



Supplement of

Evaluated kinetic and photochemical data for atmospheric chemistry: Volume IX – gas-phase reactions of halogenated alkanes, alkenes, and oxygenated compounds

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51 Detailed data sheets for the gas phase and photochemical reactions of halogenated alkanes, alkenes,
 52 and oxygenated organic compounds implemented on the IUPAC website since 2008, IUPAC Task
 53 Group on Atmospheric Chemical Kinetic Data Evaluation, (<https://iupac.aeris-data.fr/>), access date:
 54 December 31st 2025.
 55

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| oFOx154 | NO ₃ + CF ₂ =CF ₂ (HFO-1114) → products | 96 |
| oFOx153 | NO ₃ + CF ₃ CF ₂ =CH ₂ (HFO-1234yf) → products | 97 |
| oFOx122 | NO ₃ + <i>Z</i> -CF ₃ CF=CHF (HFO-1225ye(Z)) → products | 98 |
| oFOx123 | NO ₃ + CF ₃ CF ₂ =CF ₂ (FO-1216) → products | 99 |
| oFOx155 | NO ₃ + CF ₂ =CF ₂ CF=CF ₂ → products | 100 |

| | | |
|------------------------------|---|-----|
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| oClOx97 | $\text{O}_3 + \text{CH}_2=\text{CHCl}$ (vinyl chloride) \rightarrow products | 120 |
| oFOx132 | $\text{O}_3 + E\text{-CF}_3\text{CH}=\text{CHCl}$ (HCFO-1233zd(E)) \rightarrow products | 121 |
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| oFOx99 | $\text{HO} + n\text{-C}_3\text{F}_7\text{CHO}$ \rightarrow products | 162 |
| oFOx100 | $\text{HO} + n\text{-C}_4\text{F}_9\text{CHO}$ \rightarrow products | 164 |
| oFOx101 | $\text{HO} + \text{CF}_3\text{CH}_2\text{CHO}$ \rightarrow products | 166 |
| oFOx102 | $\text{HO} + n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHO}$ \rightarrow products | 169 |
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| oFOx140 | $\text{HO} + \text{CHF}_2\text{OCF}_3$ \rightarrow products | 185 |
| oFOx141 | $\text{HO} + \text{CH}_3\text{OCHF}_2\text{CF}_3$ \rightarrow products | 187 |
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| oFOx143 | $\text{HO} + \text{CH}_3\text{OCH}_2\text{CF}_3$ \rightarrow products | 191 |
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| oFOx145 | $\text{HO} + n\text{-C}_3\text{F}_7\text{OCH}_3$ \rightarrow products | 196 |
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| oFOx147 | $\text{HO} + \text{C}_4\text{F}_9\text{OCH}_3$ \rightarrow products | 201 |
| oFOx148 | $\text{HO} + \text{CH}_3\text{OCH}(\text{CF}_3)_2$ \rightarrow products | 205 |
| oFOx149 | $\text{HO} + \text{CH}_2\text{FOCH}(\text{CF}_3)_2$ (Sevoflurane) \rightarrow products | 207 |
| oFOx150 | $\text{HO} + \text{CHF}_2\text{OCHF}_2\text{CF}_3$ (Desflurane) \rightarrow products | 210 |

Halogenated vinyl ethers

| | | |
|---------|---|-----|
| oFOx133 | HO + CF ₃ OCF=CF ₂ → products | 212 |
| oFOx134 | HO + C ₂ F ₅ OCF=CF ₂ → products | 214 |

Peroxy radicals

| | | |
|---------|---|-----|
| oFOx160 | CF ₃ C(O)O ₂ + HO ₂ → CF ₃ C(O)OOH + O ₂ (1) | 216 |
| | → CF ₃ C(O)OH + O ₃ (2) | |
| | → CF ₃ C(O)O + HO (3) | |
| <hr/> | | |
| | Overall | |
| oFOx161 | CF ₃ C(O)O ₂ + NO → CF ₃ C(O)O + NO ₂ | 218 |
| oFOx162 | CF ₃ C(O)O ₂ + NO ₂ + M → CF ₃ C(O)O ₂ NO ₂ + M | 220 |
| oFOx163 | CF ₃ C(O)O ₂ NO ₂ + M → CF ₃ C(O)O ₂ + NO ₂ + M | 221 |

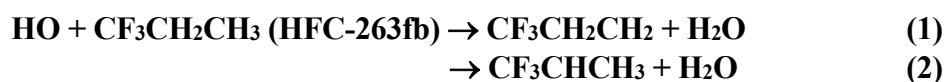
| | | |
|------|--|-----|
| PF5 | CHF ₂ CHO + hν → products | 224 |
| PF6 | C ₂ F ₅ CHO + hν → products | 227 |
| PF7 | <i>n</i> -C ₃ F ₇ CHO + hν → products | 231 |
| PF8 | <i>n</i> -C ₄ F ₉ CHO + hν → products | 234 |
| PF9 | CF ₃ CH ₂ CHO + hν → products | 237 |
| PF10 | <i>n</i> -C ₆ F ₁₃ CH ₂ CHO + hν → products | 241 |

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60

61 **oFOx72: HO + CF₃CH₂CH₃ (HFC-263fb)**
 62 Last evaluated: June 2025; Last change in preferred values: June 2009.



66
 67 **Rate coefficient data ($k = k_1 + k_2$)**
 68

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(4.00 \pm 0.13) \times 10^{-14}$ | 295 | Nelson et al. (1995) | DF-LIF (a) |
| $4.36 \times 10^{-12} \exp[-(1290 \pm 40)/T]$ | 238-373 | Rajakumar et al. (2006) | PLP-LIF (b) |
| 5.50×10^{-14} | 297 | | |

69
 70 **Comments**

- 71
 72 (a) HO radicals produced via the H + NO₂ reaction. Experiments were performed in 1.1-2.0 Torr (1.5-
 73 2.7 mbar) of helium diluent.
 74 (b) HO radicals produced by 248 nm photolysis of H₂O₂. Experiments were performed in 50-210 Torr
 75 (67-280 mbar) of helium diluent. The value given at 297 K is the average of the four determinations
 76 reported.

77
 78 **Preferred Values**
 79

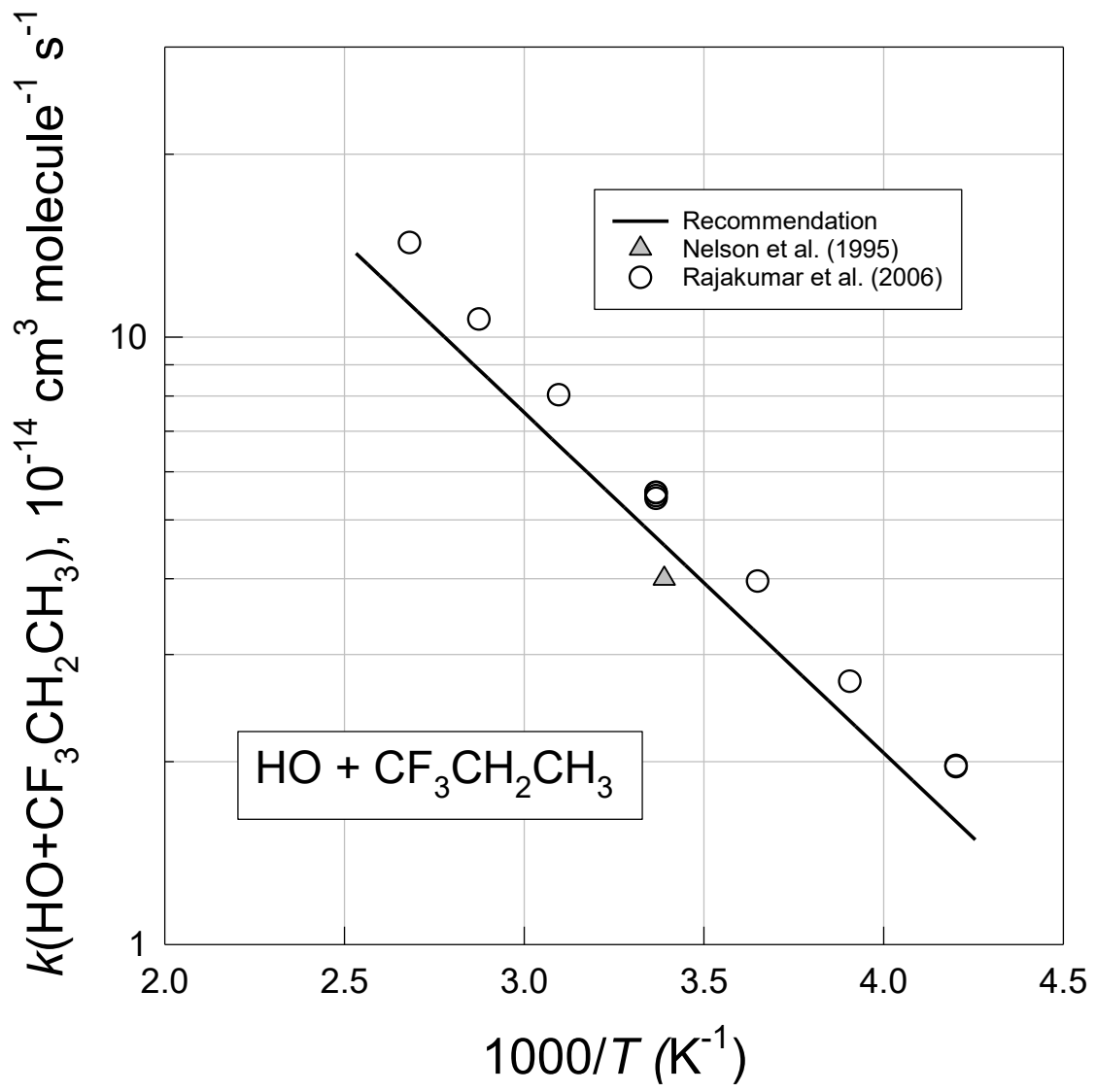
| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 4.9×10^{-14} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $3.7 \times 10^{-12} \exp(-1290/T)$ | 240-370 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |
| $\Delta E/R$ | ± 300 | 240-370 |

80
 81
 82 **Comments on Preferred Values**

83
 84
 85 The result from Nelson et al. (1995) lies approximately 25% below that from Rajakumar et al.
 86 (2006). Such a difference is within the combined uncertainties from the two studies. Adjusting the rate
 87 coefficients reported at 295 K by Nelson et al. (1995) and at 297 K by Rajakumar et al. (2006) using the
 88 temperature dependence reported by Rajakumar et al. (2006) and taking an average gives the preferred
 89 value of $k = 4.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The temperature dependence is taken from
 90 Rajakumar et al. (2006) with the pre-exponential factor adjusted to be consistent with the preferred rate
 91 coefficient at 298 K.

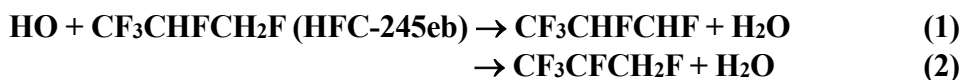
92
 93 **References**

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 95 Nelson Jr., D. D., Zahniser, M. S., Kolb, C. E., and Magid, H.: J. Phys. Chem., 99, 16301, 1995.
 96 Rajakumar, B., Portmann, R.W., Burkholder, J. B., and Ravishankara, A. R.: J. Phys. Chem. A, 110,
 97 6724, 2006.
 98



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101

102 **oFOx73: HO + CF₃CHFCH₂F (HFC-245eb)**
 103 Last evaluated: June 2025; Last change in preferred values: June 2009.



107
 108 **Rate coefficient data ($k = k_1 + k_2$)**
 109

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.37 \pm 0.03) \times 10^{-14}$ | 294 | Nelson et al. (1995) | DF-LIF (a) |
| $1.23 \times 10^{-12} \exp[-(1250 \pm 40)/T]$ | 238-374 | Rajakumar et al. (2006) | PLP-LIF (b) |
| 1.80×10^{-14} | 297 | | |

110
 111 **Comments**
 112

- 113 (a) HO radicals produced via the H + NO₂ reaction. Experiments were performed in 1.4-2.9 Torr (1.9-
 114 3.9 mbar) of helium diluent.
 115 (b) HO radicals produced by 248 nm photolysis of H₂O₂. Experiments were performed in 49-210 Torr
 116 (65-280 mbar) of helium diluent. The value given at 297 K is the average of the four determinations
 117 reported.
 118

119 **Preferred Values**
 120

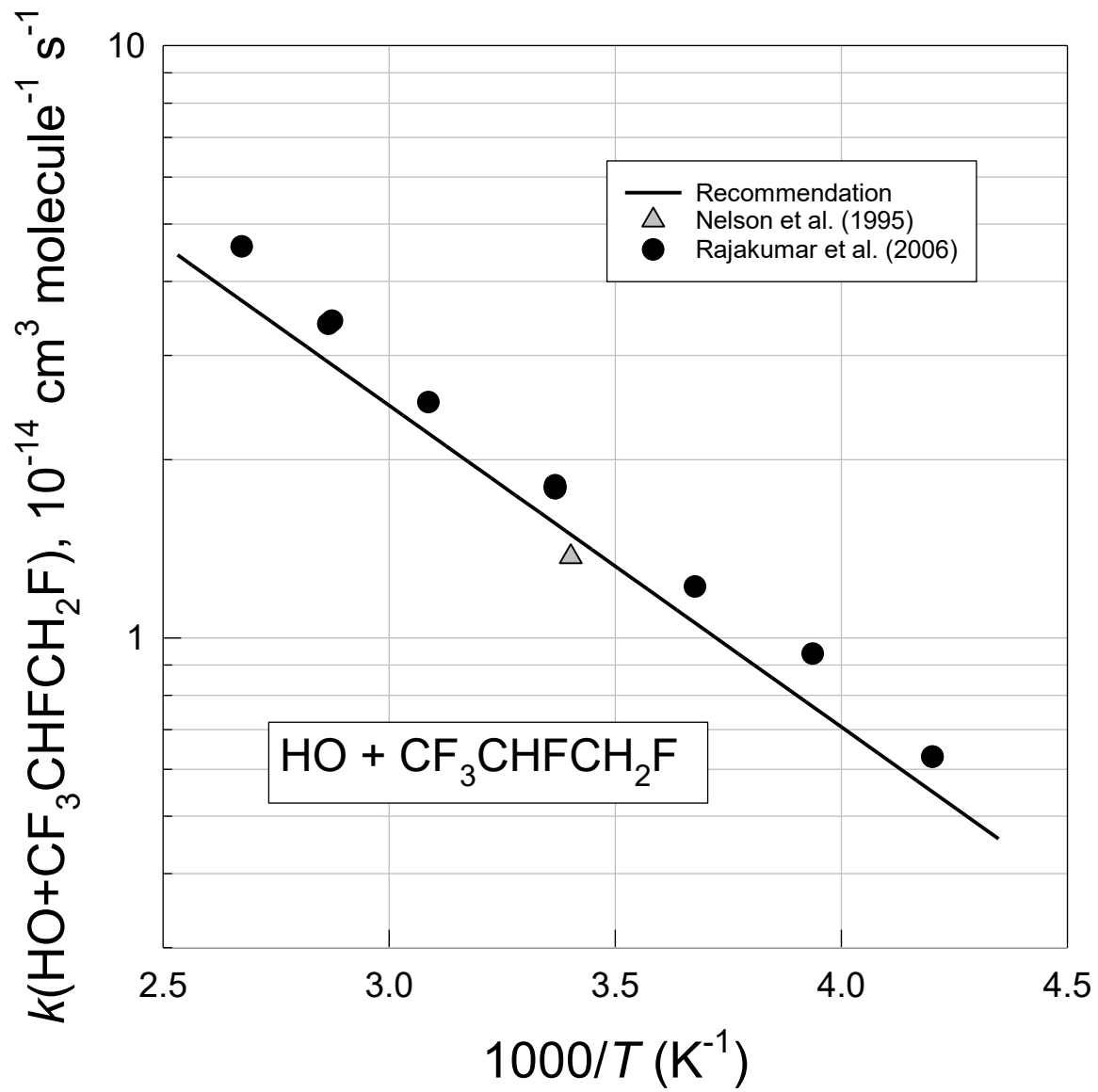
| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.6×10^{-14} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.1 \times 10^{-12} \exp(-1250/T)$ | 240-380 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |
| $\Delta E/R$ | ± 300 | 240-380 |

121
 122
 123 **Comments on Preferred Values**

124 The rate coefficient reported by Nelson et al. (1995) at 294 K is approximately 25% below that
 125 reported by Rajakumar et al. (2006) at 297 K. Adjusting both rate coefficients to values expected at 298
 126 K using the temperature dependence reported by Rajakumar et al. (2006) reduces the difference between
 127 the studies to approximately 20%. Such a difference is just within the combined uncertainties from the
 128 two studies. The preferred value at 298 K is the average of the values derived from Nelson et al. (1995)
 129 and Rajakumar et al. (2006). The temperature dependence is taken from Rajakumar et al. (2006) with the
 130 pre-exponential factor adjusted to be consistent with the $k(298 \text{ K})$ value.
 131

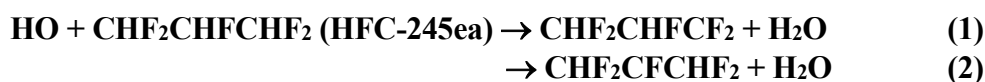
132
 133 **References**
 134

- 135 Nelson Jr., D. D., Zahniser, M. S., Kolb, C. E. and Magid, H.: J. Phys. Chem., 99, 16301, 1995.
 136 Rajakumar, B., Portmann, R.W., Burkholder, J. B. and Ravishankara, A. R.: J. Phys. Chem. A, 110, 6724,
 137 2006.
 138



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141

142 **oFOx74: HO + CHF₂CHFCHF₂ (HFC-245ea)**
 143 Last evaluated: June 2025; Last change in preferred values: June 2009.



147
 148 **Rate coefficient data ($k = k_1 + k_2$)**
 149

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.52 \pm 0.15) \times 10^{-14}$ | 294 | Nelson et al. (1995) | DF-LIF (a) |
| $1.91 \times 10^{-12} \exp[-(1375 \pm 100)/T]$ | 238-374 | Rajakumar et al. (2006) | PLP-LIF (b) |
| 1.93×10^{-14} | 297 | | |

150
 151 **Comments**
 152

- 153 (a) HO radicals were produced via the H + NO₂ reaction. Experiments were performed in 1.2-2.1 Torr
 154 (1.6-2.9 mbar) of helium diluent.
 155 (b) HO radicals were produced by 248 nm photolysis of H₂O₂. Experiments were performed in 51-205
 156 Torr (68-270 mbar) of helium diluent. The value given at 297 K is the average of the four
 157 determinations reported.
 158

159 **Preferred Values**
 160

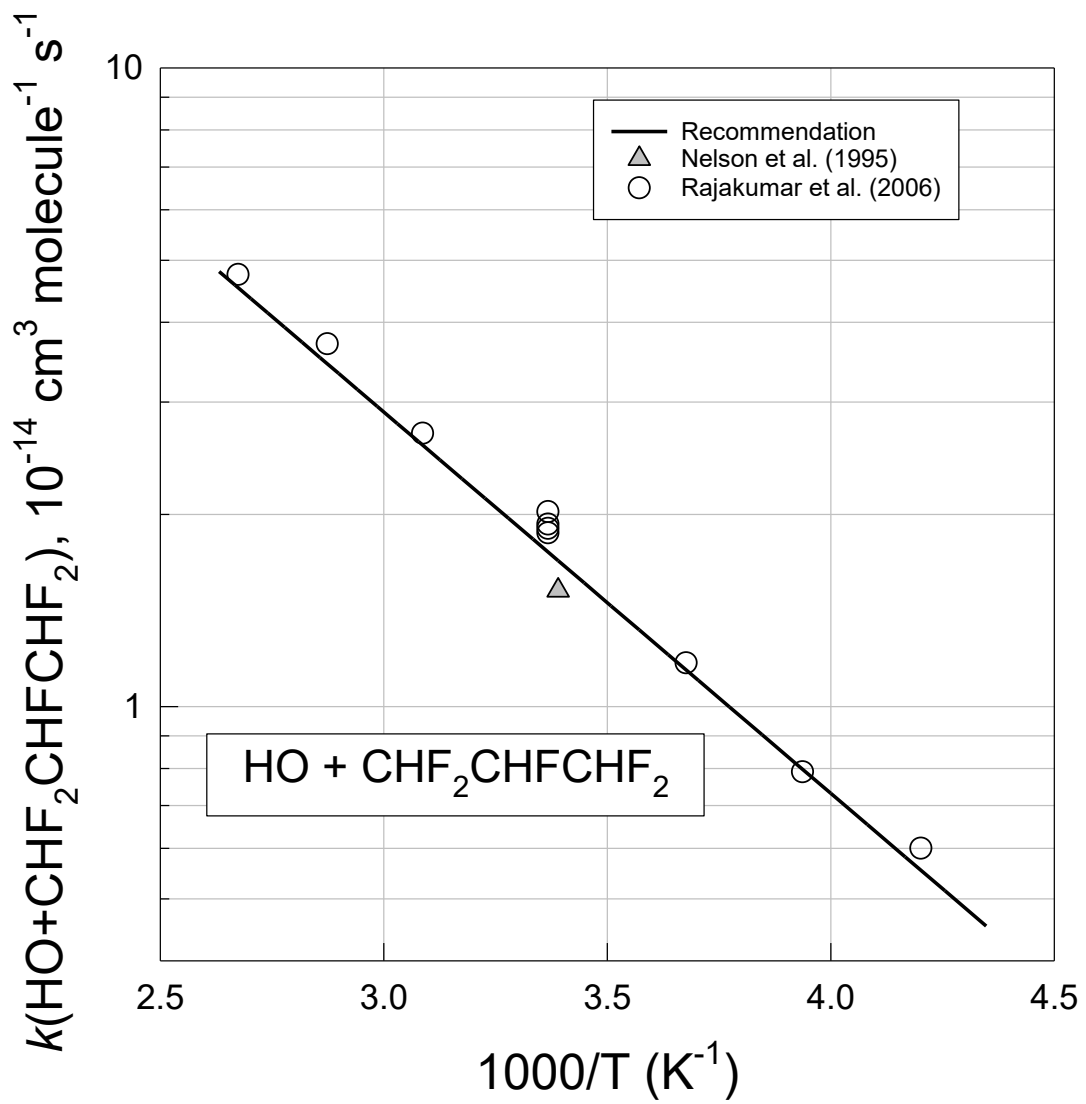
| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.8×10^{-14} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.8 \times 10^{-12} \exp(-1375/T)$ | 240-380 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |
| $\Delta E/R$ | ± 300 | 240-380 |

161
 162
 163 **Comments on Preferred Values**

164 The rate coefficient reported by Nelson et al. (1995) at 294 K is approximately 20% below that
 165 reported by Rajakumar et al. (2006) at 297 K. Adjusting both rate coefficients to values expected at 298
 166 K using the temperature dependence reported by Rajakumar et al. (2006) reduces the difference between
 167 the studies to approximately 15%. Such a difference is within the likely combined uncertainties from the
 168 two studies. The preferred value at 298 K is the average of the values derived from Nelson et al. (1995)
 169 and Rajakumar et al. (2006). The temperature dependence is taken from Rajakumar et al. (2006) with the
 170 pre-exponential factor adjusted to be consistent with the $k(298 \text{ K})$ value.
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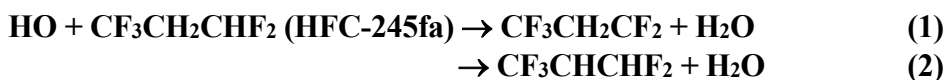
173 **References**
 174

- 175 Nelson Jr., D. D., Zahniser, M. S., Kolb, C. E., and Magid, H.: J. Phys. Chem., 99, 16301, 1995.
 176 Rajakumar, B., Portmann, R.W., Burkholder, J. B., and Ravishankara, A. R.: J. Phys. Chem. A, 110,
 177 6724, 2006.
 178



179
 180
 181
 182
 183

184 **oFOx75: HO + CF₃CH₂CHF₂ (HFC-245fa)**
 185 Last evaluated: June 2025; Last change in preferred values: June 2009.



189 **Rate coefficient data ($k = k_1 + k_2$)**
 190
 191

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|----------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(6.12 \pm 0.22) \times 10^{-15}$ | 294 | Nelson et al. (1995) | DF-LIF (a) |
| $6.32 \times 10^{-12} \exp[-(1331 \pm 43)/T]$ | 273-370 | Orkin et al. (1996) | FP-RF (b) |
| $(7.24 \pm 0.02) \times 10^{-15}$ | 298 | | |

192 **Comments**

- 193
 194 (a) HO radicals produced via the H + NO₂ reaction. Experiments were performed in 2.2-3.1 Torr (0.3-
 195 0.4 kPa) of helium diluent.
 196 (b) HO radicals were produced from the photolysis of H₂O vapor using a xenon flash lamp. HO radicals
 197 were monitored by their resonance fluorescence near 308 nm using microwave discharge resonance
 198 lamp. Experiments were performed in 100 Torr (13.33 kPa) of argon diluent.
 199

200 **Preferred Values**
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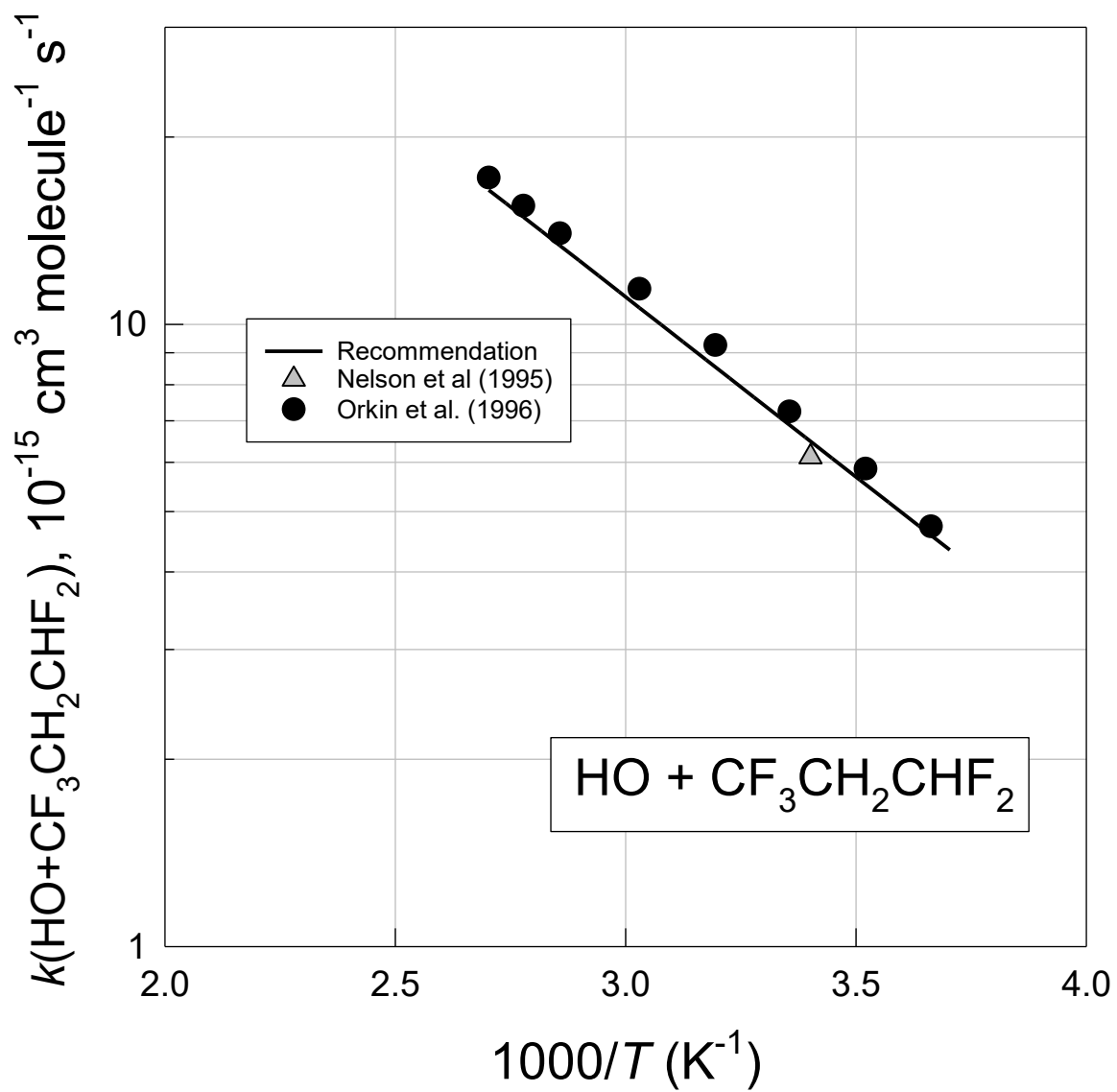
| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 6.9×10^{-15} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $6.0 \times 10^{-13} \exp(-1331/T)$ | 270-370 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.12 | 298 |
| $\Delta E/R$ | ± 300 | 270-370 |

202
 203 *Comments on Preferred Values*

204
 205 Adjusting the rate coefficient at 294 K reported by Nelson et al. (1995) to the value expected at 298
 206 K using the temperature dependence reported by Orkin et al. (1996) gives $k(298\text{K}) = 6.50 \times 10^{-15} \text{ cm}^3$
 207 $\text{molecule}^{-1} \text{ s}^{-1}$ which is 10% below the $k(298\text{K})$ value reported by Orkin et al. (1996). Such a difference is
 208 well within the combined uncertainties from the two studies. The preferred value at 298 K is the average
 209 of the values from Nelson et al. (1995) and Orkin et al. (1996). The temperature dependence is taken
 210 from Orkin et al. (1996) with the pre-exponential factor adjusted to be consistent with the $k(298\text{K})$ value.
 211
 212

213 **References**

- 214
 215
 216 Nelson Jr., D. D., Zahniser, M. S., Kolb, C. E., and Magid, H.: J. Phys. Chem., 99, 16301, 1995.
 217 Orkin, V. L., Huie, R. E., and Kurylo, M. J.: J. Phys. Chem., 100, 8907, 1996.
 218
 219



220
 221
 222
 223

224 **oFOx76: HO + CF₃CH₂CF₂CH₃ (HFC-365mfc)**
 225 Last evaluated: June 2025; Last change in preferred values: June 2009.



229
 230 **Rate coefficient data ($k = k_1 + k_2$)**
 231

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $1.68 \times 10^{-12} \exp[-(1585 \pm 80)/T]$ | 269-370 | Mellouki et al. (1995) | PLP-LIF (a) |
| 8.69×10^{-15} | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $1.39 \times 10^{-12} \exp[-1651/T]$ | 278-323 | Barry et al. (1997) | RR (b) |
| 5.46×10^{-15} | 298 | | |

232
 233 **Comments**

- 234
 235 (a) HO radicals were produced by the 248 nm photolysis of H₂O₂. Experiments were performed in 100
 236 Torr (133 mbar) of helium diluent.
 237 (b) HO radicals were produced by the 254 nm photolysis of O₃ in the presence of H₂O. Experiments
 238 were performed in 1 bar of air diluent. Rate coefficient ratios were placed on an absolute basis using
 239 $k(\text{OH}+\text{CH}_3\text{CCl}_3) = 1.2 \times 10^{-12} \exp(-1440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008).
 240

241 **Preferred Values**
 242

| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 7.1×10^{-15} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.6 \times 10^{-12} \exp(-1620/T)$ | 270-380 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.2 | 298 |
| $\Delta E/R$ | ± 200 | 270-380 |

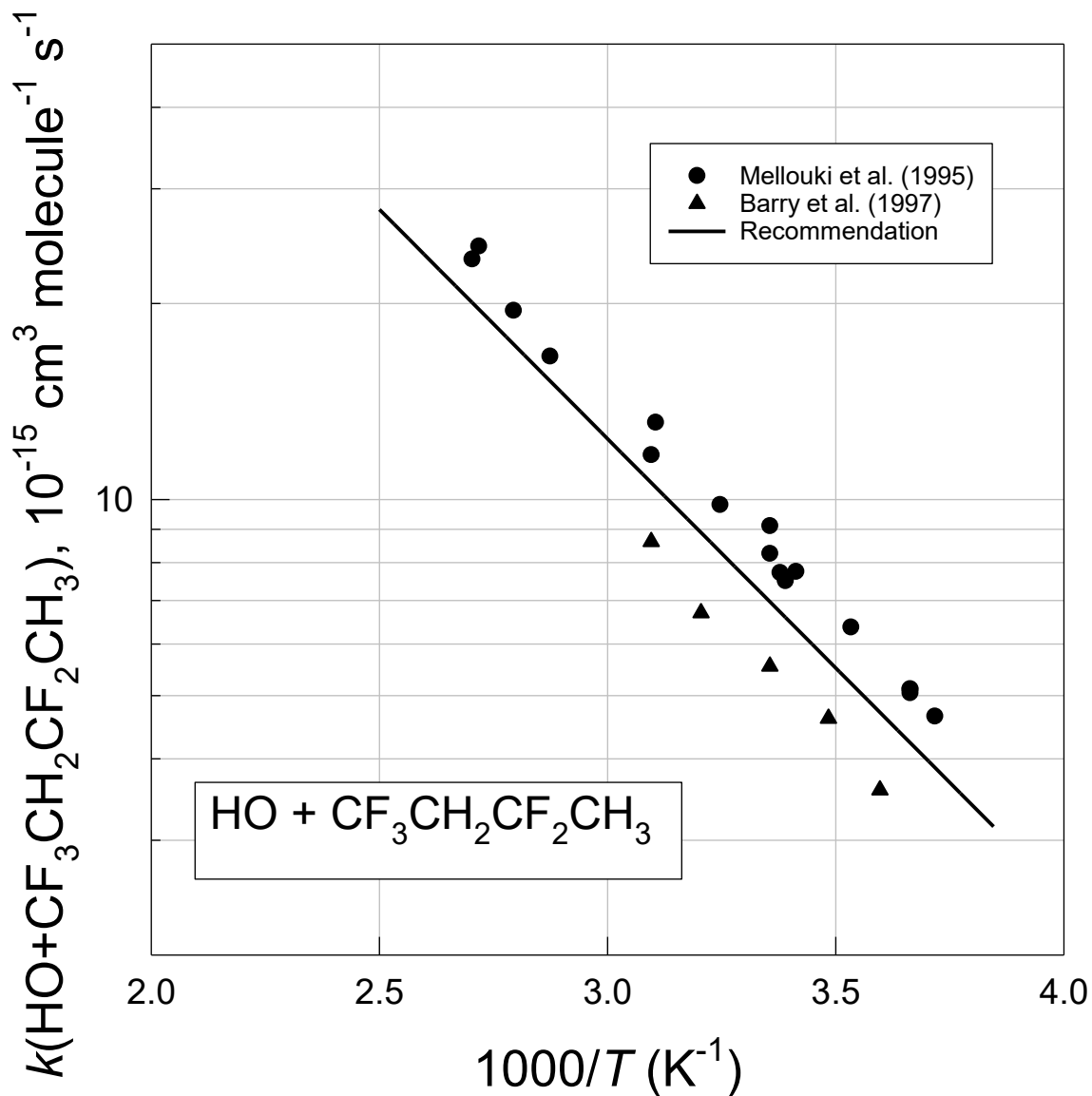
243
 244
 245 *Comments on Preferred Values*

246
 247
 248 The rate coefficient at 298 K reported in the absolute rate study by Mellouki et al. (1995) is
 249 approximately 60% greater than that measured in the relative rate study by Barry et al. (1997). A possible
 250 explanation for this discrepancy is the presence of reactive impurities in the sample used by Mellouki et
 251 al. (1995). This explanation should lead to an increasing discrepancy between the two studies with
 252 decreasing temperature, but no such trend is evident. The temperature dependencies of the rate
 253 coefficients reported in the two studies are in good agreement. There being no obvious reason to prefer
 254 either study, we prefer an average of the $k(298\text{K})$ values and temperature dependencies from the two
 255 studies with the pre-exponential A factor chosen for consistency with the $k(298\text{K})$. As discussed by Barry
 256 et al. (1997) and Inoue et al. (2008), the OH radical initiated atmospheric oxidation of CF₃CH₂CF₂CH₃ is
 257 expected to lead to the formation of CF₃CH₂CF₂CHO as the main primary product. Oxidation of
 258 CF₃CH₂CF₂CHO will generate CF₃CHO and COF₂ as secondary products. Oxidation of CF₃CHO will
 259 produce COF₂.
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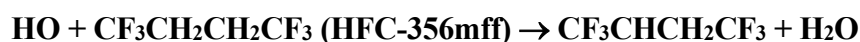
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- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: *Atmos. Chem. Phys.*, 8, 4141, 2008.
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- Mellouki, A., Téton, S., and Le Bras, G.: *Geophys. Res. Lett.*, 22, 389, 1995.



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273
274

275 **oFOx77: HO + CF₃CH₂CH₂CF₃ (HFC-356mff)**
 276 Last evaluated: June 2025; Last change in preferred values: June 2009.



279 **Rate coefficient data (*k*)**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|----------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 2.94 × 10 ⁻¹² exp[-(1734 ± 87)/ <i>T</i>] | 260-365 | Zhang et al. (1994) | FP-RF (a) |
| (8.17±1.04) × 10 ⁻¹⁵ | 296 | | |
| (6.73±0.14) × 10 ⁻¹⁵ | 296 | Nelson et al. (1995) | DF-LIF (b) |

283 **Comments**

- 284 (a) HO radicals were produced by photolysis of H₂O using a xenon flash lamp at λ >165 nm.
 285 Experiments were performed in 35 Torr (47 mbar) of argon diluent.
 286 (b) HO radicals were produced by the reaction of H atoms with NO₂. Experiments were performed in
 287 2.0 Torr (2.7 mbar) of helium diluent.
 288
 289

290 **Preferred Values**

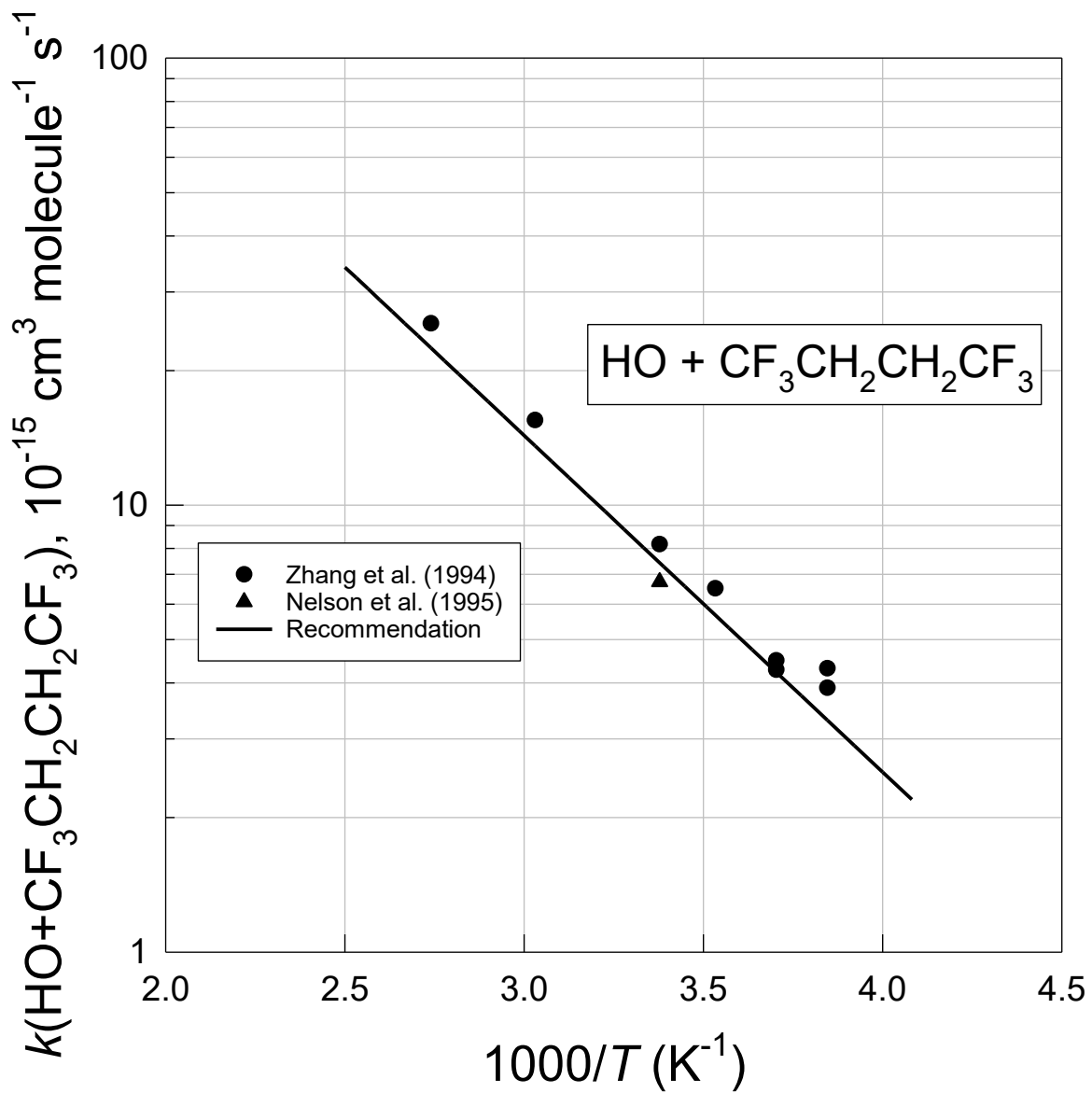
| Parameter | Value | <i>T</i> /K |
|--|---|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 7.8 × 10 ⁻¹⁵ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.6 × 10 ⁻¹² exp(-1734/ <i>T</i>) | 260-370 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |
| Δ E/R | ± 300 | 260-370 |

295 **Comments on Preferred Values**

296 There is good agreement in the rate coefficients reported by Zhang et al. (1994) and Nelson et al.
 297 (1995) at 296 K. Adjusting these rate coefficients to 298 K using the temperature dependence reported by
 298 Zhang et al. (1994) and taking an average gives our preferred rate coefficient at 298 K. Taking the
 299 temperature dependence reported by Zhang et al. (1994) and choosing a pre-exponential factor to be
 300 consistent with the rate coefficient at 298 K gives the preferred Arrhenius expression.
 301
 302

303 **References**

- 304 Nelson Jr., D. D., Zahniser, M. S, Kolb, C. E, and Magid, H.: J. Phys. Chem., 99 16301, 1995.
 305 Zhang, Z., Padmaja, S., Saini, R. D., Huie, R. E., and Kurylo, M. J.: J. Phys. Chem., 98, 4312, 1994.
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313 **oFOx78: HO + CF₃CF₂CH₂CH₂F (HFC-356mcf)**
 314 Last evaluated: June 2025; Last change in preferred values: June 2009.



318
 319 **Rate coefficient data ($k = k_1 + k_2$)**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|----------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $1.74 \times 10^{-12} \exp[-(1108 \pm 120)/T]$ | 252-366 | Nelson et al. (1995) | DF-LIF (a) |
| $(4.05 \pm 0.23) \times 10^{-14}$ | 295 | | |

321
 322 **Comments**

323
 324 (a) HO radicals were produced by the reaction of H atoms with NO₂. Experiments were performed in
 325 1.5-3.0 Torr (2-4 mbar) of helium diluent.

326
 327 **Preferred Values**

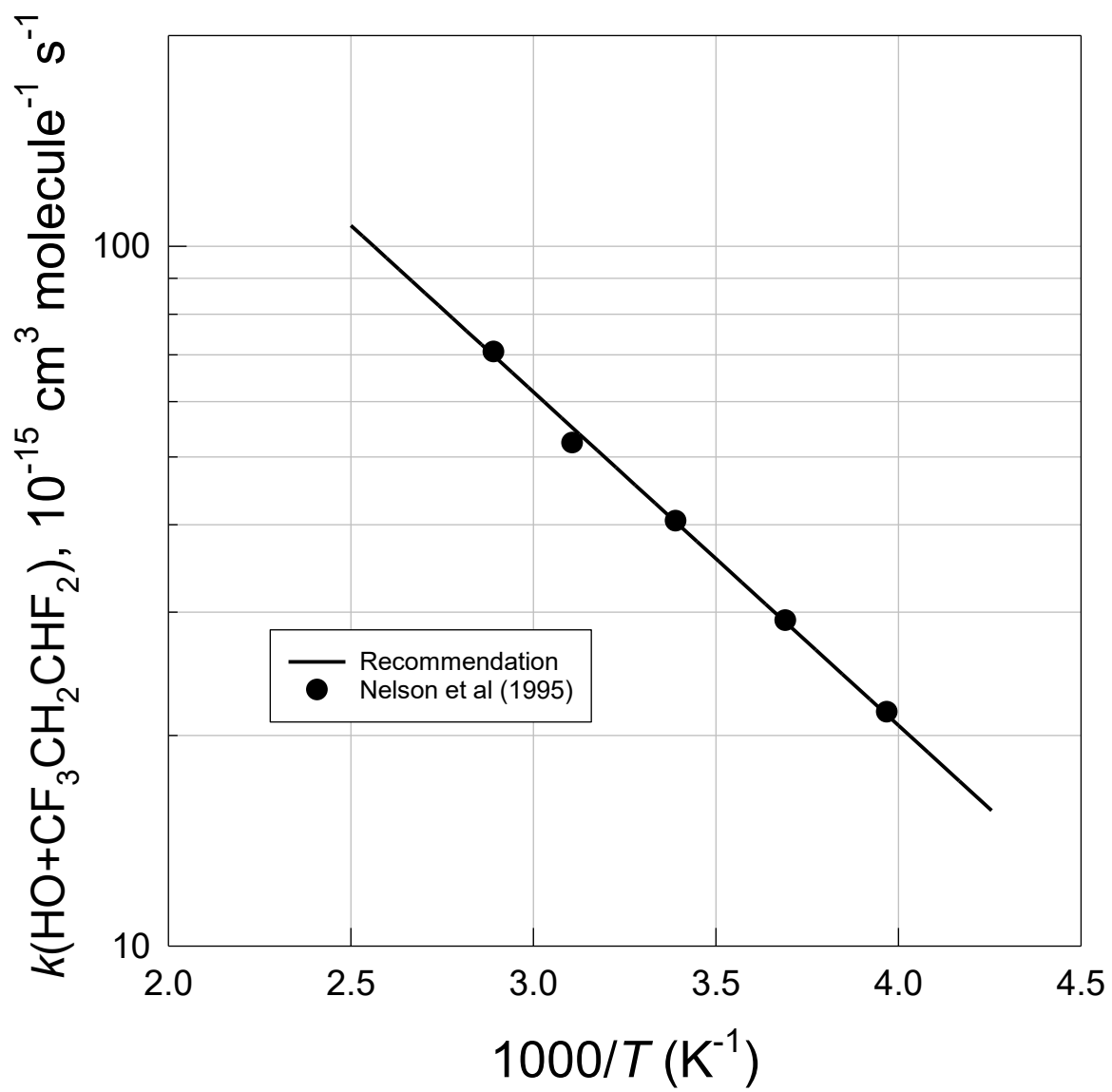
| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 4.2×10^{-14} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.7 \times 10^{-12} \exp(-1108/T)$ | 250-370 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |
| $\Delta E/R$ | ± 300 | 250-370 |

331
 332 *Comments on Preferred Values*

333
 334 The preferred values are based on the results from the study by Nelson et al. (1995).

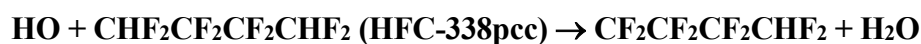
335
 336 **References**

337
 338 Nelson Jr., D. D., Zahniser, M. S, Kolb, C. E, and Magid, H.: J. Phys. Chem., 99, 16301, 1995.
 339



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341
342
343
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345 **oFOx79: HO + CHF₂CF₂CF₂CHF₂ (HFC-338pcc)**
 346 Last evaluated: June 2025; Last change in preferred values: June 2009.



350 **Rate coefficient data (*k*)**
 351

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|----------------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 7.8 × 10 ⁻¹³ exp[-(1510±260)/ <i>T</i>] (4.18 ± 0.30) × 10 ⁻¹⁵ | 245-419 296 | Zhang et al. (1992) | FP-RF (a) |
| 7.71 × 10 ⁻¹³ exp[-(1550±60)/ <i>T</i>] (3.87 ± 0.27) × 10 ⁻¹⁵ | 232-378 297 | Schmoltner et al. (1993) | FP/PLP-LIF (b) |

352
 353 **Comments**
 354

- 355 (a) HO radicals were produced by the flash photolysis ($\lambda \geq 165$ nm) of H₂O in 35 Torr (47 mbar) of
 356 argon diluent.
 357 (b) HO radicals were produced by the flash photolysis (185 nm $\geq \lambda \geq 165$ nm) of H₂O and pulsed laser
 358 photolysis ($\lambda = 355$ nm) of HONO.
 359

360 **Preferred Values**

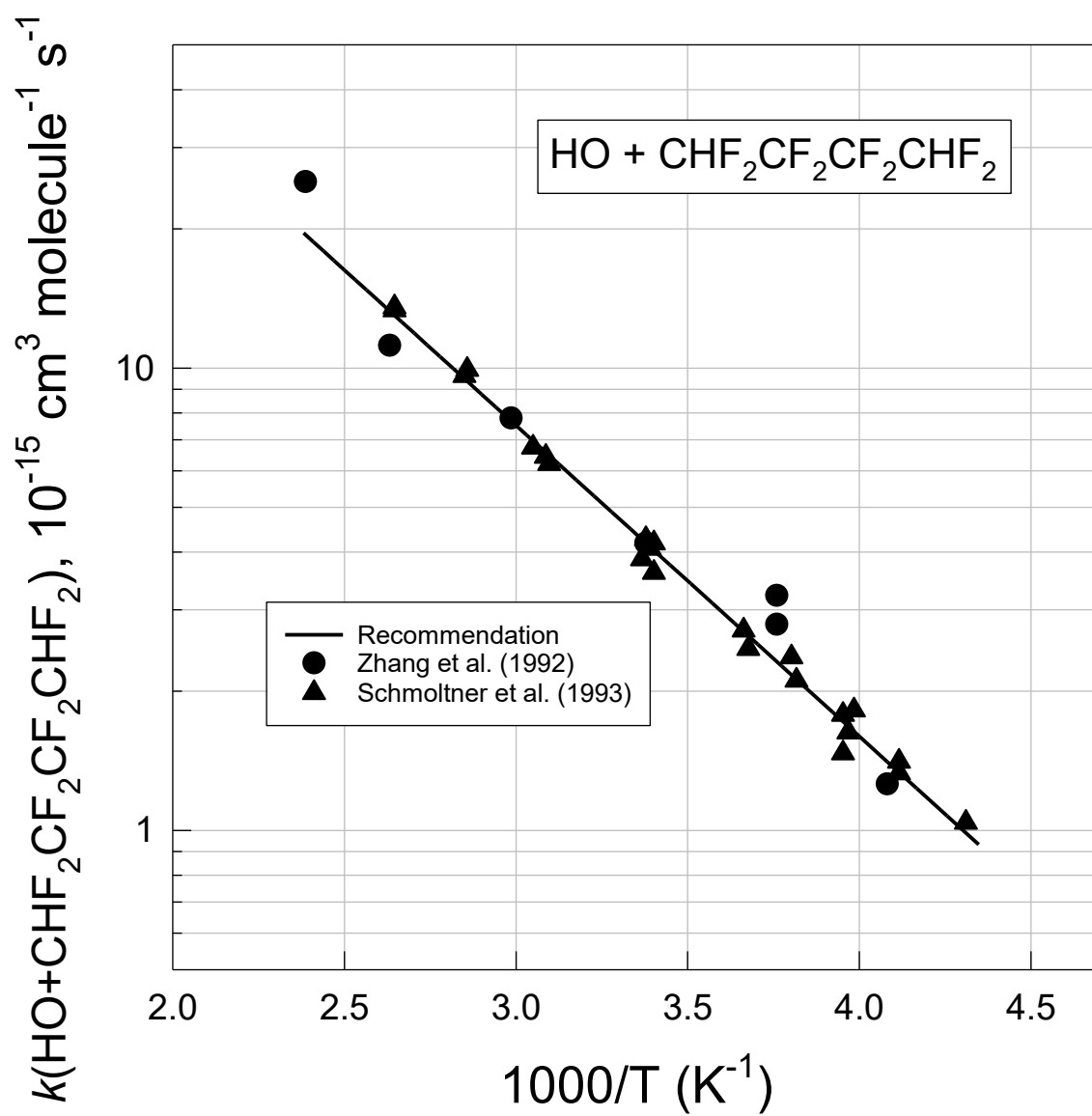
| Parameter | Value | <i>T</i> /K |
|--|---|----------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 4.3 × 10 ⁻¹⁵ 7.82 × 10 ⁻¹³ exp(-1548/ <i>T</i>) | 298 230-420 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.08 | 298 |
| Δ E/R | ± 200 | 230-420 |

363 *Comments on Preferred Values*
 364
 365

366 The results of the two studies are in good agreement. A fit of the Arrhenius expression to the
 367 combined data set from the two studies gives $k(\text{OH}+\text{CHF}_2\text{CF}_2\text{CF}_2\text{CHF}_2) = 7.82 \times 10^{-13} \exp(-1548/T)$
 368 cm³ molecule⁻¹ s⁻¹. This expression gives $k(\text{OH}+\text{CHF}_2\text{CF}_2\text{CF}_2\text{CHF}_2) = 4.34 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹
 369 at 298 K.
 370

371 **References**
 372

- 373 Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E.: Chem. Phys. Lett., 200, 230, 1992.
 374 Schmoltner, A. M., Talukdar, R. K., Warren, R. F., Mellouki, A., Goldfarb, L., Gierczak, T., McKeen, S.
 375 A., and Ravishankara, A. R.: J. Phys. Chem., 97, 8976, 1993.



376
377
378
379

380 **oFOx80: HO + CF₃CH₂CF₂CH₂CF₃ (HFC-458mfcf)**
381 Last evaluated: June 2025; Last change in preferred values: June 2009.

382

383 **HO + CF₃CH₂CF₂CH₂CF₃ (HFC-458mfcf) → CF₃CHCF₂CH₂CF₃ + H₂O**

384

385 **Rate coefficient data (*k*)**

386

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 1.23 × 10 ⁻¹² exp[-1833/ <i>T</i>] | 278-354 | Nelson et al. (1995) | FP-RF (a) |
| (2.55 ± 0.15) × 10 ⁻¹⁵ | 298 | | |

387

388

389

Comments

390 (a) HO radicals were produced by the reaction of H atoms with NO₂. Experiments were
391 performed in 0.8-6.4 Torr (1.1-8.5 mbar) of helium diluent.

392

393

394

Preferred Values

| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.6 × 10 ⁻¹⁵ | 298 |
| | 1.23 × 10 ⁻¹² exp(-1833/ <i>T</i>) | 270-360 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.15 | 298 |
| Δ <i>E</i> / <i>R</i> | ± 300 | 270-360 |

397

398

399

Comments on Preferred Values

400

401

402

The Arrhenius expression from Nelson et al. (1995), $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_3) = 1.23 \times 10^{-12} \exp(-1833/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is adopted. This expression gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_3) = 2.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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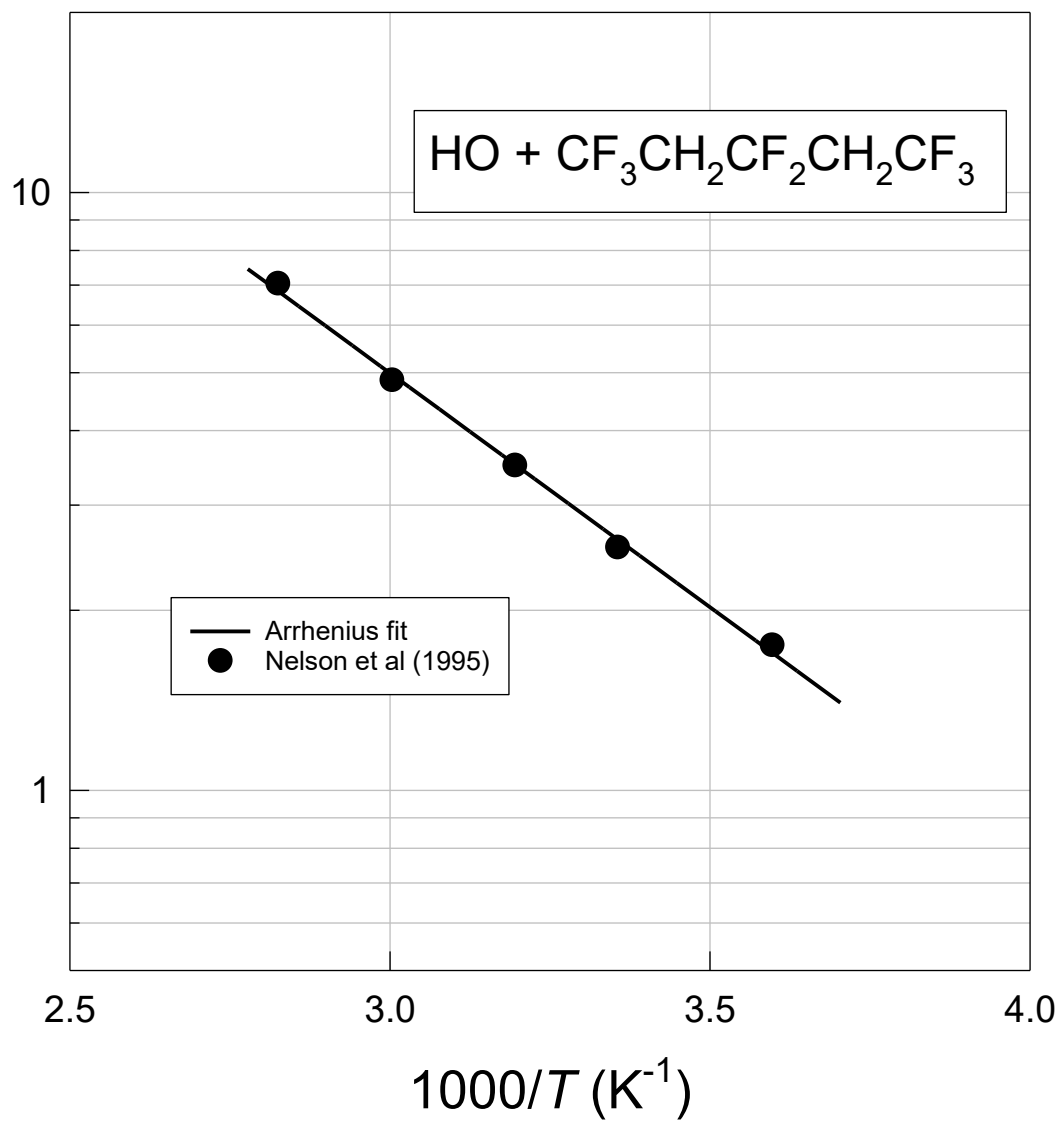
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References

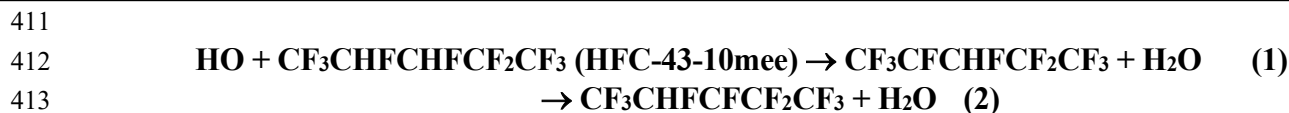
Nelson Jr., D. D., Zahniser, M. S, Kolb, C. E, and Magid, H.: J. Phys. Chem., 99 16301, 1995.

$k(\text{HO} + \text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_3), 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$



407
408

409 **oFOx81: HO + CF₃CHFCHFCF₂CF₃ (HFC-43-10mee)**
 410 Last evaluated: June 2025; Last change in preferred values: June 2009.



414
 415 **Rate coefficient data ($k = k_1 + k_2$)**
 416

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $4.21 \times 10^{-13} \exp[-(1400 \pm 180)/T]$ | 250-400 | Zhang et al. (1992) | FP-RF (a) |
| $(3.87 \pm 0.38) \times 10^{-15}$ | 295 | | |
| $6.46 \times 10^{-13} \exp[-(1600 \pm 50)/T]$ | 251.5-375 | Schmoltner et al. (1993) | FP-LIF (b) |
| $(2.88 \pm 0.20) \times 10^{-15}$ | 296 | | |

417
 418 **Comments**

- 419
 420 (a) HO radicals were produced by the flash photolysis ($\lambda \geq 165 \text{ nm}$) of H₂O in 35 Torr (47 mbar)
 421 of argon diluent.
 422 (b) HO radicals were produced by the flash photolysis ($185 \text{ nm} \geq \lambda \geq 165 \text{ nm}$) of H₂O.

423
 424 **Preferred Values**
 425

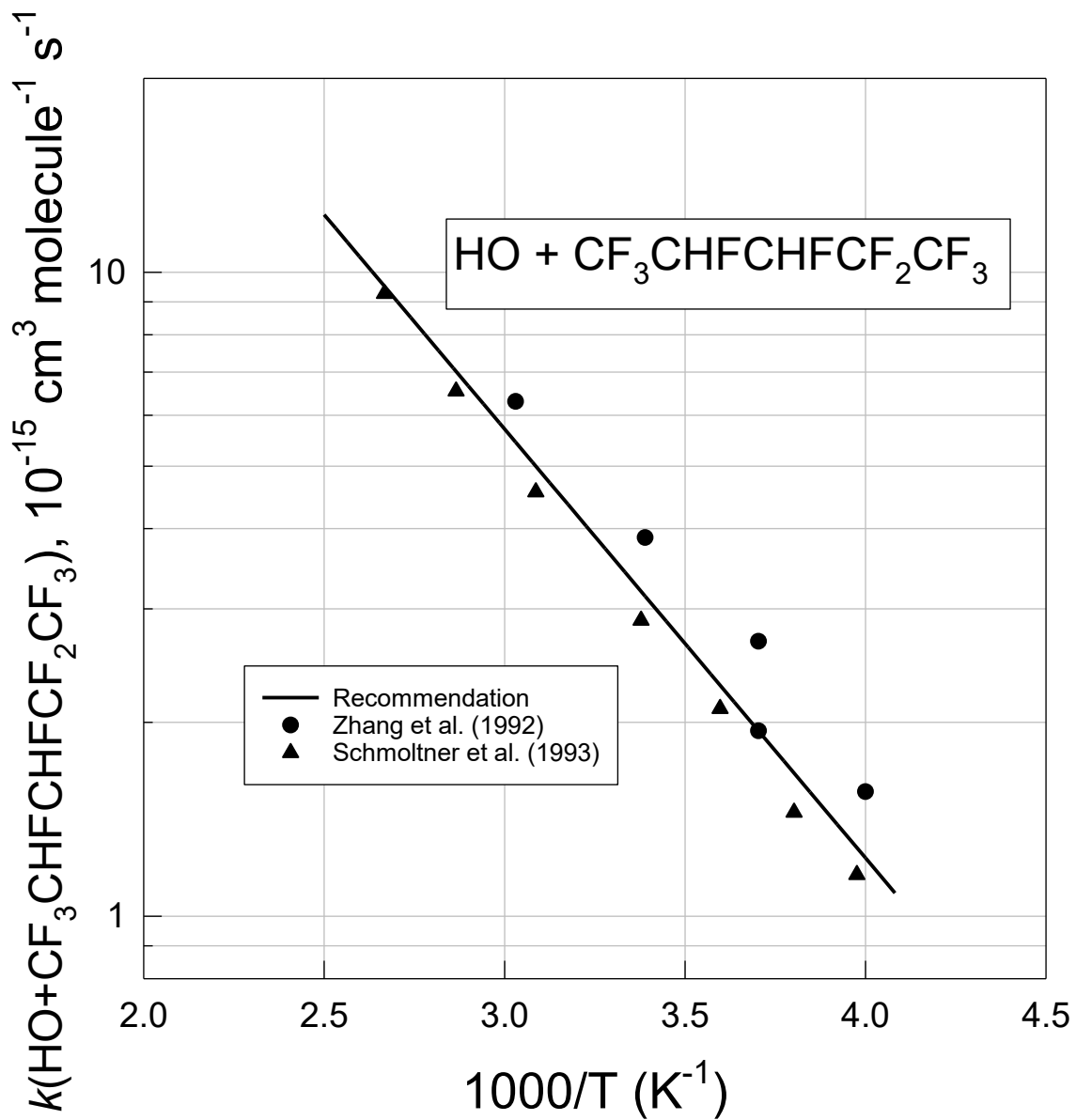
| Parameter | Value | T/K |
|--|--------------------------------------|--------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 3.3×10^{-15} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $5.68 \times 10^{-13} \exp(-1534/T)$ | 240-400 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.12 | 298 |
| $\Delta E/R$ | ± 300 | 240-400 |

426
 427
 428 **Comments on Preferred Values**

429
 430
 431 The rate coefficients measured by Schmoltner et al. (1993) are approximately 20% lower than,
 432 but consistent with the experimental uncertainties with, those reported by Zhang et al. (1992). The
 433 temperature dependence of the rate coefficients reported by Schmoltner et al. (1993) and Zhang et
 434 al. (1992) are in good agreement. There being no obvious reason to prefer either study we have fit
 435 the Arrhenius expression to the combined data set from Zhang et al. (1992) and Schmoltner et al.
 436 (1993) to give the preferred expression.

437
 438 **References**

- 439
 440 Zhang, Z., Saini, R.D., Kurylo, M. J., and Huie, R. E.: Chem. Phys. Lett., 200, 230, 1992.
 441 Schmoltner, A. M., Talukdar, R. K., Warren, R. F., Mellouki, A., Goldfarb, L., Gierczak, T.,
 442 McKeen, S. A., and Ravishankara, A. R.: J. Phys. Chem., 97, 8976, 1993.



443
444
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446

447 **oFOx82: HO + CF₃CF₂CH₂CH₂CF₂CF₃ (HFC-55-10mcf)**

448 Last evaluated: June 2025; Last change in preferred values: June 2009.

449

450 **HO + CF₃CF₂CH₂CH₂CF₂CF₃ (HFC-55-10mcf) → CF₃CF₂CHCH₂CF₂CF₃ + H₂O**

451

452 **Rate coefficient data (*k*)**

453

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (7.87±0.38) × 10 ⁻¹⁵ | 295 | Nelson et al. (1995) | DF-LIF (a) |

454

455 **Comments**

456

457 (a) HO radicals were produced by the reaction of H atoms with NO₂. Experiments were
458 performed in 1.6-2.7 Torr (2.1-3.6 mbar) of helium diluent.

459

460 **Preferred Values**

461

| Parameter | Value | <i>T</i> /K |
|--|-------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 8.3 × 10 ⁻¹⁵ | 298 |
| <i>Reliability</i> Δ log <i>k</i> | 0.2 | 298 |

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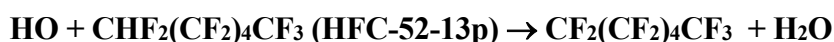
475

Comments on Preferred Values

Nelson et al. measured $k(\text{HO}+\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_3) = (7.87 \pm 0.38) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K. Using an activation energy estimated to be 3.2 kcal mol⁻¹ (13.4 kJ mol⁻¹), Nelson et al. derived a value of $k(\text{HO}+\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_3) = (8.3 \pm 0.9) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K which is our preferred value.

References

Nelson Jr., D. D., Zahniser, M. S, Kolb, C. E, and Magid, H.: J. Phys. Chem., 99, 16301, 1995.



480 **Rate coefficient data (*k*)**

481

482

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|--------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 7.36 × 10 ⁻¹² exp[-(1820 ± 60)/ <i>T</i>] | 250-430 | Chen et al. (2004) | FP-LIF/ PLP-LIF (a) |
| (1.69±0.07) × 10 ⁻¹⁵ | 298 | | FP-LIF (b) |
| (1.72±0.07) × 10 ⁻¹⁵ | 298 | | PLP-LIF (c) |
| <i>Relative Rate Coefficients</i> | | | |
| 4.87 × 10 ⁻¹³ exp[-1661/ <i>T</i>] | 253-328 | Chen et al. (2004) | RR (d) |
| 1.87 × 10 ⁻¹⁵ | 298 | | |
| 2.61 × 10 ⁻¹³ exp[-1422/ <i>T</i>] | 253-328 | Chen et al. (2004) | RR (e) |
| 2.28 × 10 ⁻¹⁵ | 298 | | |

483 **Comments**

- 484
- 485
- 486 (a) Experiments were conducted using two different absolute rate methods. The sample of
 487 CHF₂(CF₂)₄CF₃ was determined to be 99.998% pure. In the FP-LIF experiments the HO
 488 radicals were produced by the photolysis of H₂O using a Xe flash lamp and experiments were
 489 performed in 20-100 Torr (27-133 mbar) of argon bath gas. In the PLP-LIF experiments the
 490 HO radicals were produced by the 193 nm photolysis of N₂O in the presence of H₂O.
 491 Experiments were performed in 20-100 Torr (27-133 mbar) of either argon or helium bath gas.
 492 The Arrhenius expression is that given by Chen et al. (2004) from a fit to the absolute rate data.
 493 (b) Result obtained using FP-LIF technique at 298 K in 40-100 Torr (53-133 mbar) total pressure
 494 of argon bath gas.
 495 (c) Result obtained using PLP-LIF technique at 298 K in 40-100 Torr (53-133 mbar) total pressure
 496 of argon or helium bath gas.
 497 (d) Relative rate method with HO radicals produced by the 254 nm photolysis of O₃ in the
 498 presence of H₂O vapor in 200-500 Torr (267-665 mbar) of helium diluent. CHF₂Cl was used as
 499 a reference compound. The rate coefficient ratios $k(\text{HO}+\text{CHF}_2(\text{CF}_2)_4\text{CF}_3)/k(\text{HO}+\text{CHF}_2\text{Cl})$
 500 were placed on an absolute basis using $k(\text{HO}+\text{CHF}_2\text{Cl}) = 7.9 \times 10^{-13} \exp(-1530/T) \text{ cm}^3$
 501 $\text{molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008).
 502 (e) Relative rate method with HO radicals produced by the 254 nm photolysis of O₃ in the
 503 presence of H₂O vapor in 200-500 Torr (267-665 mbar) of helium diluent. CH₂FCF₃ was used
 504 as a reference compound. The rate coefficient ratios $k(\text{HO}+\text{CHF}_2(\text{CF}_2)_4\text{CF}_3)/k(\text{HO}+\text{CH}_2\text{FCF}_3)$
 505 were placed on an absolute basis using $k(\text{HO}+\text{CH}_2\text{FCF}_3) = 4.9 \times 10^{-13} \exp(-1395/T) \text{ cm}^3$
 506 $\text{molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008).

507

508

509

510 **Preferred Values**

511

| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.8 × 10 ⁻¹⁵ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 5.76 × 10 ⁻¹³ exp(-1726/ <i>T</i>) | 250-430 |

| | | |
|-----------------|-----------|---------|
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta E/R$ | ± 300 | 250-430 |

514

515 *Comments on Preferred Values*

516

517 The results obtained using two absolute rate methods by Chen et al. (2004) are in good agreement.
 518 An Arrhenius fit to the absolute rate data reported by Chen et al. (2004) gives $k(\text{HO}+\text{CHF}_2(\text{CF}_2)_4\text{CF}_3) =$
 519 $5.76 \times 10^{-13} \exp(-1726/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is preferred. The relative rate experiments using
 520 CHF_2Cl reference are in excellent agreement with the results from the absolute rate study. The relative
 521 rate experiments using CH_2FCF_3 reference lie somewhat above but are consistent within the
 522 experimental uncertainties with the preferred values.

523

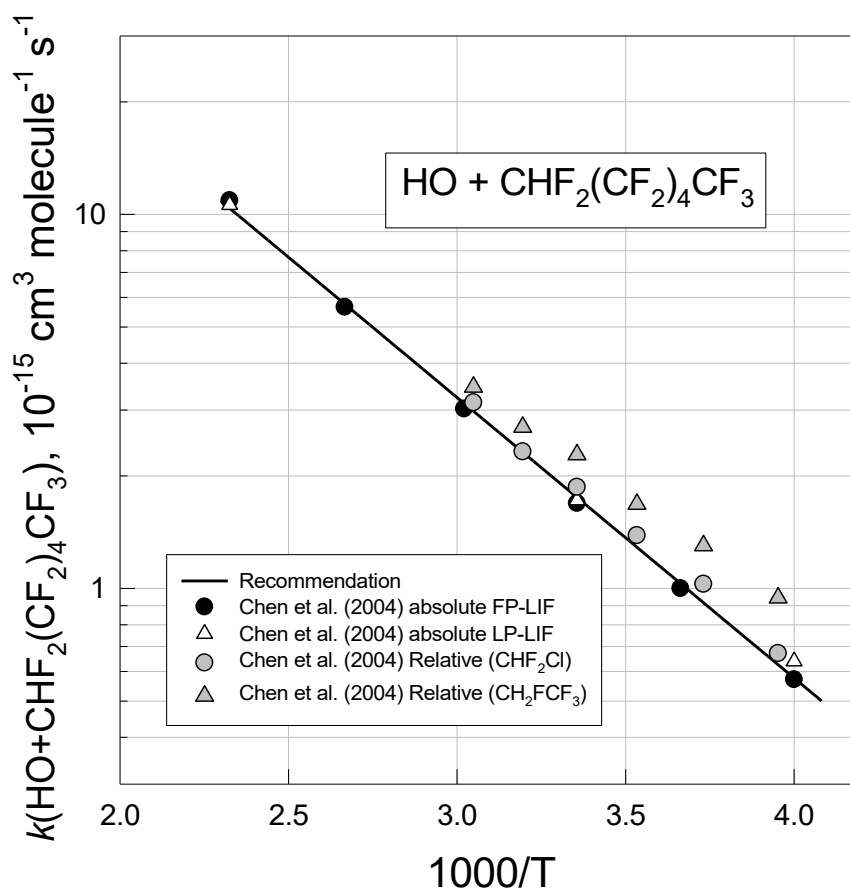
524

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530

531

532 **oClOx86: HO + CH₃CH₂Cl**
 533 Last evaluated: June 2025; Last change in preferred values: June 2009.



537
 538 **Rate coefficient data ($k = k_1 + k_2$)**
 539

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(3.9 \pm 0.7) \times 10^{-13}$ | 296 | Howard and Evenson (1976) | DF-LMR (a) |
| $(3.94 \pm 0.53) \times 10^{-13}$ | 297 | Paraskevopoulos et al. (1981) | FP-RA (b) |
| $2.96 \times 10^{-13} (T/300)^{2.59} \exp[-(28 \pm 75/T)]$ | 295-789 | Kasner et al. (1990) | FP-LIF (c) |
| $2.4 \times 10^{-11} \exp(-1082/T)$ | 295-360 | Markert and Nielsen (1992) | PR-RA (d) |
| $(4.3 \pm 0.5) \times 10^{-13}$ | 295 | | |
| $1.5 \times 10^{-13} T^{0.5} \exp(-637/T)$ | 223-426 | Herndon et al. (2001) | PLP-LIF (e) |
| $(2.92 \pm 0.12) \times 10^{-13}$ | 296 | | |

540
 541 **Comments**

- 542
 543 (a) HO radicals were generated by the reaction of H atoms with NO₂ in 0.1-1.0 kPa (1-10 mbar) of
 544 helium.
 545 (b) HO radicals produced by the flash photolysis of H₂O ($\lambda \geq 165$ nm) in 20-30 Torr (27-40 mbar) of
 546 helium.
 547 (c) HO radicals were produced by the 193 nm (ArF excimer laser) photolysis of N₂O to produce O(¹D)
 548 atoms in the presence of H₂O in 1 bar of helium.
 549 (d) HO radicals were produced by the pulsed radiolysis of argon (1 bar) containing 15 mbar of H₂O.
 550 (e) HO radicals were produced by either the photolysis of HONO at 355 nm (third harmonic Nd:YAG
 551 laser) or the photolysis of H₂O₂ at 248 nm (KrF excimer laser) in approximately 100 Torr (133
 552 mbar) of helium.
 553

554 **Preferred Values**
 555

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 3.7×10^{-13} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $4.25 \times 10^{-12} \exp(-727/T)$ | 220-400 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.1 | 298 |
| $\Delta E/R$ | ± 200 | 220-400 |

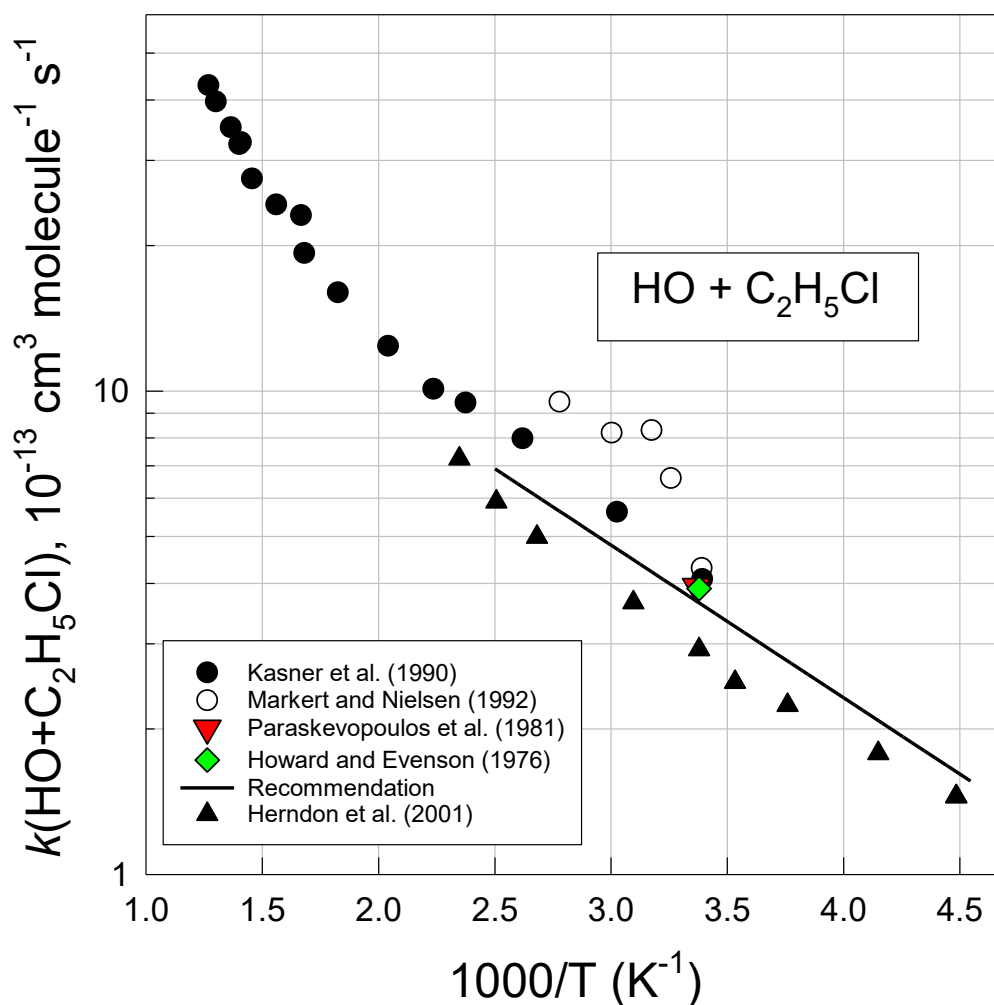
558
 559 **Comments on Preferred Values**
 560

561 The room temperature rate coefficients reported by Howard and Evenson (1976),
 562 Paraskevopoulos et al. (1981), Kasner et al. (1990), and Markert and Nielsen (1992) are in excellent
 563 agreement. However, there is disagreement between the temperature dependences reported by Kasner
 564 et al. (1990) and Markert and Nielsen (1992). The data of Markert and Nielsen (1992) are more
 565 scattered than those from Kasner et al. (1990). The rate coefficients reported by Herndon et al. (2001)
 566 lie approximately 20-30% below those from the other studies. Herndon et al. (2001) argue that the

567 presence of reactive impurities and/or complications caused by photolysis or radiolysis of the C₂H₅Cl
 568 sample may have led to overestimation of $k(\text{OH} + \text{C}_2\text{H}_5\text{Cl})$ in previous studies. However, the
 569 discharge flow experiments by Howard and Evenson (1976) would not suffer from photolysis or
 570 radiolysis of the C₂H₅Cl sample. Also, the impact of an unsaturated reactive impurity such as ethene
 571 or isobutene would be reduced at the low pressures used. Averaging the results obtained by Howard
 572 and Evenson (1976), Paraskevopoulos et al. (1981), Kasner et al. (1990), and Herndon et al. (2001)
 573 gives our preferred value of $k(\text{HO} + \text{C}_2\text{H}_5\text{Cl}) = 3.71 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Fitting the
 574 three parameter equation $k = CT^2 \exp(-D/T)$ to the data from Herndon et al. (2001) gives $k = 5.19 \times 10^{-13}$
 575 $\text{T}^2 \exp(-131/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which when centered at 298 K with $A = C e^2 T^2$ and $B = D + 2T$
 576 gives $k = 3.41 \times 10^{-12} \exp(-727/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Adjusting the A factor to match the 298 K
 577 preferred value of $k(\text{HO} + \text{C}_2\text{H}_5\text{Cl}) = 3.71 \times 10^{-13}$ gives our preferred Arrhenius expression of $k = 4.25$
 578 $\times 10^{-12} \exp(-727/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

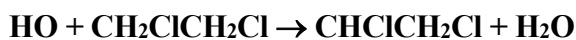
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588
589

590 **oClOx87: HO + CH₂ClCH₂Cl**
 591 Last evaluated: June 2025; Last change in preferred values: June 2009.



593 **Rate coefficient data (*k*)**

594

595

596

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|---------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (2.2±0.5) × 10 ⁻¹³ | 296 | Howard and Evenson (1976) | DF-LMR (a) |
| 4.08×10 ⁻¹² (<i>T</i> /300) ^{1.0} exp[-(825±88/ <i>T</i>)] | 292-775 | Taylor et al. (1991) | PLP-LIF (b) |
| (2.48±0.38) × 10 ⁻¹³ | 292 | | |
| 1.05 × 10 ⁻¹¹ exp[-(1141±107)/ <i>T</i>] | 292-363 | Qiu et al. (1992) | DF-RF (c) |
| 2.14 × 10 ⁻¹³ | 295 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (2.50±0.54) × 10 ⁻¹³ | 297 | Arnts et al. (1989) | RR (d) |

597 **Comments**

- 598
- 599
- 600 (a) HO radicals were generated by the reaction of H atoms with NO₂ in 0.1-1.0 kPa (0.7-7 Torr) of
 601 helium diluent.
- 602 (b) HO radicals were produced by the 193 nm (ArF eximer laser) photolysis of N₂O to produce O(¹D)
 603 atoms in the presence of H₂O in 730-750 Torr (973-1000 mbar) of helium diluent.
- 604 (c) HO radicals were produced by the reaction of F atoms with H₂O in 2-3 Torr (2.7-4.0 mbar) of argon
 605 diluent gas.
- 606 (d) The rate coefficient ratio $k(\text{HO}+\text{CH}_2\text{ClCH}_2\text{Cl})/k(\text{HO}+\text{C}_2\text{H}_6) = 1.02 \pm 0.22$ was placed on an
 607 absolute basis using $k(\text{HO}+\text{C}_2\text{H}_6) = 1.49 \times 10^{-17} T^2 \exp(-499/T)$ cm³ molecule⁻¹ s⁻¹ (Atkinson et
 608 al., 2006).

609 **Preferred Values**

610

611

| Parameter | Value | T/K |
|--|--|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.4 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 8.57 × 10 ⁻¹² exp(-1070/ <i>T</i>) | 290-360 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.08 | 298 |
| Δ <i>E</i> / <i>R</i> | ± 200 | 290-360 |

612 **Comments on Preferred Values**

613

614

615 The rate coefficients of Howard and Evenson (1976), Arnts et al. (1989), Taylor et al. (1991),
 616 and Qiu et al. (1992) are in good agreement. Adjusting the rate coefficients reported by Howard and
 617 Evenson (1976), Taylor et al. (1991), and Qiu et al. (1992) at 292 – 296 K using the temperature
 618 dependence reported by Qiu et al. (1992) and taking an average give the preferred value of 2.4 × 10⁻¹³
 619 cm³ molecule⁻¹ s⁻¹ at 298 K. Fitting the three-parameter equation $k = CT^2 \exp(-D/T)$ to the data from
 620 Howard and Evenson (1976), Arnts et al. (1989), Taylor et al. (1991), and Qiu et al. (1992) and
 621 adjusting the C factor to reproduce the preferred value at 298 K gives $k = 1.06 \times 10^{-17} T^2 \exp(-410/T)$
 622 cm³ molecule⁻¹ s⁻¹. Centering this expression at 330 K with $A = C e^2 T^2$ and $B = D + 2T$ gives $k = 8.57$
 623 cm³ molecule⁻¹ s⁻¹.
 624

625 $\times 10^{-12} \exp(-1070/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

626

627

628

References

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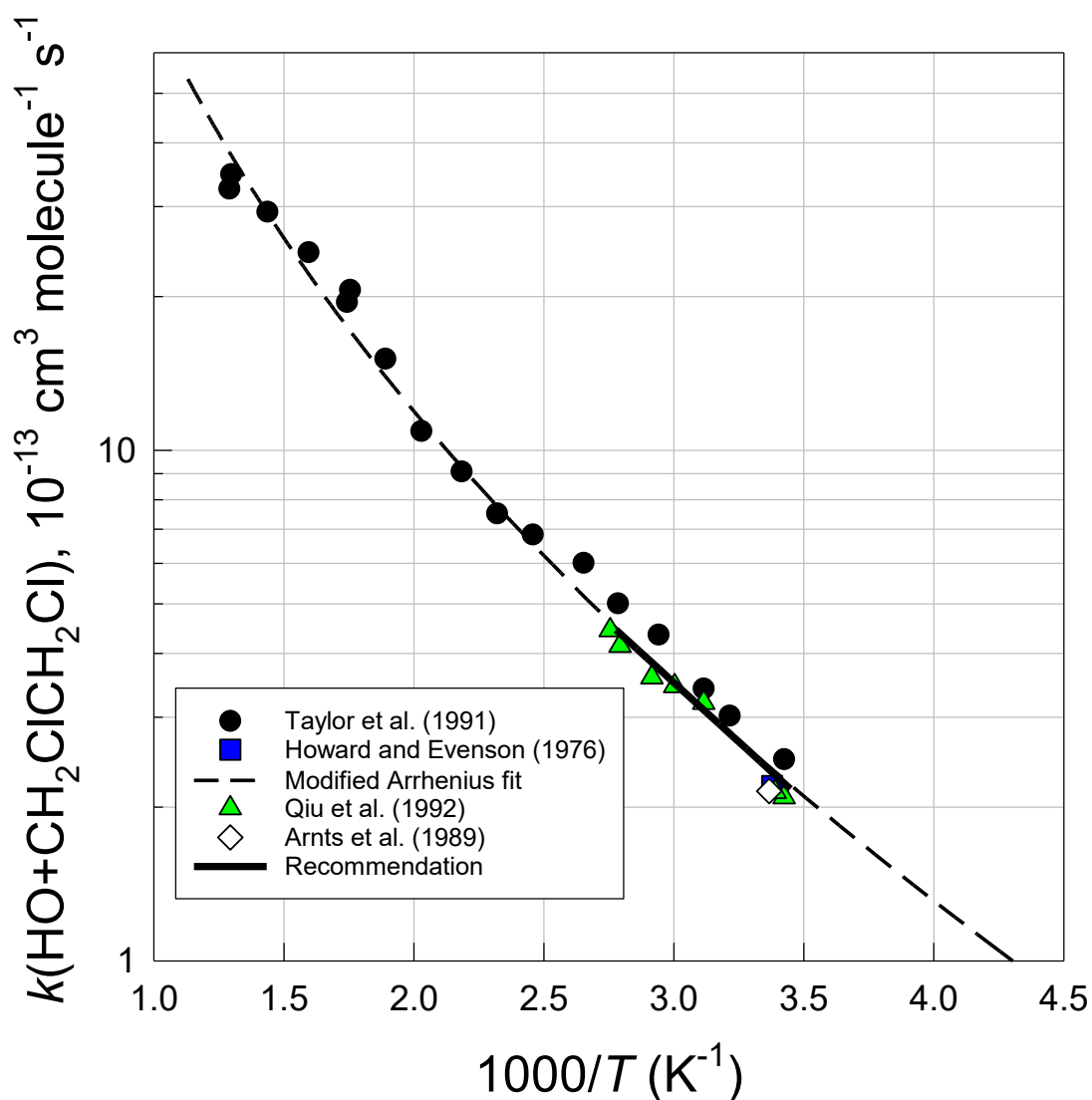
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643
 644 **oClOx88: HO + CH₃CHCl₂**
 645 Last evaluated: June 2025; Last change in preferred values: June 2009.



649
 650 **Rate coefficient data ($k = k_1 + k_2$)**
 651

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|---------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.6 \pm 0.6) \times 10^{-13}$ | 296 | Howard and Evenson (1976) | DF-LMR (a) |
| $(8.29 \pm 0.36) \times 10^{-14} (T/300)^{2.67} \exp(387 \pm 18)/T$ | 294-800 | Jiang et al. (1992) | PLP-LIF (b) |
| $(2.82 \pm 0.14) \times 10^{-13}$ | 294 | | |

652
 653 **Comments**

- 654
 655 (a) HO radicals were generated by the reaction of H atoms with NO₂ in 0.1-1.0 kPa of helium.
 656 (b) HO radicals were produced by the 193 nm photolysis of N₂O to give O(¹D) atoms in the presence of
 657 H₂O vapor in 740 ± 10 Torr (986 ± 13 mbar) of helium.
 658

659 **Preferred Values**
 660

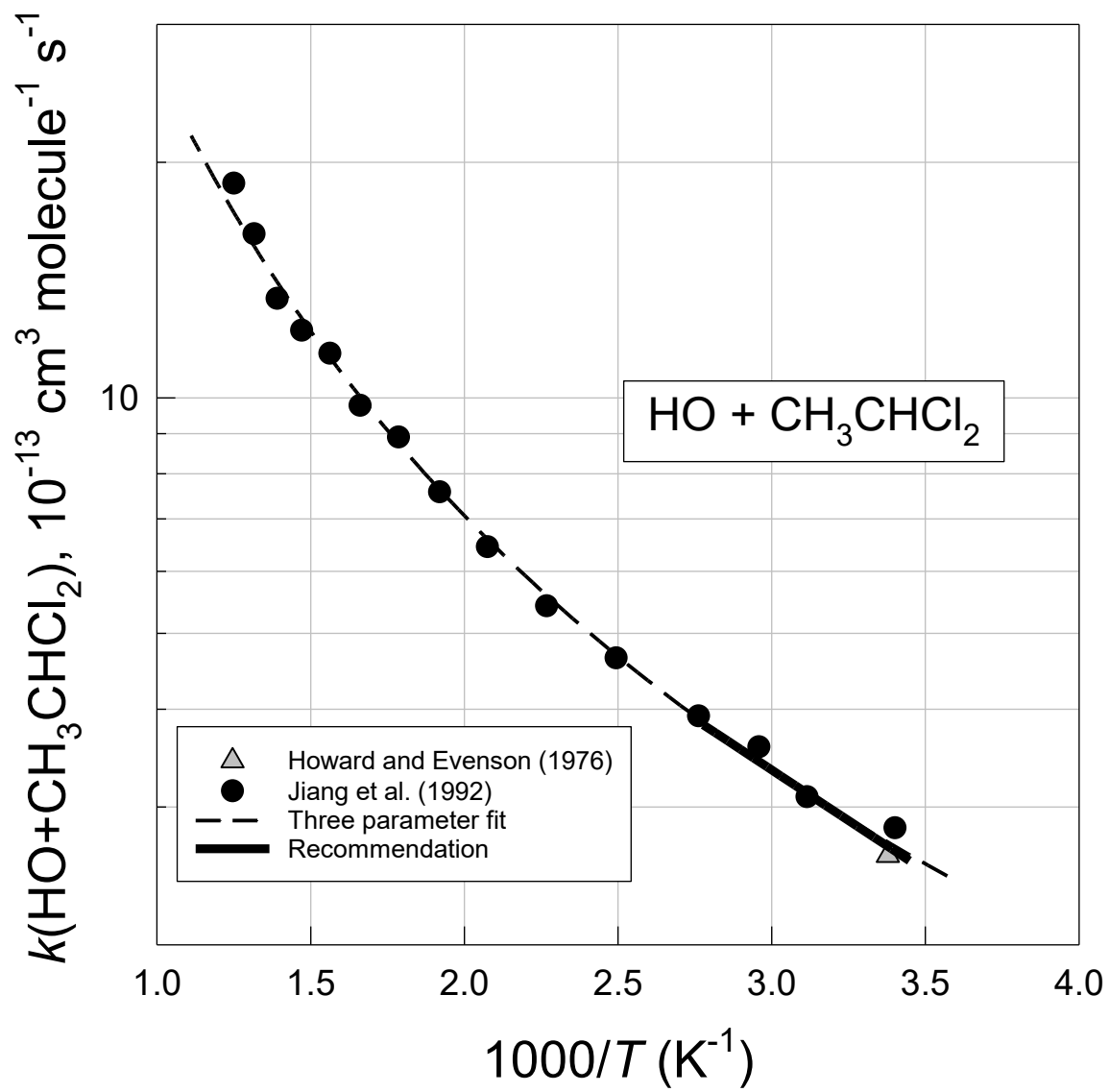
| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.76×10^{-13} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $2.04 \times 10^{-12} \exp(-596/T)$ | 290-370 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.1 | 298 |
| $\Delta E/R$ | ± 300 | 290-370 |

661
 662 **Comments on Preferred Values**

663
 664 The rate coefficients of Howard and Evenson (1976) and Jiang et al. (1992) at room temperature
 665 are in excellent agreement. Fitting the three-parameter equation $k = CT^2 \exp(-D/T)$ to the data from
 666 Howard and Evenson (1976) and Jiang et al. (1992) gives $k = 2.53 \times 10^{-18} T^2 \exp(64/T) \text{ cm}^3 \text{ molecule}^{-1}$
 667 s^{-1} . Centering this expression at 330 K with $A = C e^2 T^2$ and $B = D + 2T$ gives $k = 2.04 \times 10^{-12} \exp(-$
 668 $596/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 669
 670

671
 672 **References**

- 673
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 675 Jiang, Z., Taylor, P. H., and Dellinger, B.: J. Phys. Chem., 96, 8964, 1992.
 676



677
678

681 **HO + CHBr₃ → CBr₃ + H₂O**

682 **Rate coefficient data (*k*)**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|---|----------------|---------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 9.94 × 10 ⁻¹³ exp[(-387±22)/ <i>T</i>] (2.69 ± 0.04) × 10 ⁻¹³ | 230-370 298 | Orkin et al. (2013) | FP-RF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| 1.31 × 10 ⁻¹² exp(-584/ <i>T</i>) 1.86 × 10 ⁻¹³ | 298-366 298 | DeMore (1996) | RR (b) |

686 **Comments**

- 687
- 688
- 689 (a) HO radicals were generated by the VUV pulsed photolysis of H₂O in 30 Torr (40 mbar) of
 690 argon. HO radicals were monitored by resonance fluorescence near 308 nm. The purity of
 691 the CHBr₃ sample was checked using GC-MS. Results measured using an older version of
 692 the FP-RF system with a different gas handling system and higher flash energies were
 693 consistent with those using a newer version of the experimental apparatus.
- 694 (b) HO radicals produced by photolysis of O₃ at 254 nm in the presence of H₂O vapor in
 695 argon diluent (total pressure was not specified). CH₂Cl₂ was used as the reference
 696 compound. The loss of CHBr₃ and CH₂Cl₂ was measured using FTIR spectroscopy. A rate
 697 coefficient ratio $k(\text{HO}+\text{CHBr}_3)/k(\text{HO}+\text{CH}_2\text{Cl}_2) = (0.73 \pm 0.16) \exp[(276 \pm 71)/T]$ was
 698 reported. Using $k(\text{HO}+\text{CH}_2\text{Cl}_2) = 1.8 \times 10^{-12} \exp(-860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et
 699 al., 2008) gives $k(\text{HO}+\text{CHBr}_3) = 1.31 \times 10^{-12} \exp(-584/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

700 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|---|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.7 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.00 × 10 ⁻¹² exp(-388/ <i>T</i>) | 290-370 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.15 | 298 |
| Δ E/R | ± 300 | 290-370 |

705 **Comments on Preferred Values**

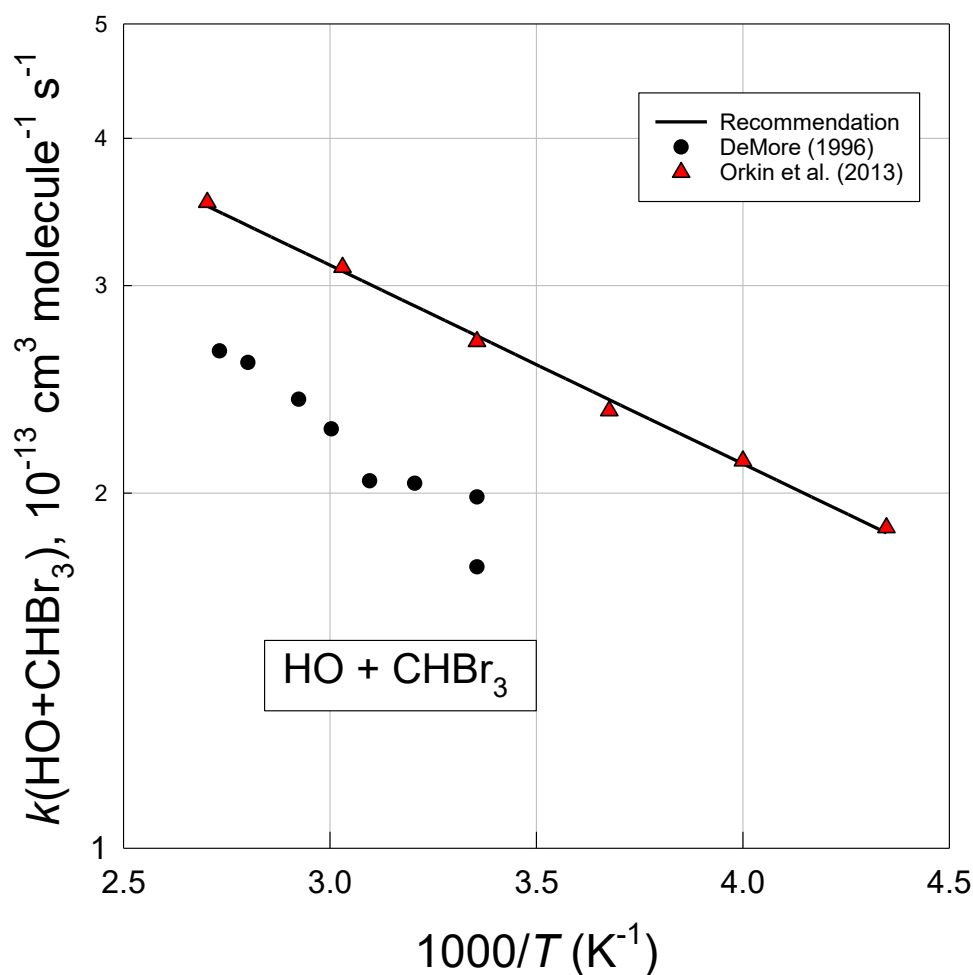
706
 707
 708 There is a substantial disagreement between the results from the relative rate study by
 709 DeMore (1996) and the absolute rate study by Orkin et al. (2013). Considerable efforts were
 710 made by Orkin et al. (2013) to assure the purity of the CHBr₃ sample and it is unlikely that
 711 the discrepancy reflects the presence of a reactive impurity in the work of Orkin et al.
 712 (2013). Orkin et al. (2013) obtained consistent results using two different versions of their
 713 experimental system over a period of several years. DeMore (1996) used CH₂Cl₂ as a
 714 reference compound. In the presence of O₂ the degradation of CH₂Cl₂ produces chlorine
 715 atoms (Niki et al., 1980). At 298 K, the rate coefficient ratio $k(\text{Cl}+\text{CHBr}_3)/k(\text{Cl}+\text{CH}_2\text{Cl}_2) =$
 716 0.79 (Atkinson et al., 2008; Kamboures et al, 2002) is about a factor of 3 lower than the rate

717 coefficient ratio $k(\text{HO}+\text{CHBr}_3)/k(\text{HO}+\text{CH}_2\text{Cl}_2) = 2.7$ (present work; Atkinson et al., 2008).
718 Additional loss of CH_2Cl_2 via reaction with chlorine atoms is a likely explanation of the
719 discrepancy between the results from DeMore (1996) and the absolute rate study by Orkin et
720 al. (2013). The preferred Arrhenius expression is derived from a fit to the data from Orkin et
721 al. (2013).

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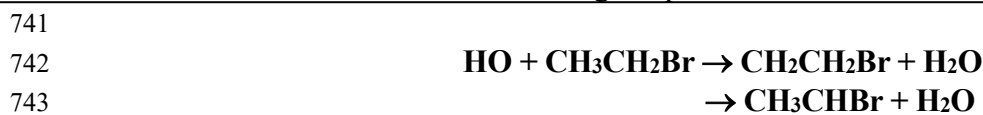
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736



737
738

739 **oBrOx17: HO + CH₃CH₂Br**
 740 Last evaluated: June 2025; Last change in preferred values: June 2009.



744
 745 **Rate coefficient data ($k = k_1 + k_2$)**
 746

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|---------------------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.77 \pm 0.34) \times 10^{-12} \exp[-(1344 \pm 86)/T]$ | 292-418 | Qiu et al. (1992), Xing et al. (1992) | DF-RF (a) |
| 3.05×10^{-13} | 298 | | |
| $1.7 \times 10^{-13} T^{0.5} \exp(-641/T)$ | 233-422 | Herndon et al. (2001) | PLP-LIF (b) |
| 3.29×10^{-13} | 297 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(2.18 \pm 0.07) \times 10^{-13}$ | 300 | Donaghy et al. (1993) | RR (c) |

747
 748 **Comments**

- 749
 750 (a) HO radicals were produced by the reaction of F atoms with H₂O in 2-3 Torr (2.7-4.0 mbar)
 751 of argon diluent gas. There is substantial overlap in the data set reported by Qiu et al. (1992)
 752 and Xing et al. (1992). For simplicity we refer to the combined data set published in these
 753 two papers as Qiu et al. (1992). Experiments were performed before and after pumping on,
 754 and removing a third of the sample. There was no discernable difference in the measured
 755 rate coefficients suggesting the absence of complications from volatile impurities. The value
 756 given at 298 K above is the average of the measurements reported by Qiu et al. (1992).
 757 (b) HO radicals were produced by either the photolysis of HONO at 355 nm or the photolysis of
 758 H₂O₂ at 248 nm in approximately 100 Torr (133 mbar) of helium. The value given at 296 K
 759 above is the average of the measurements reported by Herndon et al. (2001). The C₂H₅Br
 760 sample was checked for impurities using gas chromatography; none were found.
 761 (c) HO radicals were produced by the photolysis of CH₃ONO in one atmosphere pressure of air.
 762 Ethane was used as the reference compound and a rate coefficient ratio of
 763 $k(\text{HO}+\text{C}_2\text{H}_5\text{Br})/k(\text{HO}+\text{C}_2\text{H}_6) = 0.885 \pm 0.030$ was reported. Using $k(\text{HO}+\text{C}_2\text{H}_6) = 6.9 \times 10^{-12}$
 764 $\exp(-1000/T)$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{C}_2\text{H}_5\text{Br}) = (2.18 \pm 0.07) \times 10^{-13} \text{ cm}^3$
 765 $\text{molecule}^{-1} \text{ s}^{-1}$.

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 767 **Preferred Values**

| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 3.3×10^{-13} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $2.25 \times 10^{-12} \exp(-576/T)$ | 230-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |
| $\Delta E/R$ | ± 300 | 230-300 |

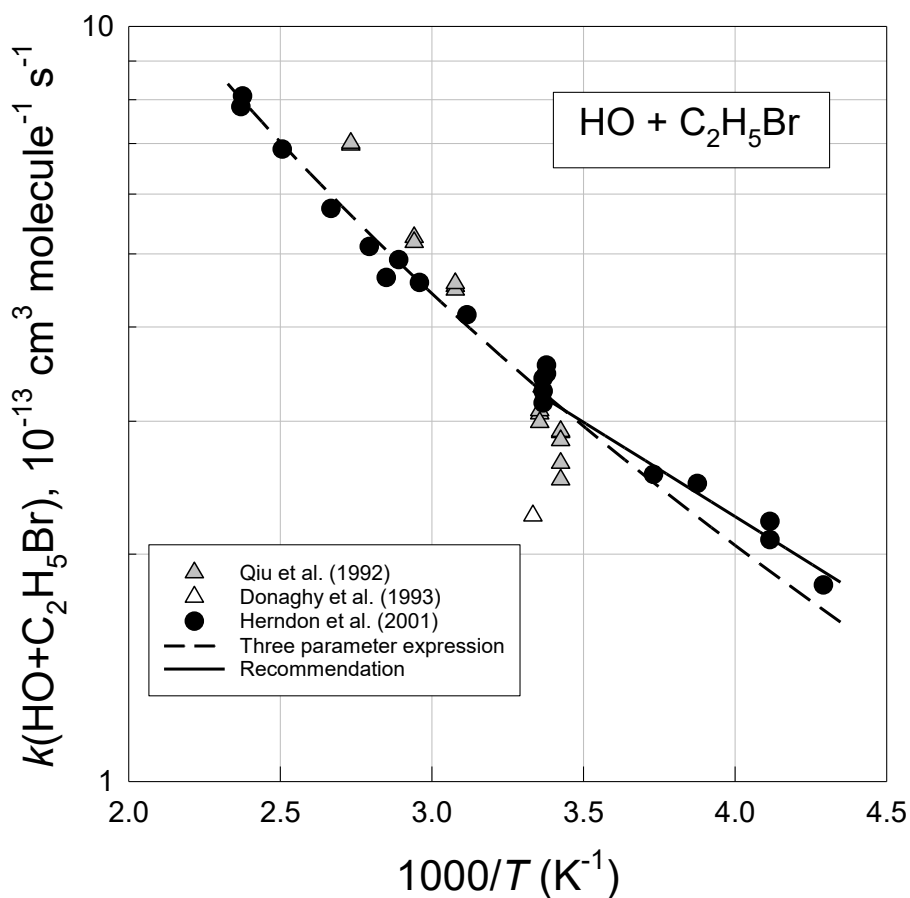
771
 772 *Comments on Preferred Values*

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 774 With the exception of the highest temperature data point (418 K from Xing et al., 1992), the

775 absolute rate coefficients of Qiu et al. (1992) and Herndon et al. (2001) are in reasonable
 776 agreement over the temperature range over which measurements were conducted. In contrast, the
 777 rate coefficient reported in the relative rate study of Donaghy et al. (1993) is significantly lower
 778 than those reported by Qiu et al. (1992) and Herndon et al. (2001). The temperature dependence
 779 reported by Qiu et al. (1992) is substantially greater than that reported by Herndon et al. (2001).
 780 Fitting the three-parameter equation $k = CT^2 \exp(-D/T)$ to the data from Qiu et al. (1992)
 781 [excluding the data point at 418 K] and Herndon et al. (2001) gives $k = 7.12 \times 10^{-18} T^2 \exp(-$
 782 $193/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Taking an average of the rate coefficients reported by Qiu et al. (1992)
 783 and Herndon et al. (2001) at 296-298 K gives our preferred value of $3.26 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 784 at 298 K. Fitting the Arrhenius expression to this data and that at lower temperatures reported
 785 by Herndon et al. (2001) gives $k = 2.25 \times 10^{-12} \exp(-576/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is
 786 preferred over the range 230-300 K.

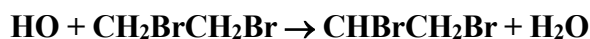
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801 **oBrOx18: HO + CH₂BrCH₂Br**
 802 Last evaluated: June 2025; Last change in preferred values: June 2009.
 803



807 **Rate coefficient data (*k*)**
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| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|---------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (2.50 ± 0.55) × 10 ⁻¹³ | 296 | Howard and Evenson (1976) | DF-LMR (a) |
| (1.46 ± 0.26) × 10 ⁻¹¹ exp[-(1283 ± 136)/ <i>T</i>] | 294-365 | Qiu et al. (1992) | DF-RF (b) |
| 1.86 × 10 ⁻¹³ | 294 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (2.15 ± 0.45) × 10 ⁻¹³ | 300 | Arnts et al. (1989) | RR (c) |

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 810 **Comments**
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- 812 (a) HO radicals were generated by the reaction of H atoms with NO₂ in 0.1-1.0 kPa (1-10 mbar) of
 813 helium.
 814 (b) HO radicals were produced by the reaction of F atoms with H₂O in 2-3 Torr (2.7-4.0 mbar) of
 815 argon. The results reported by Qiu et al. (1992) are an extension of the data set reported by
 816 Xing et al. (1992).
 817 (c) The rate coefficient ratio $k(\text{HO}+\text{CH}_2\text{BrCH}_2\text{Br})/k(\text{HO}+\text{C}_2\text{H}_6) = 0.88 \pm 0.18$ was placed on an
 818 absolute basis using $k(\text{HO}+\text{C}_2\text{H}_6) = 1.49 \times 10^{-17} T^2 \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson
 819 et al., 2006).
 820

821 **Preferred Values**
 822

| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.22 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 7.69 × 10 ⁻¹² exp(-1056/ <i>T</i>) | 290-370 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.1 | 298 |
| Δ <i>E</i> / <i>R</i> | ± 300 | 290-370 |

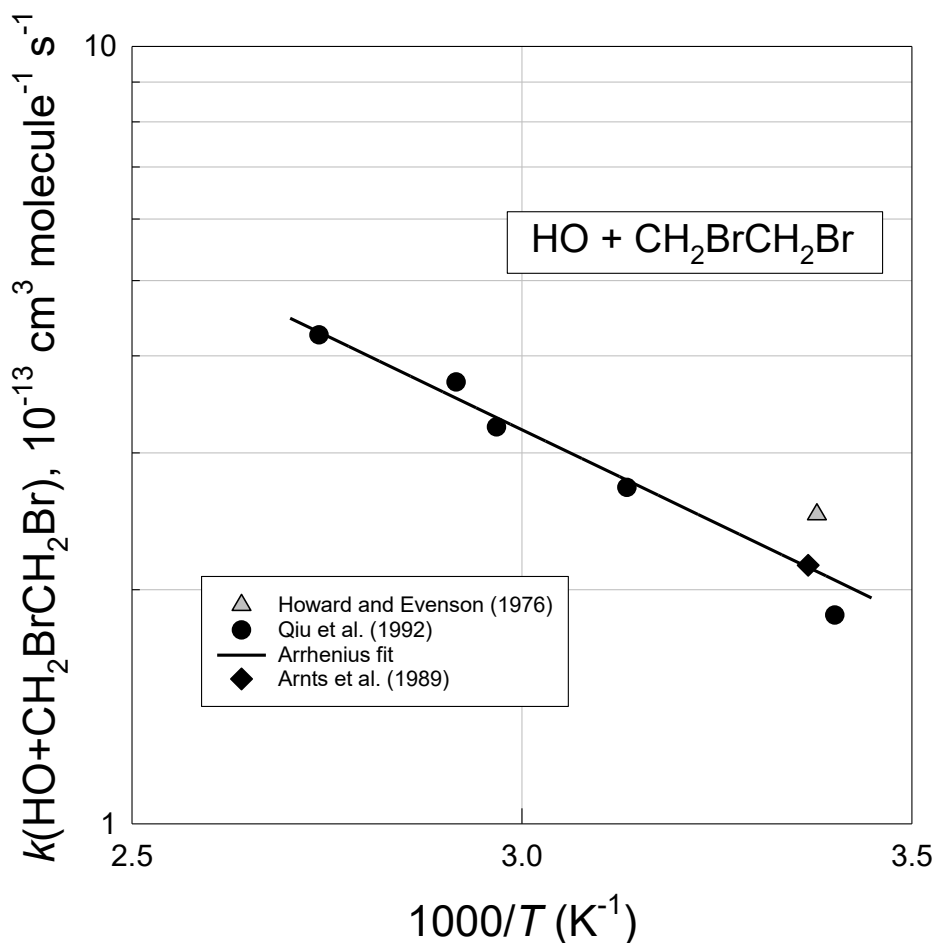
823
 824 **Comments on Preferred Values**
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826 The absolute rate coefficients of Howard and Evenson (1976), Qiu et al. (1992), and Arnts et al.
 827 (1989) are in reasonable agreement at ambient temperature. Fitting the Arrhenius expression to
 828 the combined data set from the three studies gives $k = 7.69 \times 10^{-12} \exp(-1056/T) \text{ cm}^3 \text{ molecule}^{-1}$
 829 s^{-1} (Calvert et al., 2010) which is preferred over the range 290-370 K.
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833 **References**
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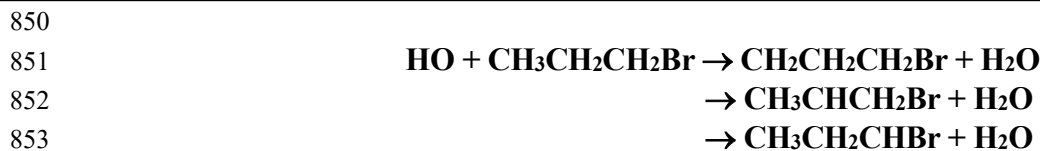
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848 **oBrOx19: HO + CH₃CH₂CH₂Br**
 849 Last evaluated: June 2025; Last change in preferred values: June 2009.



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 855 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**
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| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(5.29 \pm 0.29) \times 10^{-12} \exp[-(456 \pm 31)/T]$ | 233-372 | Téton et al. (1996) | PLP-LIF (a) |
| 1.17×10^{-12} | 298 | | |
| $(5.75 \pm 0.90) \times 10^{-12} \exp[-(504 \pm 50)/T]$ | 294-365 | Nelson et al. (1997) | DF-LIF (b) |
| $(1.01 \pm 0.10) \times 10^{-12}$ | 295 | | |
| $9.1 \times 10^{-14} T^{0.5} \exp(-157/T)$ | 230-386 | Herndon et al. (2001) | PLP-LIF (c) |
| $(8.8 \pm 0.4) \times 10^{-13}$ | 298 | | |
| $(6.6 \pm 0.52) \times 10^{-18} T^2 \exp(154 \pm 24)$ | 230-360 | Gilles et al. (2002) | PLP-LIF (d) |
| $(9.72 \pm 0.32) \times 10^{-13}$ | 297 | | |
| $2.99 \times 10^{-13} (T/298)^{2.79} \exp(369/T)$ | 210-480 | Kozlov et al. (2003) | FP-RF (e) |
| $(1.01 \pm 0.15) \times 10^{-12}$ | 298 | | |
| $1.32 \times 10^{-17} T^{1.95} \exp(25/T)$ | 297-725 | Brykov et al. (2007) | PLP-LIF (f) |
| 9.51×10^{-13} | 297 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.10 \pm 0.06) \times 10^{-12}$ | 300 | Donaghy et al. (1993) | RR (g) |

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 858 **Comments**

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 860 (a) HO radicals were generated by the photolysis of H₂O₂ at 248 nm in approximately 100 Torr
 861 (133 mbar) of helium.
 862 (b) HO radicals were generated by the reaction of H atoms with NO₂ in 1.1-2.3 Torr (1.5-3.1 kPa)
 863 of helium.
 864 (c) HO radicals were produced by the photolysis of HONO at 355 nm (third harmonic Nd:YAG
 865 laser) in approximately 100 Torr (133 mbar) of helium diluent.
 866 (d) HO radicals were generated by the photolysis of HONO at 351 nm in 50 Torr (67 kPa) of
 867 helium.
 868 (e) HO radicals were generated by the photolysis of H₂O using a xenon flash lamp. Experiments
 869 were performed in 30 Torr (4 mbar) of argon.
 870 (f) HO radicals were generated by either the photolysis of N₂O at 193 nm (ArF excimer laser) to
 871 make O(¹D) atoms in the presence of H₂O vapor, or the photolysis of HNO₃ at 248 nm (KrF
 872 excimer laser) in 6.69-26.73 kPa of helium.
 873 (g) The rate coefficient ratio $k(\text{HO} + \text{C}_3\text{H}_5\text{Br})/k(\text{HO} + \text{cyclohexane}) = 0.156 \pm 0.008$ was placed on
 874 an absolute basis using $k(\text{HO} + \text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(-262/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 875 (Atkinson, 2003).
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Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.0×10^{-12} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $3.91 \times 10^{-12} \exp(-399/T)$ | 210-300 |
| k_1/k | 0.32 | |
| k_2/k | 0.56 | |
| k_3/k | 0.12 | |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.1 | 298 |
| $\Delta \log E/R$ | ± 200 | 210-300 |
| $\Delta k_1/k$ | 0.10 | |
| $\Delta k_2/k$ | 0.05 | |
| $\Delta k_3/k$ | 0.10 | |

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Comments on Preferred Values

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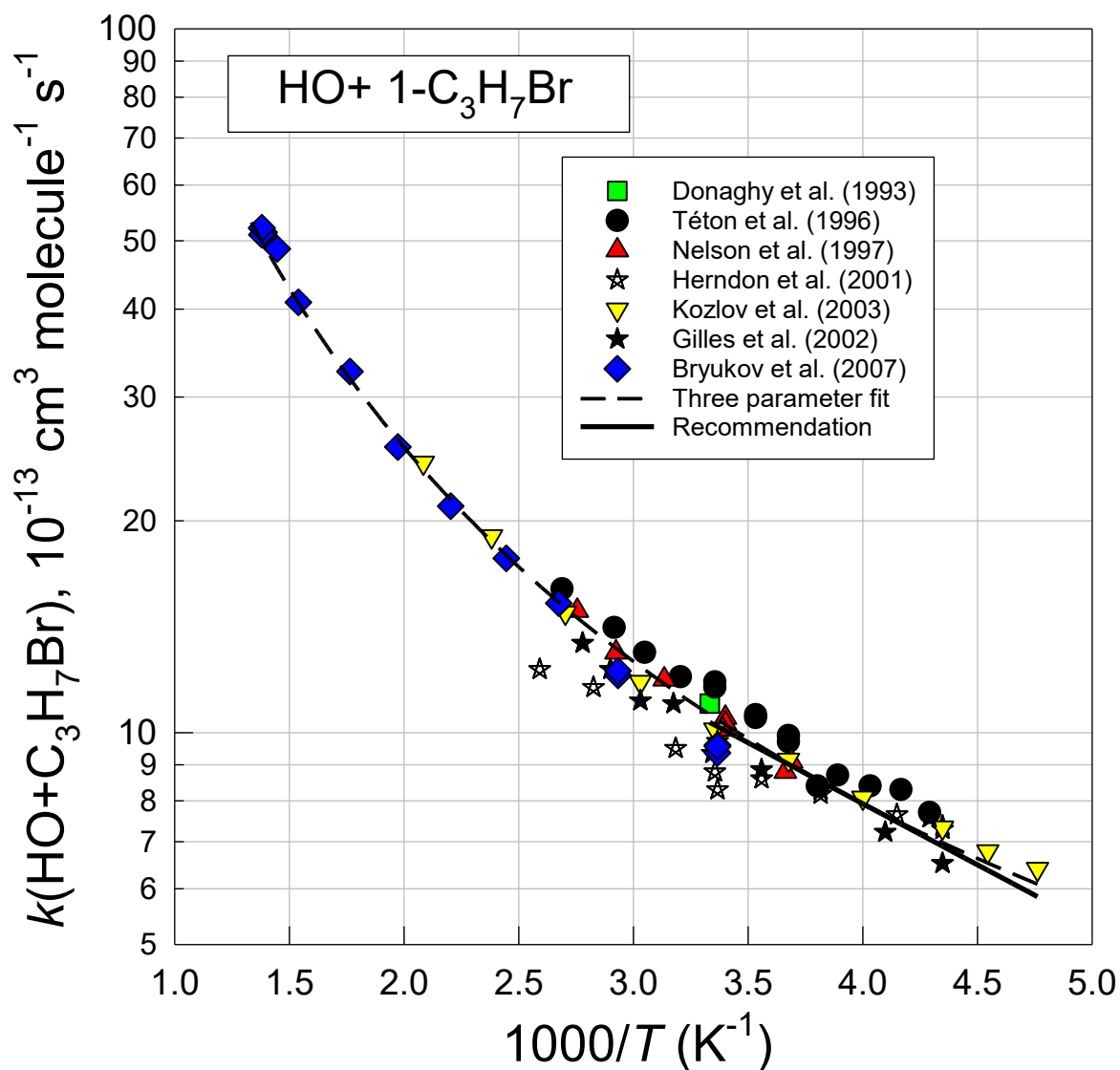
The rate coefficients obtained in the absolute rate studies by Téton et al. (1996), Nelson et al. (1997), Gilles et al. (2002), Kozlov et al. (2003), and Brykov et al. (2003) and in the relative rate study by Donaghy et al. (1993) are in good agreement. The results from the absolute rate study by Herndon et al. (2001) at ambient temperature and above lie approximately 20-30% below those from the other studies. Excluding the data from Herndon et al. (2001) and fitting the three parameter equation $k = CT^2 \exp(-D/T)$ to the remaining composite data set gives $k = 8.14 \times 10^{-18} T^2 \exp(111/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Centering this expression at 255 K with $A = Ce^2 T^2$ and $B = D + 2T$ gives $k = 3.91 \times 10^{-12} \exp(-399/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is preferred over the range 210-300 K.

From an analysis of kinetic data for the reaction of HO radicals with $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, $\text{CD}_3\text{CH}_2\text{CH}_2\text{Br}$, $\text{CD}_3\text{CH}_2\text{CD}_2\text{Br}$, $\text{CH}_3\text{CD}_2\text{CD}_2\text{Br}$, and $\text{CD}_3\text{CD}_2\text{CD}_2\text{Br}$, Gilles et al. (2002) deduced branching ratios at 298 K for abstraction at the 1-, 2-, and 3- positions in $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ of 0.32 ± 0.08 , 0.56 ± 0.04 , and 0.12 ± 0.08 , respectively. As discussed by Calvert et al. (2008), Gilles et al. (2002) conducted a study of the products of the OH radical initiated oxidation of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ in 620 Torr of air in the presence of NO_x at room temperature. Propanal and bromoacetone were identified in molar yields of 30 ± 15 and $50 \pm 20\%$, respectively. The propanal and bromoacetone yields were indistinguishable from the branching ratios for hydrogen abstraction by OH radicals at the 1- and 2- positions deduced from the experiments with the deuterated n-propyl bromide samples. At low $[\text{O}_2]$ propene was observed as a product indicating that reaction with O_2 and dissociation via Br atom elimination are competing loss mechanisms for $\text{CH}_3\text{CHCH}_2\text{Br}$ radicals. Gilles et al. (2002) derived $k_{\text{O}_2}/k_{\text{diss}} = (4.0 \pm 0.6) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$. In one atmosphere of air $k_{\text{O}_2}[\text{O}_2]/k_{\text{diss}} = 21$, and reaction with O_2 dominates the atmospheric fate of $\text{CH}_3\text{CHCH}_2\text{Br}$ radicals. Reaction of HO radicals with $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ at the 3- position is expected to be of minor (< 20%) importance. The major products of the HO radical initiated oxidation of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ are propanal and bromoacetone.

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933 **oBrOx20: HO + CH₃CHBrCH₃**
 934 Last evaluated: June 2025; Last change in preferred values: June 2009.



939 **Rate coefficient data ($k = k_1 + k_2$)**
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| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(3.58 \pm 0.47) \times 10^{-12} \exp[-(392 \pm 75)/T]$ | 233-372 | Téton et al. (1996) | PLP-LIF (a) |
| 9.42×10^{-13} | 298 | | |
| $7.0 \times 10^{-14} T^{0.5} \exp(-145/T)$ | 215-402 | Herndon et al. (2001) | PLP-LIF (b) |
| $(7.45 \pm 0.15) \times 10^{-13}$ | 298 | | |
| $1.66 \times 10^{-13} (T/298)^{2.95} \exp(461/T)$ | 210-480 | Kozlov et al. (2003) | FP-RF (c) |
| $(7.58 \pm 0.12) \times 10^{-13}$ | 298 | | |
| $1.56 \times 10^{-17} T^{4.18} \exp(922/T)$ | 297-715 | Bryukov et al. (2007) | PLP-LIF (d) |
| 7.53×10^{-13} | 297 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(8.16 \pm 0.35) \times 10^{-13}$ | 298 | Donaghy et al. (1993) | RR (e) |

941 **Comments**

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 944 (a) The value at 298 K is the average of the five determinations reported by Téton et al. (1996) at
 945 this temperature.
 946 (b) HO radicals were produced by the photolysis of HONO at 355 nm (third harmonic Nd:YAG
 947 laser) in approximately 100 Torr (133 mbar) of helium.
 948 (c) HO radicals were generated by the photolysis of H₂O using a xenon flash lamp. Experiments
 949 were performed in 30 Torr (4 mbar) of argon.
 950 (d) The value at 297 K is the average of the five determinations reported by Bryukov et al. (2003)
 951 at this temperature.
 952 (e) The rate coefficient ratio $k(\text{HO} + \text{C}_3\text{H}_5\text{Br})/k(\text{HO} + \text{cyclohexane}) = 0.117 \pm 0.005$ was placed on
 953 an absolute basis using $k(\text{HO} + \text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(-262/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 954 (Atkinson, 2003).
 955

956 **Preferred Values**
 957

| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 7.58×10^{-13} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.96 \times 10^{-12} \exp(-283/T)$ | 210-335 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.06 | 298 |
| $\Delta E/R$ | ± 200 | 210-335 |

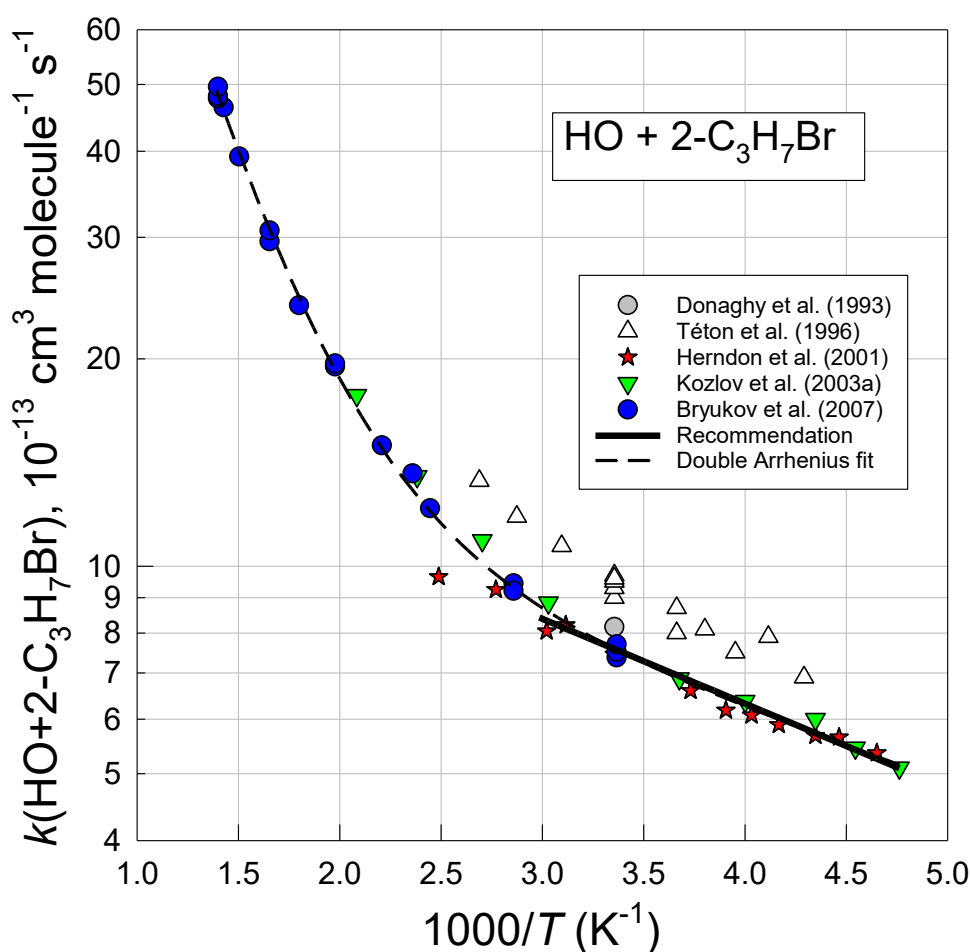
960 **Comments on Preferred Values**
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963 The rate coefficients obtained in the absolute rate studies by Herndon et al. (2001), Kozlov et al.
 964 (2003), and Bryukov et al. (2003) and in the relative rate study by Donaghy et al. (1993) are in
 965 good agreement over the temperature ranges where comparison is possible. Results from the

966 absolute rate study by Téton et al. (1996) lie approximately 20% above those from the other
 967 studies with a similar dependence on temperature. The three parameter equation $k = CT^2 \exp(-$
 968 $D/T)$ is not able to capture the magnitude of the curvature evident in the Arrhenius plot. Fitting a
 969 double Arrhenius expression of $k = A \exp(-B/T) + C \exp(-D/T)$ to the composite data set
 970 (excluding the data from Téton et al. (1996)) gives $k = 1.07 \times 10^{-10} \exp(-2413/T) + 1.66 \times 10^{-$
 971 $12 \exp(-246/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which provides a good description of the reported rate
 972 coefficients over the temperature range 210-720 K. For inclusion into atmospheric chemistry
 973 models we prefer the Arrhenius expression $k = 1.96 \times 10^{-12} \exp(-283/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 974 obtained by fitting the Arrhenius expression to the data from Donaghy et al. (1993), Herndon
 975 et al. (2001), Kozlov et al. (2003), and Bryukov et al. (2003) over the range 210-335 K.

976 977 978 979 980 981 982 983 984 985 986

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 Téton, S., El Boudali, A., and Mellouki, A.: J. Chim. Phys., 93, 274, 1996.



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989 **oBrOx21: HO + CH₃CH₂CH₂CH₂Br**
990 Last evaluated: June 2025; Last change in preferred values: June 2009.

991 **HO + CH₃CH₂CH₂CH₂Br → products**

992 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|-----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| (2.29 ± 0.07) × 10 ⁻¹² | 299 | Donaghy et al. (1993) | RR (a) |

996 **Comments**

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999 (a) The rate coefficient ratio $k(\text{HO}+\text{C}_4\text{H}_9\text{Br})/k(\text{HO}+\text{cyclohexane}) = 0.327 \pm 0.010$ was placed on
1000 an absolute basis using $k(\text{HO}+\text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(-262/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
1001 (Atkinson, 2003).

1002 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|-------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.3 × 10 ⁻¹² | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.20 | 298 |

1003 *Comments on Preferred Values*

1004
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1008 The rate coefficient reported by Donaghy et al. (1993) at 299 K is the sole study and the basis of
1009 the preferred value. There are no product studies of this reaction.

1010 **References**

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1012 Donaghy, T., Shanahan, I., Hande, M., and Fitzpatrick, S.: Int. J. Chem. Kinet., 25, 273,
1013 1993.

1019 **oBrOx22: HO + CH₃CH₂CH₂CH₂CH₂Br**
1020 Last evaluated: June 2025; Last change in preferred values: June 2009.

1021
1022 **HO + CH₃CH₂CH₂CH₂CH₂Br → products**

1023
1024 **Rate coefficient data**

1025

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|-----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| (3.71 ± 0.13) × 10 ⁻¹² | 304 | Donaghy et al. (1993) | RR (a) |

1026
1027 **Comments**

1028
1029 (a) The rate coefficient ratio $k(\text{HO}+\text{C}_5\text{H}_{11}\text{Br})/k(\text{HO}+\text{cyclohexane}) = 0.520 \pm 0.018$ was placed on
1030 an absolute basis using $k(\text{HO}+\text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(-262/T)$ cm³ molecule⁻¹ s⁻¹
1031 (Atkinson, 2003).

1032
1033 **Preferred Values**

1034

| Parameter | Value | <i>T</i> /K |
|--|-------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 3.7 × 10 ⁻¹² | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.20 | 298 |

1035
1036
1037 *Comments on Preferred Values*

1038
1039
1040 The rate coefficient reported by Donaghy et al. (1993) at 304 K is the sole study and the basis
1041 of the preferred value. There are no product data available for this reaction.

1042
1043 **References**

1044
1045 Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.
1046 Donaghy, T., Shanahan, I., Hande, M., and Fitzpatrick, S.: Int. J. Chem. Kinet., 25, 273,
1047 1993.
1048

1049 **oBrOx23: HO + CH₃CH₂CH₂CH₂CH₂CH₂Br**
1050 Last evaluated: June 2025; Last change in preferred values: June 2009.

1051
1052 **HO + CH₃CH₂CH₂CH₂CH₂CH₂Br → products**
1053
1054 **Rate coefficient data**
1055

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|-----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| (5.48 ± 0.19) × 10 ⁻¹² | 306 | Donaghy et al. (1993) | RR (a) |

1056
1057 **Comments**

1058
1059 (a) The rate coefficient ratio $k(\text{HO}+\text{C}_6\text{H}_{13}\text{Br})/k(\text{HO}+\text{cyclohexane}) = 0.763 \pm 0.027$ was placed on
1060 an absolute basis using $k(\text{HO}+\text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(-262/T)$ cm³ molecule⁻¹ s⁻¹
1061 (Atkinson, 2003).

1062
1063 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|-------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 5.5 × 10 ⁻¹² | 298 |
| <i>Reliability</i> Δ log <i>k</i> | ± 0.20 | 298 |

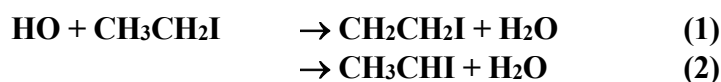
1067
1068 *Comments on Preferred Values*

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1070 The rate coefficient reported by Donaghy et al. (1993) at 306 K is the sole study and the basis
1071 of the preferred value. There are no product data available for this reaction.

1072
1073 **References**

1074
1075 Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.
1076 Donaghy, T., Shanahan, I., Hande, M., and Fitzpatrick, S.: Int. J. Chem. Kinet., 25, 273,
1077 1993.
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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|----------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $5.55 \times 10^{-12} \exp[-(830 \pm 90)/T]$ | 297-372 | Zhang et al. (2012) | FP-RF (a) |
| $(3.24 \pm 0.08) \times 10^{-13}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(7.7 \pm 1.0) \times 10^{-13}$ | 298 | Cotter et al. (2003) | DF-RF (b) |

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Comments

- (a) HO radicals were generated by the VUV flash photolysis of H₂O in 188 Torr (250 mbar) of helium. HO radicals were monitored using resonance fluorescence at 308 nm.
- (b) HO radicals were generated by the reaction of H atoms with NO₂ in 1.5 or 5.0 Torr (2.0 or 6.7 mbar) of helium diluent at 298 ± 2 K. There was no discernable effect of total pressure over the range studied. It was recognized that the measured rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_5\text{I}) = (7.7 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ could be an overestimation because of secondary loss of HO radicals via reaction with products of the HO + C₂H₅I reaction. Cotter et al. (2003) estimated that correction of the rate coefficient for possible additional loss of HO radicals via secondary reactions in their experiments would lower the rate coefficient to $5.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 3.43×10^{-13} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $5.55 \times 10^{-12} \exp(-830/T)$ | 290-380 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta E/R$ | 200 | 298 |

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Comments on Preferred Values

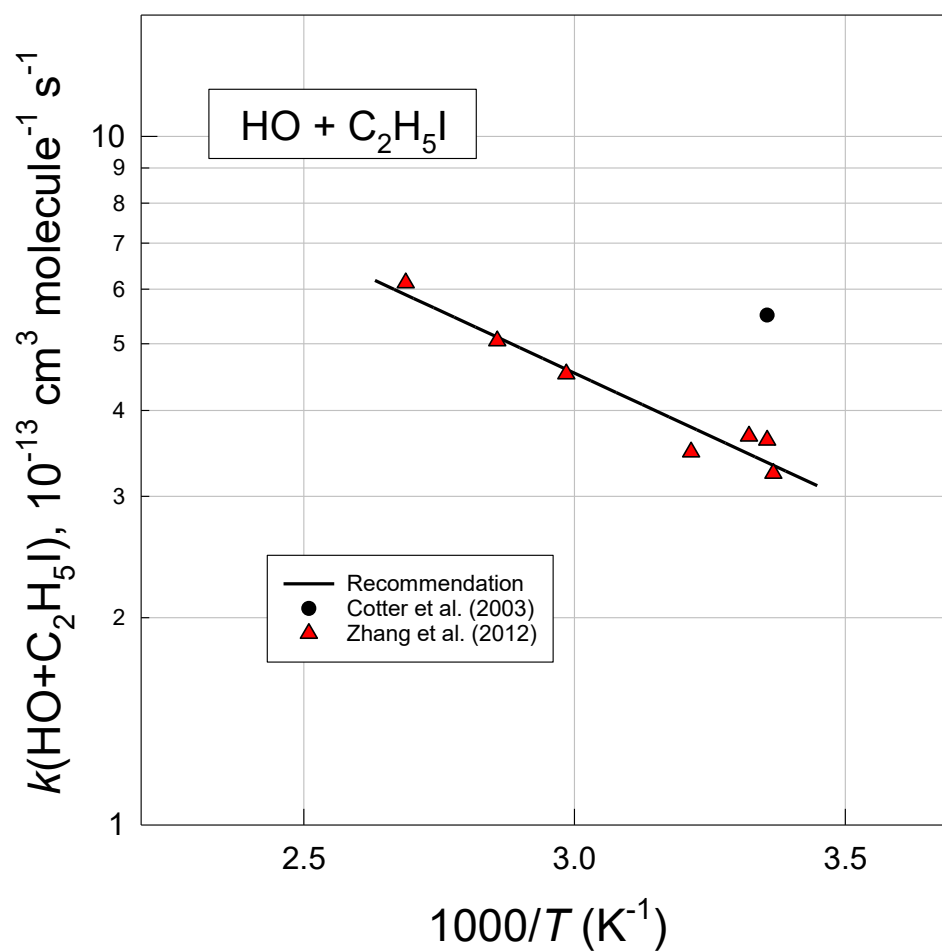
The rate coefficient at 298 K reported by Cotter et al. (2003) is significantly larger than that reported by Zhang et al. (2012). Cotter et al. (2003) considered their determination to be an upper limit because of the likely contribution of secondary reactions to the observed HO loss. The preferred expression is taken from Zhang et al. (2012) and gives $k(\text{HO} + \text{C}_2\text{H}_5\text{I}) = 3.43 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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References

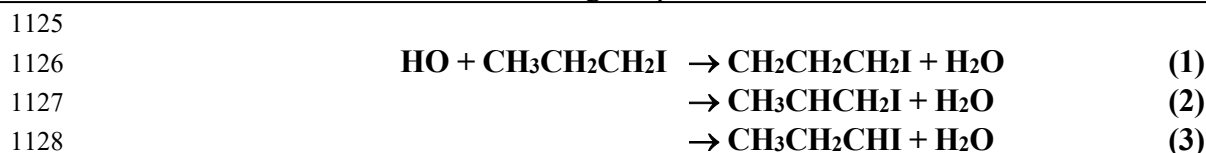
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1115 Cotter, E. S. N., Canosa-Mas, C.E., Manners, C. R., Wayne, R. P., and Shallcross, D. E.: Atmos.

1116 Environ., 37, 1125, 2003.
1117 Zhang, S., Strekowski, R.S., Monod, A., Bosland, L., and Zetzsch, C.: J. Phys. Chem. A, 116, 9497,
1118 2012.
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1123 **oIOx5: HO + CH₃CH₂CH₂I**
 1124 Last evaluated: June 2025; Last change in preferred values: June 2014



1129
 1130 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**
 1131

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.47 \pm 0.08) \times 10^{-12}$ | 298 | Carl and Crowley (2001) | PLP-RF (a) |
| $1.65 \times 10^{-11} \exp[-(780 \pm 90)/T]$ | 300-370 | Zhang et al. (2012) | FP-RF (b) |
| $(1.24 \pm 0.06) \times 10^{-12}$ | 300 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(2.5 \pm 0.3) \times 10^{-12}$ | 298 | Cotter et al. (2003) | DF-RF (c) |

1132
 1133 **Comments**

- 1134
 1135 (a) HO radicals were generated by the two photon 439.44 nm (Nd-YAG pumped dye laser) photolysis
 1136 of NO₂ (generating O(¹D) and O(³P) atoms) in the presence of H₂. Experiments were conducted in
 1137 20 Torr (27 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence at 308
 1138 nm.
 1139 (b) HO radicals were generated by the VUV flash photolysis of H₂O in 188 Torr (250 mbar) of helium
 1140 diluent. HO radicals were monitored using resonance fluorescence at 308 nm.
 1141 (c) HO radicals were generated by the reaction of H atoms with NO₂ in 1.5 or 5.0 Torr (2.0 or 6.7 mbar)
 1142 of helium diluent at 298 ± 2 K. There was no discernible effect of total pressure over the range
 1143 studied. It was noted that the measured rate coefficient could be an upper limit to $k(\text{HO}+\text{C}_3\text{H}_7\text{I})$
 1144 because of additional loss of HO radicals via reaction with products of the HO+C₃H₇I reaction.
 1145 Cotter et al. (2003) estimated that correction of the rate coefficient for possible additional loss of HO
 1146 radicals via secondary reactions would lower the rate coefficient to $1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

1147
 1148 **Preferred Values**

| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.86 \times 10^{-11} \exp(-780)/T$ | 290 -380 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.36×10^{-12} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.08 | 298 |
| $\Delta E/R$ | 200 | 290 -380 |

1152
 1153 **Comments on Preferred Values**

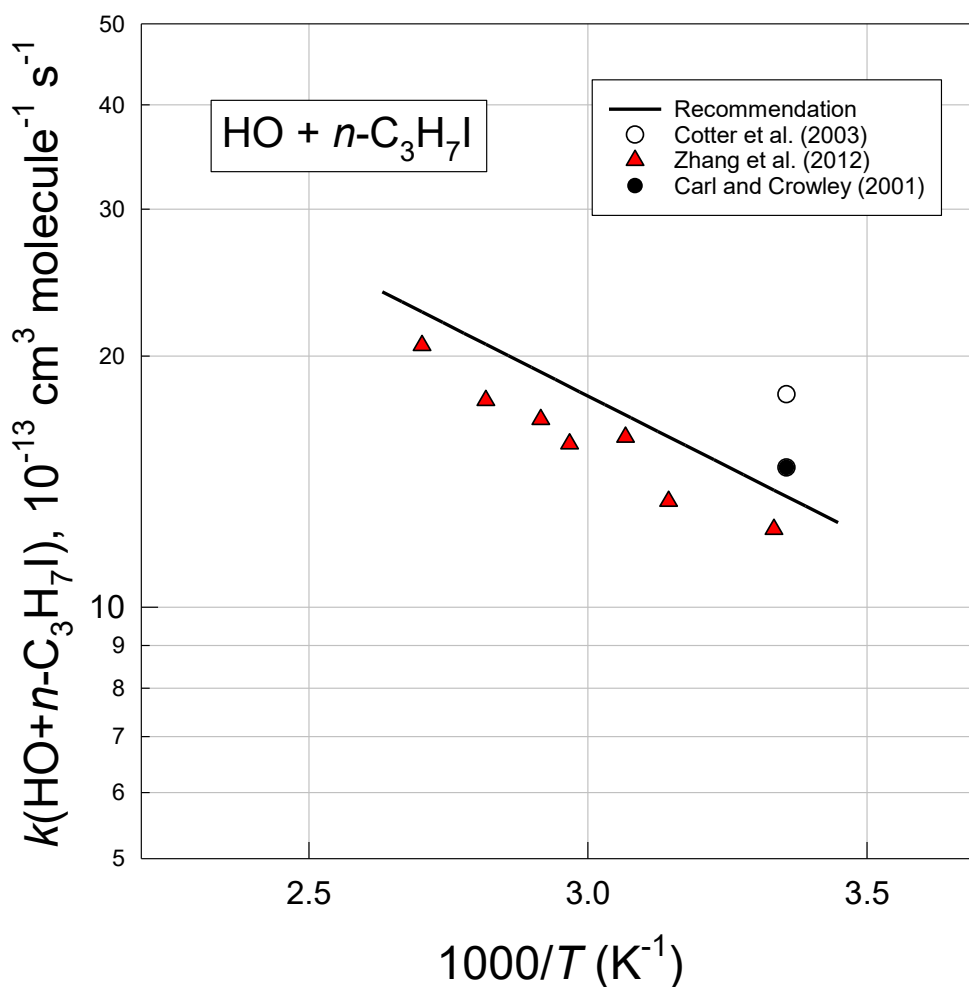
1154
 1155 Recognizing the possible contribution of secondary loss of HO radicals, Cotter et al. (2003)
 1156 considered their rate coefficient determination to be an upper limit. The value derived by Cotter et al.
 1157 (2003) corrected for possible secondary reactions is consistent, within the combined experimental
 1158 uncertainties, with that from Carl and Crowley (2001) and Zhang et al. (2012). The results from Carl and

1159 Crowley (2001) and Zhang et al. (2012) are in good agreement within the combined uncertainties. Our
1160 preferred value at 298 K is the average from Carl and Crowley (2001) and Zhang et al. (2012). The
1161 temperature dependence is taken from a fit to the work by Zhang et al. (2012) with the A-factor adjusted
1162 to reproduce the preferred value at 298 K.

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References

- Carl, S. A., and Crowley, J. N.: Atmos. Chem. Phys., 1, 1, 2001.
Cotter, E. S. N., Canosa-Mas, C.E., Manners, C. R., Wayne, R. P., and Shallcross, D. E.: Atmos.
Environ., 37, 1125, 2003.
Zhang, S., Strekowski, R.S., Monod, A., Bosland, L., and Zetzsch, C.: J. Phys. Chem. A, 116, 9497,
2012.



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1175 **oIOx6: HO + CH₃CHICH₃**
 1176 Last evaluated: June 2025; Last change in preferred values: June 2014



1181 **Rate coefficient data ($k = k_1 + k_2$)**
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| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.22 \pm 0.06) \times 10^{-12}$ | 298 | Carl and Crowley (2001) | PLP-RF (a) |
| $7.58 \times 10^{-12} \exp[-(530 \pm 80)/T]$ | 300-370 | Zhang et al. (2012) | FP-RF (b) |
| $(1.35 \pm 0.07) \times 10^{-12}$ | 299 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.6 \pm 0.2) \times 10^{-12}$ | 298 | Cotter et al. (2003) | DF-RF (c) |

1183

1184 **Comments**

- 1185 (a) HO radicals were generated by either the two photon 439.44 nm (Nd-YAG pumped dye laser)
 1186 photolysis of NO₂ (generating O(¹D) and O(³P) atoms) in the presence of H₂, or the photolysis of
 1187 HNO₃ at 248 nm. Experiments were conducted in 20 Torr (27 mbar) of argon. HO radicals were
 1188 monitored using resonance fluorescence.
- 1189 (b) HO radicals were generated by the VUV flash photolysis of H₂O in 188 Torr (250 mbar) of helium
 1190 diluent. HO radicals were monitored using resonance fluorescence at 308 nm.
- 1191 (c) HO radicals were generated by the reaction of H atoms with NO₂ in 1.5 or 5.0 Torr (2.0 or 6.7 mbar)
 1192 of helium diluent at 298 ± 2 K. There was no discernible effect of total pressure over the range
 1193 studied. It is possible that the measured rate coefficient is an overestimation of $k(\text{HO}+i\text{-C}_3\text{H}_7\text{I})$
 1194 because of additional loss of HO radicals via reaction with products of the HO+*i*-C₃H₇I reaction.
 1195 While secondary chemistry should manifest itself in curvature of the first order ($\ln([\text{HO}]_0/[\text{HO}]_t$
 1196 versus time) plots, Cotter et al. (2003) calculated that such curvature would not be discernable given
 1197 the data scatter. Cotter et al. (2003) estimated that correction of the rate coefficient for possible
 1198 additional loss of HO radicals via secondary reactions would lower the rate coefficient to 1.1×10^{-12}
 1199 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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1201 **Preferred Values**

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| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $7.64 \times 10^{-12} \exp(-530)/T$ | 290-380 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.29×10^{-12} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.08 | 298 |

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1206 *Comments on Preferred Values*

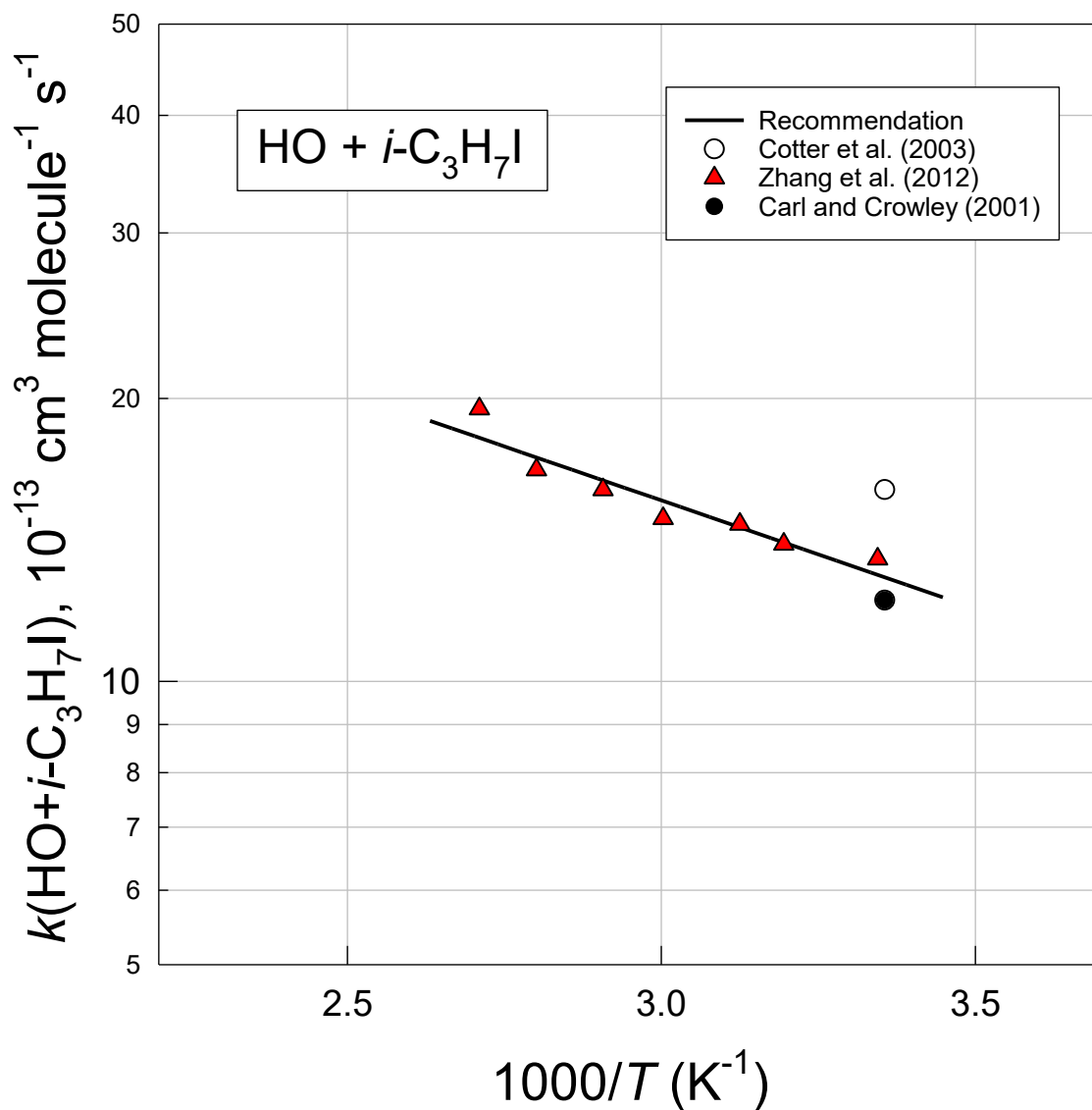
1207

1208 Recognizing the possible contribution of secondary loss of HO radicals, Cotter et al. (2003)
 1209 considered their rate coefficient determination to be an upper limit. The value derived by Cotter et al.
 1210 (2003) corrected for possible secondary reactions is consistent with those from Carl and Crowley (2001)
 1211 and Zhang et al. (2012). The results from Carl and Crowley (2001) and Zhang et al. (2012) are in good

1212 agreement within the combined uncertainties. Our recommended value at 298 K is the average from Carl
1213 and Crowley (2001) and Zhang et al. (2012). The temperature dependence is taken from a fit to the work
1214 by Zhang et al. (2012) with the A-factor adjusted to reproduce the recommended value at 298 K.
1215

1216 References

1217 Carl, S. A., and Crowley, J. N.: Atmos. Chem. Phys., 1, 1, 2001.
1218 Cotter, E. S. N., Canosa-Mas, C.E., Manners, C. R., Wayne, R. P., and Shallcross, D. E.: Atmos.
1219 Environ., 37, 1125, 2003.
1220 Zhang, S., Strekowski, R.S., Monod, A., Bosland, L., and Zetzsch, C.: J. Phys. Chem. A, 116, 9497,
1221 2012.
1222
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1227 **oFOx108: Cl + CHF₂CH₂CF₃ (HFC-245fa)**
1228 Last evaluated: June 2025; Last change in preferred values: September 2011.

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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|--------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(6.89 \pm 0.81) \times 10^{-15}$ | 297 | Chen et al. (1997) | (a) |

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Comments

1239 (a) Cl atoms were generated by the photolysis of Cl₂ in CHF₂CH₂CF₃/CF₃CHClF/Cl₂ mixtures in
1240 700 Torr (933 mbar) of N₂. The decays of CHF₂CH₂CF₃/CF₃CHClF were measured by FTIR
1241 spectroscopy. The measured rate coefficient ratio of $k(\text{Cl}+\text{CHF}_2\text{CH}_2\text{CF}_3)/k(\text{Cl}+\text{CF}_3\text{CHClF}) =$
1242 2.55 ± 0.30 was placed on an absolute basis using $k(\text{Cl}+\text{CF}_3\text{CHClF}) = 2.7 \times 10^{-15} \text{ cm}^3$
1243 $\text{molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008).

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Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 6.9×10^{-15} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.30 | 298 |

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1251 *Comments on Preferred Values*

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1253 The preferred value is based on the study by Chen et al. (1997).

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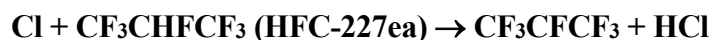
1256

References

1257 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
1258 Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 9, 4141, 2008; IUPAC Task
1259 Group on Atmospheric Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>.
1260 Chen, J., Young, V., Niki, H., and Magid, H.: J. Phys. Chem., A, 101, 2648, 1997.

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1262 **oFOx110: Cl + CF₃CHF₂CF₃ (HFC-227ea)**
 1263 Last evaluated: June 2025; Last change in preferred values: September 2011



1265 **Rate coefficient data (*k*)**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|-------------------------|------------------------|
| <i>Relative Rate Coefficients</i> | | | |
| (4.68 ± 0.52) × 10 ⁻¹⁶ | 296 | Møgelberg et al. (1996) | (a) |
| (4.10 ± 0.63) × 10 ⁻¹⁶ | 296 | | (b) |

1269 **Comments**

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 1272 (a) Cl atoms were generated by the photolysis of Cl₂ in CF₃CHF₂CF₃/CHF₂CF₃/Cl₂ and
 1273 CF₃CHF₂CF₃/CHF₂CF₂CF₃/Cl₂ mixtures in 700 Torr (933 mbar) of N₂ or air diluent. The loss of the
 1274 reactant and reference compounds was measured by FTIR spectroscopy. The measured rate
 1275 coefficient ratios of $k(\text{Cl}+\text{CF}_3\text{CHF}_2\text{CF}_3)/k(\text{Cl}+\text{CHF}_2\text{CF}_3) = 0.18 \pm 0.02$ and
 1276 $k(\text{Cl}+\text{CF}_3\text{CHF}_2\text{CF}_3)/k(\text{Cl}+\text{CHF}_2\text{CF}_2\text{CF}_3) = 0.13 \pm 0.02$ were placed on an absolute basis using
 1277 $k(\text{Cl}+\text{CHF}_2\text{CF}_3) = 2.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008) and $k(\text{Cl}+\text{CHF}_2\text{CF}_2\text{CF}_3) =$
 1278 $3.15 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Giessing et al., 1996).
 1279 (b) Using CHF₂CF₂CF₃ as reference.

1280 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|-------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 4.4 × 10 ⁻¹⁶ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.15 | 298 |

1281 **Comments on Preferred Values**

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 1286 The preferred value is the average of the relative rate determinations by Møgelberg et al. (1996).
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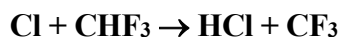
1290 **References**

- 1291
 1292 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
 1293 Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 9, 4141, 2008; IUPAC Task Group
 1294 on Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>.
 1295 Giessing, A. M. B., Feilberg, A., Møgelberg, T. E., Sehested, J., Bilde, M., Wallington, T. J., and Nielsen,
 1296 O. J.: J. Phys. Chem., 100, 6572, 1996.
 1297 Møgelberg, T. E., Sehested, J., Bilde, M., Wallington, T. J., and Nielsen, O.J.: J. Phys. Chem., 100, 8882,
 1298 1996.
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oFOx111: Cl + CHF₃

Last evaluated: June 2025; Last change in preferred values: September 2011.



$\Delta H^\circ = 17.9 \text{ kJ mol}^{-1}$

Rate coefficient data

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|---------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(4.3 \pm 1.5) \times 10^{-16}$ | 298 | Jourdain et al., 1976 | DF-MS (a) |
| <i>Relative Rate Coefficients</i> | | | |
| $4.6 \times 10^{-13} \exp[-(3520)/T]$ | 303-399 | Coomber and Whittle, 1966 | RR (b) |
| 3.4×10^{-18} | 298 | | |

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Comments

- (a) Experiments were performed in 0.3-3 Torr of helium diluent.
 (b) The reaction rate coefficients were measured using a competitive method with Cl atoms generated via photolysis of Cl₂ at 366 nm (mercury lamp). The expression in the table above was derived from the measured ratios $k_{\text{CH}_4}/k_{\text{C}_2\text{F}_5\text{H}} = 12.4 \exp[(1450 \pm 40)/RT]$ and $k_{\text{C}_2\text{F}_5\text{H}}/k_{\text{CHF}_3} = 1.16 \exp[(3080 \pm 70)/RT]$ which leads to $k_{\text{CH}_4}/k_{\text{CHF}_3} = 14.4 \exp[(4530 \pm 80)/RT] = 14.4 \exp[(2280 \pm 40)/T]$. Using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{Cl} + \text{CHF}_3) = 4.6 \times 10^{-13} \exp(-3520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. At 298 K this expression gives $k(\text{Cl} + \text{CHF}_3) = 3.4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 3.4×10^{-18} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.5 | 298 |

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Comments on Preferred Values

The rate coefficient reported by Jourdain et al. at 298 K is two orders of magnitude greater than that obtained from the data from Coomber and Whittle. The reaction endothermicity of 17.9 kJ mol⁻¹ provides a lower limit for the activation energy ($E_a/R = 2150$) which combined with an estimate of 1×10^{-12} for the A factor gives an upper limit of $k(\text{Cl} + \text{CHF}_3) < 7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. In the absolute rate study by Jourdain et al. a contribution from reaction with reactive impurities is difficult to exclude. The study by Coomber and Whittle gives a rate coefficient ratio of $k(\text{Cl} + \text{CH}_4)/k(\text{Cl} + \text{C}_2\text{HF}_5) = 144$ which is approximately a factor of two lower than the ratio of the preferred rate coefficients $k(\text{Cl} + \text{CH}_4)/k(\text{Cl} + \text{C}_2\text{HF}_5) = 385$ (Atkinson et al., 2006; 2008). The preferred value of $k(\text{Cl} + \text{CHF}_3) = 3.4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is based on the results from Coomber and Whittle and has substantial uncertainty.

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1350 **Cl + CH₃Br → HCl + CH₂Br**

1351 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|---|------------------|------------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 1.55 × 10 ⁻¹¹ exp[-(1070 ± 50)/T] (4.38 ± 0.55) × 10 ⁻¹³ | 222-393.5 298 | Gierczak et al. (1994) | PLP-RF (a) |
| 1.66 × 10 ⁻¹¹ exp[-(1072 ± 46)/T] (4.83 ± 0.12) × 10 ⁻¹³ | 273-363 303 | Kambanis et al. (1997) | VLPR-MS (b) |
| 1.02 × 10 ⁻¹⁵ T ^{1.42} exp(-605/T) 4.5 × 10 ⁻¹³ | 213-697 298 | Piety et al. (1998) | PLP-RF (c) |
| 1.55 × 10 ⁻¹¹ exp[-(1070 ± 50)/T] (4.6 ± 0.2) × 10 ⁻¹³ | 298-350 298 | Larin et al. (2018) | DF-RF (d) |
| <i>Relative Rate Coefficients</i> | | | |
| 1.26 × 10 ⁻¹¹ exp(-1565/T) 6.6 × 10 ⁻¹⁴ | 273-368 298 | Tschuikow-Roux et al. (1988) | RR (e) |
| 1.07 × 10 ⁻¹¹ exp(-935/T) 4.5 × 10 ⁻¹³ | 231-295 295 | Orlando et al. (1996) | RR (f) |
| 9.04 × 10 ⁻¹² exp(-886/T) 4.5 × 10 ⁻¹³ | 298-527 298 | Gola et al. (2010) | RR (g) |

1355 **Comments**

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- 1358 (a) The reaction rate coefficients were measured by generating Cl atoms via 308 nm laser
 1359 photolysis of Cl₂ and measuring their temporal profiles via resonance fluorescence
 1360 detection. Experiments were performed in approximately 50 Torr (66.7 mbar) of helium.
- 1361 (b) The reaction rate coefficients were measured using a very low pressure reactor, employing a
 1362 microwave discharge in Cl₂ for the generation of Cl atoms with mass spectrometric
 1363 detection of reactants and products. Experiments were performed in approximately 1 mTorr
 1364 (1.33 mbar) of helium.
- 1365 (c) The reaction rate coefficients were measured by generating Cl atoms via 266 nm laser
 1366 photolysis of Cl₂CO (or Cl₂ at 355 nm in a few experiments) and measuring their temporal
 1367 profiles via resonance fluorescence detection. Experiments were performed at 161 – 697 K
 1368 in 20 - 250 Torr (27 - 270 mbar) of nitrogen. At temperatures in the range 161 – 177 K
 1369 reversible addition of Cl atoms to give the CH₃BrCl adduct was observed. For T ≥ 213 K
 1370 where hydrogen abstraction is the dominant reaction pathway the Arrhenius expression
 1371 given in the table above was obtained.
- 1372 (d) Cl atoms generated by microwave discharge of Cl₂ in helium diluent. Cl atoms were
 1373 detected using resonance fluorescence at 118.9 nm.
- 1374 (e) Cl atoms were generated by the photolysis of Cl₂ at 424 nm, and the concentrations of the
 1375 reactions products CH₂ClBr and CH₃Cl measured by GC. The measured rate coefficient
 1376 ratio of $k(\text{Cl} + \text{CH}_3\text{Br})/k(\text{Cl} + \text{CH}_4) = (1.91 \pm 0.09) \exp[-(325 \pm 10)/T]$ is placed on an
 1377 absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et
 1378 al., 2006).
- 1379 (f) Cl atoms were generated by the photolysis of Cl₂. The decays of the reactant and reference
 1380 organic were measured by FTIR spectroscopy. Experiments were performed in

1381 approximately 700 Torr (933 mbar) of N₂. The measured rate coefficient was placed on an
 1382 absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et
 1383 al., 2006).
 1384 (g) The decays of the reactant and reference (CH₄) organic were measured by GC. The
 1385 measured rate coefficient ratios were placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times$
 1386 $10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).
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1388 Preferred Values

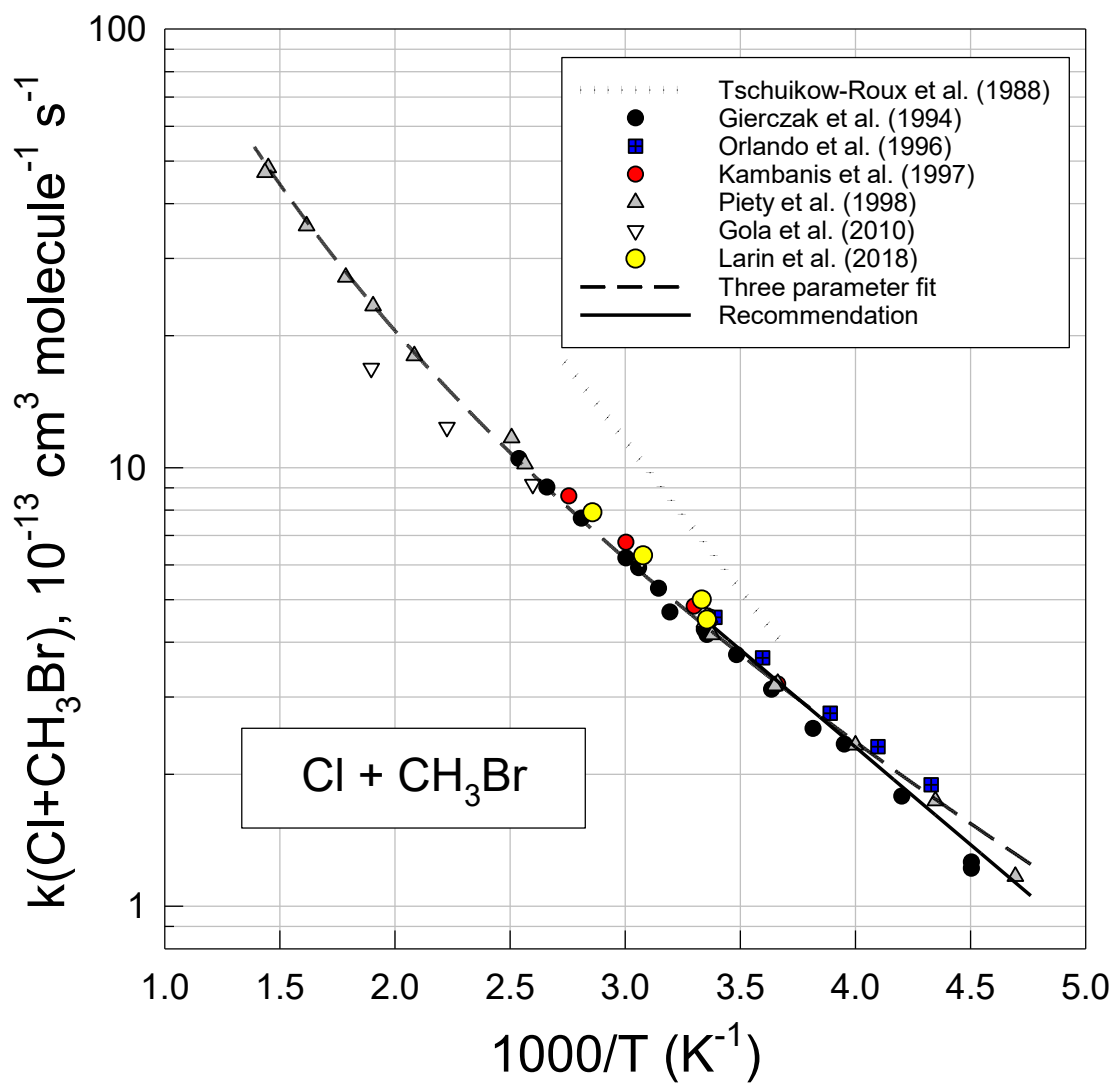
| 1389 Parameter | Value | T/K |
|--|--------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 4.5×10^{-13} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.38 \times 10^{-11} \exp(-1020/T)$ | 210-300 |
| 1390 <i>Reliability</i> | | |
| $\Delta \log k$ | 0.05 | 298 |
| $\Delta(E/R)$ | ± 100 | 210-300 |

1392 Comments on Preferred Values

1393 The preferred value at 298 K is an average of the results reported by Gierczak et al. (1994),
 1394 Kambanis et al. (1997), Piety et al. (1998), Orlando et al. (1996), and Gola et al. (2010). The
 1395 expression for the temperature dependence listed in the Table of preferred values is derived from
 1396 the fit to the data of these studies below 300 K. The values reported by Tschuikow-Roux et al.
 1397 are not used because they seem to be systematically higher than the results of the other
 1398 measurements. The results reported by Larin et al. (2018) are consistent with the preferred
 1399 value. At temperatures of 161 – 177 K the reaction leads to the reversible formation of the
 1400 adduct CH₃BrCl. For temperatures above 213 K there is no experimental evidence for
 1401 formation of the adduct and reaction proceeds via hydrogen abstraction (Piety et al., 1998;
 1402 Enami et al., 2005). For temperatures above 298 K there is some disagreement between the
 1403 results from Piety et al. (1998) and Gola et al. (2010). A fit of the modified Arrhenius expression
 1404 to the entire data set from Gierczak et al., Kambanis et al., Piety et al., Orlando et al., and Gola
 1405 et al. gives $k = 1.78 \times 10^{-17} T^2 \exp(-396/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and is preferred for 550 K > T >
 1406 298 K.
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1432 **HO + CF₂=CF₂ → products**

1433 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (1.02 ± 0.05) × 10 ⁻¹¹ | 298 | Orkin et al., 1997 | FP-RF (a) |
| 3.39 × 10 ⁻¹² exp[(323±11)/ <i>T</i>] | 250-370 | Orkin et al., 2002 | FP-RF (a) |
| (1.00 ± 0.015) × 10 ⁻¹¹ | 298 | | |
| (8.0 ± 0.3) × 10 ⁻¹² | 370 | Orkin et al., 2011 | FP-RF (a) |
| (7.09 ± 0.02) × 10 ⁻¹² | 480 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (1.07 ± 0.34) × 10 ⁻¹¹ | 298 | Acerboni et al., 1999 | RR (b) |
| (1.07 ± 0.15) × 10 ⁻¹¹ | 298 | | |

1437 **Comments**

- 1438 (a) HO radicals were generated by the photolysis of H₂O by a xenon flash lamp in 100 Torr (133
 1439 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence.
 1440 (b) Photolysis of CH₃ONO in C₂F₄-C₃H₆-NO and C₂F₄-cyclohexane-NO mixtures in 740 Torr (986
 1441 mbar) of air diluent was used to generate HO radicals and measure $k(\text{C}_2\text{F}_4)/k(\text{C}_3\text{H}_6) =$
 1442 0.375 ± 0.118 and $k(\text{C}_2\text{F}_4)/k(\text{cyclohexane}) = 1.566 \pm 0.226$. Using $k(\text{HO} + \text{C}_3\text{H}_6) = 2.85 \times 10^{-11}$
 1443 (Atkinson et al., 2006) and $k(\text{HO} + \text{cyclohexane}) = 6.85 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al.,
 1444 2015) gives $k(\text{HO} + \text{C}_2\text{F}_4) = (1.07 \pm 0.34) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(1.07 \pm 0.15) \times 10^{-11} \text{ cm}^3$
 1445 $\text{molecule}^{-1} \text{ s}^{-1}$.

1446 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.04 × 10 ⁻¹¹ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 3.84 × 10 ⁻¹² exp(297/ <i>T</i>) | 250-500 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.06 | 298 |
| Δ E/R | ± 100 | 250-500 |

1452 **Comments on Preferred Values**

1453 The preferred value at 298 K is an average of the absolute rate determinations by Orkin et al.
 1454 (1997) and (2002) and the relative rate determination by Acerboni et al. (1999). The temperature
 1455 dependence is derived from a fit to the data from Orkin et al. (2002) and (2011) with the A factor
 1456 adjusted to give the preferred rate coefficient at 298 K.

1457 The reaction proceeds via addition to the >C=C< double bond. Based upon the behavior of the
 1458 reaction of HO radicals with similar halogenated alkenes such as CH₂=CF₂ (Howard, 1976) it is
 1459 expected that the kinetics of the reaction will be at the high pressure limit for total pressures above
 1460

1463 approximately 5 Torr (7 mbar). Consistent with this expectation there is no discernable difference
 1464 between the rate coefficient measured in 100 Torr of argon diluent by Orkin et al. (1997, 2002) and
 1465 that measured in 740 Torr of air by Acerboni et al. (1999). The HO radical initiated oxidation of
 1466 $\text{CF}_2=\text{CF}_2$ will give COF_2 as the major product.

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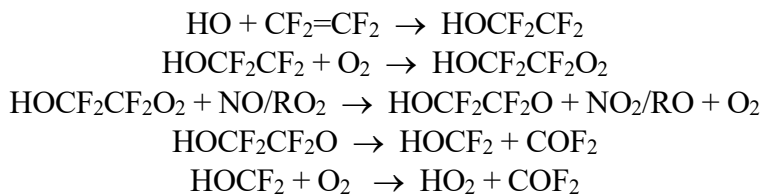
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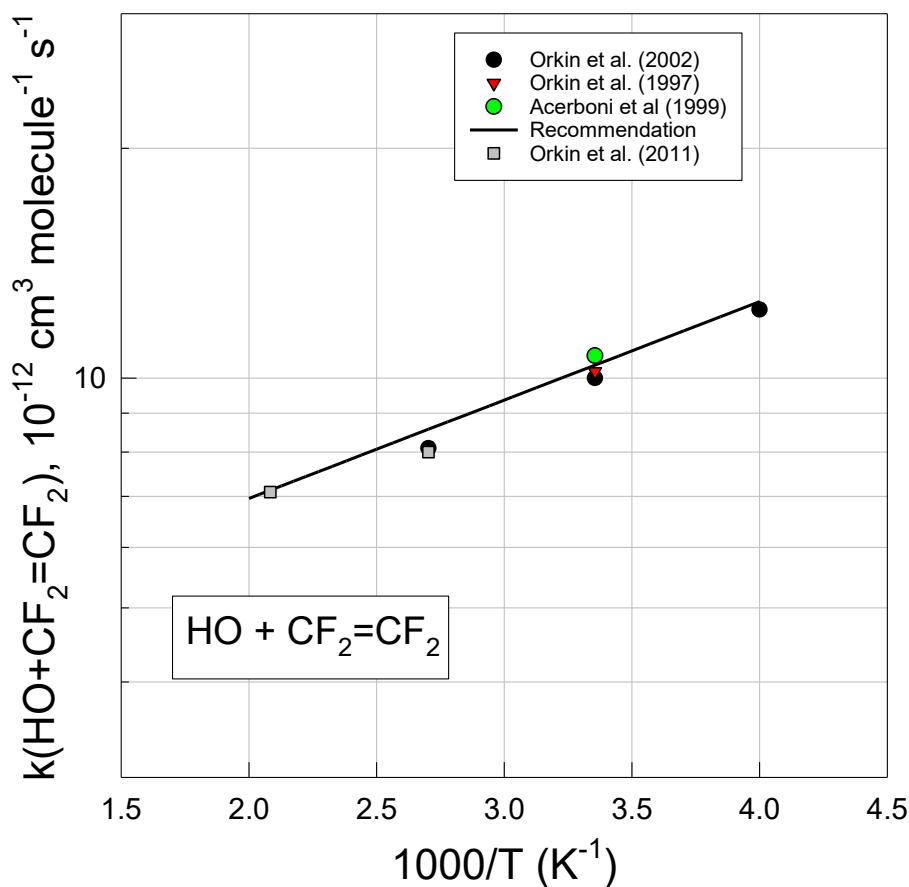
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1490 **HO + CF₃CF=CH₂ (HFO-1234yf) → products**

1491 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 1.41 × 10 ⁻¹² exp[-(64±27)/T] | 252-370 | Orkin et al. (1997) | FP-RF (a) |
| (1.12 ± 0.02) × 10 ⁻¹² | 298 | | |
| 1.26 × 10 ⁻¹² exp[-(35±10)/T] | 207-380 | Papadimitriou et al. (2008) | PLP-LIF (b) |
| (1.12 ± 0.02) × 10 ⁻¹² | 296 | | |
| 1.145 × 10 ⁻¹² exp[-13/T] | 220-298 | Orkin et al. (2010) | FP-RF (c) |
| (1.096 ± 0.007) × 10 ⁻¹² | 298 | | |
| 1.54 × 10 ⁻¹² exp[100/T] | 250-430 | Tokuhashi et al. (2018) | LP, FP-LIF (d) |
| (1.10 ± 0.01) × 10 ⁻¹² | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (9.04 ± 0.67) × 10 ⁻¹³ | 296 | Nielsen et al. (2007) | RR (e) |
| (9.82 ± 0.55) × 10 ⁻¹³ | 296 | | |

1495 **Comments**

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- 1498 (a) HO radicals were generated by the photolysis of H₂O by a xenon flash lamp in 100 Torr (133
- 1499 mbar) of argon diluent.
- 1500 (b) HO radicals were produced using the pulsed laser photolysis of either H₂O₂ or HNO₃ at 248
- 1501 nm. Experiments at 296K were conducted in a total pressure of 25-600 Torr (33-800 mbar)
- 1502 using helium, nitrogen, or SF₆ diluent. There was no discernable effect of total pressure or
- 1503 diluent on the kinetics of the reaction.
- 1504 (c) HO radicals were generated by the photolysis of H₂O by a xenon flash lamp in 30-300 Torr (40-
- 1505 400 mbar) of argon diluent.
- 1506 (d) HO radicals were generated by either flash photolysis or pulsed laser photolysis. In the flash
- 1507 photolysis experiments one chemical system (photolysis of water vapor) was employed while in
- 1508 the laser photolysis experiments three different chemical systems were used to generate HO
- 1509 radicals. There was no discernible difference in results obtained using the different methods.
- 1510 Experiments were performed in 5-200 Torr of argon or helium diluent, there was no discernible
- 1511 effect of pressure or diluent gas. The CF₃CF=CH₂ sample was purified before use and determined
- 1512 to be 99.99% pure.
- 1513 (e) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO
- 1514 radicals. The loss of CF₃CF=CH₂ was measured relative to those of C₂H₂ and C₂H₄ and used
- 1515 to measure the rate coefficient ratios $k(\text{CF}_3\text{CF}=\text{CH}_2)/k(\text{C}_2\text{H}_2) = 1.21 \pm 0.09$ and
- 1516 $k(\text{CF}_3\text{CF}=\text{CH}_2)/k(\text{C}_2\text{H}_4) = 0.125 \pm 0.007$. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ and $k(\text{HO} +$
- 1517 $\text{C}_2\text{H}_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{CF}_3\text{CF}=\text{CH}_2) = (9.04 \pm 0.67) \times 10^{-13}$
- 1518 cm³ molecule⁻¹ s⁻¹ and $(9.82 \pm 0.55) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.
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- 1520
- 1521

1522 **Preferred Values**

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| Parameter | Value | T/K |
|--|------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.12×10^{-12} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.16 \times 10^{-12} \exp(-10/T)$ | 200-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| $\Delta E/R$ | ± 100 | 200-300 |

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1527 *Comments on Preferred Values*

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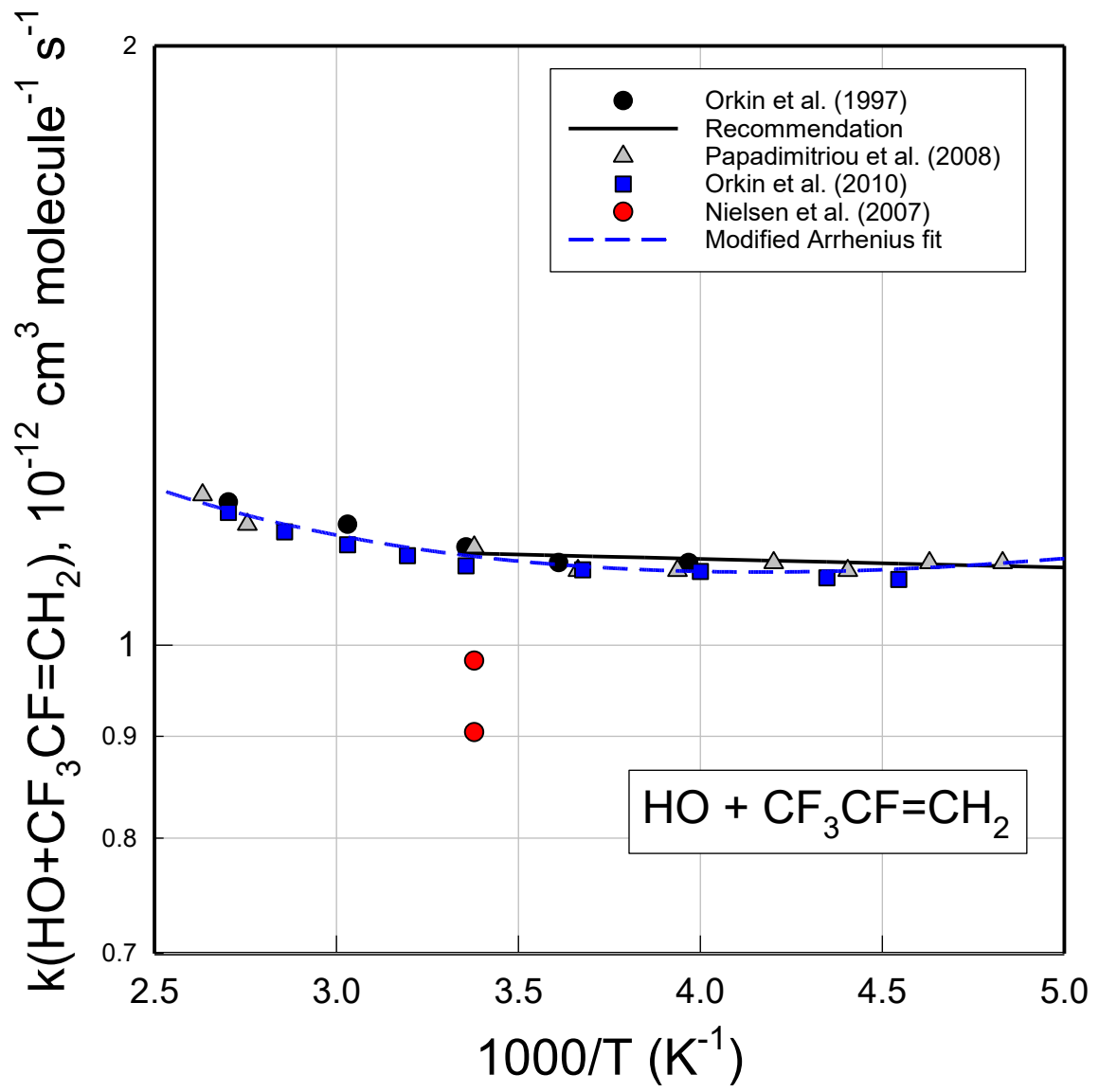
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The absolute rate measurements by Orkin et al. (1997), Papadimitriou et al. (2008), Orkin et al. (2010), and Tokuhashi et al. (2018) are in excellent agreement (within 5% at all temperatures studied) while the relative rate measurements by Nielsen et al. (2008) at 296 K lie approximately 15% below those from the absolute studies. Orkin et al. (1997), Papadimitriou et al. (2008), and Tokuhashi et al. (2018) showed that for pressures above 5 Torr there is no effect of total pressure and the reaction is at, or near, the high pressure limit. The preferred value at 298 K is the average from Orkin et al. (1997), Papadimitriou et al. (2008), and Orkin et al. (2010). The precision of the absolute rate measurements for this reaction are excellent and a small, but discernable, curvature is evident in the Arrhenius plot. A fit of a modified Arrhenius expression to the entire data set from Orkin et al. (1997), Papadimitriou et al. (2008), and Orkin et al. (2010) gives $k = 0.545 \times (T/298)^{0.882} \exp(212/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A fit of the Arrhenius expression to the data below 300 K with the A-factor adjusted to reproduce the preferred value of k at 298 K gives $k = 1.16 \times 10^{-12} \exp(-10/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The data from Tokuhashi et al. (2018) are in good agreement with the preferred value. For simplicity and consistency within the IUPAC database we prefer the simple Arrhenius expression. The HO radical initiated oxidation of $\text{CF}_3\text{CF}=\text{CH}_2$ gives $\text{CF}_3\text{C}(\text{O})\text{F}$ and HCHO as products (Hurley et al., 2008). The atmospheric fate of $\text{CF}_3\text{C}(\text{O})\text{F}$ is hydrolysis to give $\text{CF}_3\text{C}(\text{O})\text{OH}$ (trifluoroacetic acid).

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1567 **HO + E-CF₃CH=CHF (HFO-1234ze(E)) → products**

1569 **Rate coefficient data**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|---------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| See comment (a) | 220-370 | Orkin et al. (2010) | FP-RF (a) |
| $(7.11 \pm 0.05) \times 10^{-13}$ | 298 | | |
| $7.6 \times 10^{-13} (T/298)^{2.44} \exp(666/T)$ | 263-358 | Antiñolo et al. (2017) | PLP-LIF (b) |
| $(7.06 \pm 0.27) \times 10^{-13}$ | 298 | | |
| $4.8 \times 10^{-13} (T/298)^{0.727} \exp(110/T)$ | 220-430 | Tokuhashi et al. (2021) | FP, LP-LIF (c) |
| $(7.03 \pm 0.03) \times 10^{-13}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(8.00 \pm 0.82) \times 10^{-13}$ | 296 | Søndergaard et al. (2007) | RR (d) |
| $(8.72 \pm 0.47) \times 10^{-13}$ | 296 | | |
| $1.05 \times 10^{-12} \exp(-118/T)$ | 253-328 | Zhang et al. (2015) | RR (e) |
| $(7.42 \pm 0.28) \times 10^{-13}$ | 298 | | |
| $(7.14 \pm 0.34) \times 10^{-13}$ | 298 | | |

1572 **Comments**

- 1573
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- 1575 (a) HO radicals were generated by the photolysis of H₂O by a xenon flash lamp in 30-200 Torr (40-
 1576 267 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence. There was
 1577 no discernable (<5%) effect of total pressure over the range studied on the rate of reaction. A small
 1578 but distinct curvature was evident in the Arrhenius plot and a modified Arrhenius expression, $k =$
 1579 $1.115 \times 10^{-13} (T/298)^{2.03} \exp(552/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used to best represent the data.
- 1580 (b) HO radicals were generated by the pulsed laser photolysis of H₂O₂ or HNO₃ and monitored using
 1581 laser induced fluorescence in 45-300 Torr of helium diluent. There was no discernable effect of total
 1582 pressure over the range studied.
- 1583 (c) HO radicals were generated by either flash photolysis or laser photolysis and were monitored using
 1584 laser induced fluorescence. In the flash photolysis experiments photolysis of water vapor was
 1585 employed while in the laser photolysis experiments photolysis of N₂O to produce O(¹D) atoms in
 1586 the presence of either water vapor or CH₄ were used to generate HO radicals. There was no
 1587 discernible difference in results obtained using the different methods. Experiments were performed
 1588 in 5-200 Torr of argon or helium diluent, there was no discernible effect of pressure or diluent gas.
 1589 The CF₃CH=CHF sample was purified before use and the purity of the purified sample was
 1590 determined to be 99.99%.
- 1591 (d) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The
 1592 loss of E-CF₃CH=CHF was measured relative to C₂H₂ and C₂H₄ and used to measure the rate
 1593 coefficient ratios $k(\text{CF}_3\text{CH}=\text{CHF})/k(\text{C}_2\text{H}_2) = 1.07 \pm 0.11$ and $k(\text{E-CF}_3\text{CH}=\text{CHF})/k(\text{C}_2\text{H}_2) =$
 1594 0.111 ± 0.006 . Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-$
 1595 12 (Atkinson et al., 2006) gives $k(\text{HO} + \text{E-CF}_3\text{CH}=\text{CHF}) = (8.00 \pm 0.82) \times 10^{-13}$ and $(8.72 \pm 0.47) \times 10^{-$
 1596 $13 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 1597 (e) Photolysis of O₃ in the presence of water vapor in 200 Torr of helium diluent was used to generate
 1598 HO radicals. The loss of E-CF₃CH=CHF was measured relative to n-C₄H₁₀ and n-C₅H₁₂ and used to
 1599 measure rate coefficient ratios $k(\text{E-CF}_3\text{CH}=\text{CHF})/k(n\text{-C}_4\text{H}_{10})$ and $k(\text{E-CF}_3\text{CH}=\text{CHF})/k(n\text{-C}_5\text{H}_{12})$
 1600 over the temperature range 253-328 K. Rate coefficient ratios at 298 K were $k(\text{E-CF}_3\text{CH}=\text{CHF})/k(n\text{-}$
 1601 $\text{C}_4\text{H}_{10}) = 0.291 \pm 0.011$ and $k(\text{E-CF}_3\text{CH}=\text{CHF})/k(n\text{-C}_5\text{H}_{12}) = 0.187 \pm 0.009$. Using $k(\text{HO} + n\text{-C}_4\text{H}_{10}) =$

1602 $9.80 \times 10^{-12} \exp(-425/T)$ (Atkinson et al., 2006) and $k(\text{HO} + n\text{-C}_5\text{H}_{12}) = 1.81 \times 10^{-11} \exp(-452/T) \text{ cm}^3$
 1603 $\text{molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2008) gives $k(\text{HO} + E\text{-CF}_3\text{CH=CHF}) = (7.42 \pm 0.28) \times 10^{-13}$ and $(7.14$
 1604 $\pm 0.34) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

1606 Preferred Values

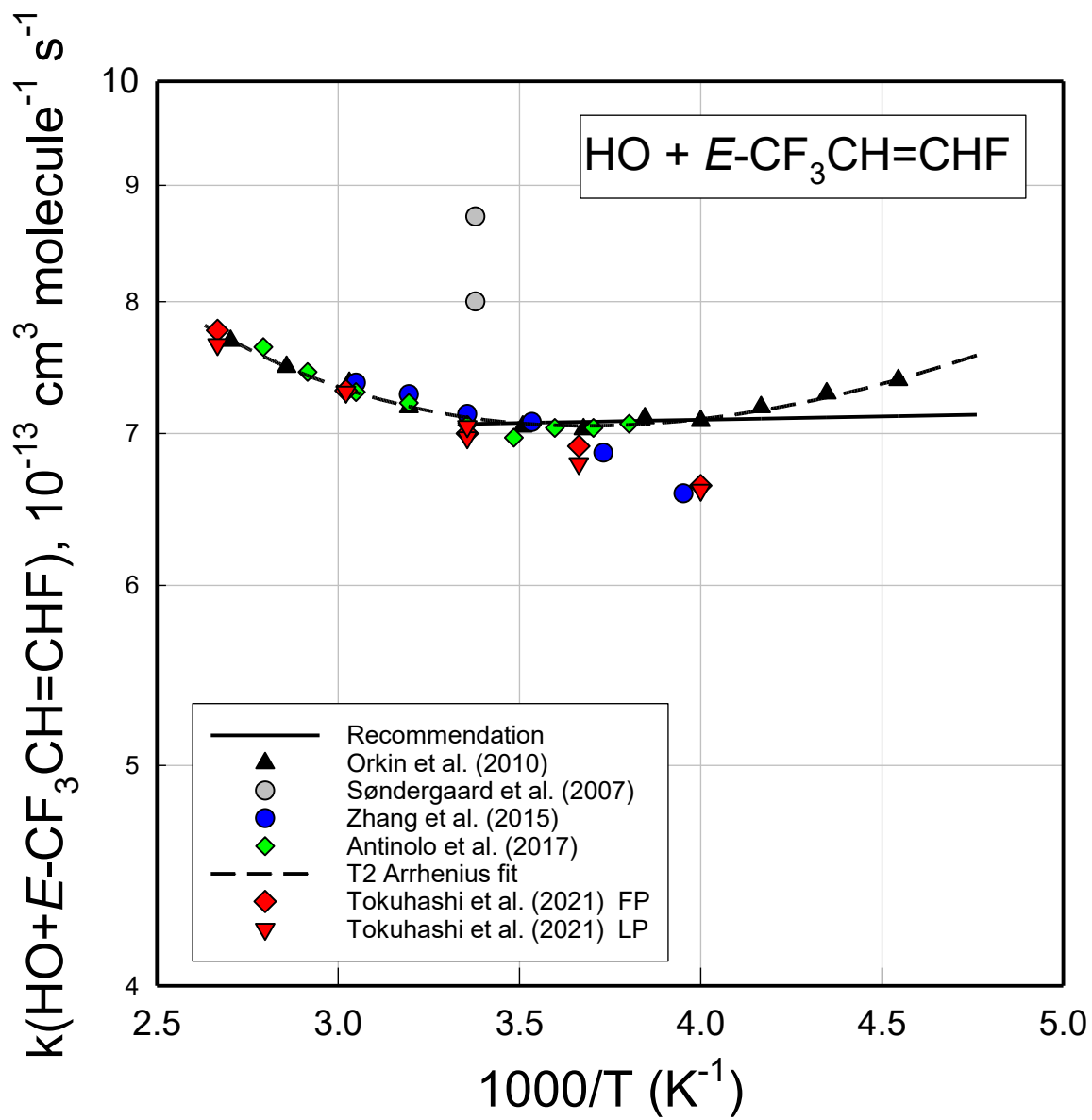
| 1607 | Parameter | Value | T/K |
|------|--|----------------------------------|---------|
| | $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 7.07×10^{-13} | 298 |
| | $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $6.91 \times 10^{-13} \exp(7/T)$ | 210-300 |
| 1608 | <i>Reliability</i> | | |
| | $\Delta \log k$ | ± 0.06 | 298 |
| | $\Delta E/R$ | ± 100 | 210-300 |

1611 Comments on Preferred Values

1612 There is good agreement between the rate coefficients measured in the absolute rate studies by
 1613 Orkin et al. (2010), Antiñolo et al. (2017), and Tokuhashi et al. (2021) and the relative rate study
 1614 by Zhang et al. (2015). The results of the relative rate study by Søndergaard et al. (2007) lie
 1615 approximately 15% higher. There was no discernible effect of total pressure over the range 5-200
 1616 Torr in the studies by Orkin et al. (2010), Antiñolo et al. (2017), and Tokuhashi et al. (2021)
 1617 indicating that the reaction is at, or near, the high-pressure limit for pressures above 5 Torr. The
 1618 measurements by Orkin et al. (2010) and Antiñolo et al. (2017) indicate a slight curvature in the
 1619 Arrhenius plot which is however not apparent in the results from Zhang et al. (2015) and
 1620 Tokuhashi et al. (2021). A fit of a modified Arrhenius expression to the combined data set from
 1621 Orkin et al. (2010) and Antiñolo et al. (2017) gives $k = 1.30 \times 10^{-18} T^2 \exp(551/T) \text{ cm}^3 \text{ molecule}^{-1}$
 1622 s^{-1} . Taking an average of the rate coefficients reported by Orkin et al. (2010), Antiñolo et al.
 1623 (2017), and Tokuhashi et al. (2021) gives our preferred value at 298 K. A fit of the Arrhenius
 1624 expression to the data from all studies below 300 K, except from Søndergaard et al. (2007), and
 1625 adjusting the A factor to match the preferred value at 298 K gives $k = 6.91 \times 10^{-13} \exp(7/T) \text{ cm}^3$
 1626 $\text{ molecule}^{-1} \text{ s}^{-1}$. For simplicity and consistency within the IUPAC database we prefer the simple
 1627 Arrhenius expression. The HO radical initiated oxidation of $\text{CF}_3\text{CH=CHF}$ in air gives $\text{CF}_3\text{C(O)H}$
 1628 and HC(O)F as products (Javadi et al., 2008).

1631 References

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1653 **HO + Z-CF₃CH=CHF (HFO-1234ze(Z)) → products**

1654 **Rate coefficient data**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $1.4 \times 10^{-13} (T/298)^{1.91} \exp(640/T)$ | 263-358 | Antiñolo et al. (2017) | PLP-LIF (a) |
| $(1.21 \pm 0.03) \times 10^{-12}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.02 \pm 0.06) \times 10^{-12}$ | 296 | Nilsson et al. 2009 | RR (b) |
| $(1.15 \pm 0.10) \times 10^{-12}$ | 296 | | |
| $9.11 \times 10^{-13} \exp(-114/T)$ | 253-328 | Zhang et al. (2015) | RR (c) |
| $(1.38 \pm 0.02) \times 10^{-12}$ | 298 | | |
| $(1.42 \pm 0.03) \times 10^{-12}$ | 298 | | |

1658 **Comments**

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- 1661 (a) HO radicals were generated by the pulsed laser photolysis of H₂O₂ or HNO₃ and monitored using
 1662 laser induced fluorescence in 45-300 Torr of helium diluent. There was no discernible effect of total
 1663 pressure on the rate coefficient over the range studied.
- 1664 (b) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The
 1665 loss of Z-CF₃CH=CHF was measured relative to C₂H₂ and C₂H₄ and used to measure the rate
 1666 coefficient ratios $k(\text{Z-CF}_3\text{CH=CHF})/k(\text{C}_2\text{H}_2) = 1.37 \pm 0.11$ and $k(\text{Z-CF}_3\text{CH=CHF})/k(\text{C}_2\text{H}_4) =$
 1667 0.146 ± 0.012 . Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$
 1668 s^{-1} (Atkinson et al., 2006) gives $k(\text{HO} + \text{Z-CF}_3\text{CH=CHF}) = (1.02 \pm 0.06) \times 10^{-12}$ and $(1.15 \pm 0.10) \times$
 1669 $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 1670 (c) Photolysis of O₃ in the presence of water vapor in 200 Torr of helium diluent was used to generate
 1671 HO radicals. The loss of E-CF₃CH=CHF was measured relative to n-C₄H₁₀ and n-C₅H₁₂ to derive
 1672 rate coefficient ratios $k(\text{Z-CF}_3\text{CH=CHF})/k(n\text{-C}_4\text{H}_{10})$ and $k(\text{Z-CF}_3\text{CH=CHF})/k(n\text{-C}_5\text{H}_{12})$ over the
 1673 temperature range 253-328 K. Rate coefficient ratios at 298 K were $k(\text{Z-CF}_3\text{CH=CHF})/k(n\text{-C}_4\text{H}_{10})$
 1674 $= 0.585 \pm 0.009$ and $k(\text{Z-CF}_3\text{CH=CHF})/k(n\text{-C}_5\text{H}_{12}) = 0.358 \pm 0.007$. Using $k(\text{HO} + n\text{-C}_4\text{H}_{10}) = 9.80 \times$
 1675 $10^{-12} \exp(-425/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) and $k(\text{HO} + n\text{-C}_5\text{H}_{12}) = 1.81 \times 10^{-11}$
 1676 $\exp(-452/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2008) gives $k(\text{HO} + \text{Z-CF}_3\text{CH=CHF}) = (1.38 \pm 0.02)$
 1677 $\times 10^{-12}$ and $(1.42 \pm 0.03) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
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Preferred Values

| Parameter | Value | T/K |
|--|------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.21×10^{-12} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $8.46 \times 10^{-13} \exp(106/T)$ | 260-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.15 | 298 |
| $\Delta E/R$ | ± 100 | 260-300 |

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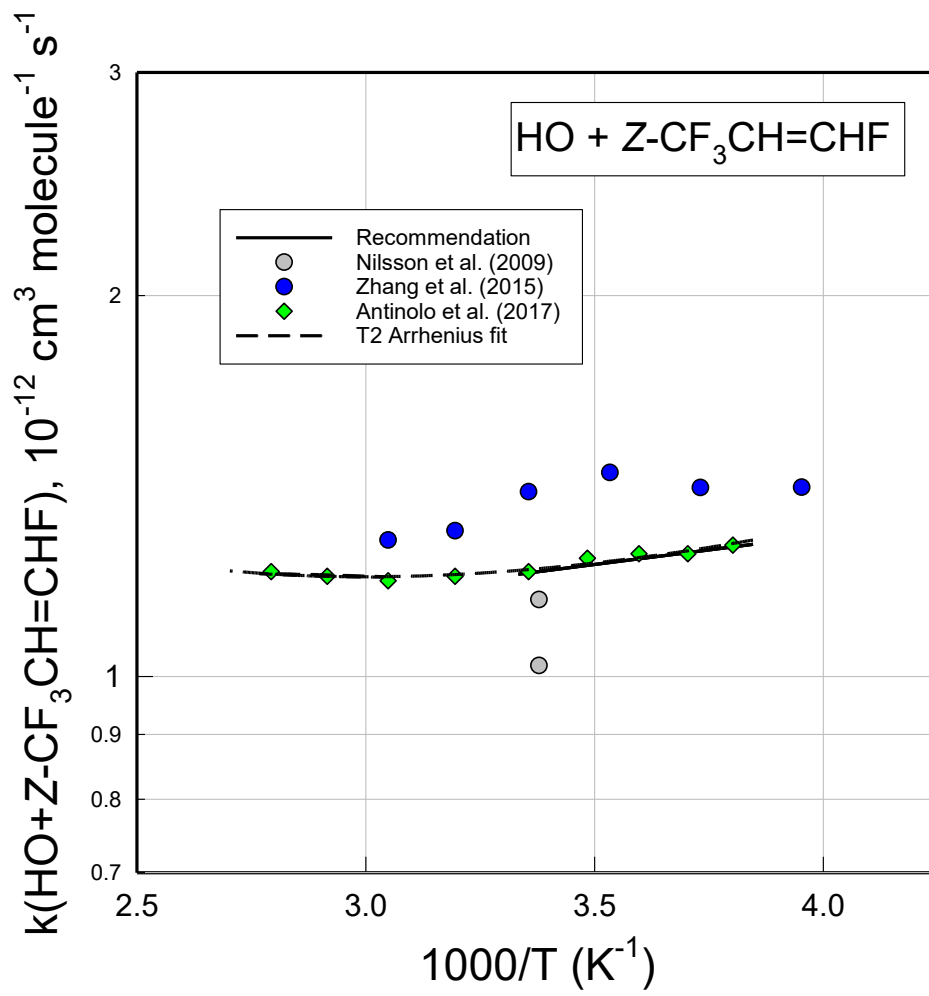
Comments on Preferred Values

1684 There is good agreement between the rate coefficients measured in the absolute rate study by Antiñolo
1685 et al. (2017) and the relative rate studies by Nilsson et al. (2009) and Zhang et al. (2015). There was
1686 no discernible effect of total pressure over the range 45-300 Torr in the study by Antiñolo et al. (2017)
1687 indicating that the reaction is at, or near, the high-pressure limit for pressures above 45 Torr. The
1688 preferred rate coefficient at 298 K is taken from the study by Antiñolo et al. (2017). The absolute rate
1689 measurements reveals a small curvature in the Arrhenius plot. A fit of a modified Arrhenius expression
1690 to the data set from Antiñolo et al. (2017) gives $k = 1.46 \times 10^{-18} T^2 \exp(666/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The
1691 preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 280 K and is derived from the three-
1692 parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.
1693 The HO radical initiated oxidation of $\text{CF}_3\text{CH}=\text{CHF}$ in air yields $\text{CF}_3\text{C}(\text{O})\text{H}$ and $\text{HC}(\text{O})\text{F}$ as products
1694 (Javadi et al., 2008).

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1714 **oFOx118: HO + E-CF₃CF=CHF**
1715 Last evaluated: June 2025; Last change in preferred values: January 2023.

1716
1717 **HO + E-CF₃CF=CHF → products**

1718
1719 **Rate coefficient data**

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| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| (2.05 ± 0.20) × 10 ⁻¹² | 296 | Hurley et al. (2007) | RR (a) |
| (2.12 ± 0.23) × 10 ⁻¹² | 296 | | |

1721
1722 **Comments**

1723
1724 (a) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals.
1725 The loss of E-CF₃CF=CHF was measured relative to those of C₂H₂ and C₂H₄ and used to
1726 measure the rate coefficient ratios $k(E-CF_3CF=CHF)/k(C_2H_2) = 2.74 \pm 0.27$ and $k(E-$
1727 $CF_3CF=CHF)/k(C_2H_4) = 0.27 \pm 0.03$. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) =$
1728 7.85×10^{-12} (Atkinson et al., 2006) gives $k(HO + E-CF_3CF=CHF) = (2.05 \pm 0.20) \times 10^{-12}$ and
1729 $(2.12 \pm 0.23) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

1730
1731 **Preferred Values**

1732

| Parameter | Value | T/K |
|--|-------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.2 × 10 ⁻¹² | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.15 | 298 |

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1734 *Comments on Preferred Values*

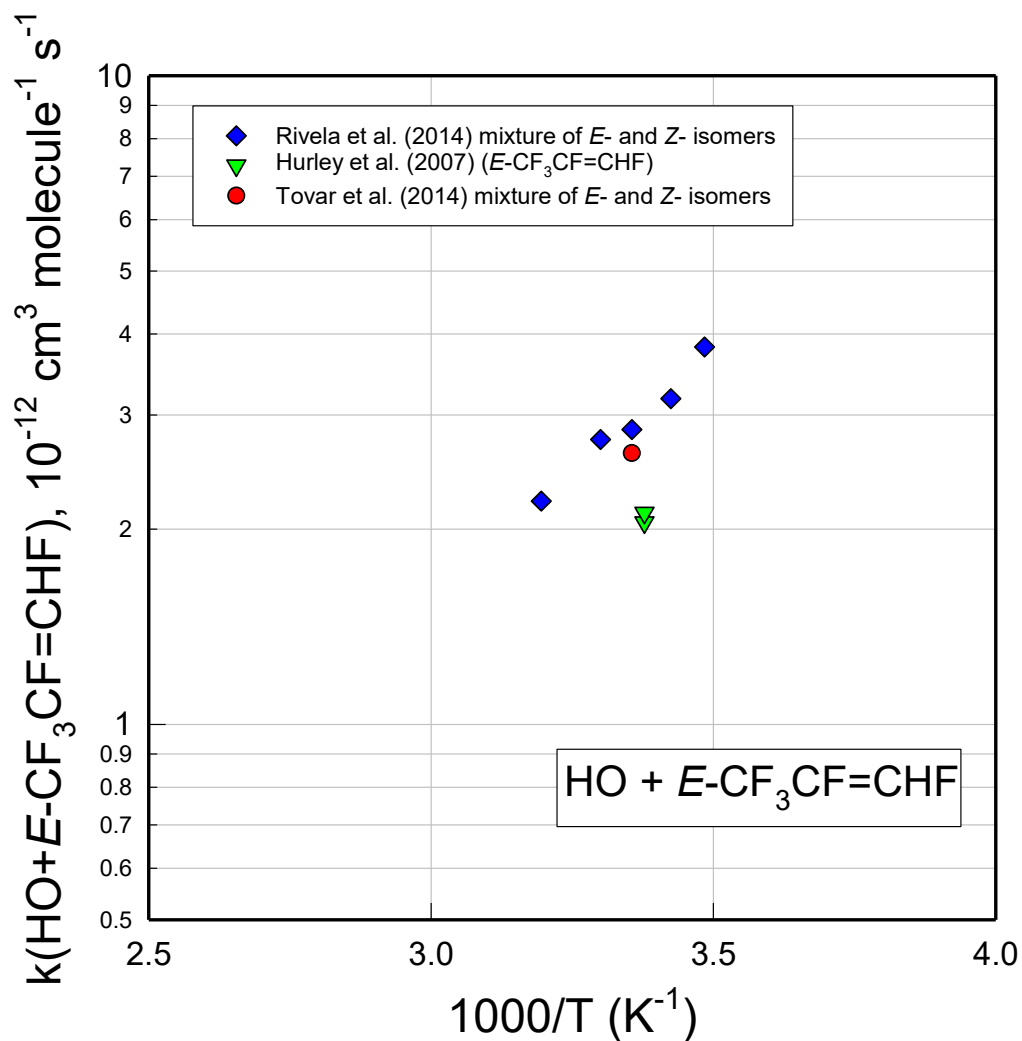
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1736 The preferred rate coefficient at 298 K is based on the results from the study by Hurley et al.
1737 (2007). Tovar et al. (2014) and Rivela et al. (2019) reported the results of a relative rate study of the
1738 reaction of a mixture of the two isomers E- and Z-CF₃CF=CHF over the temperature range 287-313
1739 K. The isomeric composition of the sample was not measured and the IR feature(s) used to follow the
1740 loss of (E/Z)-CF₃CF=CHF were not stated so it is unclear which isomer(s) was being studied.
1741 However, judging from the similarity of the reported rate coefficient at 298 K with that for E-
1742 CF₃CF=CHF reported by Hurley et al. (2007) it appears that Tovar et al. (2014) and Rivela et al.
1743 (2019) were mainly measuring the kinetics of the E-CF₃CF=CHF isomer. The rate coefficients
1744 reported by Tovar et al. (2014) and Rivela et al. (2019) at 298 K were (2.62 ± 0.76) × 10⁻¹² and (2.85 ±
1745 0.78) × 10⁻¹² cm³ molecule⁻¹ s⁻¹ and are consistent within the combined uncertainties with the
1746 preferred value for the E-CF₃CF=CHF isomer.

1747
1748 **References**

1749
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1752 Atmospheric Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>

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Rivela, C. B., Tovar, C. M., Teruel, M. A., Barnes, I., and Wiesen, P.: Chem. Phys. Lett., 714, 190, 2019.
Tovar, C. M., Blanco, M. B., Barnes, I., Wiesen, P., and Teruel, M. A.: Atmos. Env., 88, 107, 2014.



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oFOx119: HO + Z-CF₃CF=CHF (HFO-1225ye(Z))

Last evaluated: June 2025; Last change in preferred values: January 2023.

HO + Z-CF₃CF=CHF (HFO-1225ye(Z)) → products

Rate coefficient data

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 1.6 × 10 ⁻¹⁸ T ² exp(655/T) | 206-380 | Papadimitriou et al. (2008) | PLP-LIF (a) |
| 1.28 × 10 ⁻¹² | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (1.15 ± 0.11) × 10 ⁻¹² | 296 | Hurley et al. (2007) | RR (b) |
| (1.26 ± 0.08) × 10 ⁻¹² | 296 | | |

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Comments

- (a) HO radicals were produced using the pulsed laser photolysis of either H₂O₂ or HNO₃ at 248 nm. Experiments at 296K were conducted in a total pressure of 25-600 Torr (33-800 mbar) using helium, nitrogen, or SF₆ diluent. There was no discernable effect of total pressure or diluent on the kinetics of the reaction.
- (b) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of Z-CF₃CF=CHF was measured relative to those of C₂H₂ and C₂H₄ and used to derive rate coefficient ratios $k(\text{Z-CF}_3\text{CF=CHF})/k(\text{C}_2\text{H}_2) = 1.54 \pm 0.15$ and $k(\text{Z-CF}_3\text{CF=CHF})/k(\text{C}_2\text{H}_4) = 0.16 \pm 0.01$. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{Z-CF}_3\text{CF=CHF}) = (1.15 \pm 0.11) \times 10^{-12}$ and $(1.26 \pm 0.08) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.2 × 10 ⁻¹² | 298 |
| | 7.60 × 10 ⁻¹³ exp(155/T) | 200-300 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |
| Δ E/R | ±100 | 200-300 |

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Comments on Preferred Values

There is excellent agreement between the results from the absolute rate study by Papadimitriou et al. (2008) and the relative rate study by Hurley et al. (2007). The preferred rate constant at 298 K is taken from the temperature dependent expression provided by Papadimitriou et al. (2008). There is significant curvature in the Arrhenius plot. Fitting the three parameter equation, $k = CT^2 \exp(-D/T)$ to the data from Papadimitriou et al. (2008) gives $k(\text{HO} + \text{Z-CF}_3\text{CF=CHF}) = 1.62 \times 10^{-18} T^2 \exp(655/T)$ cm³ molecule⁻¹ s⁻¹. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K and is derived from the three-parameter equation with $A = C e^2 T^2$ and $B = D + 2T$ with the A factor adjusted to return the preferred rate coefficient at 298 K. Note that the preferred Arrhenius expression should not be used outside the specified temperature range (200-300 K); rather, the full three

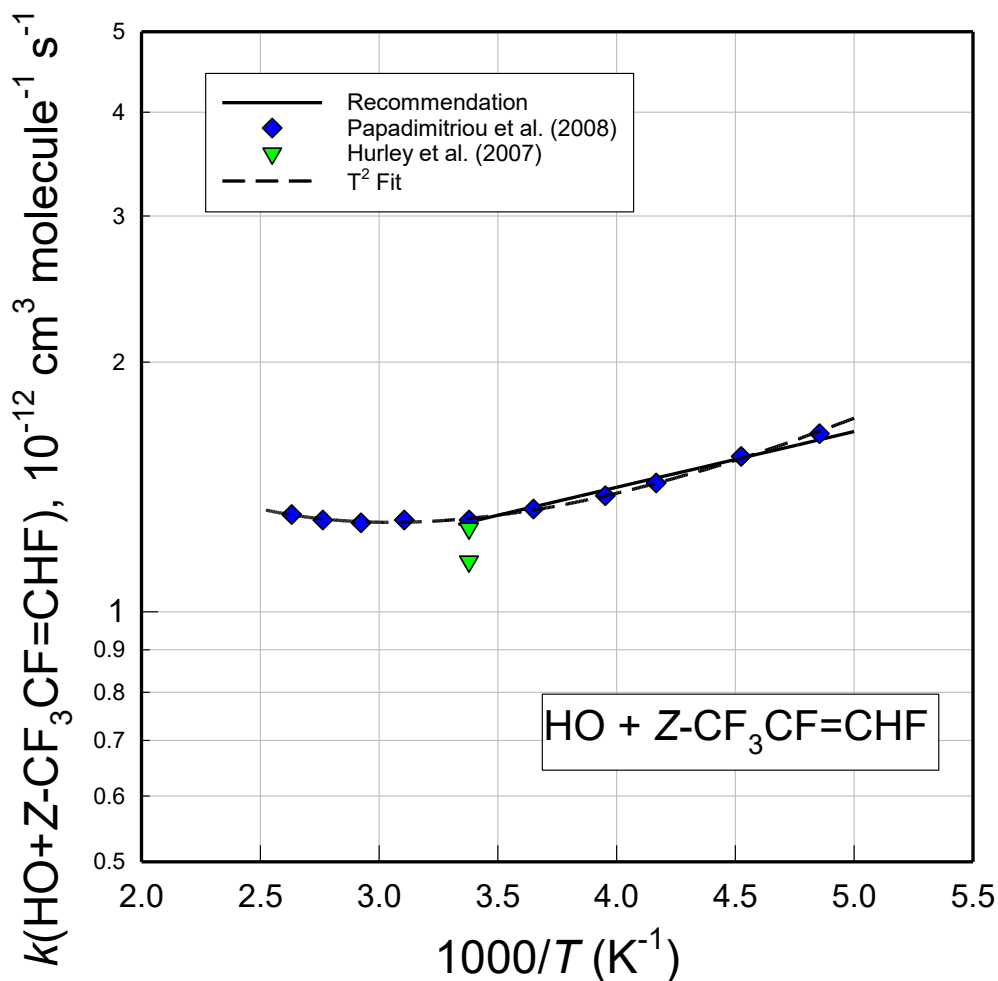
1797 parameter expression should be used.

1798 Tovar et al. (2014) and Rivela et al. (2019) have reported the results of a relative rate study of
1799 the reaction of a mixture of the two isomers *E*- and *Z*-CF₃CF=CHF over the temperature range 287-
1800 313 K. The isomeric composition of the sample was not measured and the IR feature(s) used to follow
1801 the loss of (*E/Z*)-CF₃CF=CHF were not stated. However, judging from the similarity of the reported
1802 rate coefficients at 298 K of $(2.62 \pm 0.76) \times 10^{-12}$ and $(2.85 \pm 0.78) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ with the
1803 values for $k(\text{HO} + E\text{-CF}_3\text{CF}=\text{CHF}) = (2.05 \pm 0.20) \times 10^{-12}$ and $(2.12 \pm 0.23) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹
1804 reported by Hurley et al. (2008) it appears that Tovar et al. (2014) and Rivela et al. (2019) were
1805 mainly measuring the kinetics of the *E*-CF₃CF=CHF isomer.

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References

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 1826 **HO + CF₃CF=CF₂ (FO-1216) → products**

1827
 1828 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| See comment (a) | 293-831 | McIlroy and Tully (1993) | FP-RF (a) |
| $(2.27 \pm 0.05) \times 10^{-12}$ | 293 | | |
| $5.66 \times 10^{-13} \exp(-407/T)$ | 252-370 | Orkin et al. (1997) | FP-RF (b) |
| $(2.17 \pm 0.01) \times 10^{-12}$ | 298 | | |
| $8.74 \times 10^{-13} \exp(260/T)$ | 250-430 | Tokuhashi et al. (2000) | FP-LIF (c) |
| $(2.12 \pm 0.02) \times 10^{-12}$ | 298 | | |
| $9.75 \times 10^{-14} (T/298)^{1.98} \exp(922/T)$ | 230-480 | Orkin et al. (2011) | FP-LIF (d) |
| $(2.16 \pm 0.07) \times 10^{-12}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(2.28 \pm 0.16) \times 10^{-12}$ | 296 | Mashino et al. (2000) | RR (e) |
| $(1.98 \pm 0.11) \times 10^{-12}$ | 296 | | |
| $(2.47 \pm 0.43) \times 10^{-12}$ | 298 | Acerboni et al. (2001) | RR (f) |
| $(3.29 \pm 0.91) \times 10^{-12}$ | 298 | | |

1830
 1831 **Comments**

- 1832
- 1833 (a) HO radicals were generated by the photolysis of H₂O by a xenon flash lamp in 75-750 Torr (76-
 1834 760 mbar) of argon diluent. Single-exponential decays were observed over the temperature ranges
 1835 293-489 K and 656-831 K while bi-exponential decays were observed for the intermediate
 1836 temperature range 528-641 K. There was no discernable effect of total pressure over the range
 1837 studied on the rate of reaction at 293 K. Fitting the Arrhenius expression to the data from 293-489
 1838 K gave $k = (9.95 \pm 0.64) \times 10^{-13} \exp [(486 \pm 44 \text{ cal})/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A small but distinct
 1839 curvature was evident in the Arrhenius plot and a modified Arrhenius expression, $k = 1.115 \times 10^{-13}$
 1840 $(T/298)^{2.03} \exp(552/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was used to best represent the data.
- 1841 (b) HO radicals were produced by the photolysis of H₂O by a xenon flash lamp in 100 Torr (133
 1842 mbar) of argon diluent.
- 1843 (c) HO radicals were produced by the xenon flash lamp photolysis of H₂O, or pulsed ArF excimer laser
 1844 photolysis of N₂O to produce O(¹D) atoms which were then reacted with either H₂O or CH₄ to
 1845 give HO radicals, or pulsed laser photolysis of H₂O₂. HO radicals were monitored by laser
 1846 induced fluorescence. Experiments were conducted in 5-200 Torr of helium, or argon, diluent.
 1847 There was no discernible effect of pressure or diluent gas over the range studied. Results from
 1848 experiments using four different sources of HO radicals were indistinguishable.
- 1849 (d) HO radicals were produced by the photolysis of H₂O by a xenon flash lamp in 30-100 Torr (40-
 1850 133 mbar) of argon diluent.
- 1851 (e) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals.
 1852 The loss of CF₃CF=CF₂ was measured relative to C₂H₂ and C₂H₄ and used to measure the rate
 1853 coefficient ratios $k(\text{CF}_3\text{CF}=\text{CF}_2)/k(\text{C}_2\text{H}_2) = 2.65 \pm 0.15$ and $k(\text{CF}_3\text{CF}=\text{CF}_2)/k(\text{C}_2\text{H}_4) = 0.29 \pm 0.02$.
 1854 Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives
 1855 $k(\text{HO} + \text{CF}_3\text{CF}=\text{CF}_2) = (2.28 \pm 0.16) \times 10^{-13}$ and $(1.98 \pm 0.11) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 1856 (f) Photolysis of CH₃ONO in 740 Torr (986 mbar) of air diluent was used to generate HO radicals.
 1857 The loss of CF₃CF=CF₂ was measured relative to C₂H₄ and C₃H₆ and used to measure the rate

1858 coefficient ratios $k(\text{CF}_3\text{CF}=\text{CF}_2)/k(\text{C}_2\text{H}_4) = 0.3151 \pm 0.0552$ and $k(\text{CF}_3\text{CF}=\text{CF}_2)/k(\text{C}_3\text{H}_6) =$
 1859 0.1153 ± 0.0321 . Using $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{C}_3\text{H}_6) = 2.85$
 1860 $\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{CF}_3\text{CF}=\text{CF}_2) = (2.47 \pm 0.43) \times 10^{-$
 1861 12 and $(3.29 \pm 0.91) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

1862 Preferred Values

1863

| Parameter | Value | T/K |
|--|------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.18×10^{-12} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $7.38 \times 10^{-13} \exp(322/T)$ | 240-340 |
| 1865 <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.04 | 298 |
| $\Delta E/R$ | ± 100 | 240-340 |

1866

1867 *Comments on Preferred Values*

1868

1869 The results from the absolute rate studies of McIlroy et al. (1993), Orkin et al (1997, 2011) and
 1870 Tokuhashi et al. (2000) and the relative rate studies of Aceboni et al. (2001) and Mashino et al.
 1871 (2000) are in good agreement within the experimental uncertainties. There is excellent agreement
 1872 in the reported rate coefficients from the absolute rate studies at 298 K. The preferred value at 298
 1873 K is the average of the measurements by McIlroy et al. (1993), Orkin et al (1997, 2011) and
 1874 Tokuhashi et al. (2000). There is significant curvature in the Arrhenius plot. Fitting the expression k
 1875 $= CT^2 \exp(-D/T)$ to the $240\text{K} < T < 500\text{K}$ data from McIlroy et al. (1993), Orkin et al (1997, 2011)
 1876 and Tokuhashi et al. (2000) and adjusting the pre-exponential A-factor to return the preferred value
 1877 at 298 K gives $k(\text{HO} + \text{CF}_3\text{CF}=\text{CF}_2) = 1.11 \times 10^{-18} T^2 \exp(922/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The preferred
 1878 Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three-parameter
 1879 equation with $A = C e^2 T^2$ and $B = D + 2T$. Note that the preferred Arrhenius expression should not be
 1880 used outside the specified temperature range (240-340 K); rather, the modified expression should be
 1881 used.

1882

1883

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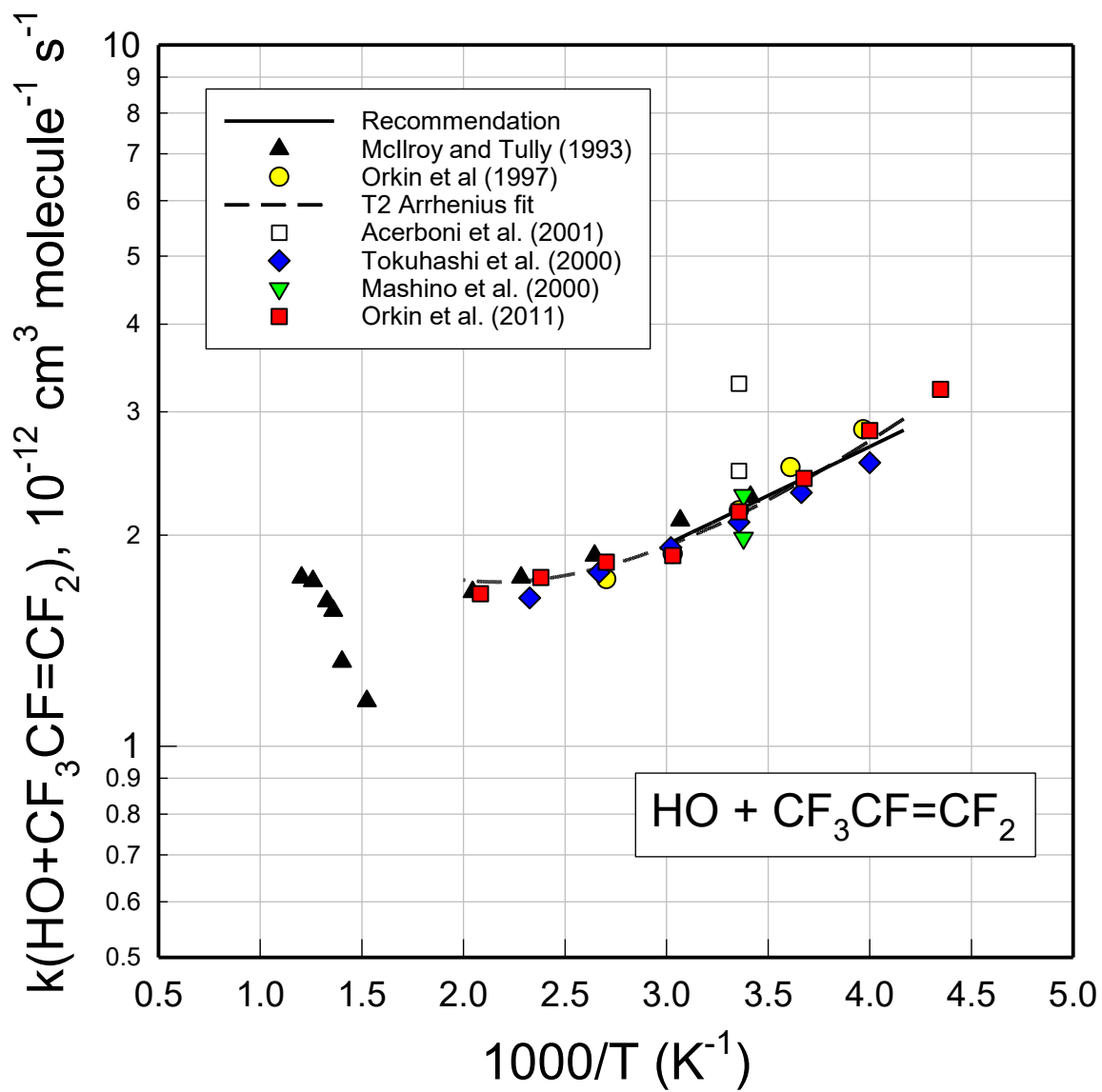
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1901



1907
 1908
 1909
 1910
 1911

HO + E-CF₃CH=CHCF₃ (HFO-1336mzz(E)) → products

Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(6.94 \pm 0.80) \times 10^{-13} \exp(-496 \pm 10/T)$ | 211-374 | Baasandorj et al. (2018) | LP-LIF (a) |
| $(1.31 \pm 0.15) \times 10^{-13}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.47 \pm 0.21) \times 10^{-13}$ | 296 | Østerstrøm et al. (2017) | RR (b) |
| $(1.88 \pm 0.24) \times 10^{-13}$ | 296 | | |
| $1.18 \times 10^{-12} \exp(-668/T)$ | 296-375 | Baasandorj et al. (2018) | RR (c) |
| $(1.21 \pm 0.10) \times 10^{-13}$ | 296 | | |
| $5.91 \times 10^{-13} \exp(-515/T)$ | 253-328 | Qing et al. (2018) | RR (d) |
| $(1.10 \pm 0.02) \times 10^{-13}$ | 298 | | |
| $4.62 \times 10^{-13} \exp(-423/T)$ | 253-328 | Qing et al. (2018) | RR (e) |
| $(1.21 \pm 0.10) \times 10^{-13}$ | 298 | | |

1912
 1913
 1914

Comments

- 1915 (a) HO radicals were generated by 248 nm laser photolysis of H₂O₂ or (CH₃)₃COOH in 2.5-200 Torr
 1916 of He or N₂ and were monitored using laser induced fluorescence. There was no discernible effect
 1917 of pressure or diluent gas on the rate coefficient.
- 1918 (b) HO radicals were generated by the photolysis of (CH₃)₂CHONO or CH₃ONO in 700 Torr air/N₂/O₂
 1919 in the presence of NO. The loss of E-CF₃CH=CHCF₃ was monitored relative to C₃H₈ and C₂H₆
 1920 using FTIR spectroscopy. Rate coefficient ratios of $k(E\text{-CF}_3\text{CH=CHCF}_3)/k(\text{C}_3\text{H}_8) = 0.14 \pm 0.02$ and
 1921 $k(E\text{-CF}_3\text{CH=CHCF}_3)/k(\text{C}_2\text{H}_6) = 0.80 \pm 0.10$ were measured. Using $k(\text{HO} + \text{C}_3\text{H}_8) = 1.05 \times 10^{-12}$ and
 1922 $k(\text{HO} + \text{C}_2\text{H}_6) = 2.35 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) at 296 K gives $k(\text{HO} + E\text{-}$
 1923 $\text{CF}_3\text{CH=CHCF}_3) = (1.47 \pm 0.21) \times 10^{-13}$ and $(1.88 \pm 0.24) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 1924 (c) HO radicals were generated by the pulsed laser photolysis of O₃ in the presence of H₂O in 100 Torr
 1925 of He at 296-375 K. The loss of E-CF₃CH=CHCF₃ was monitored relative to that of C₂H₆ by FTIR
 1926 spectroscopy. At 296 K a rate coefficient ratio of $k(E\text{-CF}_3\text{CH=CHCF}_3)/k(\text{C}_2\text{H}_6) = 0.50 \pm 0.04$ was
 1927 measured. Using $k(\text{C}_2\text{H}_6) = 6.9 \times 10^{-13} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2024) gives $k(E\text{-}$
 1928 $\text{CF}_3\text{CH=CHCF}_3) = (1.21 \pm 0.10) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Rate coefficient ratios at 296-375 K were
 1929 scaled to $k(\text{C}_2\text{H}_6) = 6.9 \times 10^{-13} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2024) and an Arrhenius fit
 1930 to the results gives $k(E\text{-CF}_3\text{CH=CHCF}_3) = 1.18 \times 10^{-12} \exp(-668/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 1931 (d) Photolysis of O₃ in the presence of water vapor in 200 Torr of helium was used to generate HO
 1932 radicals. The loss of E-CF₃CH=CHCF₃ was measured relative to C₂H₆ over the temperature range
 1933 253-328 K. A rate coefficient ratio of $k(E\text{-CF}_3\text{CH=CHCF}_3)/k(\text{C}_2\text{H}_6) = 0.458 \pm 0.002$ was reported at
 1934 298 K. Using $k(\text{C}_2\text{H}_6) = 6.9 \times 10^{-13} \exp(-1000/T)$ (IUPAC, 2024) gives $k(E\text{-CF}_3\text{CH=CHCF}_3) =$
 1935 $(1.21 \pm 0.10) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Rate coefficient ratios at 253-328 K were scaled to $k(\text{C}_2\text{H}_6) =$
 1936 $6.9 \times 10^{-13} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2024) and an Arrhenius fit to the results gives
 1937 $k(E\text{-CF}_3\text{CH=CHCF}_3) = 5.91 \times 10^{-13} \exp(-515/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 1938 (e) Photolysis of O₃ in the presence of water vapor in 200 Torr of helium was used to generate HO
 1939 radicals. The loss of E-CF₃CH=CHCF₃ was measured relative to CH₂FCH₂F over the temperature
 1940 range 253-328 K. A rate coefficient ratio of $k(E\text{-CF}_3\text{CH=CHCF}_3)/k(\text{CH}_2\text{FCH}_2\text{F}) = 1.08 \pm 0.02$ was

1941 reported at 298 K. Using $k(\text{CH}_2\text{FCH}_2\text{F}) = 1.5 \times 10^{-12} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2024)
 1942 gives $k(E\text{-CF}_3\text{CH=CHCF}_3) = (1.21 \pm 0.10) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Rate coefficient ratios at 253-
 1943 328 K were scaled to $k(\text{CH}_2\text{FCH}_2\text{F}) = 1.5 \times 10^{-12} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2024) and
 1944 an Arrhenius fit to the results gives $k(\text{HO}+E\text{-CF}_3\text{CH=CHCF}_3) = 4.62 \times 10^{-13} \exp(-423/T) \text{ cm}^3$
 1945 $\text{molecule}^{-1} \text{ s}^{-1}$.

1946 Preferred Values

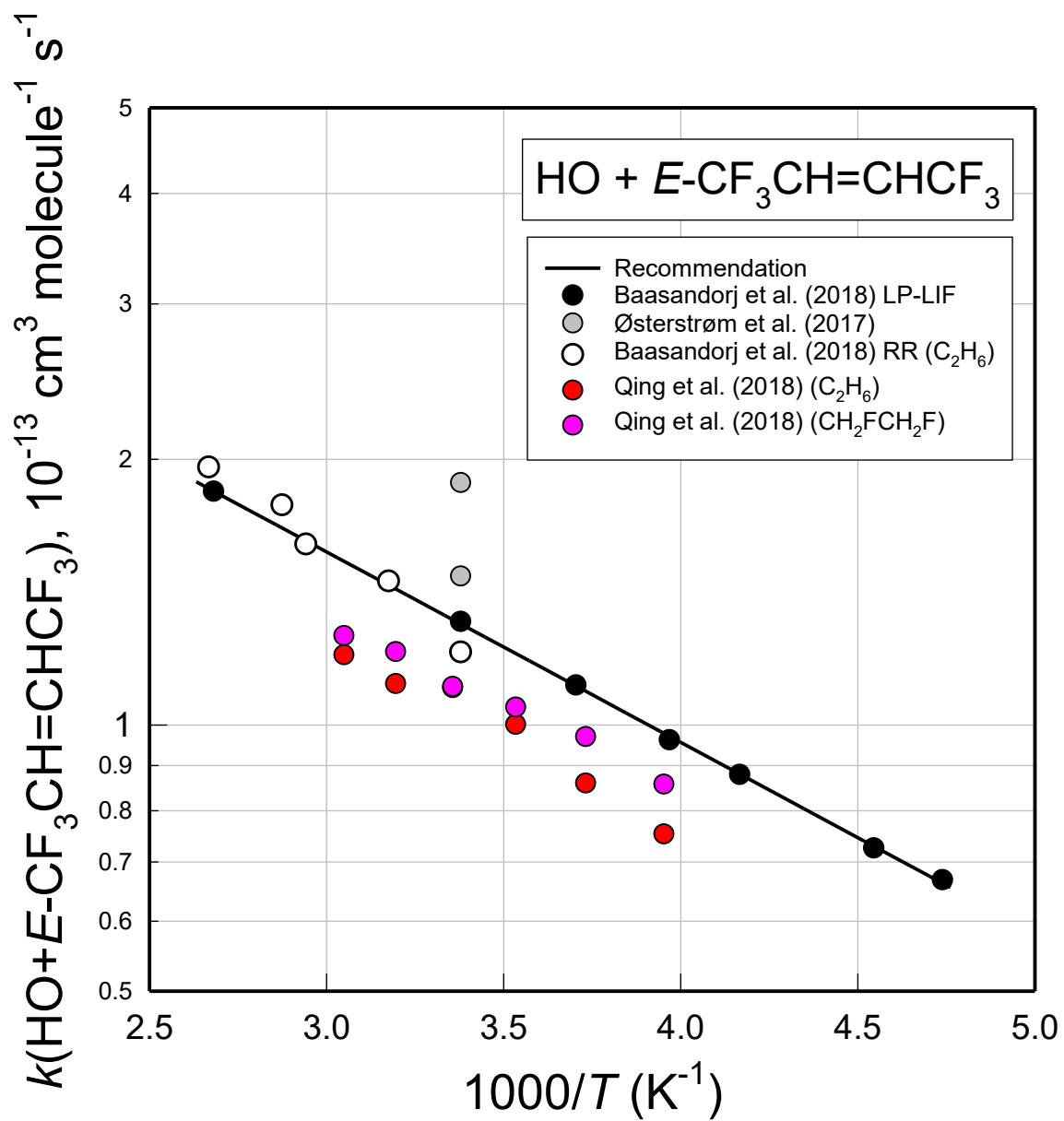
| 1947 | Parameter | Value | T/K |
|------|--|-------------------------------------|---------|
| 1948 | $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.31×10^{-13} | 298 |
| | $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $6.94 \times 10^{-13} \exp(-496/T)$ | 210-380 |
| 1949 | <i>Reliability</i> | | |
| | $\Delta \log k$ | ± 0.06 | 298 |
| | $\Delta E/R$ | ± 100 | 210-380 |

1950 Comments on Preferred Values

1951
 1952
 1953
 1954 There is good agreement between the rate coefficients measured in the absolute and relative rate
 1955 study by Baasandorj et al. (2018) and the relative rate study by Qing et al. (2018). The rate
 1956 coefficient measured using C_3H_8 as a reference by Østerstrøm et al. (2017) is in good agreement
 1957 with the results from Baasandorj et al. (2018) and Qing et al. (2018). However, the rate coefficient
 1958 ratio reported by Østerstrøm et al. using C_2H_6 as a reference compound is approximately 60%
 1959 larger than measured by Baasandorj et al. (2018) and Qing et al. (2018). A fit to the absolute rate
 1960 data from Baasandorj et al. (2018) gives the preferred expression, $k = 6.94 \times 10^{-13} \exp(-496/T) \text{ cm}^3$
 1961 $\text{molecule}^{-1} \text{ s}^{-1}$, is taken from Baasandorj et al. (2018) which gives $k = 1.31 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$
 1962 s^{-1} at 298 K.

1963 References

- 1964
 1965
 1966 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
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1974
1975
1976

1979 **HO + Z-CF₃CH=CHCF₃ (HFO-1336mzz(Z)) → products**

1980 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|----------------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 5.73 × 10 ⁻¹⁹ T ² exp(-678/T) (4.91 ± 0.50) × 10 ⁻¹³ | 212-374 296 | Baasandorj et al. (2011) | LP-LIF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (3.99 ± 0.63) × 10 ⁻¹³ (4.18 ± 0.42) × 10 ⁻¹³ | 296 296 | Østerstrøm et al. (2017) | RR (b) |
| See comment (c) (4.94 ± 0.09) × 10 ⁻¹³ | 296-375 296 | Baasandorj et al. (2018) | RR (c) |

1984 **Comments**

- 1985 (a) HO radicals were generated by 248 nm laser photolysis of H₂O₂ or (CH₃)₃COOH in 2.5-200 Torr
 1986 of He or N₂. There was no discernible effect of pressure or diluent gas on the rate coefficient.
 1987 (b) HO radicals were generated by the photolysis of (CH₃)₂CHONO or CH₃ONO in 700 Torr air/N₂/O₂
 1988 in the presence of NO. The loss of Z-CF₃CH=CHCF₃ was monitored relative to C₃H₈ and C₂H₆ using
 1989 FTIR spectroscopy. Rate coefficient ratios of $k(\text{Z-CF}_3\text{CH=CHCF}_3)/k(\text{C}_3\text{H}_8) = 0.38 \pm 0.06$ and $k(\text{Z-}$
 1990 $\text{CF}_3\text{CH=CHCF}_3)/k(\text{C}_2\text{H}_6) = 1.78 \pm 0.18$ were measured. Using $k(\text{HO} + \text{C}_3\text{H}_8) = 1.05 \times 10^{-12}$ cm³
 1991 molecule⁻¹ s⁻¹ and $k(\text{HO} + \text{C}_2\text{H}_6) = 2.35 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 2006) at 296 K
 1992 gives $k(\text{HO} + \text{Z-CF}_3\text{CH=CHCF}_3) = (3.99 \pm 0.63) \times 10^{-13}$ and $(4.18 \pm 0.42) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.
 1993 (c) HO radicals were generated by the 248 nm pulsed laser photolysis of O₃ in the presence of H₂O in
 1994 100-200 Torr of He at 296-375 K. The loss of Z-CF₃CH=CHCF₃ was monitored relative to that of
 1995 C₂H₆ by FTIR spectroscopy. At 296, 345, and 375 K rate coefficient ratios of $k(\text{Z-}$
 1996 $\text{CF}_3\text{CH=CHCF}_3)/k(\text{C}_2\text{H}_6) = 2.10 \pm 0.04$, 1.24 ± 0.02 , and 1.02 ± 0.02 were measured. Using $k(\text{C}_2\text{H}_6) =$
 1997 $6.9 \times 10^{-13} \exp(-1000/T)$ cm³ molecule⁻¹ s⁻¹ (IUPAC, 2024) gives $k(\text{Z-CF}_3\text{CH=CHCF}_3) = (4.94 \pm 0.09)$,
 1998 (4.71 ± 0.08) , and $(4.89 \pm 0.10) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 296, 345, and 375 K, respectively.
 1999
 2000
 2001
 2002
 2003

2004 **Preferred Values**

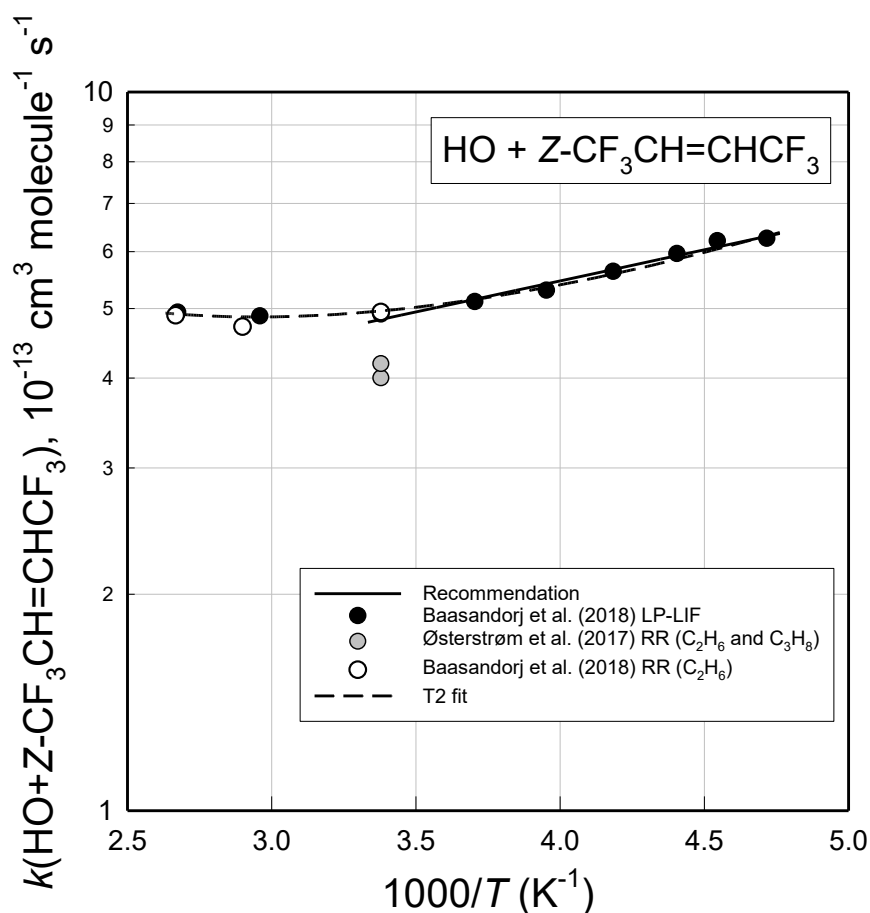
| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 4.80 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.46 × 10 ⁻¹³ exp(199/T) | 210-300 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.06 | 298 |
| Δ E/R | ± 100 | 210-300 |

2005 *Comments on Preferred Values*

2010 There rate coefficients measured in the absolute and relative rate studies by Baasandorj et al. (2011)
 2011 and the relative rate study by Østerstrøm et al. (2017) are consistent. Distinct curvature in the
 2012 Arrhenius plot is evident over temperature range studied by Baasandorj et al. (2011) and the data are
 2013 well described by the modified Arrhenius expression $k = (5.73 \pm 0.60) \times 10^{-19} T^2 \exp(-(678 \pm 10)/T) \text{ cm}^3$
 2014 $\text{molecule}^{-1} \text{ s}^{-1}$. A fit of the Arrhenius expression to the absolute rate data from Baasandorj et al. (2011)
 2015 below 300 K gives $k = 2.46 \times 10^{-13} \exp(199/T)$ which gives $k = 4.80 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298
 2016 K. For simplicity and consistency within the IUPAC database we prefer the simple Arrhenius
 2017 expression.

2020 References

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 2027 Østerstrøm, F. F., Andersen, S. T., Sølling, T. I., Nielsen, O. J., and Sulbæk Andersen, M. P.: Phys.
 2028 Chem. Chem. Phys. 19, 735–750, 2017.
 2029



2030
 2031
 2032
 2033

2034 **oClOx95: HO + CH₂=CHCl**
 2035 Last evaluated: June 2025; Last change in preferred values: June 2017.

2036 **HO + CH₂=CHCl → products**

2037 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|-----------------|---------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (2–5) × 10 ⁻¹² | 296 | Howard (1977) | DF-LMR (a) |
| 1.14 × 10 ⁻¹² exp[(526±151)/T] (6.60±0.66) × 10 ⁻¹² | 299-422 299 | Perry et al. (1977) | FP-RF (b) |
| 2.14 × 10 ⁻¹² exp[(700±120)/T] 7.55 × 10 ⁻¹² | 313-1173 313 | Liu et al. (1989) | PR-RA (c) |
| 2.72 × 10 ⁻¹² exp[(335±42)/T] (8.49±0.40) × 10 ⁻¹² | 293-730 293 | Yamada et al., 2001 | LP-LIF (d) |

2041 **Comments**

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- 2044 (a) HO radicals were produced by the reaction of H atoms with NO₂ in 0.7-7.0 Torr (0.9-9.3 mbar) of
 2045 helium. The rate coefficient was dependent on total pressure increasing from approximately 2 ×
 2046 10⁻¹² to 5 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ over the total pressure range 0.7-7.0 Torr.
- 2047 (b) Flash photolysis of H₂O in 50 or 100 Torr of argon was used as a source of HO radicals. The
 2048 decay of HO radicals was monitored using resonance fluorescence. There was no discernable
 2049 effect (<5%) of total pressure over the range studied.
- 2050 (c) Pulse radiolysis of one atmosphere of argon containing approximately 6 Torr of water vapor was
 2051 used as a source of HO radicals. Resonance absorption at 308 nm was used to monitor the decay
 2052 of HO radicals in the presence of vinyl chloride. It was deduced that the predominant reaction
 2053 channel changes from an addition-initiated reaction at temperatures below 588 K to a hydrogen
 2054 abstraction reaction for temperatures above 723 K. The rate coefficient for the addition reaction
 2055 was described by the Arrhenius expression $k = 2.14 \times 10^{-12} \exp[(700 \pm 120)/T]$ while that for the
 2056 H-abstraction reaction was described by $k = 2.98 \times 10^{-11} \exp[-(4020 \pm 700)/T]$ cm³ molecule⁻¹ s⁻¹.
- 2057 (d) Photolysis of HONO at 351 nm in 740 Torr of helium was used as a source of HO radicals.

2058 **Preferred Values**

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 7.55 × 10 ⁻¹² | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.54 × 10 ⁻¹² exp(325/T) | 280-600 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.08 | 298 |
| Δ E/R | ± 100 | 280-600 |

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2066 Howard (1976) showed that at pressures below 7 Torr of helium the rate of the reaction decreases with
 2067 total pressure. Perry et al. (1977) reported that at total pressures of 50 Torr of argon and above there is no
 2068 discernable effect of pressure on the measured rate coefficient. The rate coefficients reported by Perry et
 2069 al. (1977), Liu et al. (1989), and Yamada et al. (2001) near 298 K measured at, or near, the high pressure
 2070 limit are in reasonable agreement and an average of these gives the preferred value at 298 K. The
 2071 preferred Arrhenius expression is derived from a fit to the data obtained below 600 K by Perry et al.
 2072 (1977), Liu et al. (1989), and Yamada et al. (2001) with the pre-exponential factor adjusted to give the
 2073 preferred rate coefficient at 298 K. The preferred expression describes the high-pressure limiting rate
 2074 coefficient which is appropriate for atmospheric conditions.

2075 The reaction proceeds via addition of HO to the >C=C< double bond to give HOCH₂CHCl and
 2076 CH₂CHClOH radicals with the former expected to predominate. Elimination of a Cl atom from the
 2077 CH₂CHClOH radical will give the enol CH₂=CHOH. Addition of O₂ followed by reaction with NO is
 2078 expected to give a variety of products including HOCH₂CHO, HCHO, and HC(O)Cl.

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References

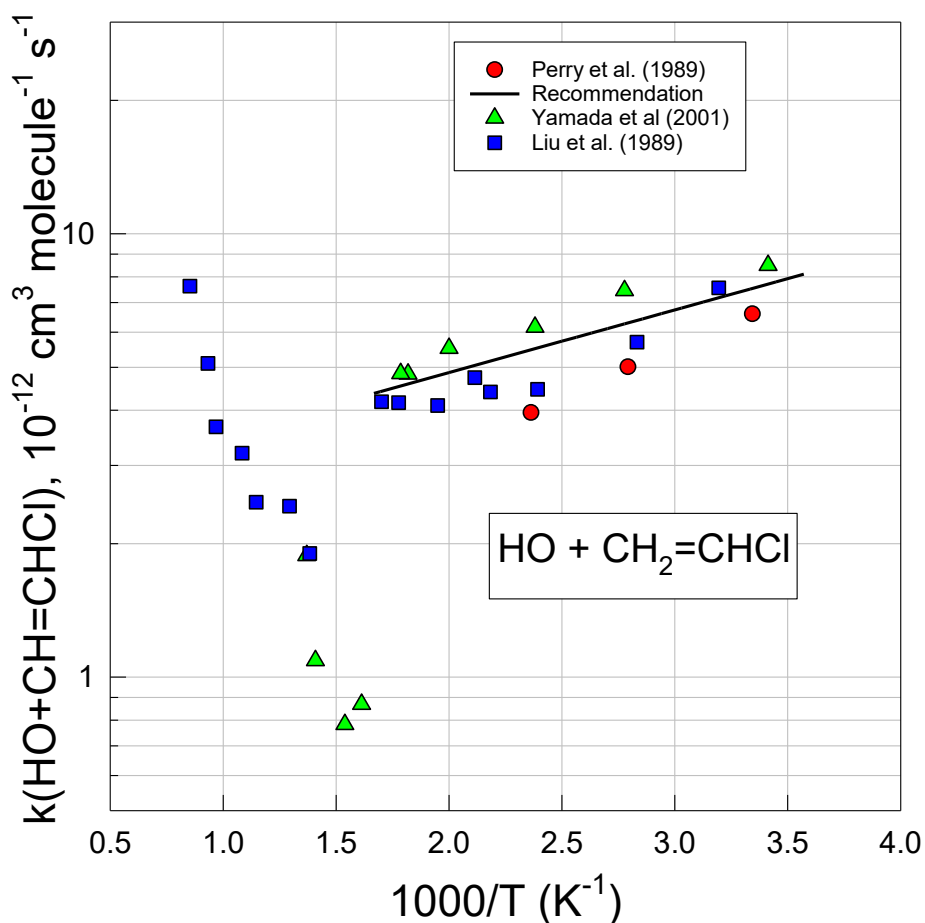
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HO + E-CF₃CH=CHCl (HCFO-1233zd(E)) → products**Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 1.025 × 10 ⁻¹³ (T/298) ^{2.29} exp(384/T) | 220-370 | Orkin et al. (2014) | FP-RF (a) |
| (3.29 ± 0.10) × 10 ⁻¹³ | 298 | | |
| 1.14 × 10 ⁻¹² exp[(-330±10)/T] | 213-376 | Gierczak et al. (2014) | PLP-LIF (b) |
| (3.76 ± 0.06) × 10 ⁻¹³ | 296 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (3.30 ± 0.30) × 10 ⁻¹³ | 296 | Andersen et al. (2015) | RR (c) |
| (3.21 ± 0.25) × 10 ⁻¹³ | 296 | | |

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Comments

- (a) HO radicals were produced by the pulsed photolysis of H₂O by a xenon flash lamp in 100 Torr (133 mbar) of argon diluent.
- (b) HO radicals were generated by the photolysis of H₂O₂, HNO₃, or (CH₃)₃COOH in 25-100 Torr (33-133 mbar) of helium or nitrogen diluent gas. There was no discernable effect of diluent gas or total pressure over the range studied.
- (c) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air. The loss of E-CF₃CH=CHCl was monitored relative to those of C₂H₄ and C₂H₂. In the initial work by Sulbaek Andersen et al. (2008) the loss of E-CF₃CH=CHCl via reaction with Cl atoms produced during the oxidation of E-CF₃CH=CHCl was not recognized. In a subsequent reanalysis by Andersen et al. (2015) corrections for such loss were computed and applied which resulted in rate coefficient ratios of $k(E-CF_3CH=CHCl)/k(C_2H_4) = 0.042 \pm 0.004$ and $k(E-CF_3CH=CHCl)/k(C_2H_2) = 0.430 \pm 0.034$. Using $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ and $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ (Atkinson et al., 2006) gives $k(E-CF_3CH=CHCl) = (3.30 \pm 0.30) \times 10^{-13}$ and $(3.21 \pm 0.25) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.

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Preferred Values

| Parameter | Value | T/K |
|--|--------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 3.53 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 8.79 × 10 ⁻¹³ exp(-272/T) | 220-300 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.06 | 298 |
| Δ E/R | ± 100 | 220-300 |

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Comments on Preferred Values

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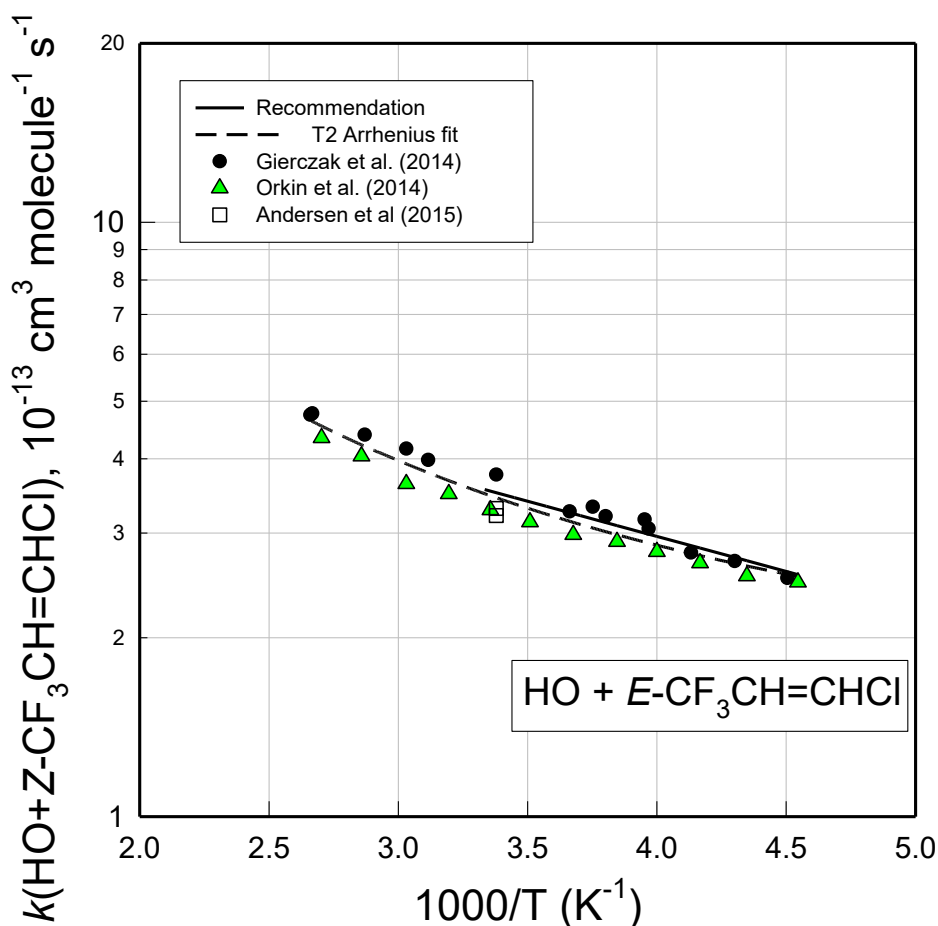
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There is good agreement in the room temperature rate coefficients reported in the absolute rate studies by Orkin et al. (2014) and Gierczak et al. (2014) and the relative rate study by Andersen et al. (2015). The preferred value at 298 K is an average from Orkin et al. (2014) and Gierczak et al. (2014). There

2123 is evidence in the combined data set from Orkin et al. (2014) and Gierczak et al. (2014) for a slight
 2124 curvature in the Arrhenius plot. Fitting the three parameter equation, $k = CT^2 \exp(-D/T)$ to the data
 2125 from Orkin et al. (2014) and Gierczak et al. (2014) gives $k(\text{HO} + E\text{-CF}_3\text{CH}=\text{CHCl}) = 1.70 \times 10^{-18} T^2$
 2126 $\exp(248/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-380 K. The preferred Arrhenius
 2127 expression, $k = A \exp(-B/T)$, is centered at 260 K and is derived from the three-parameter equation with A
 2128 $= C e^2 T^2$ and $B = D + 2T$ with the pre-exponential factor adjusted to reproduce the preferred $k(298\text{K})$
 2129 value, $k(\text{HO} + E\text{-CF}_3\text{CH}=\text{CHCl}) = 8.79 \times 10^{-13} \exp(-272/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

2130 References

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HO + Z-CF₃CH=CHCl (HCFO-1233zd(Z)) → products**Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $7.22 \times 10^{-19} T^2 \exp[(800)/T]$ | 213-376 | Gierczak et al. (2014) | PLP-LIF (a) |
| $(9.46 \pm 0.22) \times 10^{-13}$ | 296 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(8.09 \pm 1.10) \times 10^{-13}$ | 296 | Andersen et al. (2015) | RR (b) |
| $(7.17 \pm 0.61) \times 10^{-13}$ | 296 | | |

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Comments

(a) HO radicals were generated by the photolysis of H₂O₂, HNO₃, or (CH₃)₃COOH in 25-100 Torr (33-133 mbar) of helium or nitrogen diluent. There was no discernable effect of diluent gas or total pressure over the range studied.

(b) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air. The loss of Z-CF₃CH=CHCl was monitored relative to C₂H₄ and C₂H₂. Corrections for the loss of Z-CF₃CH=CHCl via reaction with Cl atoms produced during the oxidation of Z-CF₃CH=CHCl were computed and applied. Rate coefficient ratios of $k(\text{Z-CF}_3\text{CH=CHCl})/k(\text{C}_2\text{H}_4) = 0.103 \pm 0.014$ and $k(\text{Z-CF}_3\text{CH=CHCl})/k(\text{C}_2\text{H}_2) = 0.960 \pm 0.082$ were reported. Using $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12}$ and $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ (Atkinson et al., 2006) gives $k(\text{Z-CF}_3\text{CH=CHCl}) = (8.09 \pm 1.10) \times 10^{-13}$ and $(7.17 \pm 0.61) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.

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Preferred Values

| Parameter | Value | T/K |
|--|------------------------------------|---------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 9.24×10^{-13} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $3.61 \times 10^{-13} \exp(280/T)$ | 220-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.06 | 298 |
| $\Delta E/R$ | ± 100 | 220-300 |

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Comments on Preferred Values

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The results from the absolute rate study by Gierczak et al. (2014) and relative rate study of Andersen et al. (2015) at 296 K agree within the experimental uncertainties. There is significant curvature in the Arrhenius plot of the results from Gierczak et al. (2014). Gierczak et al. (2014) fitted the three parameter equation, $k = CT^2 \exp(-D/T)$ to their data giving $k(\text{HO} + \text{Z-CF}_3\text{CH=CHCl}) = 7.22 \times 10^{-19} T^2 \exp(800/T)$ cm³ molecule⁻¹ s⁻¹. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 260 K and is derived from the three-parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. Note that the preferred Arrhenius expression, $k(\text{HO} + \text{CF}_3\text{CH=CHCl}) = 3.61 \times 10^{-13} \exp(280/T)$

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2181 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ should not be used outside the specified temperature range (220-300 K); rather, the
2182 full three parameter expression should be used.

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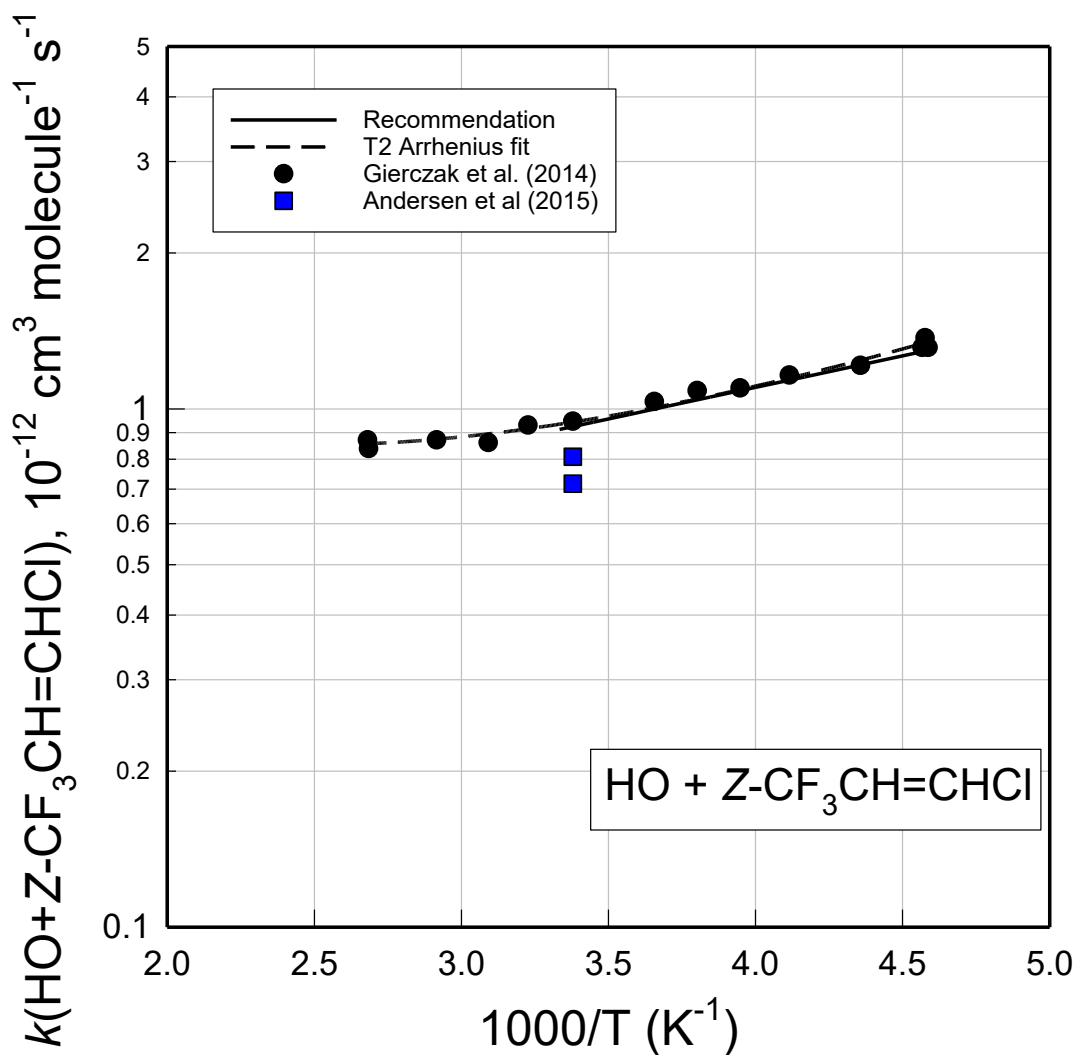
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2190 Atmospheric Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>

2191 Gierczak, T., Baasandorj, M., and Burkholder, J. B.: J. Phys. Chem. A, 118, 11015, 2014.

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2196 **oFOx165: HO + E-CF₃CF=CHCl (HCFO-1224yd(E))**
2197 Last evaluated: June 2025; Last change in preferred values: June 2024.

2198 **HO + E-CF₃CF=CHCl (HCFO-1224yd(E)) → products**

2200 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (1.09±0.03) × 10 ⁻¹² exp((50±10)/T) | 250-430 | Tokuhashi et al. (2018) | FP, LP-LIF (a) |
| (1.30 ± 0.01) × 10 ⁻¹² | 298 | | |

2203 **Comments**

2204 (a) HO radicals were generated by either flash photolysis or laser photolysis and were monitored
2205 using laser induced fluorescence. In the flash photolysis experiments photolysis of water vapor
2206 using a was employed as the source of HO radicals. In the laser photolysis experiments two
2207 photolysis of N₂O using an ArF eximer laser to produce O(¹D) atoms in the presence of either
2208 water vapor or CH₄ were used to generate HO radicals. There was no discernible difference in
2209 results obtained using the different methods. Experiments were performed in 5-200 Torr of argon
2210 or helium diluent, there was no discernible effect of pressure or diluent gas. The E-CF₃CF=CHCl
2211 sample was purified before use and the purity of the purified sample was determined to be 99.4%.

2212 **Preferred Values**

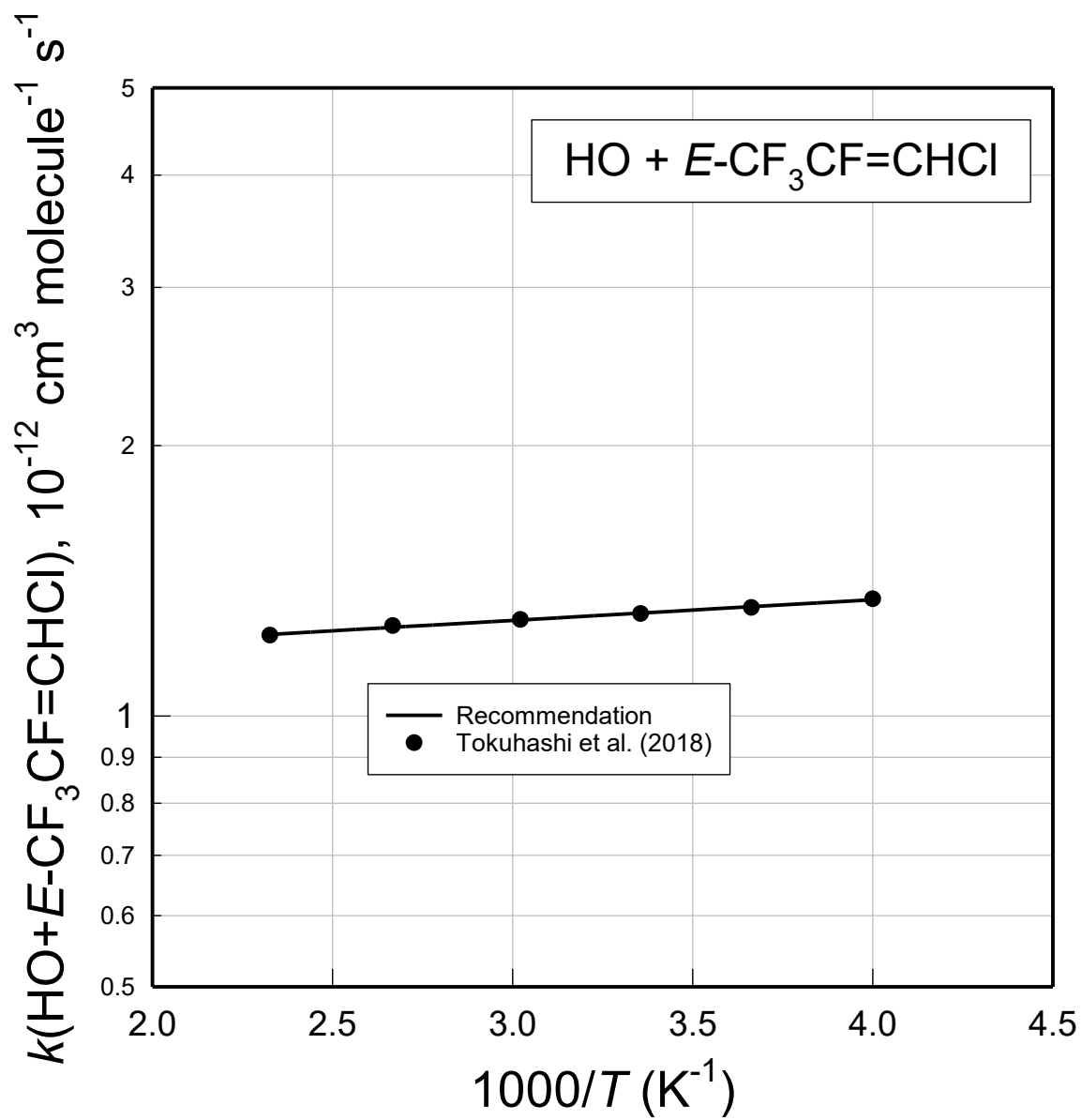
| Parameter | Value | T/K |
|--|------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.30 × 10 ⁻¹² | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.09 × 10 ⁻¹² exp(53/T) | 250-430 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.08 | 298 |
| Δ E/R | ± 100 | 250-430 |

2218 **Comments on Preferred Values**

2219 The preferred expression, $k = 1.09 \times 10^{-12} \exp(53/T)$, is a fit to the results from Tokuhashi et al.
2220 (2018) which gives $k = 1.30 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

2221 **References**

2222 Tokuhashi, K., Uchimaru, T., Takizawa, K., and Kondo, S.: J. Phys. Chem. A., 122, 3120-3127,
2223 2018.



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2234 **oFOx166: HO + Z-CF₃CF=CHCl (HCFO-1224yd(Z))**
 2235 Last evaluated: June 2025; Last change in preferred values: June 2024.

2236 **HO + Z-CF₃CF=CHCl (HCFO-1224yd(Z)) → products**

2237 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|----------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (8.02±0.19) × 10 ⁻¹³ exp(-(100±10)/T) | 250-430 | Tokuhashi et al. (2018a,b) | FP, LP-LIF (a) |
| (5.84 ± 0.03) × 10 ⁻¹³ | 298 | | |

2241 **Comments**

2242 (a) HO radicals were generated by either flash photolysis or laser photolysis and were monitored
 2243 using laser induced fluorescence. In the flash photolysis experiments photolysis of water vapor
 2244 was employed as the source of HO radicals. In the laser photolysis experiments photolysis of N₂O
 2245 to produce O(¹D) atoms in the presence of either water vapor or CH₄ were used to generate HO
 2246 radicals. There was no discernible difference in results obtained using the different methods.
 2247 Experiments were performed in 5-200 Torr of argon or helium diluent, there was no discernible
 2248 effect of pressure or diluent gas. The Z-CF₃CF=CHCl sample was purified before use and the
 2249 purity of the purified sample was determined to be 99.92%.

2252 **Preferred Values**

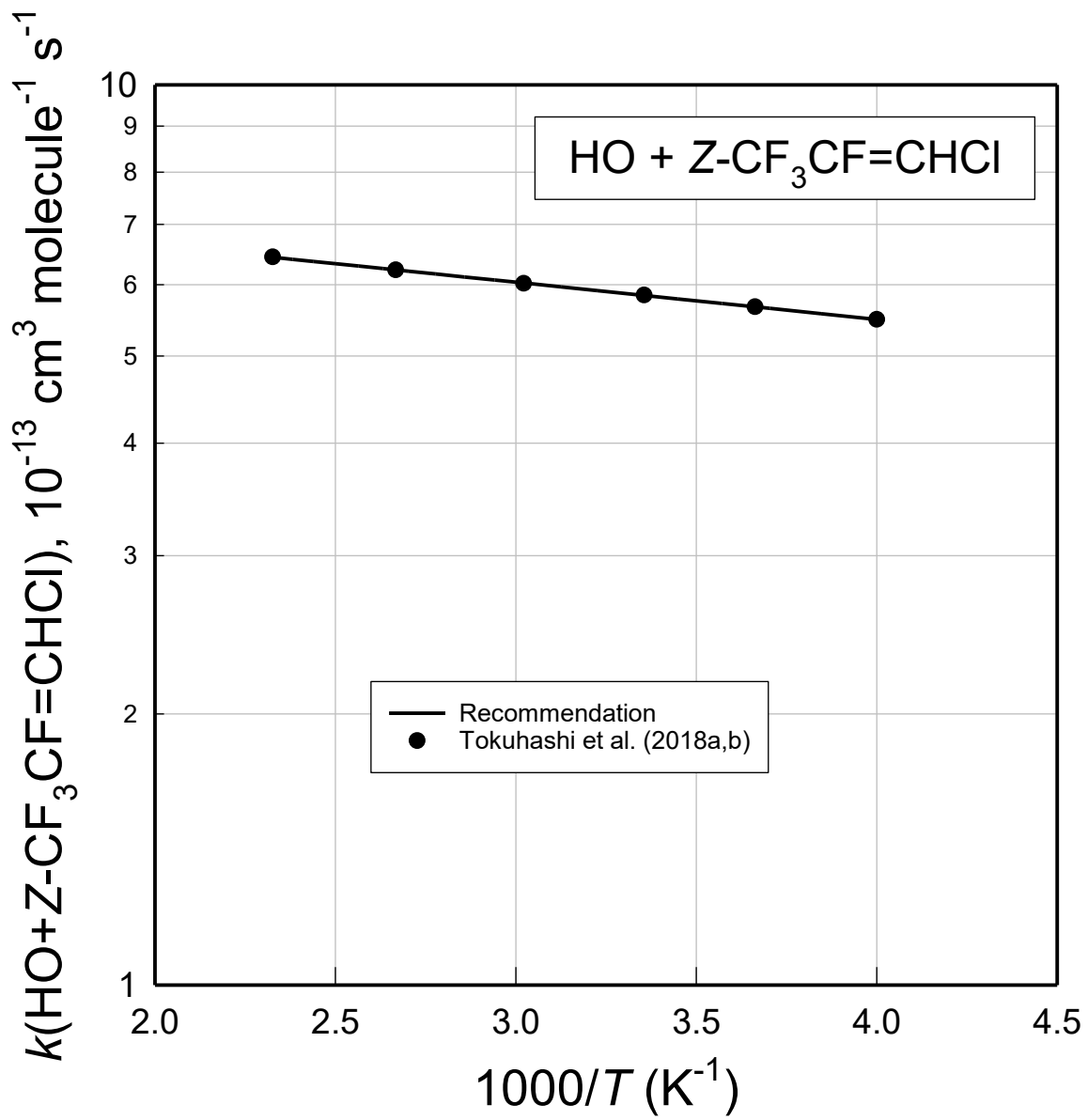
| Parameter | Value | T/K |
|--|--------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 5.83 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 8.03 × 10 ⁻¹³ exp -(95/T) | 250-430 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.08 | 298 |
| Δ E/R | ± 100 | 250-430 |

2256 **Comments on Preferred Values**

2257 The preferred expression, $k = 8.03 \times 10^{-13} \exp -(95/T)$, is a fit to the results from Tokuhashi et al.
 2258 (2018a,b) which gives $k = 5.83 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

2263 **References**

- 2264 Tokuhashi, K., Uchimaru, T., Takizawa, and K., Kondo, S.: J. Phys. Chem. A., 122, 3120-3127,
 2265 2018a.
 2266 Tokuhashi, K., Uchimaru, T., Takizawa, K., and Kondo, S.: J. Phys. Chem. A., 122, 9922-9922,
 2267 2018b.



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HO + CF₃CBr=CH₂ (HBFO-1233xfB) → products

Rate coefficient data

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (1.36±0.16) × 10 ⁻¹³ exp((317±34)/T) | 250-370 | Orkin et al. (2002) | FP-RF (a) |
| (3.88 ± 0.15) × 10 ⁻¹² | 298 | | |
| 4.85 × 10 ⁻¹³ (T/298) ^{0.92} exp(613/T) | 220-370 | Patten et al. (2011) | FP-RF (b) |
| (3.79 ± 0.02) × 10 ⁻¹² | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (3.61±0.28) × 10 ⁻¹² | 296 | Sulbaek Andersen et al. (2009) | RR (c) |
| (3.99±0.24) × 10 ⁻¹² | 296 | | |

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Comments

- (a) HO radicals were generated by flash photolysis of water. Experiments were performed in 100 Torr of argon diluent.
- (b) HO radicals were generated by flash photolysis of water. Experiments were performed in 7-30 Torr of argon diluent. There was no discernible effect of pressure suggesting the reaction is at, or near, the high-pressure limit.
- (c) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of CF₃CBr=CH₂ was measured relative to C₂H₂ and C₂H₄ and used to measure the rate coefficient ratios $k(\text{CF}_3\text{CBr}=\text{CH}_2)/k(\text{C}_2\text{H}_2) = 4.829 \pm 0.374$ and $k(\text{CF}_3\text{CBr}=\text{CH}_2)/k(\text{C}_2\text{H}_4) = 0.508 \pm 0.031$. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{CF}_3\text{CBr}=\text{CH}_2) = (3.61 \pm 0.28) \times 10^{-12}$ and $(3.99 \pm 0.24) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 3.84 × 10 ⁻¹² | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.11 × 10 ⁻¹² exp(370/T) | 250-430 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.06 | 298 |
| Δ E/R | ± 100 | 250-430 |

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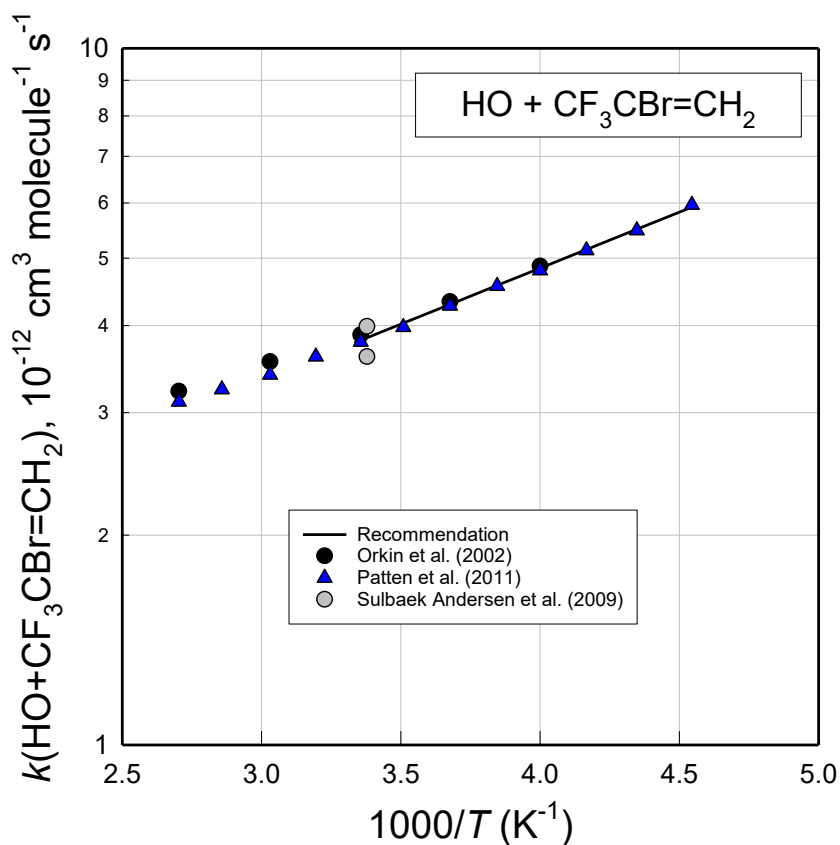
Comments on Preferred Values

There is good agreement between the results of the absolute rate studies by Orkin et al. (2002) and Patten et al. (2011) and the relative rate study by Sulbaek Andersen et al. (2009). An average of the results from Orkin et al. (2002) and Patten et al. (2011) gives $k = 3.84 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Patten et al.

2306 (2011) showed that their data and those from Orkin et al. (2002) over the entire temperature range studied
2307 (220-370 K) are well fit by the expression $k = 4.85 \times 10^{-13} (T/298)^{0.92} \exp(613/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A fit
2308 of the Arrhenius expression to the combined data set from Orkin et al. (2002) and Patten et al. (2011)
2309 below 300 K and adjusting the A factor to reproduce the preferred value at 298 K gives $k = 1.11 \times 10^{-12}$
2310 $\exp(370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For simplicity and consistency within the IUPAC database we prefer the
2311 simple Arrhenius expression.

2312 References

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2315 Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>
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2320
2321
2322



2323
2324

2325 **oFOx154: NO₃ + CF₂=CF₂**
2326 Last evaluated: June 2025; Last change in preferred values: June 2017.

2327
2328 **NO₃ + CF₂=CF₂ → products**

2329
2330 **Rate coefficient data**

2331

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| < 3 × 10 ⁻¹⁵ | 298 | Acerboni et al., 1999 | RR (a) |

2332
2333 **Comments**

2334
2335 (a) NO₃ radicals were produced by mixing O₃ with an excess of NO₂, to establish an equilibrium
2336 between NO₂, NO₃, and N₂O₅ in 740 Torr (986 mbar) of air diluent. The decay of C₂F₄ was
2337 monitored relative to that of C₃H₆ and a rate coefficient ratio $k(\text{NO}_3 + \text{C}_2\text{F}_4)/k(\text{NO}_3 + \text{C}_3\text{H}_6) =$
2338 0.159 was measured. Using $k(\text{NO}_3 + \text{C}_3\text{H}_6) = 9.5 \times 10^{-15}$ (Atkinson et al., 2006) gives $k(\text{NO}_3 +$
2339 $\text{C}_2\text{F}_4) = 1.5 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. The authors noted a “relatively large random error” in the
2340 determination of the rate coefficient ratio, although they did not quantify the uncertainty, and
2341 chose to report an upper limit for $k(\text{NO}_3 + \text{C}_2\text{F}_4) < 3 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹.

2342
2343 **Preferred Values**

2344

| Parameter | Value | T/K |
|--|-------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | < 3 × 10 ⁻¹⁵ | 298 |

2345
2346 *Comments on Preferred Values*

2347
2348 The upper limit is taken from the study by Acerboni et al. (1999).

2349
2350 **References**

2351
2352 Acerboni, G., Jensen, N. R., Rindone, B., and Hjorth, J.: Chem. Phys. Lett., 309, 364, 1999.
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2355 Atmospheric Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>.

2356

2357 **oFOx153: NO₃ + CF₃CF=CH₂ (HFO-1234yf)**
2358 Last evaluated: June 2025; Last change in preferred values: June 2017.

2359
2360 **NO₃ + CF₃CF=CH₂ (HFO-1234yf) → products**

2361
2362 **Rate coefficient data**

2363

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| < 2 × 10 ⁻¹⁶ | 233-353 | Papadimitriou et al. (2011) | FT-MS (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (2.6 ± 0.25) × 10 ⁻¹⁷ | 296 | Papadimitriou et al. (2011) | RR (b) |

2364
2365 **Comments**

- 2366
- 2367 (a) NO₃ radicals were produced by thermal decomposition of N₂O₅ in a 400 K oven attached to a
2368 low-pressure flow tube reactor. NO₃ radicals were detected using a chemical ionization mass
2369 spectrometer. Experiments were performed in 2-6 Torr of helium diluent at 233-353 K. The
2370 addition of CF₃CF=CH₂ led to a barely discernable, < 2 s⁻¹, loss of NO₃ radicals from which an
2371 upper limit of *k*(NO₃+CF₃CF=CH₂) < 2 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ was derived.
- 2372 (b) NO₃ radicals were produced by thermal decomposition of N₂O₅ in 630 Torr (840 mbar) of air
2373 diluent at 296 K. The decay of CF₃CF=CH₂ was monitored relative to that of C₂H₄ and a rate
2374 coefficient ratio *k*(NO₃ + CF₃CF=CH₂)/*k*(NO₃ + C₂H₄) = 0.124 ± 0.012 was measured. Using
2375 *k*(NO₃ + C₃H₆) = 2.1 × 10⁻¹⁶ (Atkinson et al., 2006) gives *k*(NO₃ + CF₃CF=CH₂) = (2.6 ± 0.25) ×
2376 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹.

2377
2378 **Preferred Values**

2379

| Parameter | Value | T/K |
|--|-------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.6 × 10 ⁻¹⁷ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.15 | 298 |

2380
2381 *Comments on Preferred Values*

2382
2383 The preferred value is based on the sole study of this reaction by Papadimitriou et al. (2011).

2384
2385 **References**

- 2386
2387 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
2388 Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric
2389 Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>
2390 Papadimitriou, V. C., Lazarou, Y. G., Talukdar, R. K., and Burkholder, J. B.: J. Phys. Chem. A, 115,
2391 167, 2011.

2392

2393 **oFOx122: NO₃ + Z-CF₃CF=CHF (HFO-1225ye(Z))**
 2394 Last evaluated: June 2025; Last change in preferred values: June 2018.

2395 **NO₃ + Z-CF₃CF=CHF (HFO-1225ye(Z)) → products**

2396 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| < 2 × 10 ⁻¹⁶ | 233-353 | Papadimitriou et al. (2011) | FT-MS (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (4.2 ± 0.5) × 10 ⁻¹⁸ | 296 | Papadimitriou et al. (2011) | RR (b) |

2400 **Comments**

- 2401
- 2402
- 2403 (a) NO₃ radicals were produced by thermal decomposition of N₂O₅ in a 400 K oven attached to a
 2404 low-pressure flow tube reactor. NO₃ radicals were detected using a chemical ionization mass
 2405 spectrometer. Experiments were performed in 2-6 Torr of helium diluent at 233-353 K. The
 2406 addition of CF₃CF=CHF led to a barely discernible, < 2 s⁻¹, loss of NO₃ radicals from which an
 2407 upper limit of *k*(NO₃+CF₃CF=CHF) < 2 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ was derived.
- 2408 (b) NO₃ radicals were produced by thermal decomposition of N₂O₅ in 630 Torr (840 mbar) of air
 2409 diluent at 296 K. The decay of CF₃CF=CHF was monitored relative to that of C₂H₄ and a rate
 2410 coefficient ratio *k*(NO₃ + CF₃CF=CHF)/*k*(NO₃ + C₂H₄) = 0.019 ± 0.002 was measured. Using
 2411 *k*(NO₃ + C₃H₆) = 2.1 × 10⁻¹⁶ (Atkinson et al., 2006) gives *k*(NO₃ + CF₃CF=CHF) = (4.2 ± 0.5) ×
 2412 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹.

2413 **Preferred Values**

| Parameter | Value | T/K |
|--|-------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 4.2 × 10 ⁻¹⁸ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.20 | 298 |

2416 *Comments on Preferred Values*

2417

2418 The preferred value is based on the sole study of this reaction by Papadimitriou et al. (2011).

2421 **References**

- 2422 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
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 2424 Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>.
 2425 Papadimitriou, V. C., Lazarou, Y. G., Talukdar, R. K., and Burkholder, J. B.: J. Phys. Chem. A, 115,
 2426 167, 2011.

2430 **oFOx123: NO₃ + CF₃CF=CF₂ (FO-1216)**
2431 Last evaluated: June 2025; Last change in preferred values: June 2019.

2432
2433 **NO₃ + CF₃CF=CF₂ (FO-1216) → products**

2434
2435 **Rate coefficient data**

2436

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Relative Rate Coefficients</i> < 3 × 10 ⁻¹⁵ | 298 | Acerboni et al., 2001 | RR (a) |

2437
2438 **Comments**

2439
2440 (a) NO₃ radicals were produced by mixing O₃ with an excess of NO₂, to establish an equilibrium
2441 between NO₂, NO₃, and N₂O₅ in 740 Torr (986 mbar) of air diluent. The authors specify that a
2442 relative rate method was employed, but do not specify the reference used on rate coefficient ratio
2443 result. The authors noted that the reaction was very slow and only an upper limit for the rate
2444 coefficient $k(\text{NO}_3 + \text{C}_3\text{F}_6) < 3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived.

2445
2446 **Preferred Values**

2447

| Parameter | Value | T/K |
|--|-------------------------|------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | < 3 × 10 ⁻¹⁵ | 298 |

2448
2449 *Comments on Preferred Values*

2450
2451 The preferred value was taken from the study by Acerboni et al. (2001).

2452
2453 **References**

2454
2455 Acerboni, G., Beukes, J. A., Jensen, N. R., Hjorth, J., Myhre, G., Nielsen, C. J., and Sundet, J. K. :
2456 Atmos. Environ., 35, 4113, 2001.

2457

2458 **oFOx155: NO₃ + CF₂=CFCF=CF₂**
 2459 Last evaluated: June 2025; Last change in preferred values: June 2019.

2460 **NO₃ + CF₂=CFCF=CF₂ → products**

2461 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| < 3 × 10 ⁻¹⁵ | 298 | Acerboni et al., 2001 | RR (a) |
| (1.56 ± 0.16) × 10 ⁻¹⁵ | 298 | Chen et al., 2005 | RR (b) |

2465 **Comments**

- 2466 (a) NO₃ radicals were produced by mixing O₃ with an excess of NO₂, to establish an equilibrium
 2467 between NO₂, NO₃, and N₂O₅ in 740 Torr (986 mbar) of air diluent. The authors specify that a
 2468 relative rate method was employed, but do not specify the reference used or rate coefficient ratio
 2469 result. The authors noted that the reaction was very slow and only an upper limit for the rate
 2470 coefficient $k(\text{NO}_3 + \text{C}_3\text{F}_6) < 3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived.
 2471 (b) NO₃ radicals were produced by the thermal decomposition of N₂O₅. The loss of CF₂=CFCF=CF₂
 2472 was monitored relative to that of C₃H₆ using GC-FID in 720 Torr of air diluent following the
 2473 addition of N₂O₅. A rate coefficient ratio of $k(\text{NO}_3 + \text{CF}_2=\text{CFCF}=\text{CF}_2)/k(\text{NO}_3 + \text{C}_3\text{H}_6) = 0.164 \pm$
 2474 0.017 was measured. Placing this result on an absolute basis using $k(\text{NO}_3 + \text{C}_3\text{H}_6) = 9.5 \times 10^{-15}$
 2475 (Atkinson et al., 2006) gives $k(\text{NO}_3 + \text{CF}_2=\text{CFCF}=\text{CF}_2) = (1.56 \pm 0.16) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 2476
 2477
 2478

2479 **Preferred Values**

| Parameter | Value | T/K |
|--|--------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.56 × 10 ⁻¹⁵ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.15 ± 0.04 | 298 298 |

2482 **Comments on Preferred Values**

2483 The preferred value was taken from the study by Chen et al. (2005). The upper limit reported by
 2484 Acerboni et al. (2001) is consistent with the preferred value.

2485 **References**

- 2486 Acerboni, G., Beukes, J. A., Jensen, N. R., Hjorth, J., Myhre, G., Nielsen, C. J., and Sundet, J. K.:
 2487 Atmos. Environ., 35, 4113, 2001.
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 2491 Chen, L., Kutsuna, S., Tokuhashi, K., Uchimaru, T., and Sekiya, A.: Chem. Phys. Lett., 416, 187,
 2492 2005.

2500 **NO₃ + CH₂=CHCl → products**

2501 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|---------------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (4.26 ± 0.39) × 10 ⁻¹⁶ | 295 | Noremsaune et al. (1997) | DF-Vis (a) |
| 1.8 × 10 ⁻¹³ exp(-1780/T) | 266-367 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (4.37 ± 0.19) × 10 ⁻¹⁶ | 298 | Atkinson et al. (1987) | RR (b) |
| (1.4 ± 0.9) × 10 ⁻¹⁶ | 296 | Andersson and Ljungström (1989) | RR (c) |
| (2.6 ± 0.5) × 10 ⁻¹⁶ | 296 | Noremsaune et al. (1995) | RR (d) |
| (3.74 ± 0.57) × 10 ⁻¹⁶ | 296 | Noremsaune et al. (1997) | RR (e) |

2505 **Comments**

- 2506
- 2507
- 2508 (a) NO₃ radicals were produced by the reaction of F atoms with HNO₃ and monitored by absorption at
 2509 662 nm.
- 2510 (b) NO₃ radicals were produced by the thermal decomposition of N₂O₅ in 740 Torr (986 mbar) of air at
 2511 298 K. The loss of CH₂=CHCl was monitored using GC-FID relative to that of C₂H₄ and a rate
 2512 coefficient ratio of $k(\text{NO}_3 + \text{CH}_2=\text{CHCl})/k(\text{NO}_3 + \text{C}_2\text{H}_4) = 2.08 \pm 0.09$ was measured. Using $k(\text{NO}_3 +$
 2513 $\text{C}_2\text{H}_4) = 2.1 \times 10^{-16}$ (Atkinson et al., 2006) gives $k(\text{NO}_3 + \text{CH}_2=\text{CHCl}) = (4.37 \pm 0.19) \times 10^{-16}$ cm³
 2514 molecule⁻¹ s⁻¹.
- 2515 (c) NO₃ radicals were produced by reacting NO₂ with O₃ in one atmosphere pressure of N₂ to establish
 2516 an equilibrium between NO₂, NO₃, and N₂O₅ at 296 K. The decay of N₂O₅ and CH₂=CHCl was
 2517 monitored by FTIR spectroscopy. A complex chemical mechanism was used with $k(\text{NO}_3 +$
 2518 $\text{CH}_2=\text{CHCl})$ varied to give the best fit of the decay of N₂O₅ and CH₂=CHCl. This work is
 2519 superseded by the studies by Noremsaune et al. (1995, 1997) and not considered further.
- 2520 (d) NO₃ radicals were produced by the thermal decomposition of N₂O₅ which was synthesized in situ
 2521 by mixing O₃ with excess NO₂ in 760 Torr (1 bar) of air. Experiments were performed at 295 K and
 2522 kinetic data were obtained by monitoring the decay of CH₂=CHCl in the chamber over a period of
 2523 10-60 minutes and simulating the decay using analytical and numerical methods. The rate
 2524 coefficient $k(\text{NO}_3 + \text{CH}_2=\text{CHCl})$ derived in the experiments is dependent on the NO₂ + NO₃ = N₂O₅
 2525 equilibrium constant assumed in the calculations. Unfortunately, it is unclear what equilibrium
 2526 constant was used. In the paper it is stated several times that the temperature of the experiments was
 2527 295 K, but it then stated that a value of $K_{eq} = 3.77 \times 10^{-11}$ cm³ molecule⁻¹ at 298 K (Wayne et al.
 2528 1991) was used to derive $k(\text{NO}_3 + \text{CH}_2=\text{CHCl})$. K_{eq} is very sensitive to temperature and increases
 2529 from 2.78×10^{-11} to 4.06×10^{-11} cm³ molecule⁻¹ over the temperature range 298 to 295 K
 2530 (IUPAC, 2018). Given the uncertainty in value of K_{eq} used by Noremsaune et al. (1995) we are
 2531 not able to scale their result to the latest preferred equilibrium coefficient of K_{eq} . The value in the
 2532 table above is that reported by Noremsaune et al. (1995).
- 2533 (e) NO₃ radicals were produced by mixing O₃ with an excess of NO₂, to establish an equilibrium
 2534 between NO₂, NO₃, and N₂O₅ in 740 Torr (986 mbar) of air. The decay of CH₂=CHCl was
 2535 monitored relative to that of C₂H₄ and a rate coefficient ratio $k(\text{NO}_3 + \text{CH}_2=\text{CHCl})/k(\text{NO}_3 + \text{C}_2\text{H}_4) =$
 2536 1.78 ± 0.27 was measured. Using $k(\text{NO}_3 + \text{C}_2\text{H}_4) = 2.1 \times 10^{-16}$ (Atkinson et al., 2006) gives $k(\text{NO}_3 +$
 2537 $\text{CH}_2=\text{CHCl}) = (3.74 \pm 0.57) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹.

2538
2539
2540

Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.8 \times 10^{-13} \exp(-1780/T)$ | 260-380 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 4.6×10^{-16} | 298 |
| Reliability | | |
| $\Delta \log k$ | ± 0.10 | 298 |
| $\Delta E/R$ | ± 300 | 260-380 |

2541
2542
2543

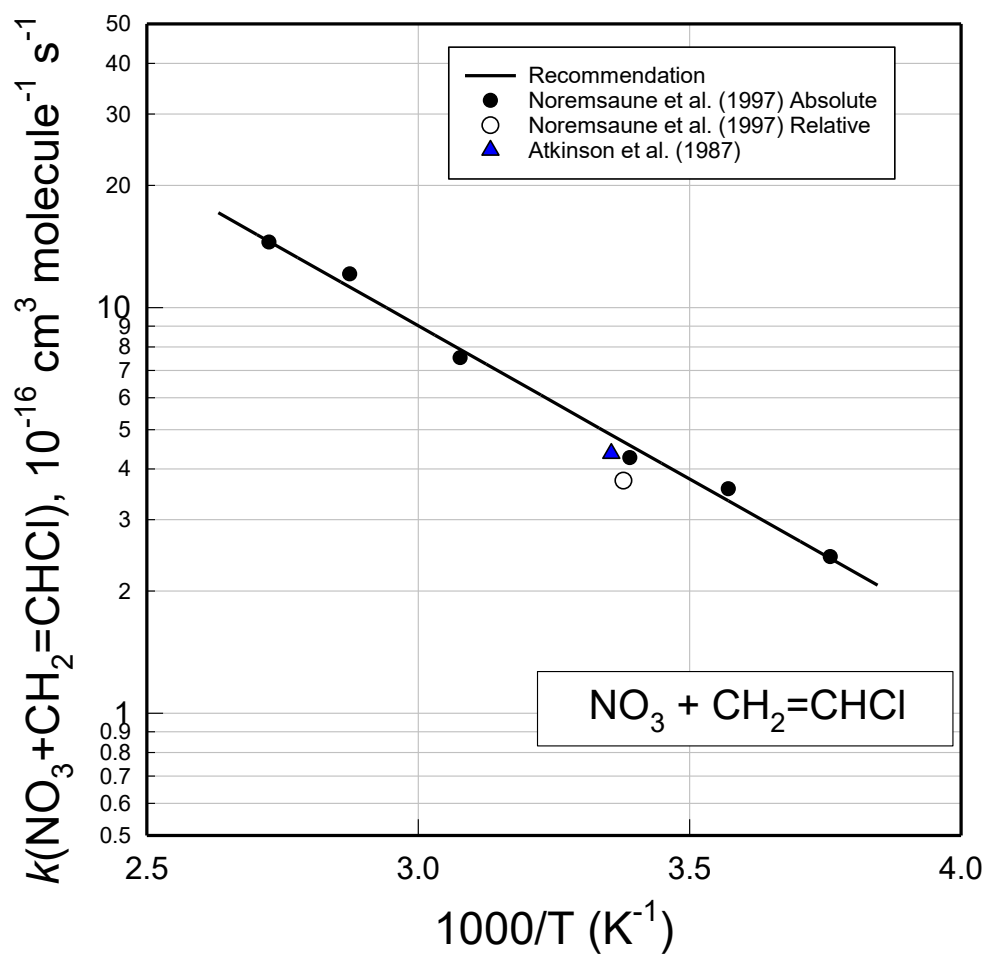
Comments on Preferred Values

2544 There is good agreement in the absolute and relative rate measurements by Noremsaune et al. (1997)
2545 and Atkinson et al. (1987). The preferred Arrhenius expression is that reported by Noremsaune et al.
2546 (1997) which gives the value at 298 K in the table above.

2547
2548
2549

References

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- 2551 Atkinson, R., Aschmann, S. M., and Goodman, M. A.: Int. J. Chem. Kinet., 19, 299, 1987.
- 2552 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi,
2553 M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical
2554 Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>.
- 2555 Noremsaune, I. M. W., Hjorth, J.; and Nielsen, C. J.: J. Atmos. Chem., 21, 223, 1995.
- 2556 Noremsaune, I. M. W., Langer, S., Ljungström, E., and Nielsen, C. J.: J. Chem. Soc., Faraday Trans., 93, 525,
2557 1997.
- 2558 Wayne, R. P., Barnes, I., Biggs, P., Burrows, J. B., Canosa-Mas, C. E., Hjorth, J., LeBras, G., Moortgat, G.,
2559 Perner, D., Poulet, G., Restelli, G., and Sidebottom, H.: Atmos. Environ. 25A, 1, 1991.
- 2560
2561
2562



2563
2564

2567
 2568 **O₃ + CF₂=CF₂ → products**

2569 **Rate coefficient data**

2570

2571

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 1.34 × 10 ⁻¹⁶ | 298 | Heicklen (1966) | S-IR (a) |
| 2.63 × 10 ⁻¹³ exp(-4780/T) | 273-373 | Toby and Toby (1976) | S-UV (b) |
| 2.84 × 10 ⁻²⁰ | 298 | | |
| (4.80 ± 0.62) × 10 ⁻²¹ | 298 | Acerboni et al., 1999 | S-FTIR (c) |

2572
 2573 **Comments**

- 2574
- 2575 (a) Kinetic data were derived by following the initial rate of formation of the reaction product COF₂
- 2576 using IR spectroscopy following the mixing of 0.7-24 Torr of O₃ with 0.2-5.7 Torr of C₂F₄.
- 2577 (b) UV absorption at 254 nm was used to follow the loss of ozone in the presence of an excess of
- 2578 C₂F₄ following mixing 0.06-0.1 Torr of O₃ with 3.0-7.9 Torr of C₂F₄.
- 2579 (c) FTIR spectroscopy was used to follow the loss of C₂F₄ (2-4 ppmv) in the presence of a large
- 2580 excess of O₃ (25-600 ppmv) in 740 Torr (986 mbar) of air at 298 K. Cyclohexane (20-60 ppmv)
- 2581 was added to scavenge radical products of the reaction of O₃ with C₂F₄ which could lead to
- 2582 unwanted secondary loss of C₂F₄. First order decay of C₂F₄ was observed and the pseudo-first
- 2583 order loss rates were linearly dependent on [O₃].

2584
 2585 **Preferred Values**

2586

| Parameter | Value | T/K |
|--|-------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 4.8 × 10 ⁻²¹ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.15 | 298 |

2587
 2588 *Comments on Preferred Values*

2589

2590 The chemical systems used by Heicklen (1966) and Toby and Toby (1976) in which high

2591 concentrations (of the order of Torr) of O₃ and C₂F₄ were mixed in the absence of diluent gas and

2592 kinetic data were obtained by monitoring the rate of formation of either COF₂ product (Heicklen,

2593 1966) or O₃ reactant (Toby and Toby, 1976). The kinetic behaviour observed was complex indicating

2594 the presence of substantial complications from secondary chemistry, and hence the rate coefficients

2595 derived are likely upper limits. The study by Acerboni et al. (1999) employed lower concentrations of

2596 reactants in 740 Torr of air diluent and derived kinetic data by monitoring the loss of C₂F₄ in the

2597 presence of excess O₃. The loss of C₂F₄ followed first order kinetics and the pseudo first order rate

2598 coefficients increased linearly with [O₃]. The preferred value is based on the result from Acerboni et

2599 al. (1999) with uncertainties increased to reflect the fact that it is based on a single study.

2600
 2601 **References**

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2604 Heicklen, J.: J. Phys. Chem., 70, 477, 1966.
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2606
2607

2610 **O₃ + CF₃CH=CH₂ (HFO-1243zf) → products**

2611 **Rate coefficient data**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(3.5 \pm 0.3) \times 10^{-19}$ | 296 | Sulbaek Andersen et al. (2005) | S-FTIR (a) |
| $(1.41 \pm 0.26) \times 10^{-20}$ | 296 | McGillen et al. (2023) | S-UV (b) |
| $7.07 \times 10^{-16} \exp(-3236/T)$ | 296-384 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(3.0 \pm 0.4) \times 10^{-19}$ | 298 | Soto et al. (2018) | RR (c) |
| $(1.15 \pm 0.23) \times 10^{-20}$ | 296 | McGillen et al. (2023) | RR (d) |
| $(1.25 \pm 0.26) \times 10^{-20}$ | 296 | | RR (e) |

2615 **Comments**

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- 2618 (a) The decay of CF₃CH=CH₂ was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of CF₃CH=CH₂, cyclohexane, and O₃ in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of CF₃CH=CH₂ via reaction with OH radicals formed in the reaction system. The loss of CF₃CH=CH₂ followed first order kinetics and the pseudo first-order rate coefficients increased linearly with [O₃].
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- 2623 (b) The decay of ozone was monitored with a commercial ozone analyser (using UV absorption) in the presence of an excess of CF₃CH=CH₂ in the presence of cyclohexane and HC(O)OH which were added as scavengers for HO radicals and stabilized Criegee intermediates, respectively. The diluent and pressure was not specified but was 1 atmosphere of air (McGillen, private communication). The loss of O₃ followed first order kinetics and the pseudo first-order rate coefficients increased linearly with [CF₃CH=CH₂].
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- 2629 (c) The loss of CF₃CH=CH₂ was measured relative to that of acrolein (CH₂=CHCHO) in 720 Torr of synthetic air. Cyclohexane was added to avoid potential problems associated with the loss of CF₃CH=CH₂ via reaction with OH radicals formed in the reaction system. A rate constant ratio of $k(\text{O}_3+\text{CF}_3\text{CH}=\text{CH}_2)/k(\text{O}_3+\text{CH}_2=\text{CHCHO}) = 0.99 \pm 0.01$ was measured which can be combined with $k(\text{O}_3+\text{CH}_2=\text{CHCHO}) = (3.0 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Treacy et al. 1992) to give $k(\text{O}_3+\text{CF}_3\text{CH}=\text{CH}_2) = (3.0 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
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- 2635 (d) The decay of CF₃CH=CH₂ was measured relative to that of HCFO-1233xf (CF₃CCl=CH₂) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge both HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(\text{O}_3+\text{CF}_3\text{CH}=\text{CH}_2)/k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2) = 3.257$ was measured and was combined with $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2) = 3.54 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (McGillen et al. 2023) to give $k(\text{O}_3+\text{CF}_3\text{CH}=\text{CH}_2) = (1.15 \pm 0.23) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
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- 2641 (e) The decay of CF₃CH=CH₂ was measured relative to that of HFO-1234yf (CF₃CF=CH₂) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge both HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(\text{O}_3+\text{CF}_3\text{CH}=\text{CH}_2)/k(\text{O}_3+\text{CF}_3\text{CF}=\text{CH}_2) = 4.885$ was measured and was combined with $k(\text{O}_3+\text{CF}_3\text{CF}=\text{CH}_2) = 2.56 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [McGillen et al. 2023] to give $k(\text{O}_3+\text{CF}_3\text{CH}=\text{CH}_2) = (1.25 \pm 0.26) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
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Preferred Values

| Parameter | Value | T/K |
|--|--|----------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.43×10^{-20} $4.65 \times 10^{-16} \exp(-3096/T)$ | 298 290-390 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.08 | 298 |
| $\Delta E/R$ | 200 | |

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Comments on Preferred Values

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2653 The preferred expression is taken from a fit to the absolute rate data from McGillen et al. (2023).
2654 The value at 298K is evaluated from the preferred Arrhenius expression. The relative rate and
2655 absolute rate results reported by McGillen et al. (2023) are in good agreement but are substantially
2656 lower than the results reported by Sulbaek Andersen et al. (2005) and Soto et al. (2018). As discussed
2657 by McGillen et al. (2023), the cyclohexane scavenger used by Sulbaek Andersen et al. (2005) and
2658 Soto et al. (2018) would be effective for HO radicals but not for Criegee intermediates. Hence, the
2659 larger rate constants reported by Sulbaek Andersen et al. (2005) and Soto et al. (2018) presumably
2660 reflect secondary loss of $\text{CF}_3\text{CH}=\text{CH}_2$ by reaction with Criegee intermediates. McGillen et al. (2023)
2661 showed that CF_3H is formed in a yield of $(0.37 \pm 0.02) \%$ in a “hot acid” reaction channel.

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References

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2665 McGillen, M. R.; Zachary, T. P.; Fried, M.; Khan, A. H.; Kuwata, K. T.; Martin, C. M.; O’Doherty, S.;
2666 Pecere, F.; Shallcross, D. E.; Stanley, K. M.; and Zhang, K.: PNAS, 120, e2312714120, 2023.

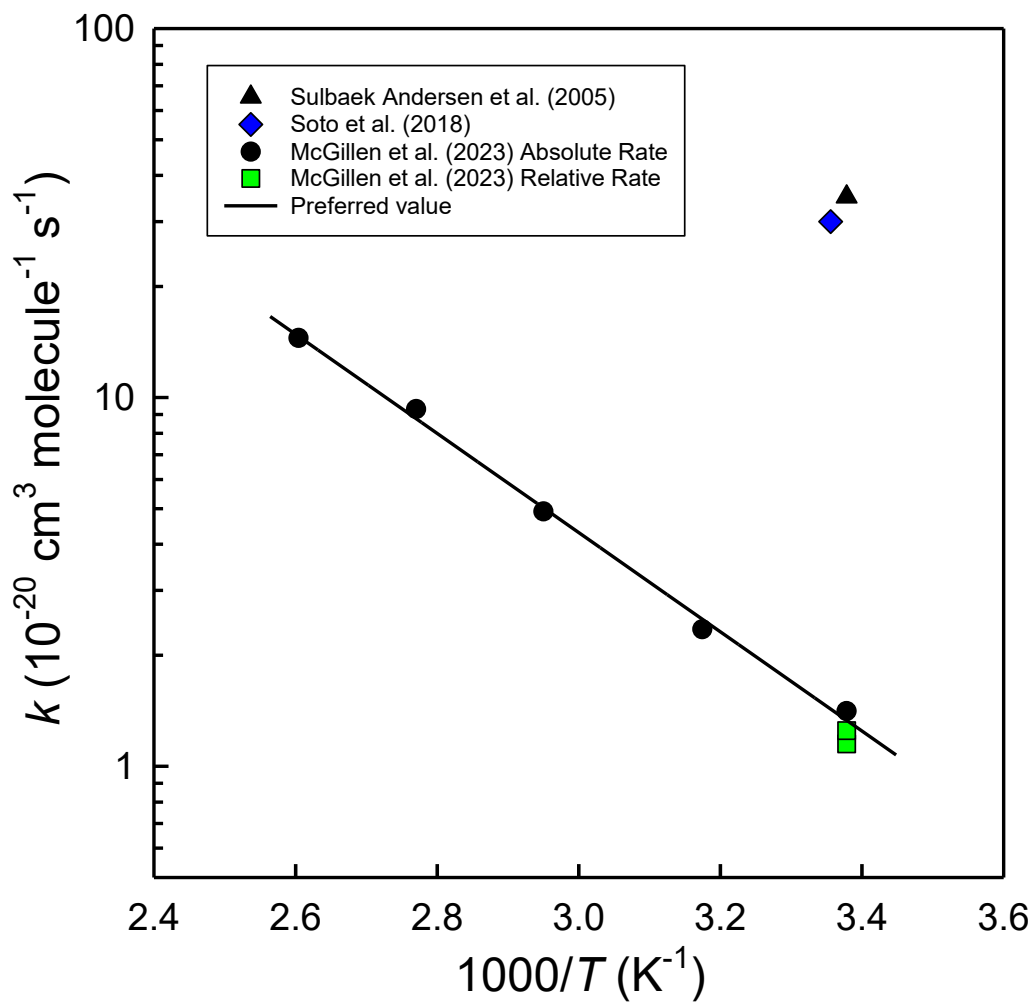
2667 Soto, A.; Ballesteros, B.; Jiménez, E.; Antinõlo, M.; Martínez, E.; and Albaladejo, J.: Chemosphere 201,
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2670 Hurley, M. D.; and Wallington, T. J.: J. Photoch. Photobio. A 176, 124–128, 2005.

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2678 **O₃ + CF₃CF=CH₂ (HFO-1234yf) → products**

2680 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (2.77 ± 0.21) × 10 ⁻²¹ | 296 | Nielsen et al. (2007) | S-FTIR (a) |
| (2.56 ± 1.42) × 10 ⁻²¹ | 296 | McGillen et al. (2023) | S-UV (b) |
| <i>Relative Rate Coefficients</i> | | | |
| (2.37 ± 0.47) × 10 ⁻²¹ | 296 | McGillen et al. (2023) | RR (c) |
| (2.58 ± 0.53) × 10 ⁻²¹ | 296 | | RR (d) |

2683 **Comments**

- 2684
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- 2686 (a) The decay of CF₃CF=CH₂ was monitored by FTIR spectroscopy when exposed to ozone in 700
 2687 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss
 2688 of CF₃CF=CH₂ via reaction with OH radicals formed in the reaction system. The loss of
 2689 CF₃CF=CH₂ followed first order kinetics and the pseudo first order rate coefficients increased
 2690 linearly with [O₃].
- 2691 (b) The decay of ozone was monitored via UV absorption in the presence of an excess of
 2692 CF₃CF=CH₂. Either *i*-propanol, or cyclohexane and HC(O)OH which were added as scavengers
 2693 for HO radicals and stabilized Criegee intermediates. The diluent and pressure was 1 atmosphere
 2694 of air (McGillen, private communication). The loss of O₃ followed first order kinetics and the
 2695 pseudo first order rate coefficients increased linearly with [CF₃CF=CH₂].
- 2696 (c) The decay of CF₃CF=CH₂ was measured relative to that of HCFO-1233xf (CF₃CCl=CH₂) in the
 2697 presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry
 2698 isopropanol was added to scavenge HO radicals and stabilized Criegee intermediates which are
 2699 formed in the system. A rate constant ratio of $k(\text{O}_3 + \text{CF}_3\text{CF}=\text{CH}_2)/k(\text{O}_3 + \text{CF}_3\text{CCl}=\text{CH}_2) = (0.669 \pm$
 2700 $0.133)$ was measured and combined with $k(\text{O}_3 + \text{CF}_3\text{CCl}=\text{CH}_2) = 3.54 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 2701 (McGillen et al., 2023) to give $k(\text{O}_3 + \text{CF}_3\text{CF}=\text{CH}_2) = (2.37 \pm 0.47) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 2702 (d) The decay of CF₃CF=CH₂ was measured relative to that of HFO-1243zf (CF₃CH=CH₂) in the
 2703 presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry
 2704 isopropanol was added to scavenge HO radicals and stabilized Criegee intermediates which are
 2705 formed in the system. A rate constant ratio of $k(\text{O}_3 + \text{CF}_3\text{CF}=\text{CH}_2)/k(\text{O}_3 + \text{CF}_3\text{CH}=\text{CH}_2) = (0.205 \pm$
 2706 $0.042)$ was measured and combined with $k(\text{O}_3 + \text{CF}_3\text{CH}=\text{CH}_2) = 1.26 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to
 2707 give $k(\text{O}_3 + \text{CF}_3\text{CF}=\text{CH}_2) = (2.58 \pm 0.53) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

2708 **Preferred Values**

| Parameter | Value | T/K |
|--|--------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.67 × 10 ⁻²¹ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.08 | 298 |

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Comments on Preferred Values

There is good agreement in the results from the absolute rate studies of Nielsen et al. (2007) and McGillen et al. (2023) and the relative rate studies by McGillen et al. (2023). The preferred value is the average of the two studies. McGillen et al. (2023) performed experiments to look for the formation of CF₄ and CF₃H as products but did not observe them.

References

McGillen, M. R.; Zachary, T. P.; Fried, M.; Khan, A. H.; Kuwata, K. T.; Martin, C. M.; O'Doherty, S.; Pecere, F.; Shallcross, D. E.; Stanley, K. M.; and Zhang, K.: PNAS, 120, e2312714120, 2023.
Nielsen, O. J.; Javadi, M. S.; Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J.; and Singh, R.: Chem. Phys. Lett. 439, 18, 2007.

2729 **oFOx129: O₃ + E-CF₃CH=CHF (HFO-1234ze(E))**
2730 Last evaluated: June 2025; Last change in preferred values: June 2024.

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O₃ + E-CF₃CH=CHF (HFO-1234ze(E)) → products

Rate coefficient data

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|---------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (2.81 ± 0.21) × 10 ⁻²¹ | 296 | Søndergaard et al. (2007) | S-FTIR (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (2.19 ± 0.43) × 10 ⁻²¹ | 296 | McGillen et al. (2023) | RR (b) |

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Comments

- 2739 (a) The decay of E-CF₃CH=CHF was monitored by FTIR spectroscopy when exposed to ozone in
2740 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the
2741 loss of E-CF₃CH=CHF via reaction with OH radicals formed in the reaction system. The loss of
2742 E-CF₃CH=CHF followed first-order kinetics and the pseudo first-order rate coefficients increased
2743 linearly with [O₃].
- 2744 (b) The decay of E-CF₃CH=CHF was measured relative to that of HCFO-1233xf (CF₃CCl=CH₂) in
2745 the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry
2746 isopropanol was added to scavenge HO radicals and stabilized Criegee intermediates which are
2747 formed in the system. A rate constant ratio of $k(\text{O}_3 + \text{E-CF}_3\text{CH=CHF})/k(\text{O}_3 + \text{CF}_3\text{CCl=CH}_2) =$
2748 0.617 ± 0.121 was measured. Combining this with $k(\text{O}_3 + \text{CF}_3\text{CCl=CH}_2) = 3.54 \times 10^{-21}$ cm³
2749 molecule⁻¹ s⁻¹ (McGillen et al., 2023) gives $k(\text{O}_3 + \text{E-CF}_3\text{CH=CHF}) = (2.19 \pm 0.43) \times 10^{-21}$ cm³
2750 molecule⁻¹ s⁻¹.

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Preferred Values

| Parameter | Value | T/K |
|--|--------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.50 × 10 ⁻²¹ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |

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Comments on Preferred Values

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The preferred value is the average from the absolute rate study by Søndergaard et al. (2007) and the relative rate study by McGillen et al. (2023). McGillen et al. (2023) showed that CF₃H is formed in a yield of (3.11 ± 0.05) % in a “hot acid” reaction channel.

References

- 2761 McGillen, M. R.; Zachary, T. P.; Fried, M.; Khan, A. H.; Kuwata, K. T.; Martin, C. M.; O’Doherty, S.;
2762 Pecere, F.; Shallcross, D. E.; Stanley, K. M.; and Zhang, K.: PNAS, 120, e2312714120, 2023.
2763 Søndergaard, R., Nielsen, O. J., Hurley, M. D., Wallington, T. J., Singh, R.: Chem. Phys. Lett, 443,
2764 199, 2007.
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2766 **oFOx156: O₃ + Z-CF₃CH=CHF (HFO-1234(Z))**
2767 Last evaluated: June 2023; Last change in preferred values: June 2019.

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O₃ + Z-CF₃CH=CHF (HFO-1234(Z)) → products

Rate coefficient data

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (1.65 ± 0.16) × 10 ⁻²¹ | 296 | Nilsson et al. (2009) | S-FTIR (a) |

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Comments

- (a) The decay of Z-CF₃CH=CHF was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of 14.7-16.2 mTorr Z-CF₃CH=CHF, 21-65 mTorr cyclohexane, and 950–2260 mTorr O₃ in 700 Torr (933 mbar) of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of Z-CF₃CH=CHF via reaction with OH radicals formed in the reaction system. The loss of Z-CF₃CH=CHF followed first order kinetics and the pseudo first order rate coefficients increased linearly with [O₃].

Preferred Values

| Parameter | Value | T/K |
|--|-------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.7 × 10 ⁻²¹ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.30 | 298 |

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Comments on Preferred Values

The preferred value is taken from the work by Nilsson et al. (2009); the only study of this reaction. As the authors did not consider the potential loss of Z-CF₃CH=CHF via reaction with Criegee intermediates, we increase the uncertainty substantially.

References

Nilsson, E. J. K., Nielsen, O. J., Johnson, M. S., Hurley, M. D., and Wallington, T. J.: Chem. Phys. Lett., 473, 233, 2009.

2800 **O₃ + CF₃CF=CF₂ (FO-1216) → products**

2801 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 2.2 × 10 ⁻¹⁷ | 298 | Heicklen (1966) | S-IR (a) |
| < 3 × 10 ⁻²¹ | 296 | Mashino et al. (2000) | S-FTIR (b) |
| (6.2 ± 1.5) × 10 ⁻²² | 298 | Acerboni et al. (2001) | S-FTIR (c) |

2805 **Comments**

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- 2808 (a) Kinetic data were derived by following the initial rate of formation of the reaction product COF₂
 2809 using IR spectroscopy following the mixing of 1.9-14.8 Torr of O₃ with 0.22-7.0 Torr of
 2810 CF₃CF=CF₂.
- 2811 (b) The decay of CF₃CF=CF₂ was monitored by FTIR spectroscopy when exposed to ozone.
 2812 Reaction mixtures consisted of 1.5-8.1 mTorr CF₃CF=CF₂ and 899–963 mTorr O₃ in 700 Torr of
 2813 O₂ diluent. There was no scavenger, such as cyclohexane, added to suppress unwanted radical
 2814 chemistry in the system. The loss of CF₃CF=CF₂ followed first order kinetics but there was a
 2815 systematic increase in the pseudo first order loss rates with increasing [CF₃CF=CF₂]. The
 2816 simplest explanation of this observation is loss of CF₃CF=CF₂ via reaction with products of the
 2817 O₃ + CF₃CF=CF₂ reaction. Mashino et al. (2000) chose to quote an upper limit based on the
 2818 lowest value of *k*(O₃+ CF₃CF=CF₂) measured in their study.
- 2819 (c) FTIR spectroscopy was used to follow the loss of CF₃CF=CF₂ (2-5 ppmv) in the presence of a large
 2820 excess of O₃ (25-600 ppmv) in 740 Torr (986 mbar) of air at 298 K. Cyclohexane was added as a
 2821 scavenge to suppress potential complications from unwanted radical reactions. First order decay of
 2822 CF₃CF=CF₂ was observed and the pseudo first order loss rates were linearly dependent on [O₃].

2823 **Preferred Values**

| Parameter | Value | T/K |
|--|-------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 6.2 × 10 ⁻²² | 298 |
| <i>Reliability</i> Δ log <i>k</i> | 0.15 | 298 |

2824 **Comments on Preferred Values**

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2827 The preferred value is based on the measurements by Acerboni et al. (2001) which were conducted using
 2828 cyclohexane to suppress radical chemistry in the system leading to additional loss of CF₃CF=CF₂.
 2829 Mashino et al. (2000) showed that in the absence of a radical scavenger such as cyclohexane there is
 2830 additional unwanted loss of CF₃CF=CF₂ and that the severity of this complication increases with the
 2831 [CF₃CF=CF₂] used in the experiment. The early experiments by Heicklen (1966) used particularly high
 2832 [CF₃CF=CF₂] and secondary losses of CF₃CF=CF₂ by radical chain reactions presumably explains the
 2833 overestimation of the rate coefficient by more than a factor of 10⁴ in the early studies.

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References

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2839 Acerboni, G., Beukes, J. A., Jensen, N. R., Hjorth, J., Myhre, G., Nielsen, C. J., and Sundet, J. K. : Atmos. Environ., 35, 4113, 2001.

2841 Heicklen, J.: J. Phys. Chem., 70, 477, 1966.

2842 Mashino, M., Ninomiya, Y., Kawasaki, M., Wallington, T. J., and Hurley, M. D.: J. Phys. Chem. A 104, 7255, 2000.

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2845 **oFOx157: O₃ + CF₂=CF₂=CF₂**
 2846 Last evaluated: June 2025; Last change in preferred values: June 2019.

2847 **O₃ + CF₂=CF₂=CF₂ → products**

2849 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (6.5 ± 0.2) × 10 ⁻²¹ | 298 | Acerboni et al. (2001) | S-FTIR (a) |
| (1.14±0.94) × 10 ⁻¹⁶ exp[-(2800±225)/T] | 225-308 | Chen et al. (2005) | S-FTIR (b) |
| (9.37±0.70) × 10 ⁻²¹ | 298 | | |

2853 **Comments**

- 2852
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- 2855 (a) FTIR spectroscopy was used to follow the loss of CF₂=CF₂=CF₂ (3-5 ppmv) in the presence of
 2856 a large excess of O₃ (25-600 ppmv) in 740 Torr (986 mbar) of air at 298 K. Cyclohexane (20-60
 2857 ppmv) was added as a scavenger to suppress potential complications from unwanted radical
 2858 reactions. First order decay of CF₂=CF₂=CF₂ was observed and the pseudo first order loss
 2859 rates were linearly dependent on [O₃].
- 2860 (b) The decay of CF₂=CF₂=CF₂ was monitored by FTIR spectroscopy when exposed to ozone.
 2861 Reaction mixtures consisted of 1.2 × 10¹⁴ molecule cm⁻³ CF₂=CF₂=CF₂ (5 ppmv) and 1.26-
 2862 6.94 × 10¹⁵ molecule cm⁻³ O₃ in 720 Torr of air diluent. Cyclohexane (5.6 × 10¹⁵ molecule cm⁻³)
 2863 was added as a scavenger to suppress unwanted radical chemistry in the system. The loss of
 2864 CF₂=CF₂=CF₂ followed first order kinetics.

2865 **Preferred Values**

| Parameter | Value | T/K |
|--|---------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 7.9 × 10 ⁻²¹ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 9.51 × 10 ⁻¹⁷ exp(-2800/T) | 220-320 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.20 | 298 |
| Δ E/R | ± 300 | |

2868 **Comments on Preferred Values**

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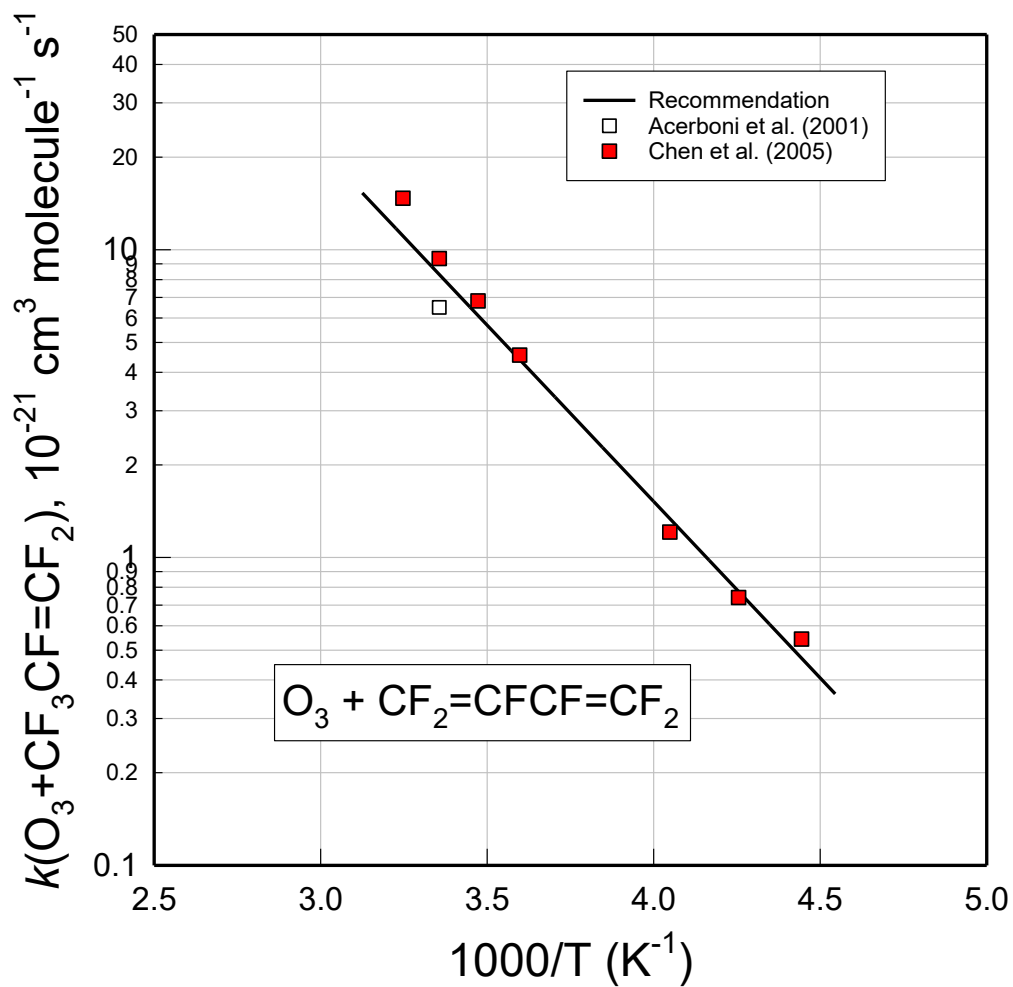
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2871 The *k*(298 K) values reported by Acerboni et al. (2001) and Chen et al. (2005) differ by approximately
 2872 30%. However, given the comment by Chen et al. that there was “a systematic uncertainty of 20% in the
 2873 measurement of O₃ concentration” in their experiments the results from the two studies are probably
 2874 consistent within the combined experimental uncertainties. The preferred value at 298 K is an average of
 2875 the results from Acerboni et al. (2001) and Chen et al. (2005). Taking the temperature dependence from
 2876 Chen et al. (2005) and adjusting the pre-exponential factor to reproduce the preferred value at 298 K
 2877 gives the preferred Arrhenius expression of *k* = 9.51 × 10⁻¹⁷ exp(-2800/T) cm³ molecule⁻¹ s⁻¹.

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References

- Acerboni, G., Beukes, J. A., Jensen, N. R., Hjorth, J., Myhre, G., Nielsen, C. J., and Sundet, J. K.: Atmos. Environ., 35, 4113, 2001.
- Chen, L., Kutsuna, S., Tokuhashi, K., Uchimaru, T., and Sekiya, A.: Chem. Phys. Lett., 416, 187, 2005.



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2893 **O₃ + *E*-CF₃CH=CHCF₃ (HFO-1336mzz(*E*)) → products**

2894 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (4.14 ± 0.42) × 10 ⁻²² | 296 | Østerstrøm et al. (2017) | S-FTIR (a) |
| (5.16 ± 0.40) × 10 ⁻²² | 296 | Baasandorj et al. (2018) | S-FTIR (b) |

2898 **Comments**

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- 2901 (a) The decay of *E*-CF₃CH=CHCF₃ was monitored by FTIR spectroscopy when exposed to ozone in
 2902 700 Torr of air or N₂/O₂ diluent. Cyclohexane was added to avoid the loss of *E*-CF₃CH=CHCF₃ via
 2903 reaction with HO radicals formed in the reaction system. The loss of *E*-CF₃CH=CHCF₃ followed
 2904 first order kinetics and the pseudo first order rate coefficients increased linearly with [O₃].
- 2905 (b) The decay of *E*-CF₃CH=CHCF₃ was monitored by FTIR spectroscopy when exposed to ozone in
 2906 10-250 Torr of He diluent. The loss of *E*-CF₃CH=CHCF₃ followed first order kinetics and the
 2907 pseudo first order rate coefficients increased linearly with [O₃].

2908 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|--------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 4.14 × 10 ⁻²² | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |

2911 **Comments on Preferred Values**

2912 The preferred value is taken from the absolute rate study by Østerstrøm et al. (2017) in which
 2913 cyclohexane was added to avoid the loss of *E*-CF₃CH=CHCF₃ via reaction with HO radicals formed in
 2914 the reaction system. The result from the study by Baasandorj et al. (2018) is approximately 25%
 2915 higher than that from Østerstrøm et al. (2017) and probably reflects additional loss of *E*-
 2916 CF₃CH=CHCF₃ from reaction with HO radicals.

2917 **References**

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- 2919
- 2920
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 2923 122, 4635-4646, 2018.
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 2925 Chem. Chem. Phys. 19, 735–750, 2017.
- 2926

2927 **oFOx124: O₃ + Z-CF₃CH=CHCF₃ (HFO-1336mzz(Z))**
 2928 Last evaluated: June 2025; Last change in preferred values: June 2024.

2929 **O₃ + Z-CF₃CH=CHCF₃ (HFO-1336mzz(Z)) → products**

2930 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (6.55 ± 0.70) × 10 ⁻²² | 296 | Østerstrøm et al. (2017) | S-FTIR (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (7.63 ± 1.53) × 10 ⁻²² | 296 | McGillen et al. (2023) | RR (b) |

2934 **Comments**

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- 2937 (a) The decay of Z-CF₃CH=CHCF₃ was monitored by FTIR spectroscopy when exposed to ozone. Cyclohexane was added to avoid potential problems associated with the loss of Z-CF₃CH=CHCF₃ via reaction with OH radicals formed in the reaction system. The loss of Z-CF₃CH=CHCF₃ was found to be approximately 15% greater in the absence of cyclohexane than in the presence of cyclohexane. The loss of Z-CF₃CH=CHCF₃ followed first order kinetics and the pseudo first order rate coefficients increased linearly with [O₃].
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- 2943 (b) The decay of Z-CF₃CH=CHCF₃ was measured relative to that of HCFO-1233xf (CF₃CCl=CH₂) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge both HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(\text{O}_3 + \text{Z-CF}_3\text{CH=CHCF}_3) / k(\text{O}_3 + \text{CF}_3\text{CCl=CH}_2) = 0.043$ was measured and was combined with $k(\text{O}_3 + \text{CF}_3\text{CCl=CH}_2) = 3.54 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (McGillen et al. 2023) to give $k(\text{O}_3 + \text{Z-CF}_3\text{CH=CHCF}_3) = (7.63 \pm 1.53) \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
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2950 **Preferred Values**

| Parameter | Value | T/K |
|--|--------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 7.09 × 10 ⁻²² | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.08 | 298 |

2951 **Comments on Preferred Values**

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2953 The results from the absolute rate study by Østerstrøm et al. (2017) and the relative rate study by

2954 McGillen et al. (2023) are in good agreement. The preferred value is an average from the two studies.

2955 The upper limit of $k < 6 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Baasandorj et al. (2011) is consistent with

2956 the preferred value. McGillen et al. (2023) observed the formation of CF₃H in a yield of 0.42 ± 0.02

2957 % and showed that this is formed via the hot acid mechanism.

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References

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2023.

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Østerstrøm, F. F.; Andersen, S. T.; Sølling, T. I.; Nielsen, O. J.; and Sulbæk Andersen, M. P.: *Phys.*

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Chem. Chem. Phys. 19, 735–750, 2017.

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2972 **oClOx97: O₃ + CH₂=CHCl**
2973 Last evaluated: June 2025; Last change in preferred values: June 2017.

2974 **O₃ + CH₂=CHCl → products**

2975 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|---------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| ~ 2.3 × 10 ⁻¹⁹ | 305 | Gay et al. (1976) | S-FTIR (a) |
| (2.45 ± 0.45) × 10 ⁻¹⁹ | 298 | Zhang et al. (1983) | S-FTIR (b) |

2979 **Comments**

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2982(a) A mixture of approximately 5 ppm of O₃ and 3 ppm of CH₂=CHCl in 1 atmosphere of air at 305 K was
2983 prepared and monitored for 4 hours. A rate coefficient of $k(\text{O}_3 + \text{CH}_2=\text{CHCl}) = 0.34 \text{ ppm}^{-1} \text{ min}^{-1}$ was
2984 estimated from the rate of loss of CH₂=CHCl.

2985(b) The loss of CH₂=CHCl in the presence of O₃ in 1 atmosphere of N₂ or air diluent was monitored by FTIR
2986 spectroscopy. CH₃CHO was added as a scavenger for Cl atoms formed in the oxidation of CH₂=CHCl.
2987 Initial concentrations of CH₂=CHCl were 12-14 mTorr and O₃ were 12-71 mTorr.

2988 **Preferred Values**

| Parameter | Value | T/K |
|--|-------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.5 × 10 ⁻¹⁹ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.2 | 298 |

2991 *Comments on Preferred Values*

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2994 The preferred value is based upon the study by Zhang et al. (1983) which is in good agreement
2995 with the earlier work by Gay et al. (1976).

2996 **References**

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2999 Gay, B. W., Hanst, P. L., and Noonan, R. C.: Environ. Sci. Technol., 10, 58, 1976.

3000 Zhang, J., Hatakeyama, S., and Akimoto, H.: Int. J. Chem. Kinet., 15 655, 1983.
3001

3002 **oFOx132: O₃ + *E*-CF₃CH=CHCl (HCFO-1233zd(E))**

3003 Last evaluated: June 2025; last change in preferred values: June 2019.

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3005 **O₃ + *E*-CF₃CH=CHCl (HCFO-1233zd(E)) → products**

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Rate coefficient data

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| (1.46 ± 0.12) × 10 ⁻²¹ | 296 | Sulbaek Andersen et al. (2008) | S-FTIR (a) |

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Comments

3013 (a) The decay of *E*-CF₃CH=CHCl was monitored by FTIR spectroscopy when exposed to ozone.
 3014 Reaction mixtures consisted of 5.9-14.2 mTorr *E*-CF₃CH=CHCl, 14.0-30.6 mTorr cyclohexane,
 3015 and 414–4360 mTorr O₃ in 700 Torr (933 mbar) of air diluent. Cyclohexane was added to avoid
 3016 potential problems associated with the loss of *E*-CF₃CH=CHCl via reaction with OH radicals
 3017 formed in the reaction system. The loss of *E*-CF₃CH=CHCl followed first order kinetics and the
 3018 pseudo first order rate coefficients increased linearly with [O₃].

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Preferred Values

| Parameter | Value | <i>T</i> /K |
|--|-------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.5 × 10 ⁻²¹ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.15 | 298 |

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Comments on Preferred Values

3025 The recommended value is taken from the work by Sulbaek Andersen et al. (2008); the only study of
 3026 this reaction.

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References

3030 Sulbaek Andersen, M. P., Nilsson, E. J. K., Nielsen, O. J., Johnson, M. S., Hurley, M. D., and
 3031 Wallington, T. J.: J. Photochem. and Photobiol. A: Chem., 199, 92, 2008.

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3033 **oFOx131: O₃ + Z-CF₃CH=CHCl (HCFO-1233zd(Z))**

3034 Last evaluated: June 2025; last change in preferred values: June 2019.

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O₃ + Z-CF₃CH=CHCl (HCFO-1233zd(Z)) → products

Rate coefficient data

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|------------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| (1.53 ± 0.12) × 10 ⁻²¹ | 296 | Andersen et al. (2015) | S-FTIR (a) |

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Comments

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- (a) The decay of Z-CF₃CH=CHCl was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of 4.07-4.17 mTorr Z-CF₃CH=CHCl, 3.96-31.79 mTorr cyclohexane, and 610–2820 mTorr O₃ in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of Z-CF₃CH=CHCl via reaction with OH radicals formed in the reaction system. The loss of Z-CF₃CH=CHCl followed first order kinetics and the pseudo first order rate coefficients increased linearly with [O₃].

Preferred Values

| Parameter | Value | T/K |
|--|--------------------------|-----|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.53 × 10 ⁻²¹ | 298 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.15 | 298 |

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Comments on Preferred Values

The recommended value is taken from the work by Andersen et al. (2015); the only study of this reaction.

References

Andersen, L. L., Østerstrøm, F. F., Sulbaek Andersen, M. P., Nielsen, O. J., and Wallington, T. J.: Chem. Phys. Lett., 639, 289, 2015.

3065 **oFOx125: O₃ + CF₃CCl=CH₂ (HCFO-1233xf)**

3066 Last evaluated: June 2025; last change in preferred values: June 2024.

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O₃ + CF₃CCl=CH₂ (HCFO-1233xf) → products**Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (3.00 ± 0.74) × 10 ⁻²¹ | 296 | McGillen et al. (2023) | S-UV (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (3.86 ± 0.79) × 10 ⁻²¹ | 296 | McGillen et al. (2023) | RR (b) |
| (3.82 ± 0.78) × 10 ⁻²¹ | 296 | McGillen et al. (2023) | RR (c) |
| (3.95 ± 0.87) × 10 ⁻²¹ | 296 | McGillen et al. (2023) | RR (d) |
| (3.15 ± 0.87) × 10 ⁻²¹ | 296 | McGillen et al. (2023) | RR (e) |

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Comments

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- (a) The decay of ozone was monitored via UV absorption in the presence of an excess of CF₃CCl=CH₂ in the presence of either *i*-propanol or cyclohexane and HC(O)OH which were added as scavengers for HO radicals and stabilized Criegee intermediates. The diluent and pressure was 1 atmosphere of air (McGillen, private communication). The loss of O₃ followed first-order kinetics and the pseudo first-order rate coefficients increased linearly with [CF₃CCl=CH₂].
- (b) The decay of CF₃CCl=CH₂ was measured relative to that of HFO-1243zf (CF₃CH=CH₂) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge both HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2)/k(\text{O}_3+\text{CF}_3\text{CH}=\text{CH}_2) = 0.307$ was measured and was combined with $k(\text{O}_3+\text{CF}_3\text{CH}=\text{CH}_2) = 1.26 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (McGillen et al. 2023) to give $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2) = (3.86 \pm 0.79) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (c) The decay of CF₃CCl=CH₂ was measured relative to that of HFO-1234yf (CF₃CF=CH₂) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge both HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2)/k(\text{O}_3+\text{CF}_3\text{CF}=\text{CH}_2) = 1.495$ was measured and was combined with $k(\text{O}_3+\text{CF}_3\text{CF}=\text{CH}_2) = 2.56 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (McGillen et al. 2023) to give $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2) = (3.82 \pm 0.78) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) The decay of CF₃CCl=CH₂ was measured relative to that of HFO-1243ze(*E*) (*E*-CF₃CH=CHF) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge both HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2)/k(\text{O}_3+\textit{E}\text{-CF}_3\text{CH}=\text{CHF}) = 1.619$ was measured and was combined with $k(\text{O}_3+\textit{E}\text{-CF}_3\text{CH}=\text{CHF}) = 2.44 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (McGillen et al. 2023) to give $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2) = (3.95 \pm 0.87) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (e) The decay of CF₃CCl=CH₂ was measured relative to that of HFO-1336mzz(*Z*) (*Z*-CF₃CH=CHCF₃) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted

3104 secondary chemistry isopropanol was added to scavenge both HO radicals and stabilized Criegee
 3105 intermediates which are formed in the system. A rate constant ratio of $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2)/k(\text{O}_3+$
 3106 $\text{Z-CF}_3\text{CH}=\text{CHCF}_3) = 4.624$ was measured and was combined with $k(\text{O}_3+ \text{Z-CF}_3\text{CH}=\text{CHCF}_3) =$
 3107 $6.81 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (McGillen et al. 2023) to give $k(\text{O}_3+\text{CF}_3\text{CCl}=\text{CH}_2) = (3.15 \pm 0.87)$
 3108 $\times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3111 Preferred Values

| 3112 | Parameter | Value | T/K |
|------|--|------------------------|-----|
| | $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 3.00×10^{-21} | 298 |
| | <i>Reliability</i> | | |
| | $\Delta \log k$ | 0.08 | 298 |

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3115 *Comments on Preferred Values*

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3117 The preferred value is taken from the absolute rate study by McGillen et al. (2023). Results from the
 3118 relative rate studies by McGillen et al. (2023) are consistent with the preferred value. McGillen et al.
 3119 (2023) did not observe formation of CF_3Cl and CF_3H as products.

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References

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3123 McGillen, M. R.; Zachary, T. P.; Fried, M.; Khan, A. H.; Kuwata, K. T.; Martin, C. M.; O'Doherty,
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 3125 e2312714120, 2023.

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3127 **oFOx84: HO + CH₂FCH₂OH**
 3128 Last evaluated: June 2025; Last change in preferred values: June 2023.

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3134 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**

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| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|-------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(5.15 \pm 0.88) \times 10^{-12} \exp[-(330 \pm 45)/T]$ | 238-355 | Rajakumar et al. (2005) | PLP-LIF (a) |
| $(1.63 \pm 0.09) \times 10^{-12}$ | 297 | | |
| $3.47 \times 10^{-14} (T/298)^{4.49} \exp(977/T)$ | 230-370 | Orkin et al. (2011) | FP-RF (b) |
| $(9.29 \pm 0.18) \times 10^{-13}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.39 \pm 0.05) \times 10^{-12}$ | 298 | Sellevåg et al. (2004) | RR (c) |

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Comments

3139 (a) HO radicals were generated by the 248 nm photolysis of H₂O₂ in 60-100 Torr (80-133 mbar) of
 3140 helium diluent. Additional experiments were performed at 355 K using DO radicals (formed via O₃
 3141 photolysis in the presence of D₂O). The rate coefficients for the reactions of DO and HO radicals
 3142 with CH₂FCH₂OH were indistinguishable. There was no evidence for the formation of HO radicals
 3143 following reaction of DO radicals with CH₂FCH₂OH.

3144 (b) HO radicals were generated by the flash photolysis of H₂O in 1.33-26.7 kPa (10-200 Torr) of argon
 3145 diluent. The rate coefficients were independent of the H₂O concentration, flash energy, flash
 3146 repetition rate, residence time of the mixture in the reactor, reactant concentration in the storage
 3147 bulb, and residence time of the reactant mixture in the delivery volume.

3148 (c) HO radicals were generated by the photolysis of O₃ in the presence of H₂O in 1013 mbar of air
 3149 diluent at 298 K. A rate coefficient ratio of $k(\text{HO} + \text{CH}_2\text{FCH}_2\text{OH})/k(\text{HO} + \text{C}_2\text{H}_6) = 5.81 \pm 0.19$ was
 3150 measured. Placing this on an absolute basis using $k(\text{HO} + \text{C}_2\text{H}_6) = 2.4 \times 10^{-13}$ (Atkinson et al., 2006)
 3151 gives $k(\text{HO} + \text{CH}_2\text{FCH}_2\text{OH}) = (1.39 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 9.12×10^{-13} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $2.23 \times 10^{-12} \exp(-266/T)$ | 230-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.08 | 298 |
| $\Delta E/R$ | ± 100 | 230-300 |

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Comments on Preferred Values

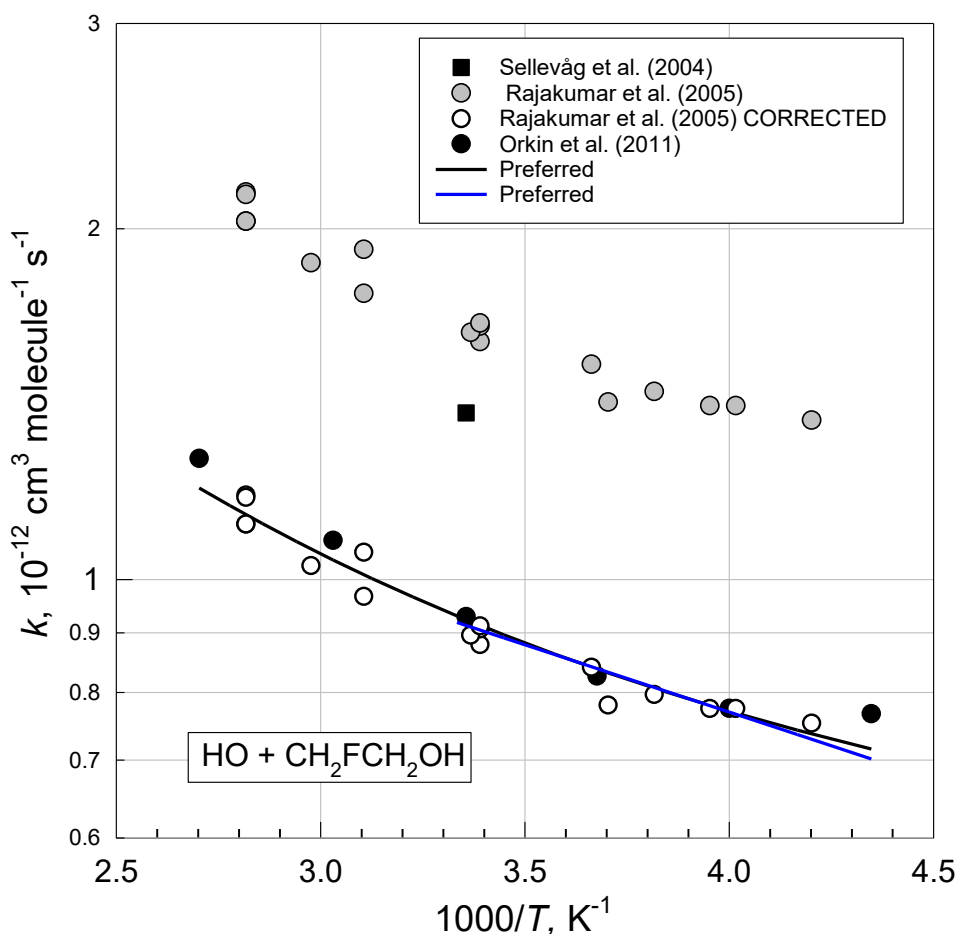
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3159 The results from the relative rate study by Sellevåg et al. (2004) and the absolute rate study of
 3160 Rajakumar et al. (2005) at ambient temperature are indistinguishable within the likely combined
 3161 experimental uncertainties. The results from the absolute rate study by Orkin et al. (2011) are
 3162 approximately a factor of 2 lower. The concentration of CH₂FCH₂OH in the study by Rajakumar et al.
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3164 was measured using absorption at 184.9 nm. Orkin et al. remeasured the absorption spectrum of
 3165 CH₂FCH₂OH and determined an absorption cross section at 184.9 nm that was 1.82 times smaller than
 3166 used by Rajakumar et al. (2005). Correction of the rate coefficients reported by Rajakumar et al. by a
 3167 factor of 1.82 brings them into good agreement with those from Orkin et al. (2011). A fit of the
 3168 modified Arrhenius expression $k = CT^2 \exp(-D/T)$, to the combined data set from Orkin et al. (2011)
 3169 and the corrected data from Rajakumar et al. (2005) gives $k = 4.28 \times 10^{-18} T^2 \exp(264/T) \text{ cm}^3$
 3170 $\text{molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230-370 K. The preferred Arrhenius expression $k = 2.23 \times$
 3171 $10^{-12} \exp(-266/T)$, is centered at 265 K and is derived from the three-parameter equation with $A = C e^2$
 3172 T^2 and $B = D + 2T$.

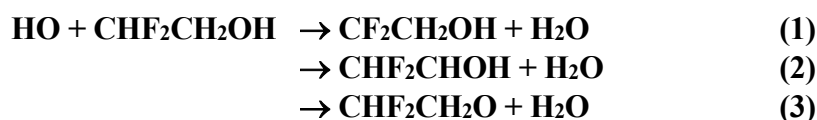
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Rate coefficient data ($k = k_1 + k_2 + k_3$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.52 \pm 0.44) \times 10^{-13}$ | 300 | Kovacs et al. (2005) | PLP-RF (a) |
| $3.87 \times 10^{-14} (T/298)^{4.25} \exp(578/T)$ | 220-370 | Orkin et al. (2011) | FP-RF (b) |
| $(2.70 \pm 0.02) \times 10^{-13}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(4.57 \pm 0.38) \times 10^{-13}$ | 298 | Sellevåg et al. (2004) | RR (c) |

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Comments

- (a) HO radicals were produced by the photolysis of HNO₃ at 248 nm in 105 ± 5 mbar of helium diluent.
 (b) HO radicals were generated by the flash photolysis of H₂O in 1.33-26.7 kPa (10-200 Torr) of argon. The rate coefficient was independent of the H₂O concentration, flash energy, flash repetition rate, residence time of the mixture in the reactor, reactant concentration in the storage bulb, and residence time of the reactant mixture in the delivery volume.
 (c) HO radicals were generated by the photolysis of O₃ in the presence of H₂O in 1013 mbar of air diluent at 298 K. A rate coefficient ratio of $k(\text{HO}+\text{CHF}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_6) = 1.903 \pm 0.016$ was measured. Placing this on an absolute basis using $k(\text{HO}+\text{C}_2\text{H}_6) = 2.4 \times 10^{-13}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{CHF}_2\text{CH}_2\text{OH}) = (4.57 \pm 0.38) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.61×10^{-13} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.63 \times 10^{-12} \exp(-545/T)$ | 220-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.08 | 298 |
| $\Delta E/R$ | ± 200 | 220-300 |

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Comments on Preferred Values

The results from the absolute rate studies at ambient temperature by Kovacs et al. (2005) and Orkin et al. (2011) are in excellent agreement. For reasons which are unclear the rate coefficient reported in the relative rate study by Sellevåg et al. (2004) is approximately 80% larger than those from the two absolute rate studies. The preferred value of $k = 2.61 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is an average of the ambient temperature measurements by Kovacs et al. (2005) and Orkin et al. (2011). There is small, but discernable, curvature in the Arrhenius plot evident in the data from Orkin et al. (2011). A fit of the modified Arrhenius expression $k = CT^2 \exp(-D/T)$, to the combined data set from Kovacs et al. (2005) and Orkin et al. (2011) gives $k = 3.44 \times 10^{-18} T^2 \exp(-35/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-370 K. The preferred Arrhenius expression $k = A \exp(-B/T)$ is centered at 255 K and was

3225 derived using $B = D + 2T$ with the value of A adjusted to give the preferred $k(298\text{K})$ value; $k = 1.63 \times$
3226 $10^{-12} \exp(-545/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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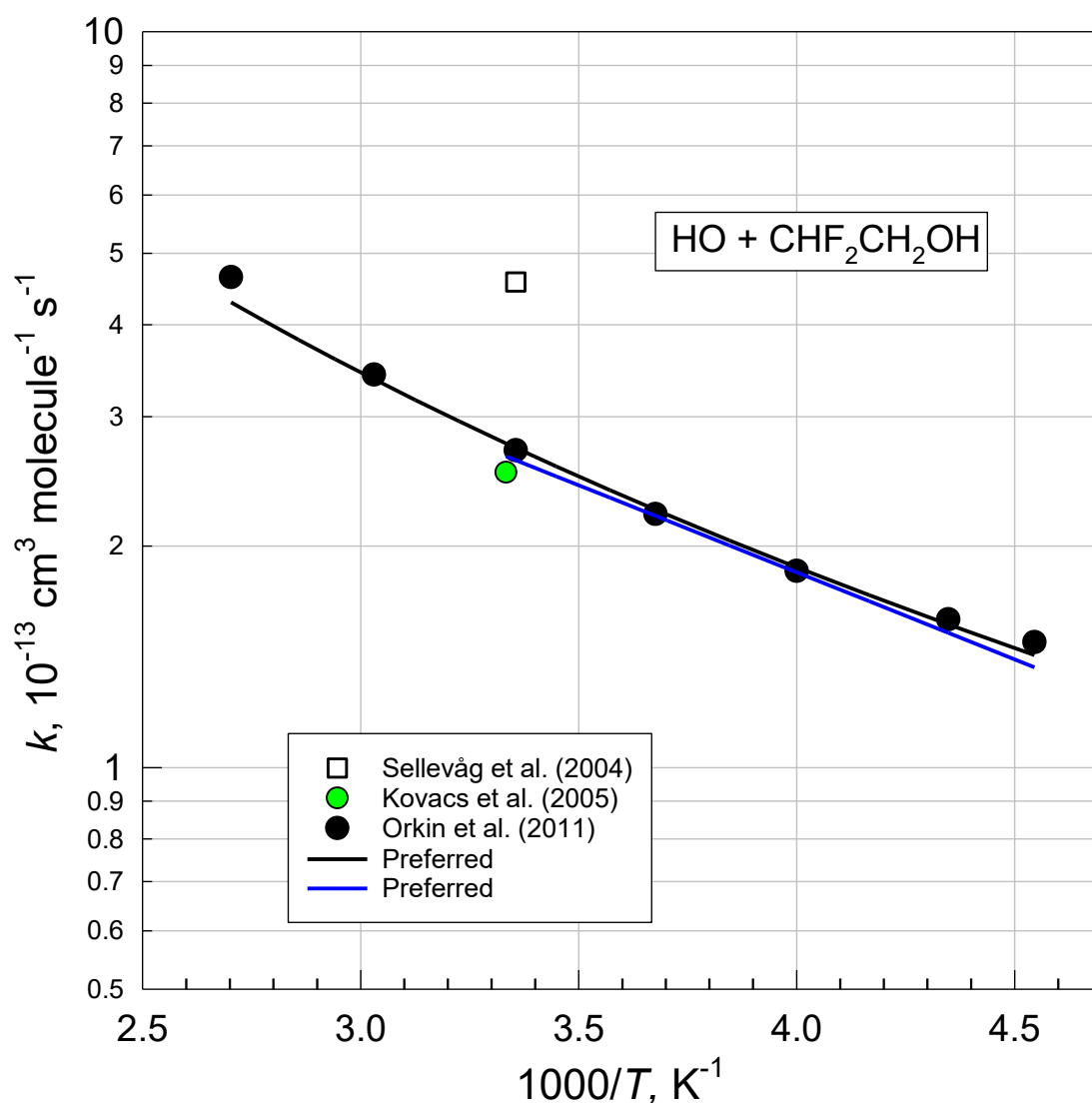
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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|--------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(9.55 \pm 0.71) \times 10^{-14}$ | 298 | Wallington et al. (1988) | FP-RF (a) |
| $(2.00 \pm 0.37) \times 10^{-12} \exp[-(890 \pm 60)/T]$ | 250-430 | Tokuhashi et al. (1999) | LP-LIF (b) |
| 1.01×10^{-13} | 298 | | FP-LIF (b) |
| | | | DF-LIF (b) |
| $(1.06 \pm 0.30) \times 10^{-13}$ | 300 | Kovacs et al. (2005) | PLP-RF (c) |
| $(1.23 \times 10^{-12} \exp[-(760 \pm 340)/T])$ | 298-363 | Indulkar et al. (2011) | LP-LIF (d) |
| $(1.03 \pm 0.11) \times 10^{-13}$ | 298 | | |
| $2.48 \times 10^{-14} (T/298)^{4.03} \exp(418/T)$ | 220-370 | Orkin et al. (2011) | FP-RF (e) |
| $(1.01 \pm 0.01) \times 10^{-13}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.31 \pm 0.05) \times 10^{-13}$ | 298 | Sellevåg et al. (2004) | RR (f) |
| $(9.4 \pm 0.8) \times 10^{-14}$ | 296 | Hurley et al. (2004) | RR (g) |

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Comments

- 3253 (a) HO radicals were generated by the photolysis ($\lambda \geq 165 \text{ nm}$) of H₂O in 25-50 Torr (33-67 mbar) of
 3254 argon diluent at 298 K.
- 3255 (b) Three different absolute rate methods were employed by Tokuhashi et al. (1999): LP-LIF, FP-LIF,
 3256 and DF-LIF. HO radicals in the LP-LIF experiments were generated by the 193 nm photolysis of
 3257 N₂O to produce O(¹D) atoms in the presence of H₂O in 15-70 Torr (20-93 mbar) of helium diluent.
 3258 HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp, $\lambda < 180$
 3259 nm) of H₂O in argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction
 3260 of H atoms with NO₂ in 4-6 Torr (5-8 mbar) of argon diluent. There was good agreement between
 3261 the results from experiments using the three different techniques. The value at 298 K cited above is
 3262 the average obtained using the different techniques.
- 3263 (c) HO radicals were produced by the photolysis of HNO₃ at 248 nm in 105 ± 5 mbar of helium diluent.
- 3264 (d) HO radicals were produced by the photolysis of H₂O₂ at 248 nm.
- 3265 (e) HO radicals were generated by the flash photolysis of H₂O in 1.33-26.7 kPa (10-200 Torr) of argon
 3266 diluent. The rate coefficient was independent of the H₂O concentration, flash energy, flash repetition
 3267 rate, residence time of the mixture in the reactor, reactant concentration in the storage bulb, and
 3268 residence time of the reactant mixture in the delivery volume.
- 3269 (f) HO radicals were generated by the photolysis of O₃ in the presence of H₂O in 1013 mbar of air
 3270 diluent at 298 K. A rate coefficient ratio of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_6) = 0.547 \pm 0.019$ was
 3271 measured. Placing this on an absolute basis using $k(\text{HO}+\text{C}_2\text{H}_6) = 2.4 \times 10^{-13}$ (Atkinson et al., 2006)
 3272 gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH}) = (1.31 \pm 0.05) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 3273 (g) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air. A rate
 3274 coefficient ratio of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_2) = 0.12 \pm 0.01$ was reported. Using
 3275 $k(\text{HO}+\text{C}_2\text{H}_2) = 7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH}) =$
 3276 $(9.4 \pm 0.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.00×10^{-13} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.25 \times 10^{-12} \exp(-754/T)$ | 220-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.06 | 298 |
| $\Delta E/R$ | ± 100 | 220-300 |

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3281*Comments on Preferred Values*3282
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Except for the measurement by Sellevåg et al. (2004), there is excellent agreement in the room temperature rate coefficients reported for this reaction. The preferred value at 298 K is an average of the results from the remaining six studies. The rate coefficients reported by Indulkar et al. (2011) at 318 and 333 K are approximately 20% below those reported by Tokuhashi et al. (1999) and Orkin et al. (2011) but are within the likely combined uncertainties of the studies. The rate coefficients reported by Indulkar et al. (2011) at 348 and 363 K are in excellent agreement with those expected based on the studies by Tokuhashi et al. (1999) and Orkin et al. (2011). The temperature dependencies reported by Tokuhashi et al. (1999), Indulkar et al. (2011), and Orkin et al. (2011) over the range 250-370 K are in good agreement. There is evidence of curvature in the Arrhenius plot in the results from Orkin et al. (2011) particularly below 250 K. A fit of the modified Arrhenius expression $k = CT^2 \exp(-D/T)$, to the combined data set from Tokuhashi et al. (1999) and Orkin et al. (2011) gives $k = 2.41 \times 10^{-18} T^2 \exp(-224/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-430 K. The preferred Arrhenius expression $k = A \exp(-B/T)$ is centered at 265 K and was derived using $B = D + 2T$ with the value of A adjusted to give the preferred $k(298\text{K})$ value; $k = 1.25 \times 10^{-12} \exp(-754/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Hurley et al. (2004) have reported the formation of CF_3CHO in a molar yield of $97 \pm 3\%$ following the chlorine-atom-initiated oxidation of $\text{CF}_3\text{CH}_2\text{OH}$ in 700 Torr of air. HO and chlorine atom reaction with $\text{CF}_3\text{CH}_2\text{OH}$ are expected to proceed via the same mechanism; hydrogen abstraction from the $-\text{CH}_2-$ group. The HO radical initiated oxidation of $\text{CF}_3\text{CH}_2\text{OH}$ is expected to lead to quantitative conversion of $\text{CF}_3\text{CH}_2\text{OH}$ into CF_3CHO (Calvert et al., 2011).

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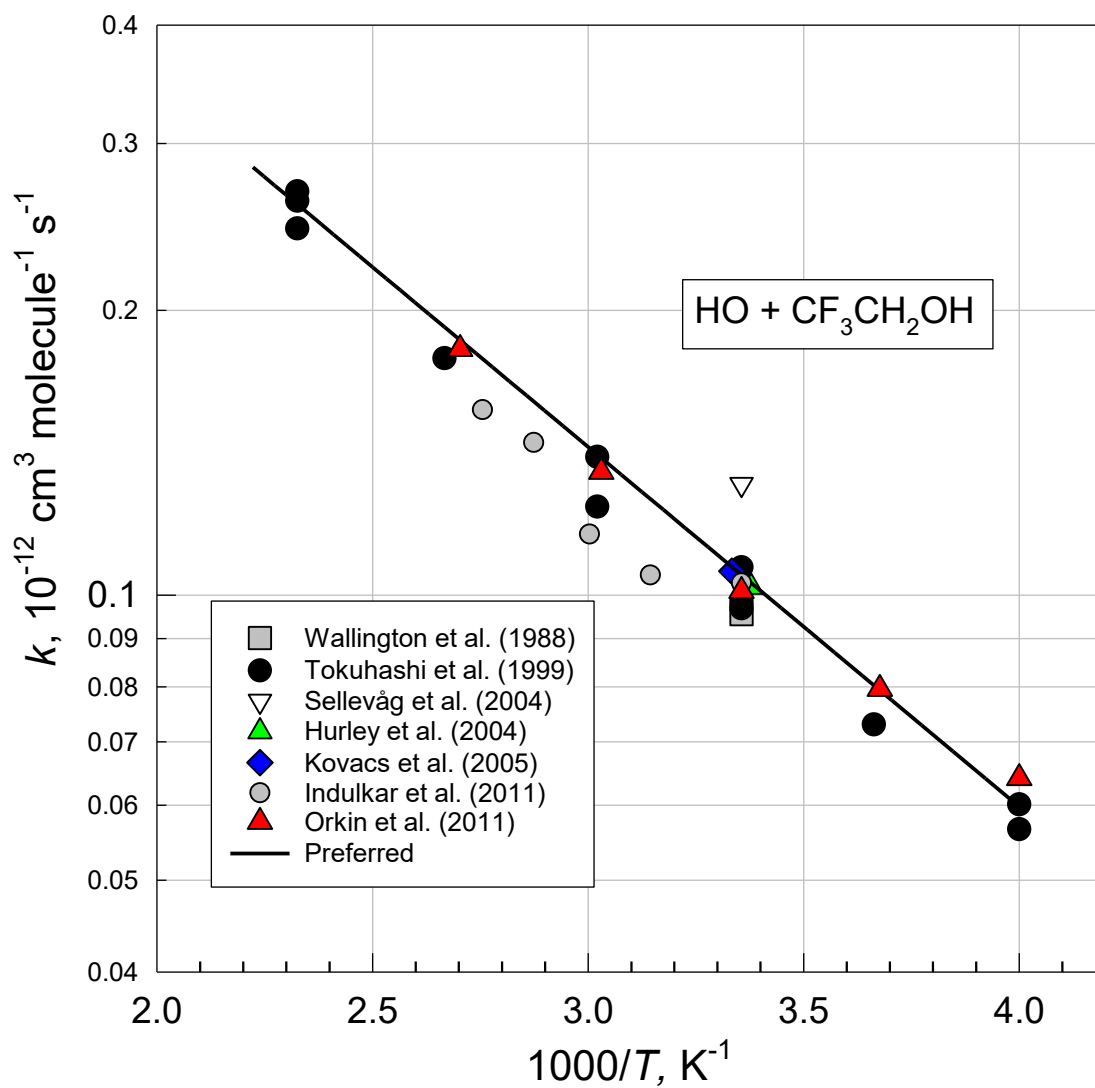
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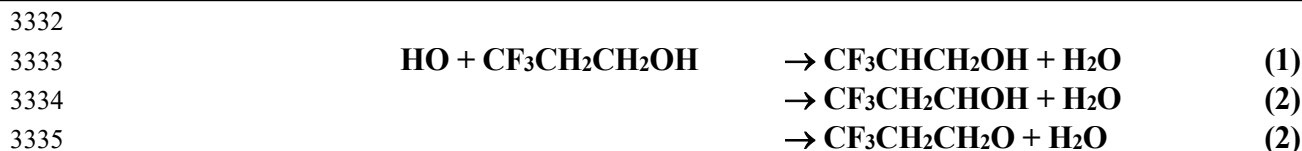
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3330 **oFOx87: HO + CF₃CH₂CH₂OH**
 3331 Last evaluated: June 2025; Last change in preferred values: June 2014.



3336 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(0.89 \pm 0.03) \times 10^{-12}$ | 298 | Kelly et al. (2005) | PLP-LIF (a) |
| $(0.97 \pm 0.11) \times 10^{-12}$ | 298 | Jiménez et al. (2010) | PLP-LIF (b) |
| $2.82 \times 10^{-12} \exp[-(302 \pm 139)/T]$ | 263-358 | Antiñolo et al. (2011) | PLP-LIF (c) |
| $(1.03 \pm 0.11) \times 10^{-12}$ | 287 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.06 \pm 0.04) \times 10^{-12}$ | 298 | Kelly et al. (2005) | RR (d) |
| $(1.05 \pm 0.05) \times 10^{-12}$ | | | RR (d) |
| $(1.43 \pm 0.03) \times 10^{-12}$ | | | RR (d) |
| $(0.68 \pm 0.07) \times 10^{-13}$ | 296 | Hurley et al (2005) | RR (e) |
| $(0.70 \pm 0.08) \times 10^{-13}$ | | | RR (e) |

3339 **Comments**

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 3342 (a) HO radicals were generated by the 248 nm photolysis of H₂O₂ in 100 Torr (133 mbar) of helium
 3343 diluent at 298 K.
 3344 (b) HO radicals were produced by 248 nm photolysis of H₂O₂ in 47-211 Torr (63-281 mbar) of helium
 3345 diluent at 298 K.
 3346 (c) HO radicals were produced by 248 nm photolysis of H₂O₂ in 46-95 Torr (61-127 mbar) of helium
 3347 diluent at 263-358 K.
 3348 (d) HO radicals were generated by the 254 nm (Hg lamp) photolysis of either H₂O₂ or O₃ (in the
 3349 presence of H₂O vapor) in one atmosphere of air. Rate coefficient ratios of
 3350 $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{HC}(\text{O})\text{OC}_4\text{H}_9) = 0.30 \pm 0.01$, $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+n$
 3351 $\text{hexane}) = 0.20 \pm 0.01$, and $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH}) = 0.95 \pm 0.02$ were
 3352 determined. Placing these ratios on an absolute basis using $k(\text{HO}+\text{HC}(\text{O})\text{OC}_4\text{H}_9) = 3.54 \times 10^{-12}$ (Le
 3353 Calvé et al., 1997), $k(\text{HO}+n\text{-hexane}) = 5.27 \times 10^{-12}$ (Calvert et al., 2008), and $k(\text{HO}+\text{CF}_3\text{CH}_2\text{OH}) =$
 3354 $1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (present recommendation) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}) = (1.06 \pm$
 3355 $0.04) \times 10^{-12}$, $(1.05 \pm 0.05) \times 10^{-12}$, and $(1.43 \pm 0.03) \times 10^{-12}$, respectively.
 3356 (e) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air. Rate
 3357 coefficient ratios of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_2) = 0.87 \pm 0.09$ and
 3358 $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_4) = 0.089 \pm 0.010$ were reported. Using $k(\text{HO}+\text{C}_2\text{H}_2) = 7.8$
 3359 $\times 10^{-13}$ and $k(\text{HO}+\text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}) = (6.79$
 3360 $\pm 0.70) \times 10^{-13}$ and $(7.03 \pm 0.79) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3361 **Preferred Values**

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 9.6×10^{-13} | 298 |

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $2.72 \times 10^{-12} \exp(-305/T)$

260-360

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3365 *Reliability* $\Delta \log k$

0.10

298

 $\Delta E/R$ ± 200

260-360

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3367 *Comments on Preferred Values*

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There is significant scatter in the room temperature rate coefficients reported in the relative rate studies by Kelly et al. (2005) and Hurley et al. (2005). The room temperature rate coefficients reported in the absolute rate studies by Kelly et al. (2005) and Jiménez et al. (2010) are in good agreement. The absolute rate determinations at 298 K by Kelly et al. (2005) and Jiménez et al. (2010) lie in the center of the scatter in the results from the relative rate studies of Kelly et al. (2005) and Hurley et al. (2005). The preferred rate coefficient at 298 K is an average from the results of the absolute rate studies by Kelly et al. (2005) and Jiménez et al. (2010). An interpolation of the absolute rate data at 263 – 358 K reported by Antiñolo et al. (2011) is in good agreement with the preferred rate coefficient at 298 K. The preferred temperature dependence is taken from a fit to the data from Antiñolo et al. (2011) with the pre-exponential factor adjusted to be consistent with the preferred rate coefficient at 298K. The majority of reaction is believed to occur via hydrogen abstraction from the $-\text{CH}_2-$ group bearing the alcohol functionality (Calvert et al., 2010). Subsequent reaction of the $\text{CF}_3\text{CH}_2\text{CHOH}$ with O_2 will give $\text{CF}_3\text{CH}_2\text{CHO}$. The HO radical initiated oxidation of $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$ is expected to give $\text{CF}_3\text{CH}_2\text{CHO}$ in a yield close to 100%. Consistent with this expectation, Hurley et al. (2005) observed the formation of $\text{CF}_3\text{CH}_2\text{CHO}$ as the sole product of the chlorine-atom-initiated oxidation of $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$ in one atmosphere of air.

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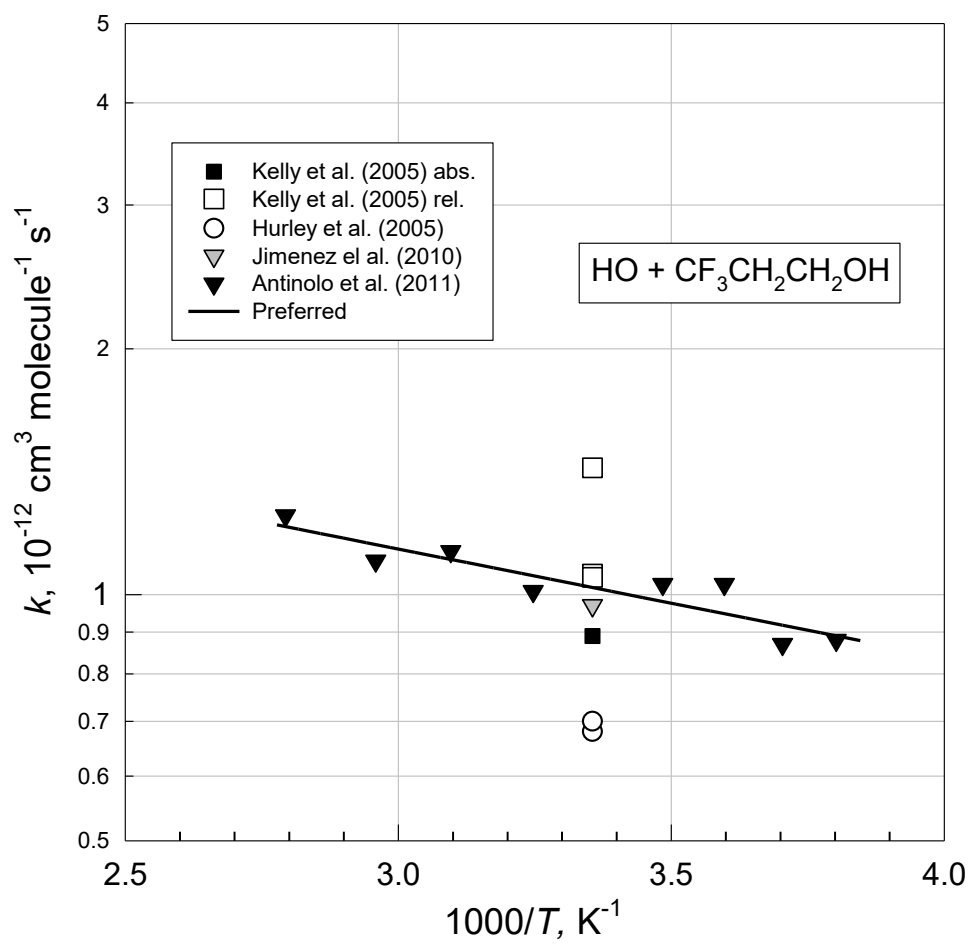
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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|-------------------------|--------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.40 \pm 0.27) \times 10^{-12} \exp[-(780 \pm 60)/T]$ | 250-430 | Tokuhashi et al. (1999) | LP-LIF (a) |
| 1.00×10^{-13} | 298 | | FP-LIF (a) DF-LIF (a) |
| $1.36 \times 10^{-12} \exp[-(730 \pm 43)/T]$ | 263-358 | Antiñolo et al. (2012) | PLP-LIF (b) |
| $(1.19 \pm 0.03) \times 10^{-13}$ | 287 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $1.5 \times 10^{-12} \exp[-(818)/T]$ | 298-356 | Chen et al. (2000) | RR(c) |
| 9.84×10^{-14} | 298 | | |
| $(9.4 \pm 0.8) \times 10^{-14}$ | 296 | Hurley et al. (2004) | RR (d) |

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Comments

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- 3419 (a) Three different absolute rate methods were employed by Tokuhashi et al. (1999): LP-LIF, FP-LIF,
 3420 and DF-LIF. HO radicals in the LP-LIF experiments were generated by the 193 nm photolysis of
 3421 N₂O to produce O(¹D) atoms in the presence of H₂O in 15-70 Torr (20-93 mbar) of helium diluent.
 3422 HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp, $\lambda \geq 180$
 3423 nm) of H₂O in argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction
 3424 of H atoms with NO₂ in 4-6 Torr (5-8 mbar) of argon diluent. There was good agreement between
 3425 the results from experiments using the three different techniques. The value at 298 K cited above is
 3426 the average obtained using the different techniques.
- 3427 (b) HO radicals were produced by 248 nm photolysis of H₂O₂ in 43-214 Torr (57-285 mbar) of helium
 3428 diluent at 263-358 K. No effect of total pressure was reported over the range studied.
- 3429 (c) HO radicals were generated by the photolysis of O₃ in the presence of water vapor in 1 bar of O₂
 3430 diluent. The decay of C₂F₅CH₂OH was monitored relative to that of CH₂Cl₂. Chen et al. (2000)
 3431 used the expression $k(\text{HO}+\text{CH}_2\text{Cl}_2) = 3.8 \times 10^{-12} \exp(-1050/T)$ to place their results on an absolute
 3432 basis. Rescaling using $k(\text{HO}+\text{CH}_2\text{Cl}_2) = 1.8 \times 10^{-12} \exp(-860/T)$ (Atkinson et al., 2008) and fitting
 3433 an Arrhenius expression to the results gives $k(\text{HO}+\text{C}_2\text{F}_5\text{CH}_2\text{OH}) = 1.5 \times 10^{-12} \exp(-818/T) \text{ cm}^3$
 3434 $\text{molecule}^{-1} \text{ s}^{-1}$.
- 3435 (d) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air. A rate
 3436 coefficient ratio of $k(\text{HO}+\text{C}_2\text{F}_5\text{CH}_2\text{OH})/k(\text{HO}+\text{C}_2\text{H}_2) = 0.12 \pm 0.01$ was reported. Using
 3437 $k(\text{HO}+\text{C}_2\text{H}_2) = 7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{C}_2\text{F}_5\text{CH}_2\text{OH}) =$
 3438 $(9.4 \pm 0.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.05×10^{-13} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.28 \times 10^{-12} \exp(-748/T)$ | 250-430 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.06 | 298 |
| $\Delta E/R$ | ± 200 | 250-430 |

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3451*Comments on Preferred Values*

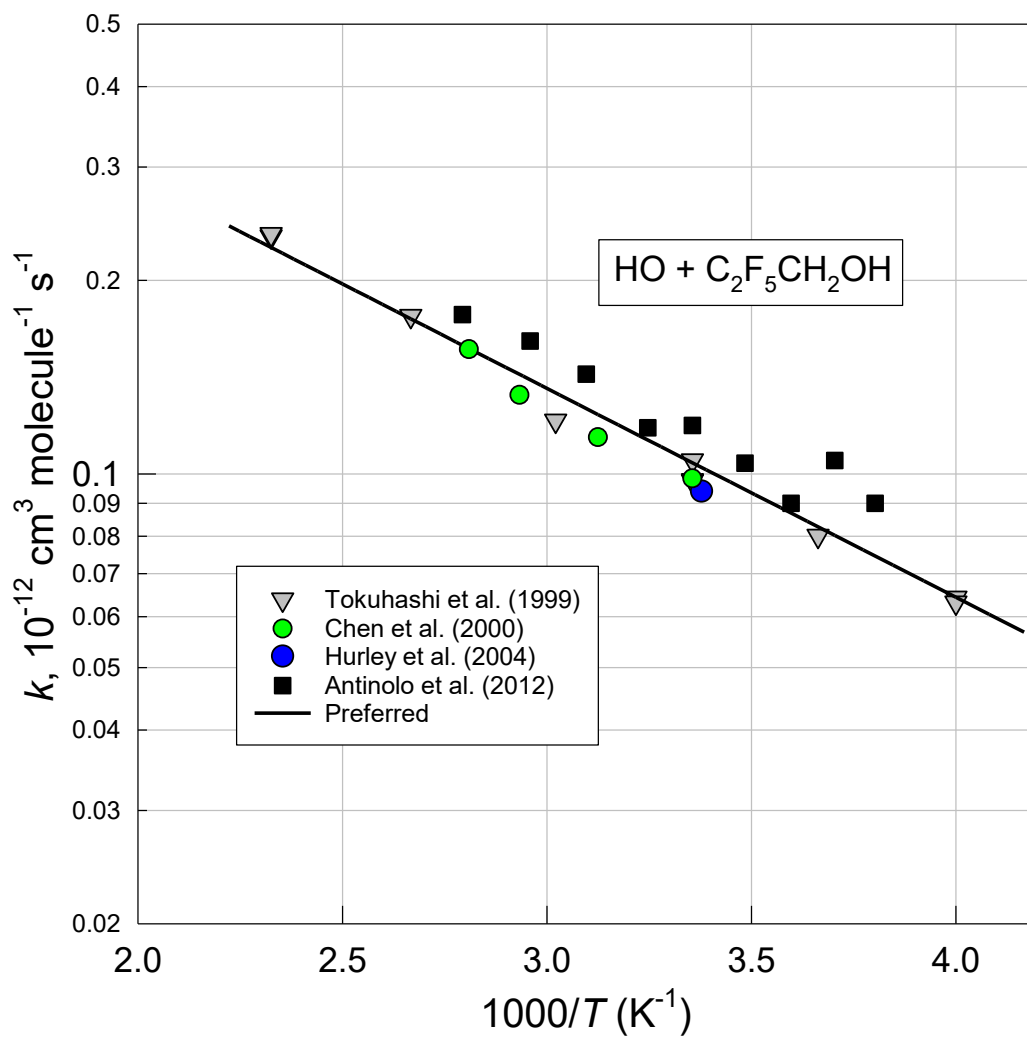
The rate coefficients reported in the absolute rate studies by Tokuhashi et al. (1997) and Antiñolo et al. (2012) and the relative rate studies by Chen et al. (2000) and Hurley et al. (2004) are in good agreement. Taking an average of the determinations by Tokuhashi et al. (1997) and Antiñolo et al. (2012) gives $k(\text{HO} + \text{C}_2\text{F}_5\text{CH}_2\text{OH}) = 1.05 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Fitting the Arrhenius expression to the data from Tokuhashi et al. (1997) and Antiñolo et al. (2012) and adjusting the pre-exponential factor to reproduce the preferred value at 298 K gives $k(\text{HO} + \text{C}_2\text{F}_5\text{CH}_2\text{OH}) = 1.28 \times 10^{-12} \exp(-748/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The HO radical initiated oxidation of $\text{C}_2\text{F}_5\text{CH}_2\text{OH}$ is expected to lead to quantitative conversion into $\text{C}_2\text{F}_5\text{CHO}$ (Calvert et al., 2011).

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References

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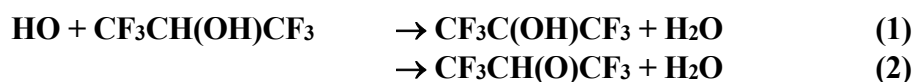
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3485 **oFOx89: HO + CF₃CH(OH)CF₃**
 3486 Last evaluated: June 2025; Last change in preferred values: June 2019.

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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|-------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(6.99 \pm 1.56) \times 10^{-13} \exp[-(990 \pm 70)/T]$ | 250-430 | Tokuhashi et al. (1999) | LP-LIF (a) |
| 2.52×10^{-14} | 298 | | FP-LIF (a) |
| | | | DF-LIF (a) |
| $1.19 \times 10^{-12} \exp(-1207/T) + 7.85 \times 10^{-16} \exp(502/T)$ | 220-370 | Orkin et al. (2012) | FP-RF (b) |
| $(2.47 \pm 0.03) \times 10^{-14}$ | 298 | | |

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Comments

- (a) Three different absolute rate methods were employed by Tokuhashi et al. (1999): LP-LIF, FP-LIF, and DF-LIF. HO radicals in the LP-LIF experiments were generated by the 193 nm photolysis of N₂O to produce O(¹D) atoms in the presence of H₂O in 15-70 Torr (20-93 mbar) of helium diluent. HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp, $\lambda \geq 180$ nm) of H₂O in argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction of H atoms with NO₂ in 4-6 Torr (5-8 mbar) of argon diluent. There was good agreement between the results from experiments using the three different techniques. The value at 298 K cited above is the average obtained using the different techniques.
- (b) HO radicals were generated using the flash photolysis of H₂O vapor in 30 Torr (40 mbar) of argon.

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Preferred Values

| Parameter | Value | T/K |
|--|---|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.43×10^{-14} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $3.94 \times 10^{-15} (T/298)^{4.57} \exp(542/T)$ | 220-430 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.12 | 298 |

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 3512

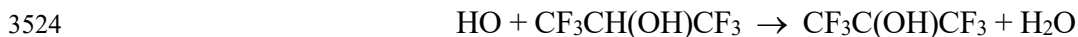
Comments on Preferred Values

The results from Tokuhashi et al. (1997) and Orkin et al. (2012) are in excellent agreement. The preferred value at 298 K is an average of the values from Tokuhashi et al. (1997) and Orkin et al. (2012). There is significant curvature in the Arrhenius plot which is particularly evident in the data below 250 K. A fit of the modified Arrhenius expression to the combined data set from Tokuhashi et al. (1997) and Orkin et al. (2012) with the first term adjusted so the expression returns the preferred value at 298 K gives $k(\text{HO} + \text{CF}_3\text{CH}(\text{OH})\text{CF}_3) = 3.94 \times 10^{-15} (T/298)^{4.57} \exp(542/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which fits the data over the temperature range 220-430 K.

3520

3521 The HO radical initiated oxidation of $\text{CF}_3\text{CH}(\text{OH})\text{CF}_3$ is expected to lead to quantitative conversion into
3522 $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ (Calvert et al., 2011).

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References

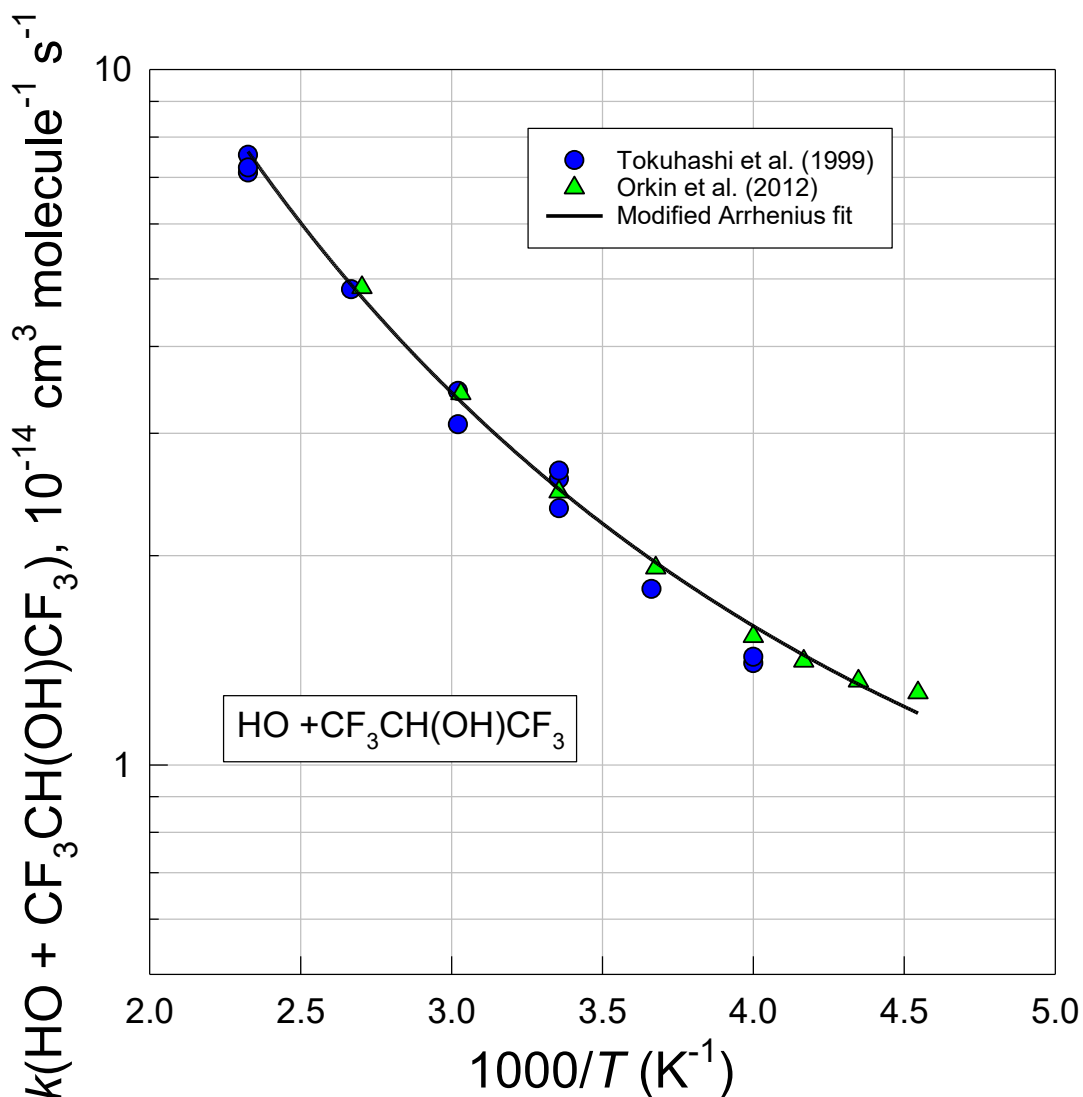
3529 Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M., and Wallington T. J.: The Mechanisms of
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3533 Suga, A.: J. Phys. Chem. A, 103, 2664, 1999.

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3543 **oFOx158: HO + (CF₃)₂C(OH)CH₃**
 3544 Last evaluated: June 2025; Last change in preferred values: September 2019.



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 3549 **Rate coefficient data ($k = k_1 + k_2$)**
 3550

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|---------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $1.68 \times 10^{-12} \exp(-1718/T) + 7.32 \times 10^{-16} \exp(371/T)$ | 230-370 | Orkin et al. (2012) | FP-RF (b) |
| $(7.84 \pm 0.12) \times 10^{-15}$ | 298 | | |

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 3552 **Comments**

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 3554 (a) HO radicals were generated using the flash photolysis of H₂O vapor in 30 Torr (40 mbar) of argon
 3555 diluent and monitored using resonance fluorescence.

3556
 3557 **Preferred Values**

| Parameter | Value | T/K |
|--|--|---------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 7.71×10^{-15} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.90 \times 10^{-18} (T/298)^{11.5} \exp(2476/T)$ | 230-370 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.12 | 298 |

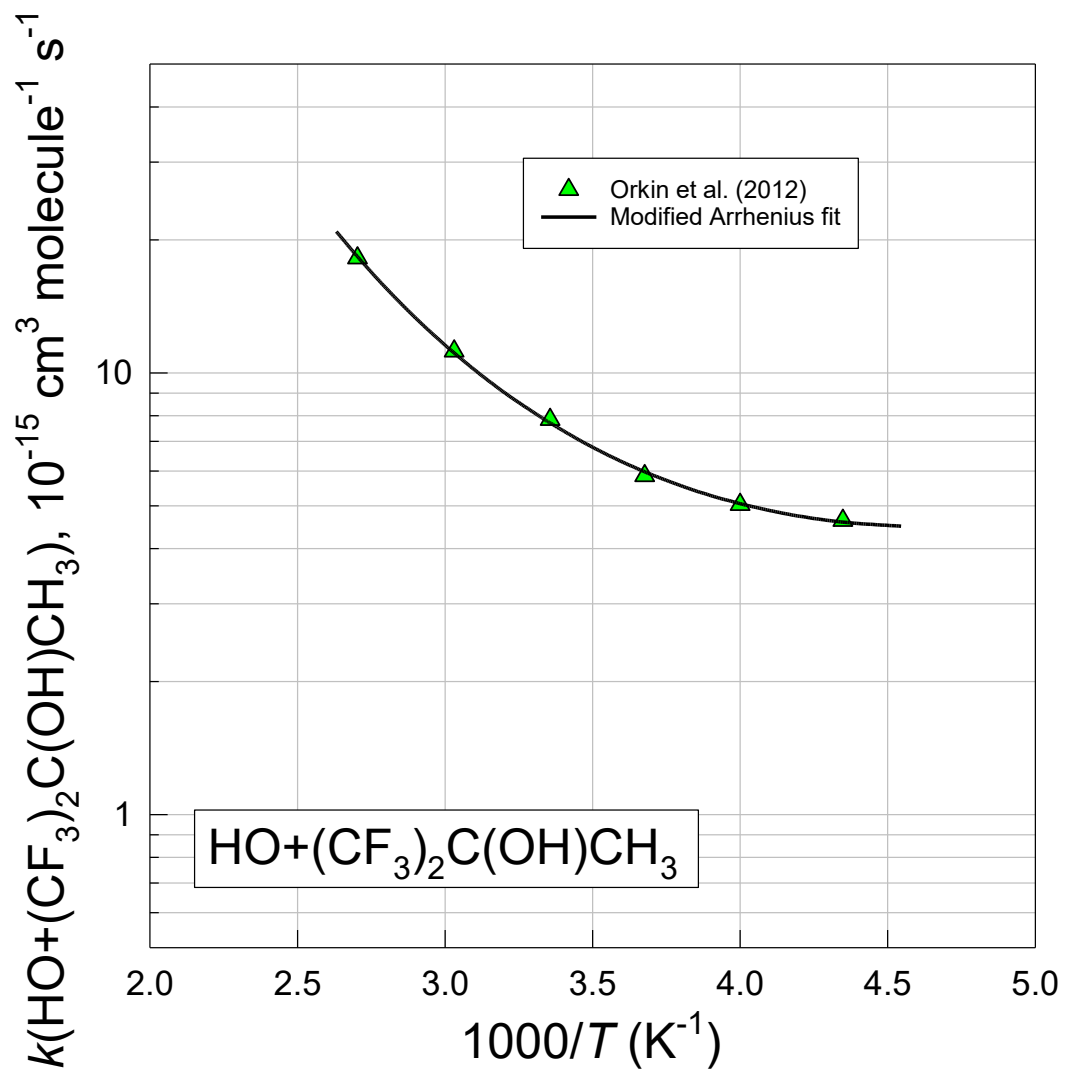
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 3562 *Comments on Preferred Values*

3563
 3564 The preferred value at 298 K is taken from Orkin et al. (2012). There is significant curvature in the
 3565 Arrhenius plot which is particularly evident in the data below 250 K. A fit of the modified Arrhenius
 3566 expression to the data set from Orkin et al. (2012) gives $k(\text{HO} + (\text{CF}_3)_2\text{C}(\text{OH})\text{CH}_3) = 1.90 \times 10^{-18}$
 3567 $(T/298)^{11.5} \exp(2476/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230-370 K.

3568
 3569
 3570 **References**

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 3572 Orkin, V. L., Khamaganov, V. G., and Kurylo, M. J.: J. Phys. Chem. A, 116, 6188, 2012.

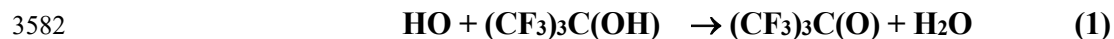
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3579 **oFOx159: HO + (CF₃)₃C(OH)**
 3580 Last evaluated: June 2025; Last change in preferred values: June 2019.

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Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|----------------|---------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $3.0 \times 10^{-20} (T/298)^{11.3} \exp(3060/T)$ $(8.6 \pm 0.2) \times 10^{-16}$ | 230-370 298 | Orkin et al. (2012) | FP-RF (b) |

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Comments

3589 (a) HO radicals were generated using the flash photolysis of H₂O vapor in 30 Torr (40 mbar) of argon
 3590 diluent and monitored using resonance fluorescence.

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Preferred Values

| Parameter | Value | T/K |
|--|---|---------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 8.6×10^{-16} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $3.0 \times 10^{-20} (T/298)^{11.3} \exp(3060/T)$ | 230-370 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.12 | 298 |

3596

Comments on Preferred Values

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3599 There is significant curvature in the Arrhenius plot. The $k(298\text{K})$ value and modified Arrhenius
 3600 expression from Orkin et al. (2012) are preferred. The HO radical initiated oxidation of (CF₃)₃C(OH) is
 3601 expected to lead to quantitative conversion into CF₃C(O)CF₃ (Calvert et al., 2011).

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References

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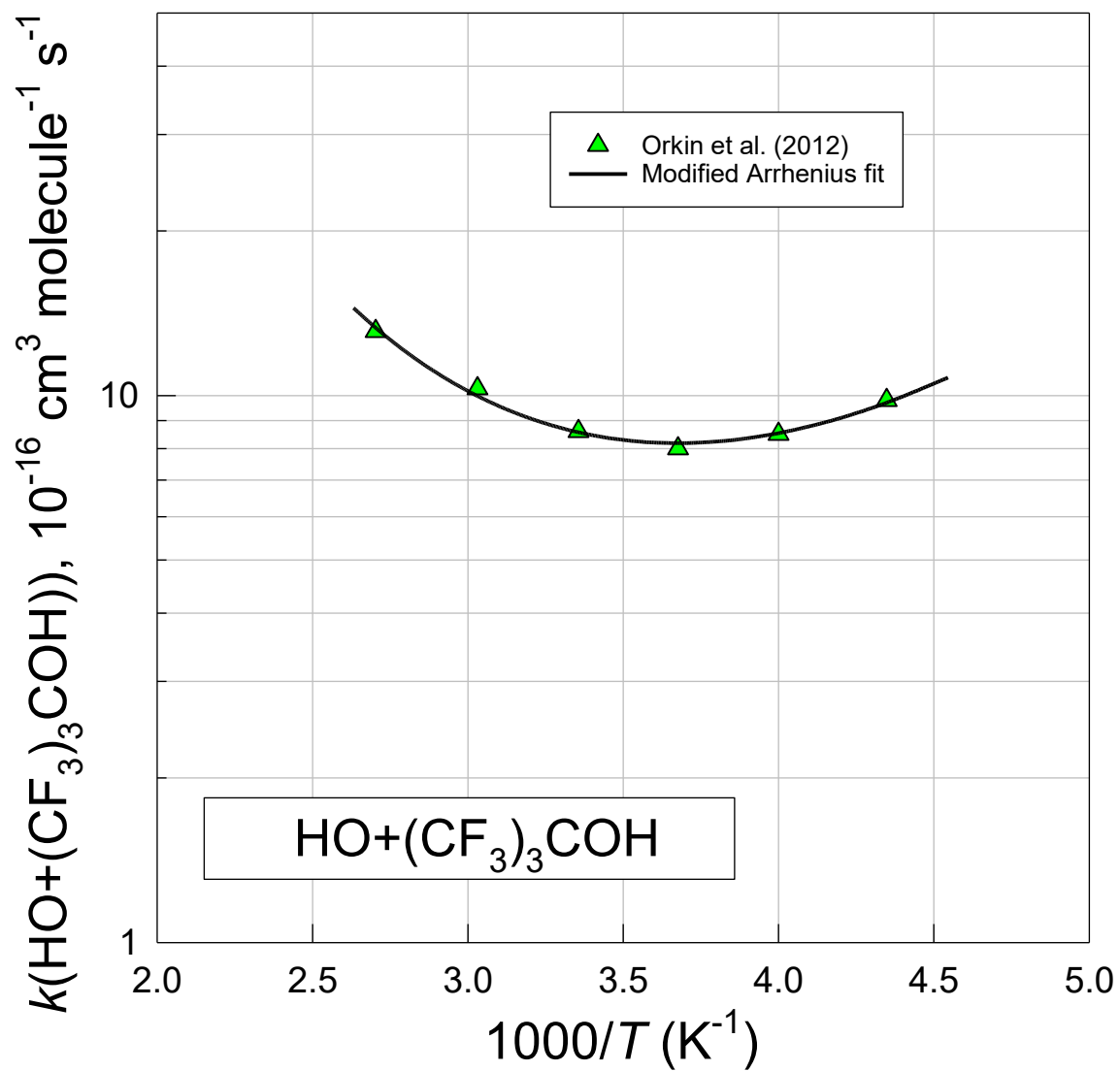
3608 Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M., and Wallington T. J.: The Mechanisms of
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3610 Orkin, V. L., Khamaganov, V. G., and Kurylo, M. J.: J. Phys. Chem. A, 116, 6188, 2012.

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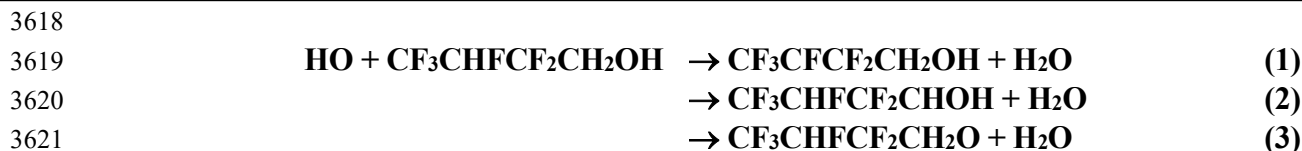
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3616 **oFOx90: HO + CF₃CHF₂CF₂CH₂OH**
 3617 Last evaluated: June 2025; Last change in preferred values: June 2009.



3622 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**
 3623
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| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|---|--------------|--------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.46 \pm 0.26) \times 10^{-12} \exp[-(880 \pm 40)/T]$ | 250-430 | Chen et al. (2003) | LP-LIF (a) |
| 1.3×10^{-13} | 298 | | FP-LIF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| $6.03 \times 10^{-13} \exp(-510/T)$ | 230-308 | Chen et al. (2003) | RR (b) |
| $(1.04 \pm 0.04) \times 10^{-13}$ | 298 | | |
| $9.41 \times 10^{-13} \exp(-591/T)$ | 230-308 | Chen et al. (2003) | RR (b) |
| $(1.27 \pm 0.03) \times 10^{-13}$ | 298 | | |

3625 **Comments**

- 3626
 3627 (a) Two different absolute rate methods were employed by Chen et al. (2003): LP-LIF and FP-LIF. HO
 3628 radicals in the LP-LIF experiments were generated by the 193 nm photolysis of N₂O to produce
 3629 O(¹D) atoms in the presence of H₂O in 20-80 Torr (27-107 mbar) of helium diluent. HO radicals in
 3630 the FP-LIF experiments were generated by the photolysis (Xe flash lamp) of H₂O in 20-80 Torr (27-
 3631 107 mbar) of argon diluent. There was good agreement between the results from experiments using
 3632 the two different techniques. The Arrhenius expression is from a fit to the combined data set from
 3633 both sets of absolute rate experiments. The value at 298 K cited above is the average obtained using
 3634 the different techniques.
 3635 (b) HO radicals were generated by the photolysis of O₃ at $\lambda \geq 260$ nm using the output from Xe arc
 3636 lamps in the presence of H₂O vapor in 100 Torr (133 mbar) of helium diluent. CH₂Cl₂ and CHCl₃
 3637 were used as reference compounds. Arrhenius fits to the rate coefficient ratios reported by Chen et
 3638 al. (2003) give $k(\text{HO} + \text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH})/k(\text{HO} + \text{CH}_2\text{Cl}_2) = 0.335 \exp(350/T)$ and
 3639 $k(\text{HO} + \text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH})/k(\text{HO} + \text{CHCl}_3) = 0.523 \exp(259/T)$. Placing these ratios on an absolute
 3640 basis using $k(\text{HO} + \text{CH}_2\text{Cl}_2) = 1.8 \times 10^{-12} \exp(-860/T)$ and $k(\text{HO} + \text{CHCl}_3) = 1.8 \times 10^{-12} \exp(-850/T)$
 3641 (Atkinson et al., 2008) gives $k(\text{HO} + \text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}_2\text{OH}) = 6.03 \times 10^{-13} \exp(-510/T)$ and 9.41×10^{-13}
 3642 $\exp(-591/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Over the temperature range where comparison is
 3643 possible, the results from the relative rate studies are consistent with those from the absolute study.
 3644

3645 **Preferred Values**
 3646

| Parameter | Value | T/K |
|--|-------------------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.3×10^{-13} | 298 |
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $2.26 \times 10^{-12} \exp(-848/T)$ | 250-430 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.12 | 298 |
| $\Delta E/R$ | ± 200 | 250-430 |

3648 *Comments on Preferred Values*

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3658 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi,
3659 M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 8, 4141, 2008; IUPAC Subcommittee for Gas
3660 Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>.

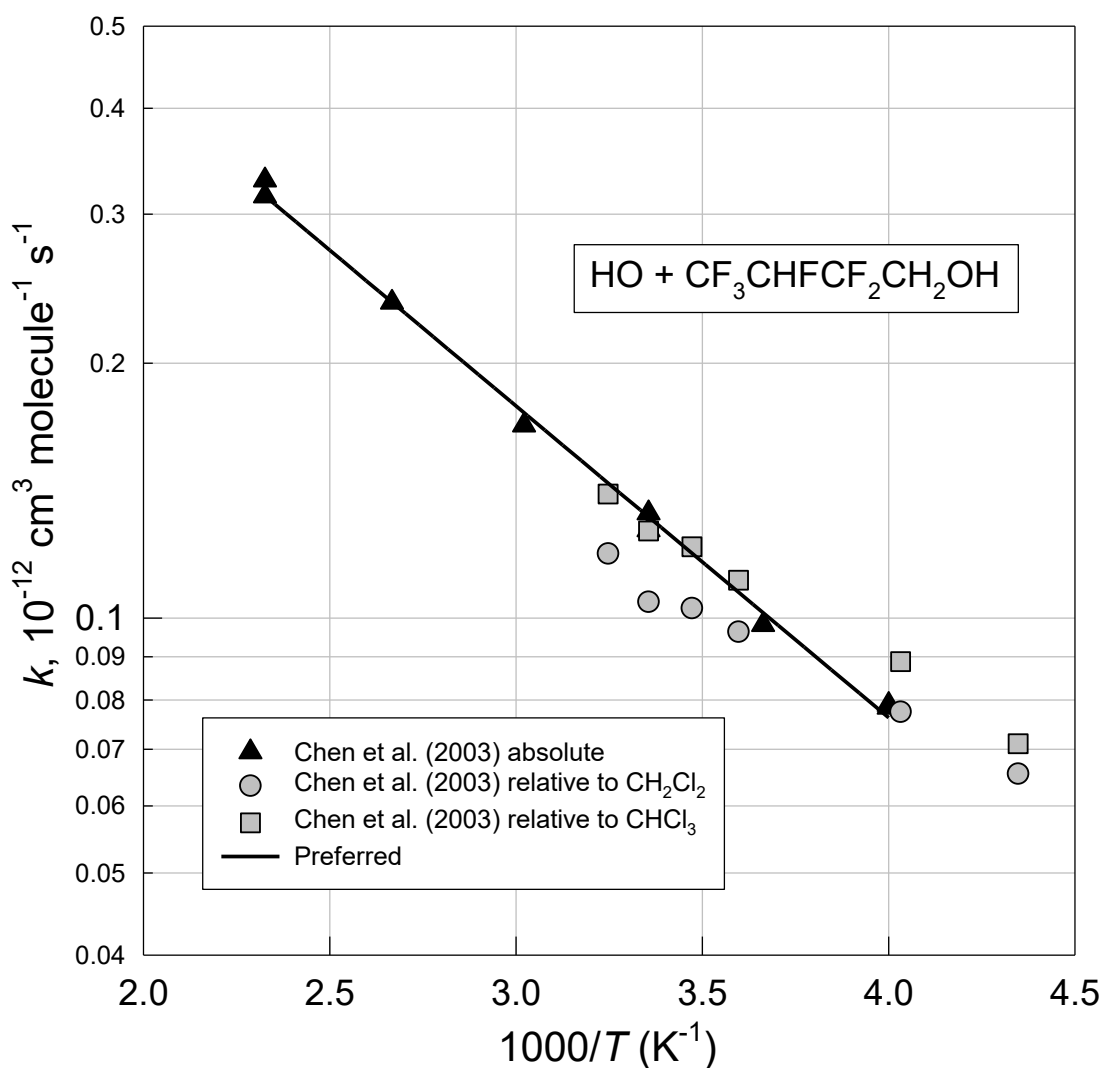
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3664 2003.

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References



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3669 **oFOx91: HO + *n*-C₃F₇CH₂OH**
 3670 Last evaluated: June 2025; Last change in preferred values: June 2025.



3674
 3675 **Rate coefficient data (*k* = *k*₁ + *k*₂)**
 3676

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|---|-------------|------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (1.4 ^{+0.3} _{-0.2}) × 10 ⁻¹¹ exp [-(1460±120)/ <i>T</i>] | 290-368 | Bravo et al. (2010) | DF-MS (a) |
| (1.07 ± 0.05) × 10 ⁻¹³ | 298 | | |
| (1.54 × 10 ⁻¹² exp[-(765±170)/ <i>T</i>]) | 298-363 | Indulkar et al. (2011) | LP-LIF (b) |
| (1.15 ± 0.12) × 10 ⁻¹³ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (9.4 ± 0.8) × 10 ⁻¹⁴ | 296 | Hurley et al. (2004) | RR (c) |

3677
 3678 **Comments**

3679
 3680(a) F atoms produced in a microwave discharge of F₂/He mixtures were reacted with H₂O to generate HO
 3681 radicals. Experiments were conducted in a flow tube at a pressure of 1 Torr of helium diluent. HO
 3682 radicals were monitored by mass spectroscopy by adding I₂ and detecting the HOI product.
 3683(b) HO radicals were produced by the photolysis of H₂O₂ at 248 nm and monitored by laser induced
 3684 fluorescence in 55 Torr of helium diluent.
 3685(c) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air. A rate
 3686 coefficient ratio of *k*(HO+C₃F₇CH₂OH)/*k*(HO+C₂H₂) = 0.12 ± 0.01 was reported. Using *k*(HO+C₂H₂) =
 3687 7.8 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 2006) gives *k*(HO+C₃F₇CH₂OH) = (9.4 ± 0.8) × 10⁻¹⁴ cm³
 3688 molecule⁻¹ s⁻¹.

3689
 3690 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.11 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 6.06 × 10 ⁻¹² exp(-1192/ <i>T</i>) | 280-370 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | ± 0.10 | 298 |
| Δ E/R | ± 200 | 280-370 |

3694
 3695 **Comments on Preferred Values**

3696
 3697 The results from the absolute rate studies by Bravo et al. (2010), Indulkar et al. (2011), and the
 3698 relative rate study by Hurley et al. (2005) at ambient temperature are in good agreement. The preferred
 3699 rate coefficient at 298 K is an average from the two absolute rate studies. The Arrhenius expression was
 3700 obtained using the temperature dependence derived from fitting an Arrhenius expression to the combined
 3701 data set from Bravo et al. (2010) and Indulkar et al. (2011) and adjusting the pre-exponential factor to

3702 match the preferred rate coefficient at 298 K.

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References

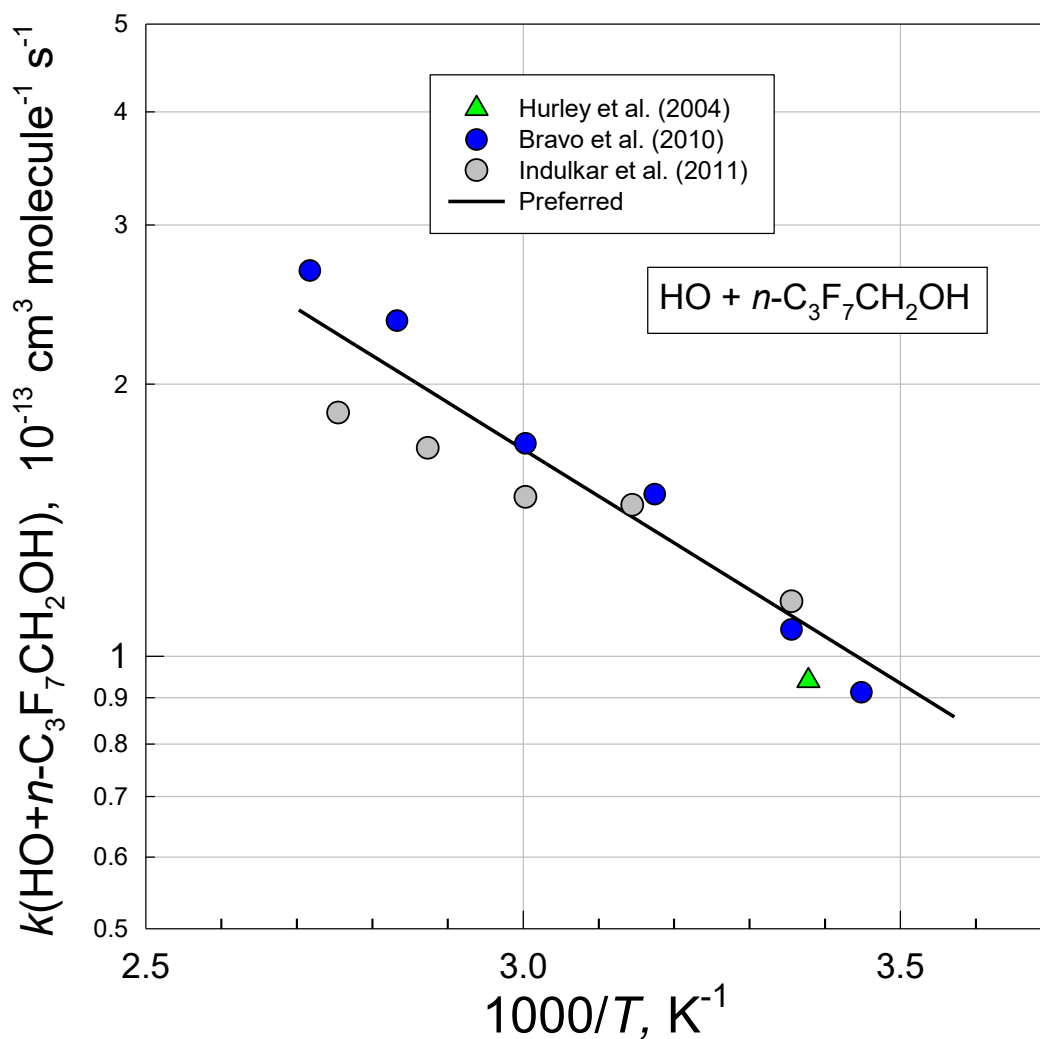
3706 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
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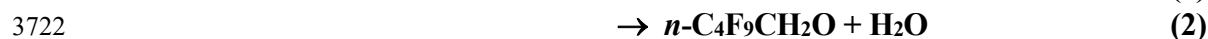
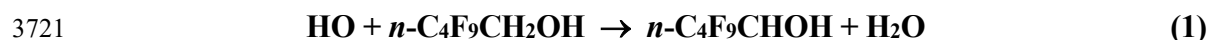


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3718 **oFOx92: HO + n-C₄F₉CH₂OH**
3719 Last evaluated: June 2025; Last change in preferred values: June 2009.

3720



3723

3724 **Rate coefficient data ($k = k_1 + k_2$)**

3725

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(9.4 \pm 0.8) \times 10^{-14}$ | 296 | Hurley et al. (2004) | RR (a) |

3726

3727

3728

Comments

3729 (a) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air.
3730 Experiments were performed with C_xF_{2x+1}CH₂OH (x= 1, 2, 3, and 4). There was no discernable
3731 difference in the reactivity of C_xF_{2x+1}CH₂OH molecules investigated and the composite data set was
3732 analyzed together. A rate coefficient ratio of $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CH}_2\text{OH})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.12 \pm 0.01$ was
3733 reported. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives
3734 $k(\text{HO} + \text{C}_4\text{F}_9\text{CH}_2\text{OH}) = (9.4 \pm 0.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3735

3736

3737

Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 9.4×10^{-14} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.15 | 298 |

3740

3741 *Comments on Preferred Values*

3742

3743 The preferred value is based upon the sole study of this reaction by Hurley et al. (2004).

3744

3745

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3746

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3749 Data Evaluation, <https://iupac.aeris-data.fr/>.

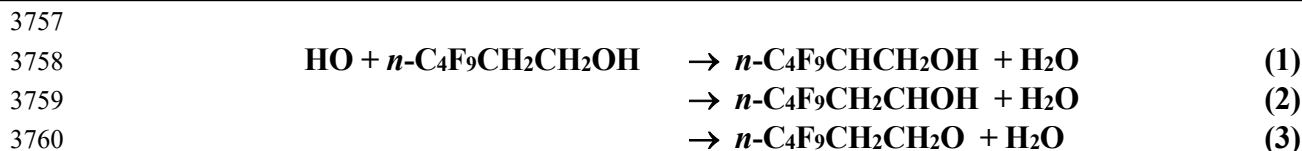
3750 Hurley, M. D., Wallington, T. J., Andersen, M. P. S., Ellis, D. A., Martin, J. W., and Mabury, S. A.: J.
3751 Phys. Chem. A, 108, 1973, 2004.

3752

3753

3754

3755 **oFOx93: HO + *n*-C₄F₉CH₂CH₂OH**
 3756 Last evaluated: June 2025; Last change in preferred values: June 2009.



3761 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|---------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(0.92 \pm 0.12) \times 10^{-12}$ | 296 | Ellis et al. (2003) | RR (a) |
| $(1.03 \pm 0.14) \times 10^{-12}$ | 296 | | |

3764

3765 **Comments**

3766

3767 (a) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air.

3768 Experiments were performed with *n*-C₄F₉CH₂CH₂OH, *n*-C₆F₁₃CH₂CH₂OH, and *n*-

3769 C₈F₁₇CH₂CH₂OH. There was no discernable difference in the reactivity of the three alcohols and the

3770 composite data set was analyzed together. Rate coefficient ratios of

3771 $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO} + \text{C}_2\text{H}_2) = 1.18 \pm 0.15$ and $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CH}_2\text{CH}_2\text{OH})/$

3772 $k(\text{HO} + \text{C}_2\text{H}_4) = 0.131 \pm 0.018$ were reported. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_2) =$

3773 $7.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO} + n\text{-C}_4\text{F}_9\text{CH}_2\text{CH}_2\text{OH}) = (0.92 \pm$

3774 $0.12) \times 10^{-12}$ and $(1.03 \pm 0.14) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3775

3776 **Preferred Values**

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.0×10^{-12} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

3777

3778 **Comments on Preferred Values**

3781

3782

3783 The preferred value is based upon the average of the two determinations by Ellis et al. (2003). As

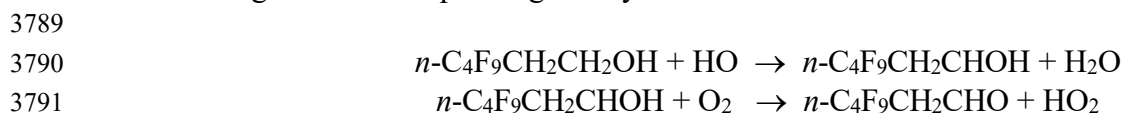
3784 discussed by Calvert et al. (2011), HO radicals are approximately an order of magnitude less reactive

3785 towards C_xF_{2x+1}CH₂OH than towards C_xF_{2x+1}CH₂CH₂OH and presumably the majority (>90%) of

3786 reaction of HO with *n*-C₄F₉CH₂CH₂OH proceeds via attack on the terminal –CH₂– group. As with

3787 other α-hydroxy alkyl radicals, the atmospheric fate of *n*-C₄F₉CH₂CHOH radicals will be reaction

3788 with O₂ to give the corresponding aldehyde.



3792

3793 Product studies of the chlorine atom initiated oxidation of *n*-C₄F₉CH₂CH₂OH in 700 Torr of air at 296

3794 K by Hurley et al. (2004) and Andersen et al. (2005) have shown that *n*-C₄F₉CH₂CH₂OH is oxidized

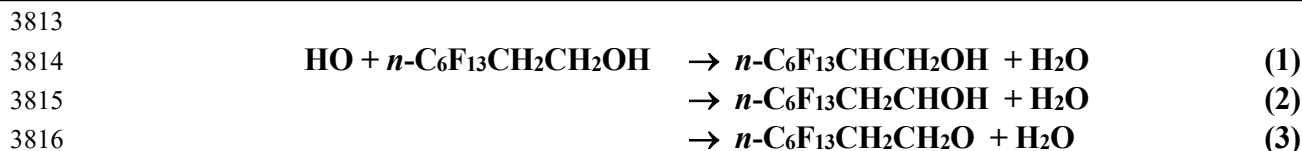
3795 to give *n*-C₄F₉CH₂CHO in a yield which is indistinguishable from 100%.

3796

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3798
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3807 *Environ. Sci. Technol.*, 37, 3816, 2003.
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3809 A.: *J. Phys. Chem. A*, 108, 5635, 2004.
- 3810

3811 **oFOx94: HO + *n*-C₆F₁₃CH₂CH₂OH**
 3812 Last evaluated: June 2025; Last change in preferred values: June 2009.



3818 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**
 3819

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|---------------------|------------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(9.2 \pm 1.2) \times 10^{-13}$ | 296 | Ellis et al. (2003) | RR (a) |
| $(7.79 \pm 0.35) \times 10^{-13}$ | 298 | Kelly et al. (2005) | RR (b) |
| $(7.91 \pm 0.53) \times 10^{-13}$ | 298 | | RR (b) |

3820
 3821 **Comments**
 3822

- 3823 (a) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air.
 3824 Experiments were performed with *n*-C₄F₉CH₂CH₂OH, *n*-C₆F₁₃CH₂CH₂OH, and *n*-
 3825 C₈F₁₇CH₂CH₂OH. There was no discernable difference in the reactivity of the three alcohols and the
 3826 composite data set was analyzed together. A rate coefficient ratio of
 3827 $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO} + \text{C}_2\text{H}_2) = 1.18 \pm 0.15$ was reported. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8 \times$
 3828 $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO} + n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{OH}) = (9.2 \pm 1.2) \times 10^{-13}$
 3829 $\text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 3830 (b) HO radicals were generated by the photolysis of either H₂O₂ or O₃ (in the presence of H₂O vapor) in
 3831 one atmosphere of air. Experiments were performed using two different reference compounds;
 3832 HC(O)OC₄H₉ and *n*-C₆H₁₄. Rate coefficient ratios of
 3833 $k(\text{HO} + \text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO} + \text{HC}(\text{O})\text{OC}_4\text{H}_9) = 0.22 \pm 0.01$ and
 3834 $k(\text{HO} + \text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO} + n\text{-C}_6\text{H}_{14}) = 0.15 \pm 0.01$ were reported. Using $k(\text{HO} + \text{HC}(\text{O})\text{OC}_4\text{H}_9)$
 3835 $= 3.54 \times 10^{-12}$ (Le Calvé et al., 1997) and $k(\text{HO} + n\text{-C}_6\text{H}_{14}) = 3.27 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert
 3836 et al., 2008) gives $k(\text{HO} + n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{OH}) = (7.79 \pm 0.35) \times 10^{-13}$ and $(7.91 \pm 0.53) \times 10^{-13} \text{ cm}^3$
 3837 $\text{ molecule}^{-1} \text{ s}^{-1}$.
 3838

3839 **Preferred Values**
 3840

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 8.3×10^{-13} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

3841
 3842 **Comments on Preferred Values**
 3843

3844 The rate coefficients reported in the relative rate studies by Ellis et al. (2003) and Kelly et al.
 3845 (2005) are in agreement and an average gives our preferred value. As discussed by Calvert et al. (2011),
 3846 HO radicals are approximately an order of magnitude less reactive towards C_xF_{2x+1}CH₂CH₂OH than
 3847 towards C_xF_{2x+1}CH₂CH₂OH and it seems likely that the majority (>90%) of reaction of HO with *n*-
 3848 C₆F₁₃CH₂CH₂OH proceeds via attack on the terminal –CH₂– group. As with other α-hydroxy alkyl
 3849
 3850

3851 radicals, the atmospheric fate of $n\text{-C}_6\text{F}_{13}\text{CH}_2\text{CHOH}$ radicals will be reaction with O_2 to give the
3852 corresponding aldehyde.



3855

3856

References

3857

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3869 Kelly, T., Bossoutrot, V., Magneron, I., Wirtz, K., Treacy, J., Mellouki, A., Sidebottom, H., and Le Bras,
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3871 Le Calvé, S., Le Bras, G., and Mellouki, A.: J. Phys. Chem. A 101, 5489, 1997.

3872

3873

3874 **oFOx95: HO + *n*-C₆F₁₃CH₂CH₂OH**
 3875 Last evaluated: June 2025; Last change in preferred values: June 2009.

3876



3880

3881 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**

3882

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|---------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(9.2 \pm 1.2) \times 10^{-13}$ | 296 | Ellis et al. (2003) | RR (a) |

3883

3884

3885

Comments

3886 (a) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air.
 3887 Experiments were performed with *n*-C₄F₉CH₂CH₂OH, *n*-C₆F₁₃CH₂CH₂OH, and *n*-
 3888 C₈F₁₇CH₂CH₂OH. There was no discernable difference in the reactivity of the three alcohols and the
 3889 composite data set was analyzed together. A rate coefficient ratio of
 3890 $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CH}_2\text{CH}_2\text{OH})/k(\text{HO} + \text{C}_2\text{H}_5) = 1.18 \pm 0.15$ was reported. Using $k(\text{HO} + \text{C}_2\text{H}_5) = 7.8 \times$
 3891 $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO} + n\text{-C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}) = (9.2 \pm 1.2) \times 10^{-$
 3892 $13 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3893

3894

3895

Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 9.2×10^{-13} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

3896

3897

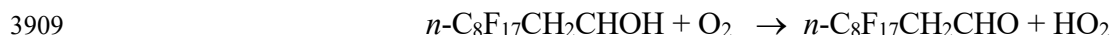
3898

Comments on Preferred Values

3900

3901 The rate coefficient reported by Ellis et al. (2003) is adopted as the preferred value. As discussed
 3902 by Calvert et al. (2011), HO radicals are approximately an order of magnitude less reactive towards
 3903 C_{*x*}F_{2*x*+1}CH₂OH than towards C_{*x*}F_{2*x*+1}CH₂CH₂OH and it seems likely that the majority (>90%) of
 3904 reaction of HO with *n*-C₈F₁₇CH₂CH₂OH proceeds via attack on the terminal –CH₂– group. As with
 3905 other α -hydroxy alkyl radicals, the atmospheric fate of *n*-C₈F₁₇CH₂CHOH radicals will be reaction
 3906 with O₂ to give the corresponding aldehyde.

3907



3910

3911 It is expected that the HO radical initiated oxidation of *n*-C₈F₁₇CH₂CH₂OH will lead to the formation
 3912 of *n*-C₈F₁₇CH₂CHO in a yield of essentially 100%. Consistent with this expectation, Chiappero et al.
 3913 (2008) measured a $92 \pm 7\%$ yield of *n*-C₈F₁₇CH₂CHO in the chlorine-atom initiated oxidation of *n*-
 3914 C₈F₁₇CH₂CH₂OH (8:2 FTOH) in 700 Torr of air.

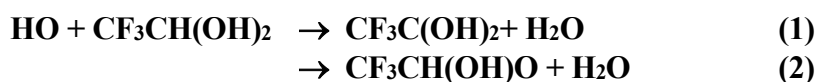
3915

3916

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3918
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3921 Data Evaluation, <https://iupac.aeris-data.fr/>.
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3925 2008.
3926 Ellis, D. A., Martin, J. W., Mabury, S. A., Hurley, M. D., Andersen, M. P. S., and Wallington, T. J.:
3927 *Environ. Sci. Technol.*, 37, 3816, 2003.
3928
3929

3930 **oFOx96: HO + CF₃CH(OH)₂**
 3931 Last evaluated: June 2025; Last change in preferred values: June 2009.



3935 **Rate coefficient data ($k = k_1 + k_2$)**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|-----|------------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(1.18 \pm 0.11) \times 10^{-12}$ | 296 | Andersen et al. (2006) | RR (a) |
| $(1.14 \pm 0.12) \times 10^{-12}$ | 296 | | |

3938 **Comments**

- 3939
 3940
 3941 (a) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air. Separate
 3942 experiments were performed using C₂H₂ and C₂H₄ as references. Rate coefficient ratios of
 3943 $k(\text{HO} + \text{CF}_3\text{CH}(\text{OH})_2)/k(\text{HO} + \text{C}_2\text{H}_2) = 0.146 \pm 0.015$ and $k(\text{HO} + \text{CF}_3\text{CH}(\text{OH})_2)/k(\text{HO} + \text{C}_2\text{H}_4) =$
 3944 0.0149 ± 0.0014 were reported. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.9 \times 10^{-12} \text{ cm}^3$
 3945 $\text{molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{CF}_3\text{CH}(\text{OH})_2) = (1.14 \pm 0.12) \times 10^{-13}$ and $(1.18 \pm$
 3946 $0.11) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3947 **Preferred Values**

| Parameter | Value | T/K |
|--|-----------------------|-----|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.2×10^{-13} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.20 | 298 |

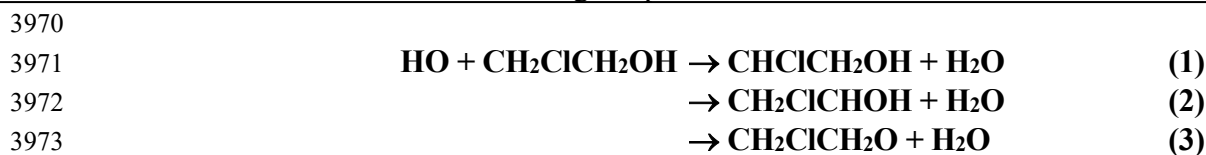
3948 **Comments on Preferred Values**

3949
 3950
 3951
 3952
 3953 The preferred value is based upon the average of the two determinations by Andersen et al.
 3954 (2006). Andersen et al. (2006) reported that the chlorine atom initiated oxidation of CF₃CH(OH)₂ in
 3955 700 Torr (933 mbar) of air gives CF₃C(O)OH in a molar yield of $101 \pm 6\%$. The HO radical initiated of
 3956 CF₃CH(OH)₂ is expected to give CF₃C(O)OH in essentially 100% yield.

3957 **References**

- 3958 Andersen, M. P. S., Nielsen, O. J., Hurley, M. D., Ball, J. C., Wallington, T. J., Ellis, D. A., Martin, J. W.,
 3959 and Mabury, S. A.: J. Phys. Chem. A, 109, 1849, 2005.
 3960 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
 3961 Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Subcommittee for Gas Kinetic
 3962 Data Evaluation, <https://iupac.aeris-data.fr/>.

3968 **oClOx90: HO + CH₂ClCH₂OH**
 3969 Last evaluated: June 2025; Last change in preferred values: June 2009



3974
 3975 **Rate coefficient data ($k = k_1 + k_2 + k_3$)**
 3976

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|--------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.28 \pm 0.09) \times 10^{-12}$ | 298 | Wallington et al. (1988) | FP-RF (a) |

3977
 3978 **Comments**

3979
 3980 (a) HO radicals were generated by the photolysis ($\lambda \geq 165 \text{ nm}$) of H₂O in 25-50 Torr (33-67 mbar) of
 3981 argon at 298 K.

3982
 3983 **Preferred Values**

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.3×10^{-12} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.20 | 298 |

3987
 3988 *Comments on Preferred Values*

3989
 3990 The absolute rate coefficient reported by Wallington et al. (1988) is adopted as the preferred value.
 3991 The enhanced uncertainty reflects the fact that there is only one study available.

3992
 3993
 3994 **References**

3995
 3996 Wallington, T. J., Dagaut, P., and Kurylo, M. J.: J. Phys. Chem., 92, 5024, 1988.

3997
 3998

3999 **oClOx91: HO + CCl₃CH₂OH**
4000 Last evaluated: June 2023; Last change in preferred values: June 2009.



4004
4005 **Rate coefficient data ($k = k_1 + k_2$)**
4006

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.45 \pm 0.24) \times 10^{-13}$ | 298 | Wallington et al. (1988) | FP-RF (a) |

4007
4008 **Comments**

4009
4010 (a) HO radicals were generated by the photolysis ($\lambda \geq 165 \text{ nm}$) of H₂O in 25-50 Torr (33-67 mbar) of
4011 argon at 298 K.

4012
4013 **Preferred Values**

| Parameter | Value | T/K |
|--|------------------------|-----|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.45×10^{-13} | 298 |
| <i>Reliability</i> $\Delta \log k$ | 0.20 | 298 |

4017
4018 *Comments on Preferred Values*

4019
4020 The absolute rate coefficient reported by Wallington et al. (1988) forms the basis of the preferred
4021 value. The enhanced uncertainty reflects the fact that there is only one study available.

4022
4023 **References**

4024
4025
4026 Wallington, T. J., Dagaut, P., and Kurylo, M. J.: J. Phys. Chem., 92, 5024, 1988.

4027

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 4031
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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.7 \pm 0.2) \times 10^{-12}$ | 298 | Scollard et al. (1993) | PLP-RF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.32 \pm 0.28) \times 10^{-12}$ | 298 | Scollard et al. (1993) | RR (b) |
| $(1.79 \pm 0.05) \times 10^{-12}$ | 298 | Sellevåg et al. (2005) | RR (c) |

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Comments

- 4039 (a) HO radicals were generated by the 248 nm photolysis of nitric acid in argon at 15-100 Torr (20 - 133
 4040 mbar) pressure. Laser fluence was varied in the range 150-300 mJ/pulse with no discernable effect
 4041 on the rate coefficient measured suggesting the absence of complications from photolysis of
 4042 CHF₂CHO.
- 4043 (b) HO radicals were generated by the photolysis of CH₃ONO (or C₂H₅ONO) in CH₃ONO (or
 4044 C₂H₅ONO)-NO-CHF₂CHO-toluene-air mixtures at 730-750 Torr (973 - 1000 mbar) pressure. The
 4045 concentrations of CHF₂CHO and toluene were measured by GC and/or FTIR spectroscopy. Scollard
 4046 et al. (1993) did not report a value for the rate coefficient ratio $k(\text{HO} + \text{CHF}_2\text{CHO})/k(\text{HO} + \text{toluene})$.
 4047 Dividing the reported value of $k(\text{HO} + \text{CHF}_2\text{CHO})$ by the value of $k(\text{HO} + \text{toluene})$ used by
 4048 Scollard et al. (1993) gives $k(\text{HO} + \text{CHF}_2\text{CHO})/k(\text{HO} + \text{toluene}) = 0.235 \pm 0.005$ which is placed on
 4049 an absolute basis in the table above using $k(\text{HO} + \text{toluene}) = 5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K
 4050 (Mellouki et al., 2022).
- 4051 (c) HO radicals were generated by the photolysis of O₃ in the presence of H₂ in 1013 mbar of air
 4052 diluent. Propane was used as the reference compound. The concentrations of CHF₂CHO and
 4053 propane were measured by FTIR spectroscopy and a rate coefficient ratio of $k(\text{HO} +$
 4054 $\text{CHF}_2\text{CHO})/k(\text{HO} + \text{propane}) = 1.626 \pm 0.042$ was reported. Placing this result on an absolute basis
 4055 using $k(\text{HO} + \text{propane}) = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO} +$
 4056 $\text{CHF}_2\text{CHO}) = (1.79 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.6×10^{-12} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

4062
 4063
 4064

Comments on Preferred Values

4065 The results from the relative and absolute rate studies by Scollard et al. (1993) and Sellevåg et
 4066 al. (2005) are in agreement within the combined experimental uncertainties. An average of the results
 4067 from Scollard et al. (1993) and Sellevåg et al. (2005) gives the preferred value of $k(\text{OH} + \text{CHF}_2\text{CHO}) =$

4068 $1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The reaction probably proceeds predominately via abstraction
4069 of the aldehydic hydrogen (channel 1) to give CHF₂C(O) radicals.

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References

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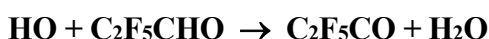
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4083 Sellevåg, S.R., Stenstrøm, V., Helgaker, T., and Nielsen, C.J.: *J. Phys. Chem. A* 109, 3652, 2005.

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4089 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|---|----------------|--------------------------------|---------------------|
| 2.56 × 10 ⁻¹² exp[-(458±36)/ <i>T</i>] (5.57 ± 0.14) × 10 ⁻¹³ | 263-358 298 | Antiñolo et al. (2014) | PLP-LIF (a) |
| <i>Relative Rate Coefficients</i> (4.63 ± 0.51) × 10 ⁻¹³ (5.10 ± 0.29) × 10 ⁻¹³ | 296 | Sulbaek Andersen et al. (2003) | RR (b) |

4092 **Comments**

- 4093 (a) HO radicals were produced by 248 nm (KrF eximer laser) photolysis of HNO₃ in 50-205 Torr (67-
 4094 273 mbar) of helium diluent at 263-358 K. HO radicals were monitored by LIF. No effect of total
 4095 pressure was reported over the range studied
 4096 (b) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air in the
 4097 presence of NO. C₂H₂ and C₂H₄ were used in separate experiments as reference compounds. The
 4098 loss of C₂F₅CHO and the reference compounds were monitored using FTIR spectroscopy. Rate
 4099 coefficient ratios of $k(\text{HO}+\text{C}_2\text{F}_5\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_2) = 0.593 \pm 0.065$ and
 4100 $k(\text{HO}+\text{C}_2\text{F}_5\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_4) = 0.0646 \pm 0.0037$ were reported. Scaling these ratios using
 4101 $k(\text{HO}+\text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and $k(\text{HO}+\text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO}+$
 4102 $\text{C}_2\text{F}_5\text{CHO}) = (4.63 \pm 0.51) \times 10^{-13}$ and $(5.10 \pm 0.29) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.

4103 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|---|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 5.2 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.42 × 10 ⁻¹² exp(-458/ <i>T</i>) | 250-360 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |
| Δ <i>E</i> / <i>R</i> | ± 200 | 250-360 |

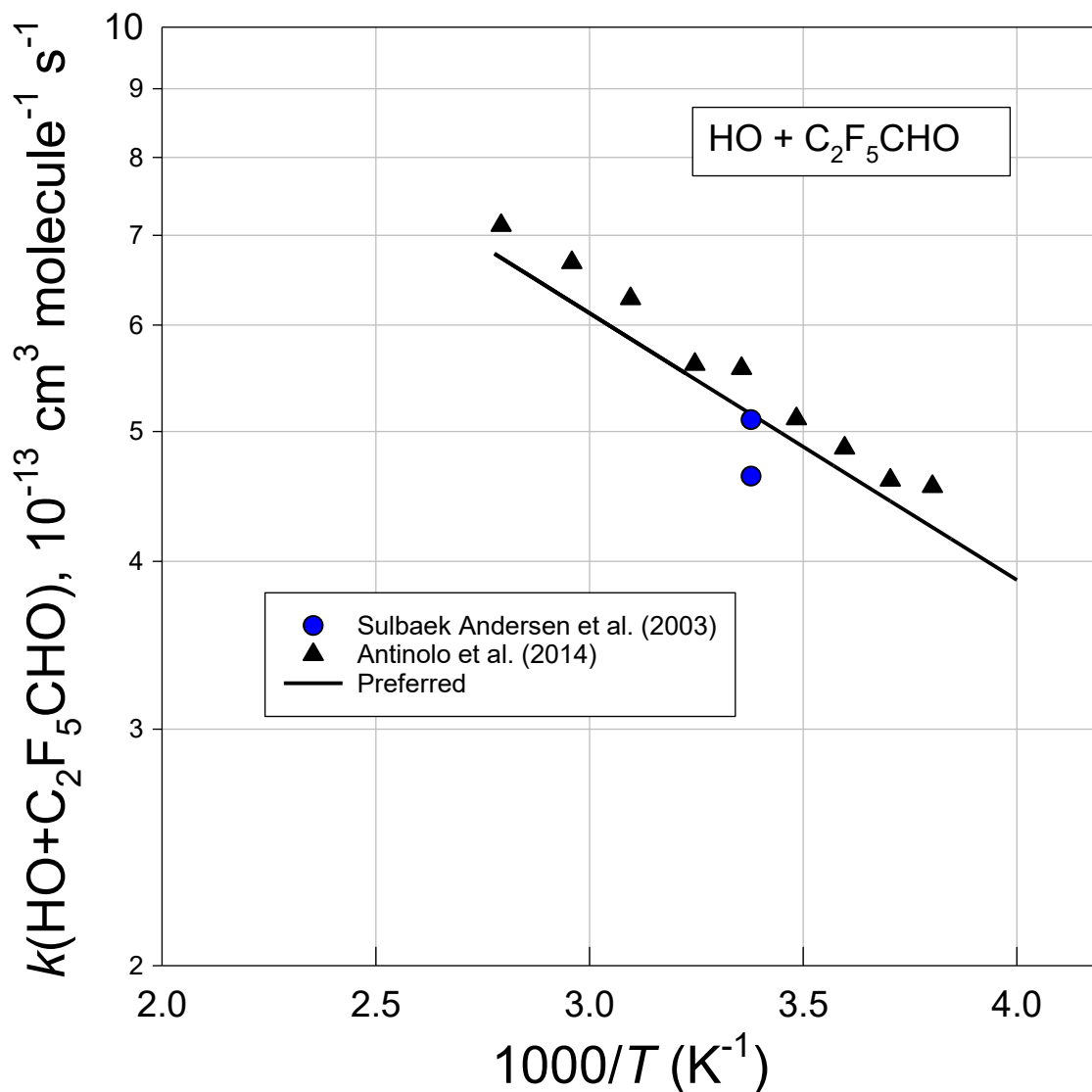
4104 **Comments on Preferred Values**

4105 The results reported by Sulbaek Andersen et al. (2003) and Antiñolo et al. (2014) near room
 4106 temperature are in agreement within the likely experimental uncertainties. Taking an average of the
 4107 results from the two studies gives the preferred value of $k(\text{OH}+\text{C}_2\text{F}_5\text{CHO}) = 5.2 \times 10^{-13}$ cm³ molecule⁻¹
 4108 s⁻¹ at 298 K. Taking the temperature dependence from Antiñolo et al. (2014) and adjusting the A factor
 4109 to reproduce the preferred rate coefficient at 298 K gives $k(\text{OH}+\text{C}_2\text{F}_5\text{CHO}) = 2.42 \times 10^{-12}$ exp(-458/*T*)
 4110 cm³ molecule⁻¹ s⁻¹. The reaction proceeds via abstraction of the aldehydic hydrogen to give C₂F₅C(O)
 4111 radicals.

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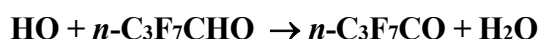
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4133 **oFOx99: HO + n-C₃F₇CHO**
 4134 Last evaluated: June 2025; Last change in preferred values: June 2019.



4136 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|--------------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (2.0 ± 0.6) × 10 ⁻¹² exp[-(369 ± 90)/ <i>T</i>] | 252 - 373 | Solignac et al. (2007) | PLP-LIF (a) |
| 5.55 × 10 ⁻¹³ | 297 | | (b) |
| <i>Relative Rate Coefficients</i> | | | |
| (5.68 ± 0.74) × 10 ⁻¹³ | 296 | Sulbaek Andersen et al. (2004) | RR (c) |
| (6.42 ± 0.75) × 10 ⁻¹³ | | | |

4140 **Comments**

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- 4143 (a) HO radicals were generated by the photolysis of H₂O₂ at 248 nm in the presence of C₃F₇CHO in 100 Torr (133 mbar) of helium diluent.
- 4144
- 4145 (b) Average of values given at 297 K
- 4146 (c) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air in the presence of NO. C₂H₂ and C₂H₄ were used as reference compounds in separate experiments. The loss of C₃F₇CHO and the reference compounds were monitored using FTIR spectroscopy. Experiments were performed using CF₃CHO, C₃F₇CHO, and C₄F₉CHO. There was no discernable difference in reactivity of the three fluorinated aldehydes. An analysis of the combined data set gave rate coefficient ratios of $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.73 \pm 0.10$ and $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO})/k(\text{HO} + \text{C}_2\text{H}_4) = 0.0813 \pm 0.0095$. Scaling these ratios using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO}) = (5.68 \pm 0.74) \times 10^{-13}$ and $(6.42 \pm 0.75) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.

4155 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 5.8 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.0 × 10 ⁻¹² exp(-369/ <i>T</i>) | 250-380 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.08 | 298 |
| Δ E/R | ± 200 | 250-380 |

4157 **Comments on Preferred Values**

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4161 There is excellent agreement between the absolute rate data reported by Solignac et al. (2007) and the relative rate data reported by Sulbaek Andersen et al. (2004) at temperatures near 298K. The Arrhenius expression $k(\text{HO} + \text{C}_3\text{F}_7\text{CHO}) = 2.0 \times 10^{-12} \exp(-369/T)$ from Solignac et al. (2007) is preferred and gives 5.8×10^{-13} cm³ molecule⁻¹ s⁻¹ at 298 K. As shown by Sulbaek Andersen et al. (2004), the reaction proceeds via abstraction of the aldehydic hydrogen to give C₃F₇C(O) radicals.

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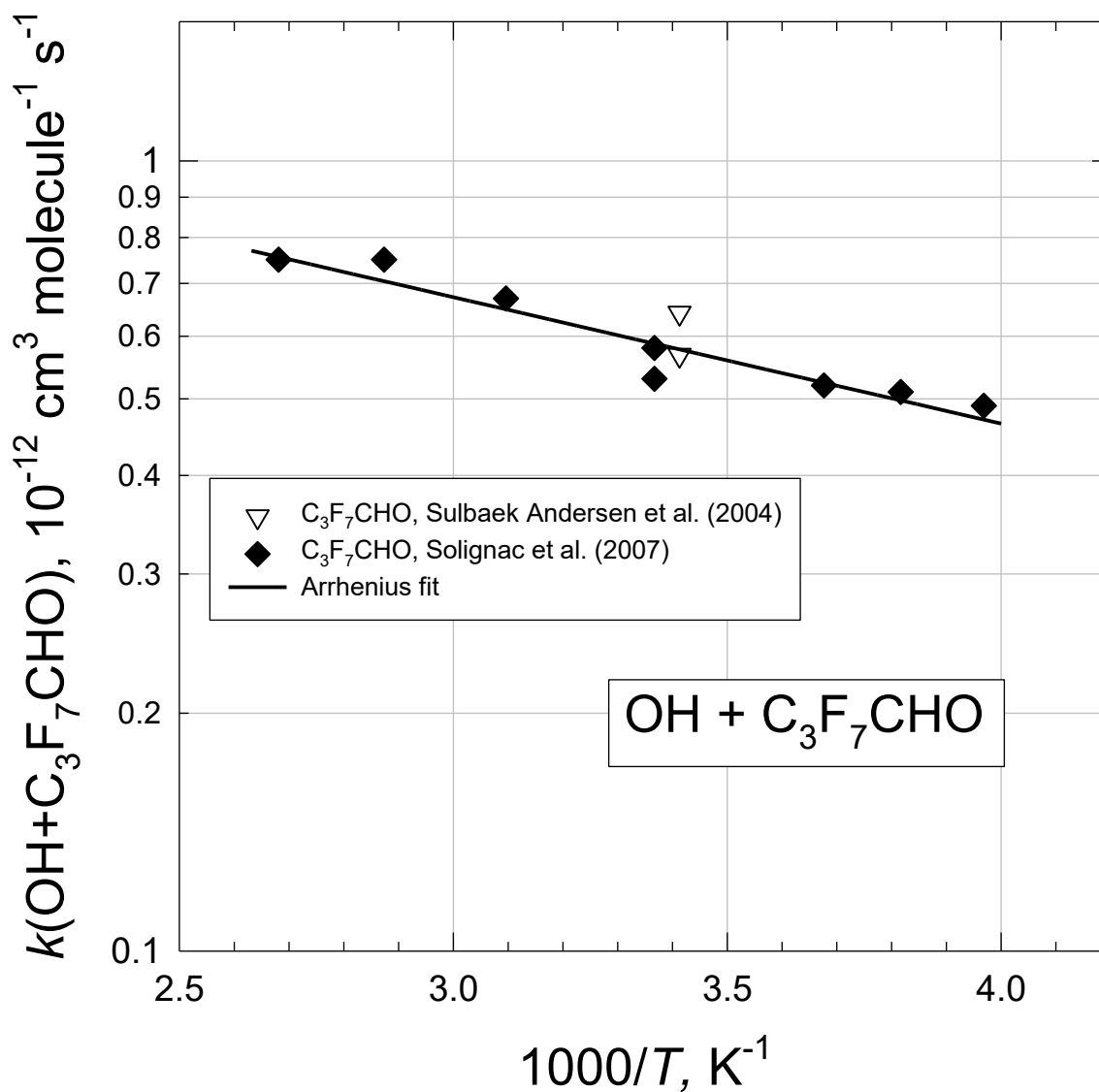
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 4187 **Rate coefficient data**
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| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|------------------|--------------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (2.0 ± 0.5) × 10 ⁻¹² exp[-(356 ± 70)/ <i>T</i>] (6.4 ± 0.3) × 10 ⁻¹³ | 253 – 373 299 | Solignac et al. (2007) | PLP-LIF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (5.68 ± 0.74) × 10 ⁻¹³ (6.42 ± 0.75) × 10 ⁻¹³ | 296 | Sulbaek Andersen et al. (2004) | RR (b) |

4189
 4190 **Comments**

- 4191
 4192 (a) HO radicals were generated by the photolysis of H₂O₂ at 248 nm in the presence of C₄F₉CHO in 100
 4193 Torr (133 mbar) of helium diluent.
 4194 (b) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air in the
 4195 presence of NO. In separate experiments C₂H₂ and C₂H₄ were used as reference compounds. The
 4196 loss of C₄F₉CHO and the reference compounds were monitored using FTIR spectroscopy.
 4197 Experiments were performed using CF₃CHO, C₃F₇CHO, and C₄F₉CHO. There was no discernable
 4198 difference in reactivity of the three fluorinated aldehydes. An analysis of the combined data set gave
 4199 rate coefficient ratios of $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.73 \pm 0.10$ and
 4200 $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO})/k(\text{HO} + \text{C}_2\text{H}_4) = 0.0813 \pm 0.0095$. Scaling these ratios using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8$
 4201 $\times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{CHO}) = (5.68 \pm$
 4202 $0.74) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ and $(6.42 \pm 0.75) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.

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 4204 **Preferred Values**
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| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 6.1 × 10 ⁻¹³ | 298 |
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.0 × 10 ⁻¹² exp(-356/ <i>T</i>) | 250-380 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.08 | 298 |
| Δ E/R | ± 150 | 250-380 |

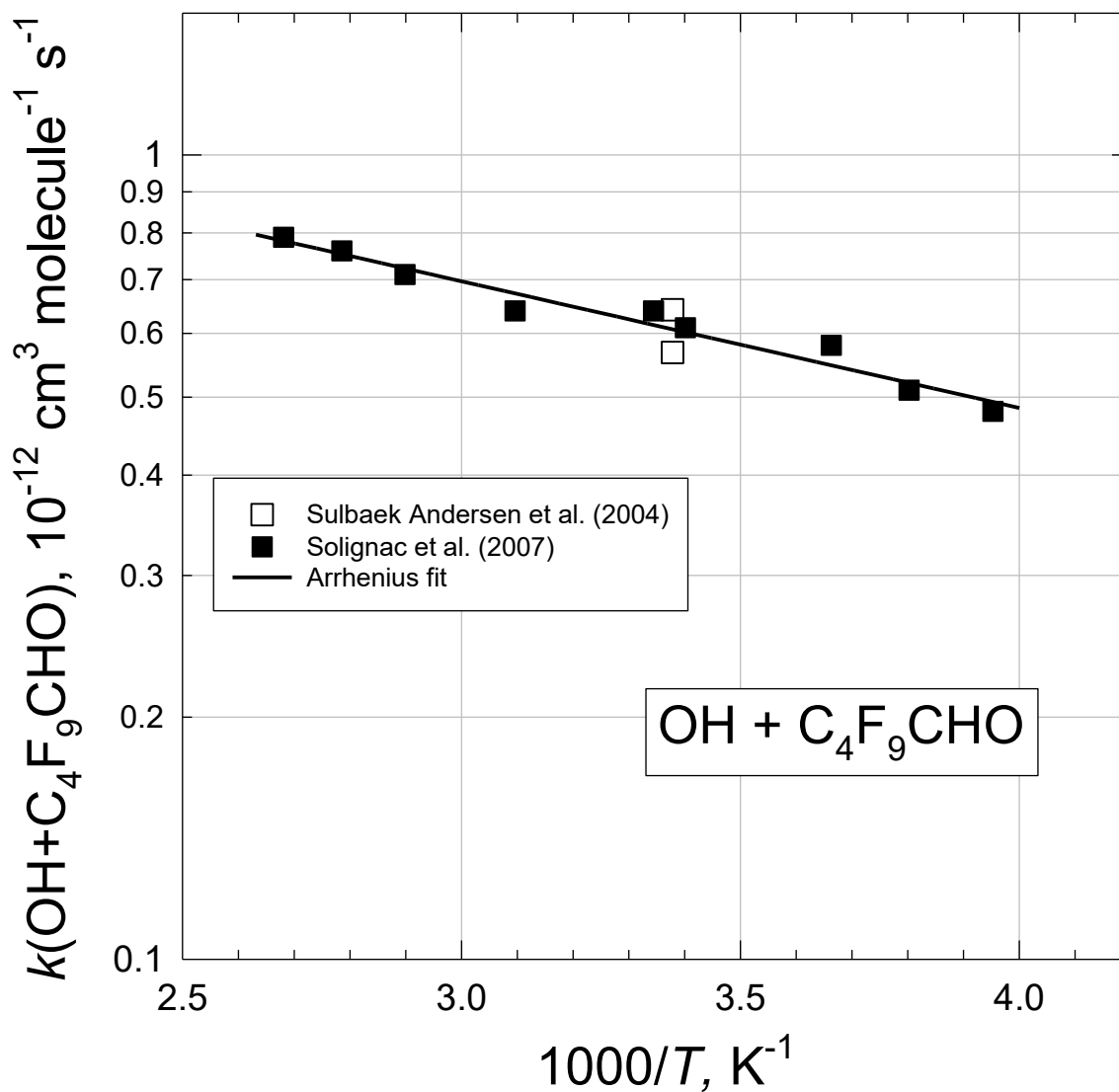
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 4207 **Comments on Preferred Values**

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 4210 There is excellent agreement between the absolute rate data reported by Solignac et al. (2007)
 4211 and the relative rate data reported by Sulbaek Andersen et al. (2004) at temperatures near 298 K. The
 4212 Arrhenius expression $k(\text{HO} + \text{C}_4\text{F}_9\text{CHO}) = 2.0 \times 10^{-12} \exp(-365/T)$ from Solignac et al. (2007) is
 4213 preferred and gives 6.1 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ at 298 K. As shown by Sulbaek Andersen et al.
 4214 (2004), the reaction proceeds via abstraction of the aldehydic hydrogen to give C₄F₉C(O) radicals.
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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.96 \pm 0.04) \times 10^{-12}$ | 298 | Kelly et al. (2005) | PLP-LIF (a) |
| $(7.8 \pm 2.2) \times 10^{-12} \exp(-314 \pm 90)/T$ | 263-358 | Antiñolo et al. (2010) | PLP-LIF (b) |
| $(2.59 \pm 0.50) \times 10^{-12}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(3.87 \pm 0.16) \times 10^{-12}$ | 298 | Sellevåg et al. (2004) | RR (c) |
| $(3.07 \pm 0.08) \times 10^{-12}$ | | | |
| $(2.48 \pm 0.27) \times 10^{-12}$ | 296 | Hurley et al. (2005) | RR (d) |
| $(2.65 \pm 0.36) \times 10^{-12}$ | | | |

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Comments

- (a) HO radicals were generated by the 248 nm photolysis of H₂O₂ in 100 Torr (133 mbar) of helium diluent at 298 K.
- (b) HO radicals were generated by the 248 nm photolysis of H₂O₂ in 50-215 Torr (67-286 mbar) of helium diluent at 263-358 K.
- (c) Experiments were performed in 1013 mbar of air diluent. HO radicals were generated by the photolysis of O₃ at $\lambda \approx 310$ nm in the presence of H₂O vapor. The loss of CF₃CH₂CHO was monitored relative to C₂H₅OH and HC(O)OC₂H₅ in separate experiments using FTIR spectroscopy and rate coefficient ratios of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_5\text{OH}) = 1.21 \pm 0.05$ and $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CHO})/k(\text{HO}+\text{HC}(\text{O})\text{OC}_2\text{H}_5) = 3.51 \pm 0.09$ were reported. Scaling these ratios using $k(\text{HO}+\text{C}_2\text{H}_5\text{OH}) = 3.2 \times 10^{-12}$ (Atkinson et al., 2006) and $k(\text{HO}+\text{HC}(\text{O})\text{OC}_2\text{H}_5) = 8.74 \times 10^{-13}$ (Calvert et al., 2011) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CHO}) = (3.87 \pm 0.16) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(3.07 \pm 0.08) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr (933 mbar) of air in the presence of NO. C₂H₂ and C₂H₄ were used as reference compounds in separate experiments. The loss of CF₃CH₂CHO and the reference compounds were monitored using FTIR spectroscopy. Rate coefficient ratios of $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_2) = 3.18 \pm 0.35$ and $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_4) = 0.336 \pm 0.045$. Scaling these ratios using $k(\text{HO}+\text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and $k(\text{HO}+\text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{CF}_3\text{CH}_2\text{CHO}) = (2.48 \pm 0.27) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(2.65 \pm 0.36) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.7×10^{-12} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $7.74 \times 10^{-12} \exp(-314/T)$ | 260-360 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |
| $\Delta (E/R)$ | ± 150 | 260-360 |

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4268*Comments on Preferred Values*4269
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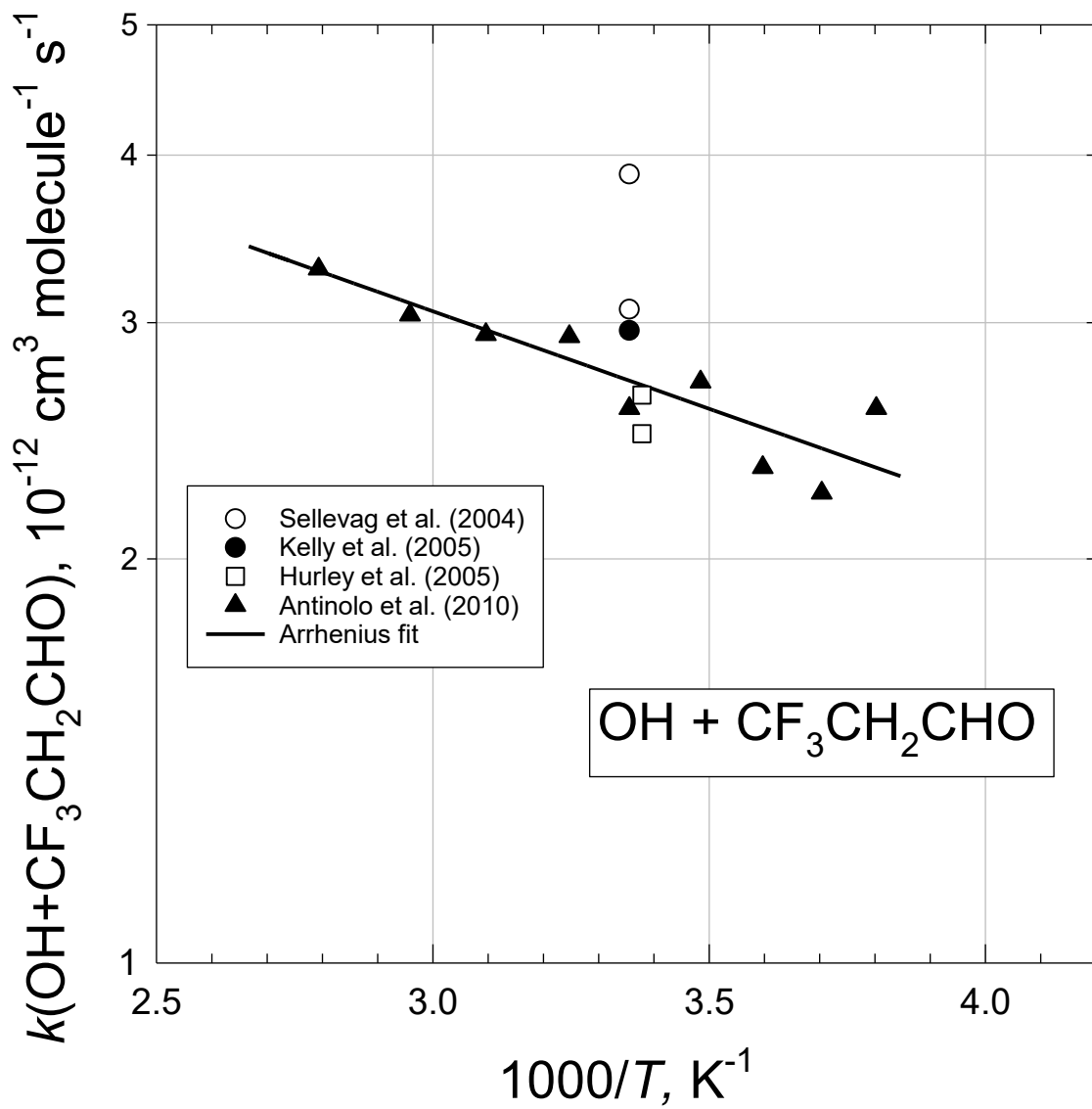
Except for one of the two relative rate determinations by Sellevåg et al. (2004), the data from the relative and absolute rate studies by Antiñolo et al. (2010), Hurley et al. (2005), Kelly et al. (2005), and Sellevåg et al. (2004) are consistent within the combined experimental uncertainties. Taking an average of the data from Antiñolo et al. (2010), Hurley et al. (2005), and Kelly et al. (2005) gives the preferred value at 298 K. The preferred Arrhenius expression is derived from taking the temperature dependence from Antiñolo et al. (2010) and adjusting the pre-exponential factor to match the preferred value at 298 K. The reaction is expected to proceed predominantly via abstraction of the aldehydic hydrogen giving $\text{CF}_3\text{CH}_2\text{C}(\text{O})$ radicals.

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References

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4299 **oFOx102: HO + n-C₆F₁₃CH₂CHO**
4300 Last evaluated: June 2025; Last change in preferred values: June 2009.

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4305 **Rate coefficient data ($k = k_1 + k_2$)**

4306

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(1.98 \pm 0.24) \times 10^{-12}$ | 296 | Chiappero et al. (2010) | RR (a) |

4307

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4309

Comments

4310 (a) HO radicals were generated by the photolysis of CH₃ONO in n-C₆F₁₃CH₂CHO/C₂H₄/CH₃ONO
4311 mixtures in 700 Torr (933 mbar) of air diluent. The loss of C₆F₁₃CH₂CHO and C₂H₄ were monitored
4312 using FTIR spectroscopy and a rate coefficient ratio of $k(\text{HO}+\text{C}_6\text{F}_{13}\text{CH}_2\text{CHO})/k(\text{HO}+\text{C}_2\text{H}_4) = 0.25$
4313 ± 0.03 was obtained. Using $k(\text{HO}+\text{C}_2\text{H}_4) = 7.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006)
4314 gives $k(\text{HO}+\text{C}_6\text{F}_{13}\text{CH}_2\text{CHO}) = (1.98 \pm 0.24) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

4315

4316

4317

Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.0×10^{-12} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

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4321 *Comments on Preferred Values*

4322

4323 The preferred value is based on the sole study of this reaction by Chiappero et al. (2010). The
4324 reaction is expected to proceed predominantly via abstraction of the aldehydic hydrogen giving
4325 C₆F₁₃CH₂C(O) radicals.

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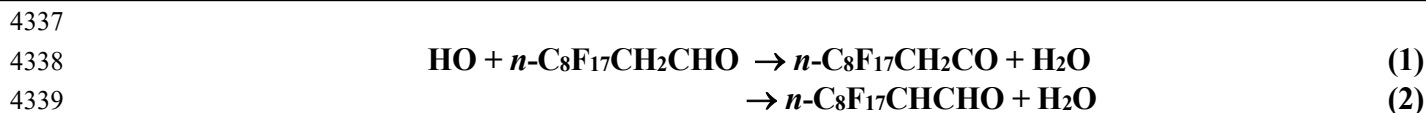
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4330 Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Subcommittee for Gas Kinetic
4331 Data Evaluation, <https://iupac.aeris-data.fr/>.

4332 Chiappero, M. S., Argüello, G. A., Hurley, M. D., and Wallington, T. J.: J. Phys. Chem. A, 114, 6131,
4333 2010.

4334

4335 **oFOx103: HO + *n*-C₈F₁₇CH₂CHO**
 4336 Last evaluated: June 2025; Last change in preferred values: June 2009.



4340
 4341 **Rate coefficient data ($k = k_1 + k_2$)**
 4342

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(1.82 \pm 0.32) \times 10^{-12}$ | 296 | Chiappero et al. (2008) | RR (a) |

4343
 4344 **Comments**

4345
 4346 (a) HO radicals were generated by the photolysis of CH₃ONO in *n*-C₈F₁₇CH₂CHO/C₂H₄/CH₃ONO
 4347 mixtures in 700 Torr (933 mbar) of air diluent. The loss of C₈F₁₇CH₂CHO and C₂H₄ were
 4348 monitored using FTIR spectroscopy and a rate coefficient ratio of
 4349 $k(\text{HO} + \text{C}_8\text{F}_{17}\text{CH}_2\text{CHO})/k(\text{HO} + \text{C}_2\text{H}_4) = 0.23 \pm 0.04$ was obtained. Using $k(\text{HO} + \text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$
 4350 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}) = (1.82 \pm 0.32) \times 10^{-12} \text{ cm}^3$
 4351 $\text{molecule}^{-1} \text{ s}^{-1}$.

4352
 4353 **Preferred Values**
 4354

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.8×10^{-12} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

4355
 4356 *Comments on Preferred Values*

4357
 4358 The preferred value is based on the sole study of this reaction by Chiappero et al. (2008). The
 4359 reaction is expected to proceed predominantly via abstraction of the aldehydic hydrogen giving
 4360 C₈F₁₇CH₂C(O) radicals.
 4361
 4362

4363
 4364 **References**

4365
 4366 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
 4367 Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Subcommittee for Gas Kinetic
 4368 Data Evaluation, <https://iupac.aeris-data.fr/>.
 4369 Chiappero, M. S., Argüello, G. A., Hurley, M. D., and Wallington, T. J.: Chem. Phys. Lett., 461, 198,
 4370 2008.
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4378 **oFOx104: HO + C₂F₅C(O)CF(CF₃)₂**
4379 Last evaluated: June 2025; Last change in preferred values: June 2009.

4380

4381 **HO + C₂F₅C(O)CF(CF₃)₂ → products** (1)

4382

4383 **Rate coefficient data ($k = k_1$)**

4384

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|-------------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $< 5 \times 10^{-16}$ | 296 | Taniguchi et al. (2003) | RR (a) |

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Comments

4388 (a) HO radicals were generated by photolysis of ozone at 254 nm in the presence of water vapor in 200
4389 Torr (266 mbar) of helium diluent. The loss of C₂F₅C(O)CF(CF₃)₂ was measured relative to CH₄
4390 and CH₃Cl. Following the generation of OH radicals in the system, CH₄ and CH₃Cl were observed
4391 to decay, but there was no discernible loss (<2%) of C₂F₅C(O)CF(CF₃)₂ (over and above that
4392 ascribed to photolysis). Using $k(\text{HO}+\text{CH}_4) = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006)
4393 an upper limit of $k(\text{HO}+\text{C}_2\text{F}_5\text{C}(\text{O})\text{CF}(\text{CF}_3)_2) < 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived.

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Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $< 5 \times 10^{-16}$ | 298 |

4397

4398 *Comments on Preferred Values*

4399

4400 The preferred value is based on the study by Taniguchi et al. (2008).

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References

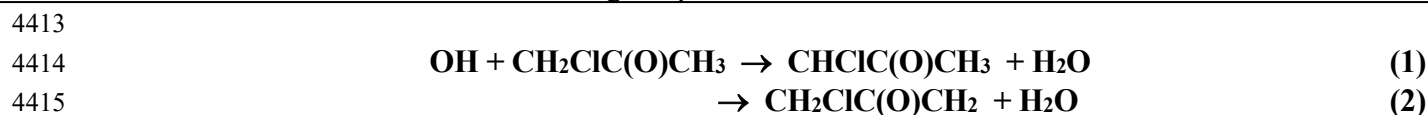
4404 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
4405 Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Subcommittee for Gas Kinetic
4406 Data Evaluation, <https://iupac.aeris-data.fr/>.

4407 Taniguchi, N., Wallington, T. J., Hurley, M. D., Guschin, A. G., Molina, L. T., and Molina, M. J.: J. Phys.
4408 Chem. A., 107, 2674, 2003.

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4410

4411 **oClOx92: OH + CH₂ClC(O)CH₃**
 4412 Last evaluated: June 2025; Last change in preferred values: June 2010



4417 **Rate coefficient data ($k = k_1 + k_2$)**
 4418

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|--------------------|------------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(4.38 \pm 0.29) \times 10^{-13}$ | 298 | Carr et al. (2003) | RR (a) |

4419
 4420 **Comments**

4421
 4422 (a) OH radicals were generated by the photolysis of O₃ at 254 nm in the presence of H₂O vapour in 1
 4423 bar of O₂ diluent. CH₂ClCH₂Cl was used as the reference compound. Chemical analysis was
 4424 achieved using FTIR spectroscopy and GC techniques and a rate coefficient ratio of
 4425 $k(\text{HO}+\text{CH}_2\text{ClC(O)CH}_3)/k(\text{HO}+\text{CH}_2\text{ClCH}_2\text{Cl}) = 1.81 \pm 0.12$ was obtained. Using
 4426 $k(\text{HO}+\text{CH}_2\text{ClCH}_2\text{Cl}) = 2.42 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2008) gives
 4427 $k(\text{HO}+\text{CH}_2\text{ClC(O)CH}_3) = (4.38 \pm 0.29) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 4428

4429 **Preferred Values**
 4430

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 4.4×10^{-13} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

4431
 4432 *Comments on Preferred Values*

4433
 4434 The preferred value is based on the study by Carr et al. (2003). The chlorine atom initiated
 4435 oxidation of CH₂ClC(O)CH₃ was studied by Carr et al. (2003) in one atmosphere of O₂ and the formation
 4436 of CO, CO₂, and HC(O)Cl products were reported. The products of the HO-initiated oxidation are
 4437 expected to be the same. Carr et al (2003) did not provide any information on the magnitude of the
 4438 consumption of CH₂ClC(O)CH₃ and the precise mechanism by which these products form is not clear.
 4439 As discussed by Calvert et al. (2011), photolysis leading to the formation of CO, CO₂, and HC(O)Cl is
 4440 probably the major atmospheric fate of CH₂ClC(O)CH₃.
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 4444 **References**

4445
 4446 Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington T. J.: Mechanisms of
 4447 Atmospheric Oxidation of the Alkanes, Oxford University Press, New York, NY, 2008.
 4448 Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington T. J.: The Mechanisms of
 4449 Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.
 4450 Carr, S., Shallcross, D.E., Canosa-Mas, C.E., Wenger, J.C., Sidebottom, H.W., Treacy, J.J., and Wayne,
 4451 R.P.: Phys. Chem. Chem. Phys., 5, 3874, 2003.
 4452

4453 **oClOx93: HO + CHCl₂C(O)CH₃**
4454 Last evaluated: June 2025; Last change in preferred values: June 2010.

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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|--------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(4.02 \pm 0.27) \times 10^{-13}$ | 298 | Carr et al. (2003) | RR (a) |

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Comments

(a) HO radicals were generated by the photolysis of O₃ at 254 nm in the presence of H₂O vapour in 1 bar of O₂ diluent. CH₂ClCH₂Cl was used as the reference compound. Chemical analysis was achieved using FTIR spectroscopy and GC techniques and a rate coefficient ratio of $k(\text{HO}+\text{CHCl}_2\text{C}(\text{O})\text{CH}_3)/k(\text{HO}+\text{CH}_2\text{ClCH}_2\text{Cl}) = 1.66 \pm 0.11$ was obtained. Using $k(\text{HO}+\text{CH}_2\text{ClCH}_2\text{Cl}) = 2.42 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2008) gives $k(\text{HO}+\text{CHCl}_2\text{C}(\text{O})\text{CH}_3) = (4.02 \pm 0.27) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 4.0×10^{-13} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.15 | 298 |

4473
4474

Comments on Preferred Values

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The preferred value is based on the study by Carr et al. (2003). The chlorine-atom initiated oxidation of CHCl₂C(O)CH₃ was studied by Carr et al. (2003) in one atmosphere of O₂ and the formation of CO, CO₂, and COCl₂ products were reported. The products of the HO-initiated oxidation are expected to be the same. Carr et al (2003) did not provide any information on the magnitude of the consumption of CHCl₂C(O)CH₃ and the precise mechanism by which these products form is not clear. As discussed by Calvert et al. (2011), photolysis leading to the formation of CO, CO₂, and COCl₂ is probably the major atmospheric fate of CHCl₂C(O)CH₃.

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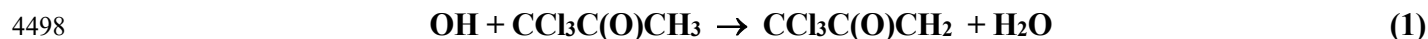
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4495 **oClOx94: OH + CCl₃C(O)CH₃**
4496 Last evaluated: June 2025; Last change in preferred values: June 2010.

4497



4499

4500 **Rate coefficient data ($k = k_1$)**

4501

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|--------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(1.54 \pm 0.15) \times 10^{-14}$ | 298 | Carr et al. (2003) | RR (a) |

4502

4503

4504

Comments

4505 (a) OH radicals were generated by the photolysis of O₃ at 254 nm in the presence of H₂O vapour in 1
4506 bar of O₂ diluent. CH₃CN was used as the reference compound. Chemical analysis was achieved using
4507 FTIR spectroscopy and GC techniques and a rate coefficient ratio of
4508 $k(\text{HO}+\text{CCl}_3\text{C}(\text{O})\text{CH}_3)/k(\text{HO}+\text{CH}_3\text{CN}) = 0.70 \pm 0.07$ was obtained. Using $k(\text{HO}+\text{CH}_3\text{CN}) = 2.2 \times 10^{-14}$
4509 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) gives $k(\text{HO}+\text{CCl}_3\text{C}(\text{O})\text{CH}_3) = (1.54 \pm 0.15) \times 10^{-14} \text{ cm}^3$
4510 $\text{molecule}^{-1} \text{ s}^{-1}$.

4511

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Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.5×10^{-14} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.15 | 298 |

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Comments on Preferred Values

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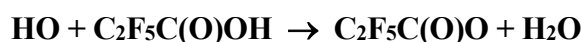
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References

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4531 Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>.
4532 Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington T. J.: The Mechanisms of
4533 Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.
4534 Carr, S., Shallcross, D. E., Canosa-Mas, C. E., Wenger, J. C., Sidebottom, H.W., Treacy, J. J., and Wayne,
4535 R. P.: Phys. Chem. Chem. Phys., 5, 3874, 2003.

4536

4537 **oFOx105: HO + C₂F₅C(O)OH**
 4538 Last evaluated: June 2025; Last change in preferred values: June 2009.



4540 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(1.54 \pm 0.17) \times 10^{-13}$ | 296 | Hurley et al. (2004) | RR (a) |
| $(1.56 \pm 0.11) \times 10^{-13}$ | | | |

4544 **Comments**

4545 (a) HO radicals were generated by the photolysis of CH₃ONO in C₂F₅C(O)OH/CH₃ONO/NO/(C₂H₂
 4546 or C₂H₄) mixtures in 700 Torr (933 mbar) of air. The loss of the reference compounds (C₂H₂ or C₂H₄)
 4547 was monitored by FTIR spectroscopy. The loss of C₂F₅C(O)OH was small and difficult to observe
 4548 directly. The loss of C₂F₅C(O)OH was calculated from the formation of COF₂ observed by FTIR
 4549 spectroscopy with a molar yield assumed to be 193% (CF₃ONO₂ and C₂F₅ONO₂ are formed in small
 4550 amounts). Experiments performed using C₂F₅C(O)OH, C₃F₇C(O)OH, and C₄F₉C(O)OH gave
 4551 indistinguishable values of the rate coefficient ratio $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{reference})$. Analysis
 4552 of the composite data set gave $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.197 \pm 0.022$ and
 4553 $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_4) = 0.0198 \pm 0.0014$. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and
 4554 $k(\text{HO} + \text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 2006) gives the values of $k(\text{HO} +$
 4555 $\text{C}_x\text{F}_{2x+1}\text{CHO})$ listed in the table above.

4556 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|-------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.559×10^{-13} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

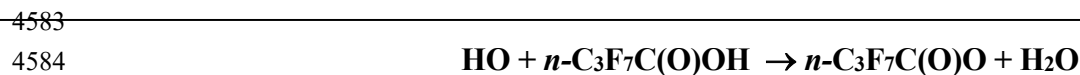
4560 **Comments on Preferred Values**

4561 The preferred value is based on the study by Hurley et al. (2004). The C₂F₅C(O)O radical
 4562 decomposes rapidly to give CO₂ and a C₂F₅ radical. As discussed by Ellis et al. (2004), in the
 4563 atmosphere the C₂F₅ radical will be converted mainly into COF₂ with CF₃C(O)OH formed as a minor
 4564 product following reaction of C₂F₅O₂ radicals with CH₃O₂ radicals. As might be expected from their
 4565 similar molecular structure, the reactivity of C₂F₅C(O)OH, C₃F₇C(O)OH, and C₄F₉C(O)OH towards HO
 4566 radicals are indistinguishable.

4567 **References**

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 4573 Hurley, M. D., Wallington, T. J., Ellis, D. A., Martin, J. W., and Mabury, S. A.: J. Phys. Chem. A, 108,
 4574 615, 2004.

4581 **oFOx106: HO + *n*-C₃F₇C(O)OH**
 4582 Last evaluated: June 2025; Last change in preferred values: June 2009.



4585
 4586 **Rate coefficient data**

4587

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | <i>T</i> /K | Reference | Technique/ Comments |
|--|-------------|----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(1.54 \pm 0.17) \times 10^{-13}$ | 296 | Hurley et al. (2004) | RR (a) |
| $(1.56 \pm 0.11) \times 10^{-13}$ | | | |

4588
 4589 **Comments**

4590
 4591 (a) HO radicals were generated by the photolysis of CH₃ONO in C₃F₇C(O)OH/CH₃ONO/NO/(C₂H₂
 4592 or C₂H₄) mixtures in 700 Torr (933 mbar) of air. The loss of the reference compounds C₂H₂ or C₂H₄ was
 4593 monitored by FTIR spectroscopy. The loss of C₃F₇C(O)OH was small and difficult to observe directly.
 4594 The loss of C₃F₇C(O)OH was calculated from the formation of COF₂ observed by FTIR spectroscopy
 4595 with a molar yield assumed to be 290% (CF₃ONO₂, C₂F₅ONO₂, and C₃F₇ONO₂ are formed in small
 4596 amounts). Experiments performed using C₂F₅C(O)OH, C₃F₇C(O)OH, and C₄F₉C(O)OH gave
 4597 indistinguishable values of the rate coefficient ratio $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{reference})$. Analysis
 4598 of the composite data set gave $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.197 \pm 0.022$ and
 4599 $k(\text{HO} + \text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH})/k(\text{HO} + \text{C}_2\text{H}_4) = 0.0198 \pm 0.0014$. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and
 4600 $k(\text{HO} + \text{C}_2\text{H}_4) = 7.9 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 2006) gives the values of $k(\text{HO} +$
 4601 $\text{C}_x\text{F}_{2x+1}\text{CHO})$ listed in the table above.

4602 **Preferred Values**

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| Parameter | Value | <i>T</i> /K |
|--|------------------------|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.55×10^{-13} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

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 4606 **Comments on Preferred Values**

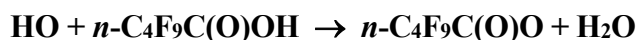
4607
 4608 The preferred value is based on the study by Hurley et al. (2004). The C₃F₇C(O)O radical
 4609 decomposes rapidly to give CO₂ and a C₃F₇ radical. As discussed by Ellis et al. (2004), the C₃F₇ radical
 4610 will be converted mainly into COF₂ with CF₃C(O)OH and C₂F₅C(O)OH formed as minor products
 4611 following reactions of C₂F₅O₂ and C₃F₇O₂ radicals with CH₃O₂ radicals. As might be expected from
 4612 their similar molecular structure, the reactivity of C₂F₅C(O)OH, C₃F₇C(O)OH, and C₄F₉C(O)OH towards
 4613 HO radicals are indistinguishable.

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 4615 **References**

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 4617 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
 4618 Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Subcommittee for Gas Kinetic
 4619 Data Evaluation, <https://iupac.aeris-data.fr/>.
 4620 Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P.,
 4621 and Wallington, T. J.: Environ. Sci. Tech., 38, 3316, 2004.
 4622 Hurley, M. D., Wallington, T. J., Ellis, D. A., Martin, J. W., and Mabury, S. A.: J. Phys. Chem. A, 108,
 4623 615, 2004.

4625 **oFOx107: HO + n-C₄F₉C(O)OH**
4626 Last evaluated: June 2025; Last change in preferred values: June 2009.

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Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | T/K | Reference | Technique/ Comments |
|--|--------------|----------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $(1.54 \pm 0.17) \times 10^{-13}$ | 296 | Hurley et al. (2004) | RR (a) |
| $(1.56 \pm 0.11) \times 10^{-13}$ | | | |

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Comments

4635 (a) HO radicals were generated by the photolysis of CH₃ONO in C₄F₉C(O)OH/CH₃ONO/NO/(C₂H₂
4636 or C₂H₄) mixtures in 700 Torr (933 mbar) of air. The loss of the reference compounds C₂H₂ or C₂H₄ was
4637 monitored by FTIR spectroscopy. The loss of C₄F₉C(O)OH was small and difficult to observe directly.
4638 The loss of C₄F₉C(O)OH was calculated from the formation of COF₂ observed by FTIR spectroscopy.
4639 with a molar yield assumed to be 384% (nitrates are formed in small amounts). Experiments performed
4640 using C₂F₅C(O)OH, C₃F₇C(O)OH, and C₄F₉C(O)OH gave indistinguishable values of the rate coefficient
4641 ratio $k(\text{HO}+\text{C}_x\text{F}_{2x+1}\text{C(O)OH})/k(\text{HO}+\text{reference})$. Analysis of the composite data set gave
4642 $k(\text{HO}+\text{C}_x\text{F}_{2x+1}\text{C(O)OH})/k(\text{HO}+\text{C}_2\text{H}_2) = 0.197 \pm 0.022$ and $k(\text{HO}+\text{C}_x\text{F}_{2x+1}\text{C(O)OH})/k(\text{HO}+\text{C}_2\text{H}_4) =$
4643 0.0198 ± 0.0014 . Using $k(\text{HO}+\text{C}_2\text{H}_2) = 7.8 \times 10^{-13}$ and $k(\text{HO}+\text{C}_2\text{H}_4) = 7.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
4644 (Atkinson et al., 2006) gives the values of $k(\text{HO}+\text{C}_x\text{F}_{2x+1}\text{CHO})$ listed in the table above.

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Preferred Values

| Parameter | Value | T/K |
|--|------------------------|--------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.55×10^{-13} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |

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Comments on Preferred Values

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The preferred value is based on the study by Hurley et al. (2004). The C₄F₉C(O)O radical decomposes rapidly to give CO₂ and a C₄F₉ radical. As discussed by Ellis et al. (2005), the C₄F₉ radical will be converted mainly into COF₂ with CF₃C(O)OH, C₂F₅C(O)OH, and C₃F₇C(O)OH formed as minor products from reactions involving CH₃O₂ radicals. As might be expected from their similar molecular structure, C₄F₉C(O)OH has a reactivity towards HO radicals which is indistinguishable from those of C₂F₅C(O)OH and C₃F₇C(O)OH.

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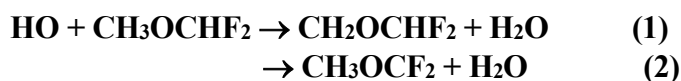
References

4661 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
4662 Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Subcommittee for Gas Kinetic
4663 Data Evaluation, <https://iupac.aeris-data.fr/>.
4664 Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P.,
4665 and Wallington, T. J.: Environ. Sci. Tech., 38, 3316, 2004.
4666 Hurley, M. D., Wallington, T. J., Ellis, D. A., Martin, J. W., and Mabury, S. A.: J. Phys. Chem. A, 108,
4667 615, 2004.

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4669 **oFOx137: HO + CH₃OCHF₂**
 4670 Last evaluated: June 2025; Last change in preferred values: June 2019.

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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---------|---------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.16 \pm 0.42) \times 10^{-11} \exp[(-1728 \pm 133)/T]$ | 298-460 | Orkin et al. (2014) | DF-EPR (a) |
| $(3.54 \pm 0.65) \times 10^{-14}$ | 298 | | |

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Comments

(a) HO radicals were generated by the reaction of H atoms with NO₂ in 2.5 Torr of helium diluent.

Preferred Values

| Parameter | Value | T/K |
|--|--------------------------------------|---------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 3.52×10^{-14} | 298 |
| | $1.16 \times 10^{-11} \exp(-1728/T)$ | 290-470 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.15 | 298 |
| $\Delta E/R$ | ± 100 | 290-470 |

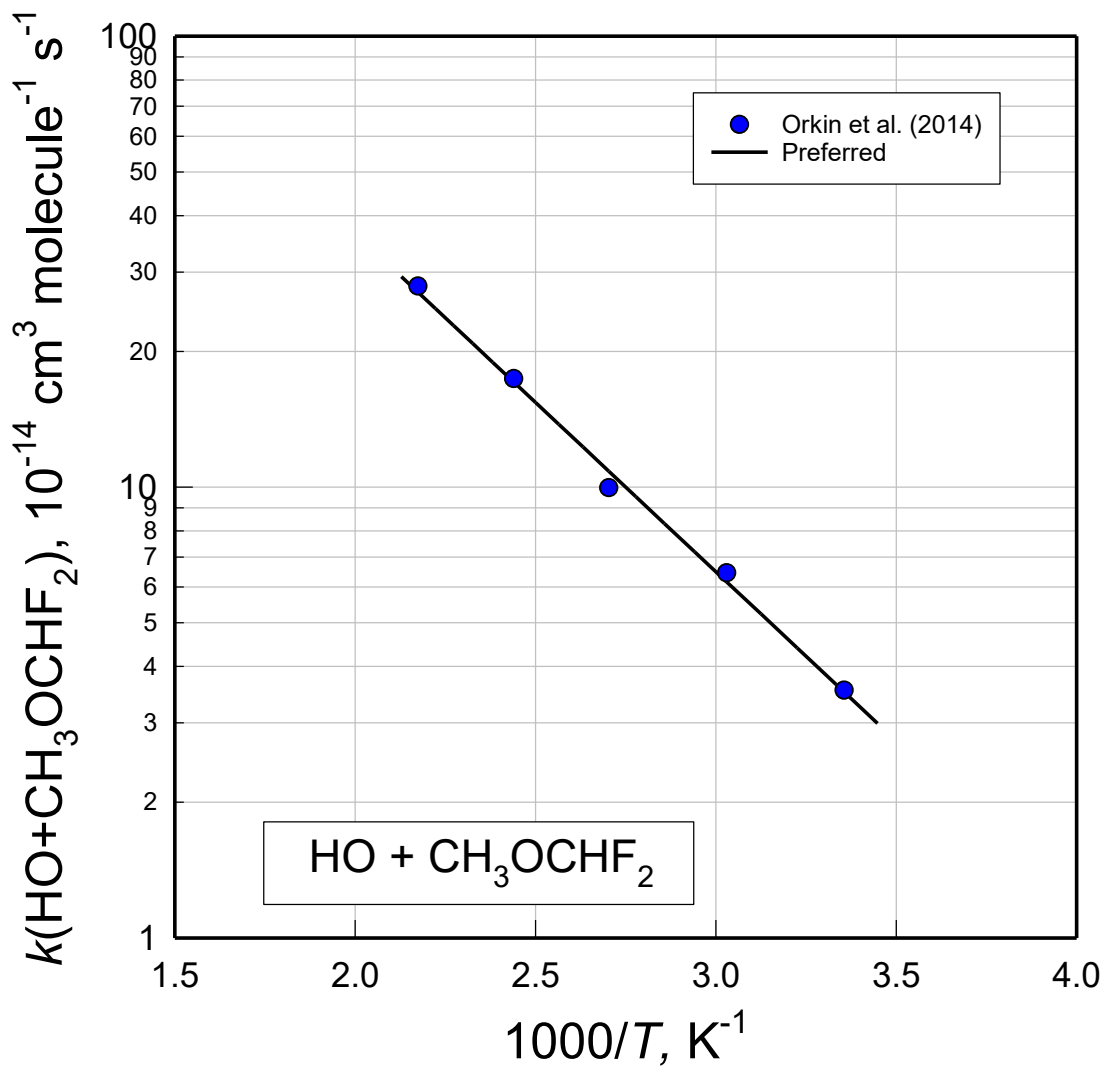
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Comments on Preferred Values

The preferred Arrhenius expression and rate coefficient at 298 K are taken from a fit to the data reported by Orkin et al. (2014).

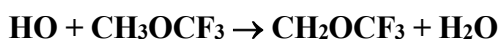
References

Orkin, V. L., Khamaganov, V. G., and Guschin, A. G.: J. Phys. Chem. A, 118, 10770, 2014.



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Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.14 \pm 0.15) \times 10^{-14}$ | 296 | Zhang et al. (1992) | FP-RF (a) |
| $(1.10 \pm 0.20) \times 10^{-12} \exp[(-1324 \pm 61)/T]$ | 298-460 | Orkin et al. (2014) | DF-EPR (b) |
| $(1.30 \pm 0.06) \times 10^{-14}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $1.18 \times 10^{-12} \exp(-1381/T)$ | 298-381 | Hsu and DeMore (1995) | RR (c) |
| 1.15×10^{-14} | 298 | | |
| $4.19 \times 10^{-12} \exp[(-1742)/T]$ | 268-308 | Chen et al. (2001) | RR (d) |
| 1.17×10^{-14} | 298 | | |

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Comments

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4705 (a) HO radicals were generated by the photolysis of water vapor in 35 Torr (47 mbar) of argon diluent
 4706 and monitored by resonance fluorescence.

4707 (b) HO radicals were generated by the reaction of H atoms with NO₂ in 2.5 Torr of helium diluent.

4708 (c) HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. Experiments
 4709 were conducted in which the loss of CF₃OCH₃ was measured relative to either CH₃CHF₂ or CHF₂Cl.
 4710 The concentrations of CF₃OCH₃, CH₃CHF₂, and CH₂F₂ were measured by FTIR spectroscopy. The
 4711 measured rate coefficient ratios of $k(\text{HO} + \text{CF}_3\text{OCH}_3)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.65 \pm 0.08) \exp[(190 \pm$
 4712 $43)/T]$ and $k(\text{HO} + \text{CF}_3\text{OCH}_3)/k(\text{HO} + \text{CH}_2\text{F}_2) = (1.55 \pm 0.10) \exp[(136 \pm 43)/T]$ are placed on an
 4713 absolute basis using $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.25 \times 10^{-12} \exp(-1070/T)$ and $k(\text{HO} + \text{CH}_2\text{F}_2) = 2.3 \times 10^{-12}$
 4714 $\exp(-1590/T)$ (Atkinson et al., 2008) to give $k(\text{HO} + \text{CF}_3\text{OCH}_3) = (8.1 \pm 1.0) \times 10^{-13} \exp[(-880 \pm$
 4715 $43)/T]$ and $(3.6 \pm 1.0) \times 10^{-12} \exp[-(1454 \pm 43)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A fit to the combined data set
 4716 (scaled using reference rate coefficients from Atkinson et al. 2008) gives $k(\text{HO} + \text{CF}_3\text{OCH}_3) = 1.18 \times$
 4717 $10^{-12} \exp(-1381/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

4718 (d) HO radicals were generated by the photolysis of ozone in the presence of water vapor in 100 Torr of
 4719 helium diluent. Separate experiments were performed in which the loss CF₃OCH₃ was measured
 4720 relative to either CH₄ or CH₃CCl₃. Placing the reported rate coefficient ratios on an absolute basis
 4721 using $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-12} \exp(-1690/T)$ and $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 1.2 \times 10^{-12} \exp(-1440/T)$
 4722 (Atkinson et al., 2008) and fitting an Arrhenius expression to the results gives $k(\text{HO} + \text{CH}_3\text{OCF}_3) =$
 4723 $(3.6 \pm 1.0) \times 10^{-12} \exp[(1454 \pm 43)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|--|----------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.29×10^{-14} $1.10 \times 10^{-12} \exp(-1324/T)$ | 298 290-470 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |

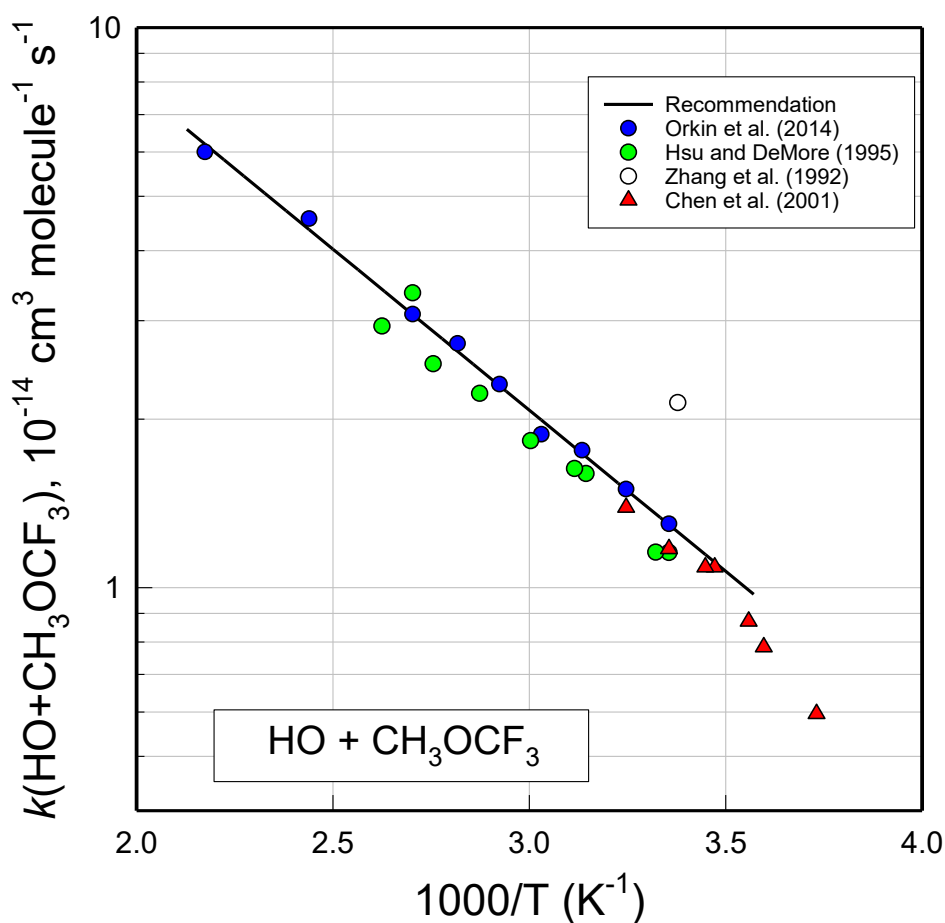
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Comments on Preferred Values

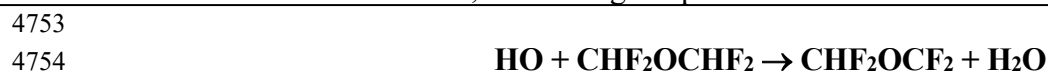
There is excellent agreement in the results from the relative rate study by Hsu and DeMore (1995), the absolute study by Orkin et al. (2014), and the $T > 285$ K results from the relative rate study by Chen et al. (2001). The rate coefficient reported by Zhang et al. (1992) at 296 K is substantially higher (by a factor of 1.6 to 1.9) than the results from Hsu and DeMore (1995), Chen et al. (2001), and Orkin et al. (2014). The origin of the discrepancy is probably the presence of reactive impurities in the sample used by Zhang et al. (1992). For reasons which are unclear, the low temperature ($T < 285$ K) results from Chen et al. (2001) appear to be anomalously low. Further work is needed to investigate the kinetics of the reaction at temperatures below 285 K. The preferred Arrhenius expression and rate coefficient at 298 K are taken from Orkin et al. (2014).

References

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Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem., 99, 11141, 1995.
Orkin, V. L., Khamaganov, V. G., and Guschin, A. G.: J. Phys. Chem. A, 118, 10770, 2014.
Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E.: J. Phys. Chem., 96, 9301, 1992.



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4755 **Rate coefficient data**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.53 \pm 0.24) \times 10^{-14}$ | 296 | Zhang et al. (1992) | FP-RF (a) |
| $(2.41 \pm 0.16) \times 10^{-14}$ | 296 | | |
| $(5.4 \pm 3.5) \times 10^{-13} \exp[-(1560 \pm 201)/T]$ | 269-312 | Garland et al. (1993) | PLP-LIF (b) |
| $(3.0 \pm 0.7) \times 10^{-15}$ | 295 | | |
| $(6.3^{+0.20}_{-0.16}) \times 10^{-12} \exp[-(1646 \pm 76)/T]$ | 277-370 | Orkin et al. (1999) | FP-RF (c) |
| $(2.47 \pm 0.12) \times 10^{-15}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $1.26 \times 10^{-12} \exp[-(1896)/T]$ | 298-381 | Hsu and DeMore (1995) | RR (d) |
| 2.23×10^{-15} | 298 | | |
| $1.01 \times 10^{-12} \exp[-(1825)/T]$ | 268-308 | Wilson et al. (2001) | RR (e) |
| 2.18×10^{-15} | 298 | | |

4758 **Comments**

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 4761 (a) HO radicals were generated by the photolysis of water vapor in 35 Torr (47 mbar) of argon and
 4762 monitored by resonance fluorescence. Two sets of experiments were performed using different
 4763 threshold voltages (3.3 kV or 4.6 kV) for the Xe flash lamp giving the values in the table.
 4764 (b) HO radicals were generated by the 248 nm photolysis of HNO₃ water vapor in 20 Torr (27 mbar) of
 4765 argon or helium diluent and monitored by LIF.
 4766 (c) HO radicals were generated by the photolysis of water vapor in 100 Torr (133 mbar) of argon diluent.
 4767 (d) HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. FTIR
 4768 spectroscopy was used to follow the loss of CHF₂OCHF₂ measured relative to CH₃CCl₃. The
 4769 measured rate coefficient ratio of $k(\text{HO} + \text{CHF}_2\text{OCHF}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = (1.05 \pm 0.20) \exp[(-456$
 4770 $\pm 62)/T]$ is placed on an absolute basis using $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 1.2 \times 10^{-12} \exp(-1440/T)$ (Atkinson
 4771 et al., 2008) to give $k(\text{HO} + \text{CHF}_2\text{OCHF}_2) = 1.26 \times 10^{-12} \exp[-(1896)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 4772 (e) HO radicals were generated by the photolysis of water vapor in helium diluent and the loss of
 4773 CHF₂OCHF₂ was measured relative to that of CF₃CF₂H by GC-MS. Placing the reported rate
 4774 coefficient ratios on an absolute basis using $k(\text{HO} + \text{CF}_3\text{CF}_2\text{H}) = 4.40 \times 10^{-13} \exp(-1630/T)$ (Atkinson
 4775 et al., 2008) and fitting an Arrhenius expression to the results gives $k(\text{HO} + \text{CHF}_2\text{OCHF}_2) = (3.6 \pm$
 4776 $1.0) \times 10^{-12} \exp[(1454 \pm 43)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|--|----------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.20×10^{-15} $1.04 \times 10^{-12} \exp(-1836/T)$ | 298 270-470 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta E/R$ | ± 100 | 270-470 |

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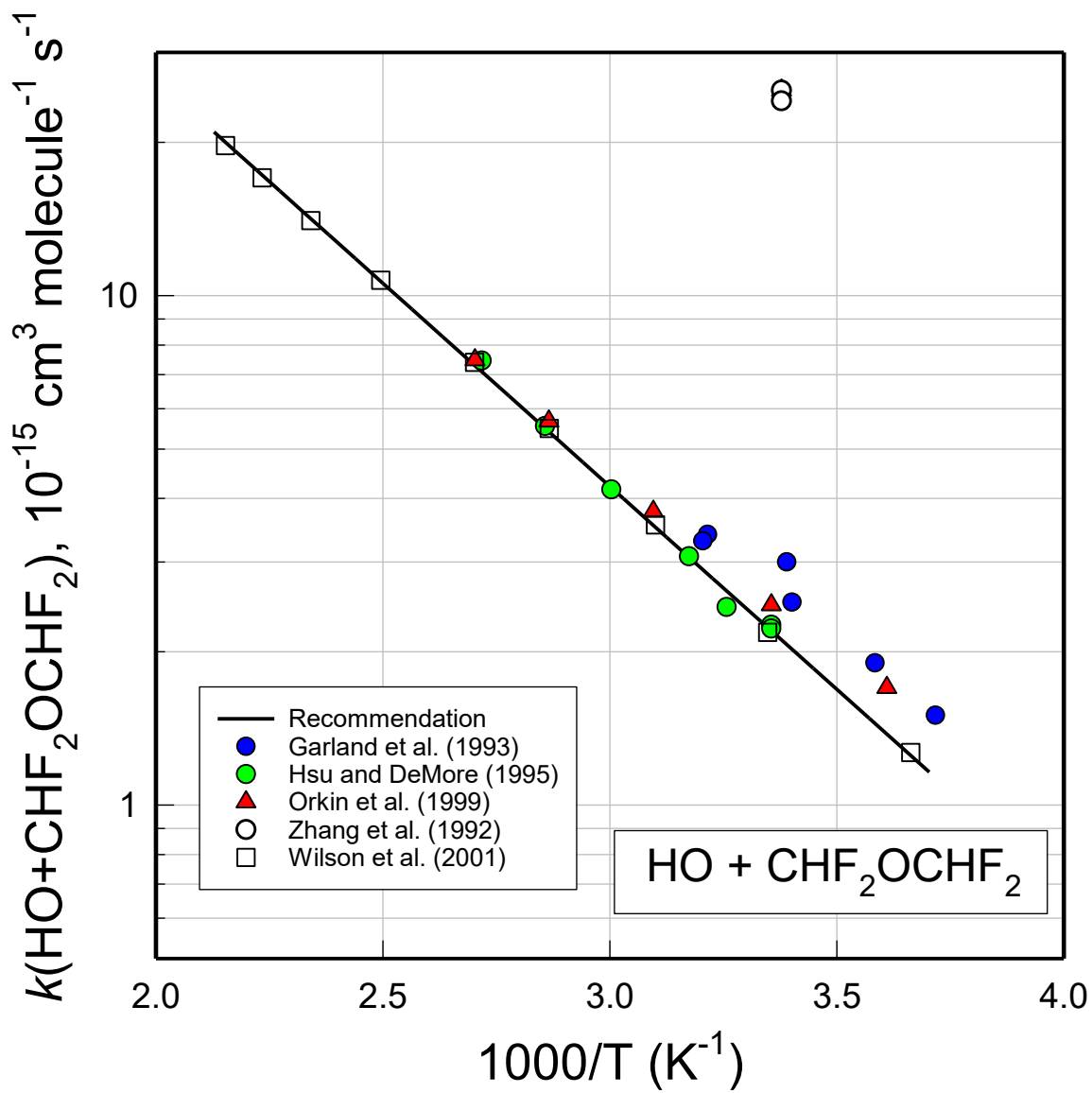
Comments on Preferred Values

4791 There is excellent agreement in the results at 298 K and higher temperatures from the relative
4792 rate studies of Hsu and DeMore (1995) and Wilson et al. (2001) and the absolute rate study by Orkin
4793 et al. (1999). The results at 298 K from the absolute rate study by Garland et al. (1993) lie
4794 approximately 20-30% above those from Orkin et al. (1999) and the relative rate studies. The results
4795 from the absolute study by Zhang et al. (1992) are approximately an order of magnitude greater than
4796 from the other studies and probably reflect the presence of reactive impurities. The results from the
4797 absolute studies by Orkin et al. (1999) and Garland et al. (1993) at temperatures below 298 K lie
4798 substantially above those from the relative rate studies. This discrepancy may indicate the effect of
4799 small amounts of reactive impurities in these studies whose effects would be more pronounced at the
4800 lower temperatures. The preferred values are based on an Arrhenius fit to the data from Hsu and
4801 DeMore (1995) and Wilson et al. (2001).

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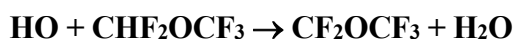
References

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4808 Wilson, E. W., Sawyer, A. A., and Sawyer, H. A.: J. Phys. Chem. A, 105, 1445, 2001.
4809 Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E.: J. Phys. Chem.: 96, 9301, 1992.
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4814 **oFOx140: HO + CHF₂OCF₃**
 4815 Last evaluated: June 2025; Last change in preferred values: June 2019.



4817 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-----------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 3.47 × 10 ⁻¹⁵ | 296 | Zhang et al. (1992) | FP-RF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| 3.09 × 10 ⁻¹³ exp[(-1942)/ <i>T</i>] | 298-381 | Hsu and DeMore (1995) | RR (b) |
| 4.57 × 10 ⁻¹⁶ | 298 | | |

4821 **Comments**

- 4822 (a) HO radicals were generated by the photolysis of water vapor in 35 Torr (47 mbar) of argon diluent
 4823 and monitored by resonance fluorescence.
 4824 (b) HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. FTIR
 4825 spectroscopy was used to follow the loss of CHF₂OCF₃ and the reference compounds CF₃H, CH₄,
 4826 and CHF₂CF₃. Placing the measured rate coefficient ratios on an absolute basis using *k*(HO + CF₃H)
 4827 = 6.90 × 10⁻¹³ exp(-2340/*T*), *k*(HO + CH₄) = 1.85 × 10⁻¹² exp(-1690/*T*), and *k*(HO + CHF₂CF₃H) =
 4828 4.40 × 10⁻¹³ exp(-1630/*T*) cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 2006, 2008) and fitting an Arrhenius
 4829 expression to the results gives *k*(HO + CHF₂OCF₃) = 3.09 × 10⁻¹³ exp[(-1942)/*T*] cm³ molecule⁻¹ s⁻¹.
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4833 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 4.57 × 10 ⁻¹⁶ | 298 |
| | 3.09 × 10 ⁻¹³ exp(-1942/ <i>T</i>) | 290-400 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |
| Δ E/R | ±100 | 290-400 |

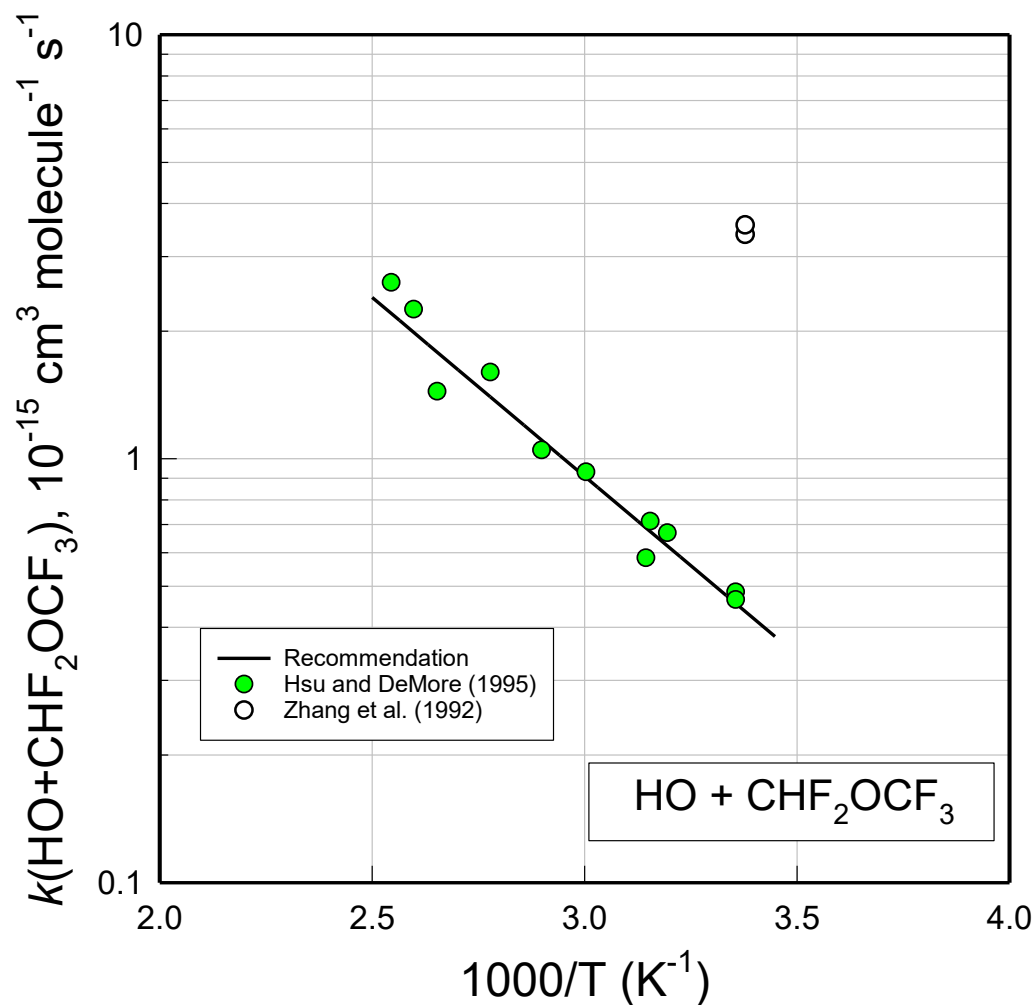
4835 **Comments on Preferred Values**

4836 The preferred values are based on a fit to the results from the relative rate study of Hsu and
 4837 DeMore (1995). The results from the absolute study by Zhang et al. (1992) at 296 K are
 4838 approximately a factor of 8 greater than from Hsu and DeMore (1995) probably reflecting the
 4839 presence of reactive impurities.
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4842 **References**

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4848 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
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4857 **oFOx141: HO + CH₃OCHF₂CF₃**
 4858 Last evaluated: June 2025; Last change in preferred values: June 2019.



4862 **Rate coefficient data ($k = k_1 + k_2$)**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------|---------------------|
| <i>Relative Rate Coefficients</i> | | | |
| $1.74 \times 10^{-12} \exp(-716/T)$ | 253-328 | Chen et al. (2006) | RR (a) |
| 1.57×10^{-13} | 298 | | |

4865 **Comments**

4866 (a) HO radicals were generated by the photolysis of ozone in the presence of water vapor in 200 Torr of
 4867 helium diluent. Separate experiments were performed in which the loss CH₃OCHF₂CF₃ was
 4868 measured relative to either C₂H₆ or CH₃CHF₂. Placing the reported rate coefficient ratios on an
 4869 absolute basis using $k(\text{HO} + \text{C}_2\text{H}_6) = 6.9 \times 10^{-12} \exp(-1000/T)$ and $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.25 \times 10^{-12}$
 4870 $\exp(-1070/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al. 2006, 2008) and fitting an Arrhenius expression to
 4871 the results gives $k(\text{HO} + \text{CH}_3\text{OCHF}_2\text{CF}_3) = 1.74 \times 10^{-12} \exp(-716/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

4872 **Preferred Values**

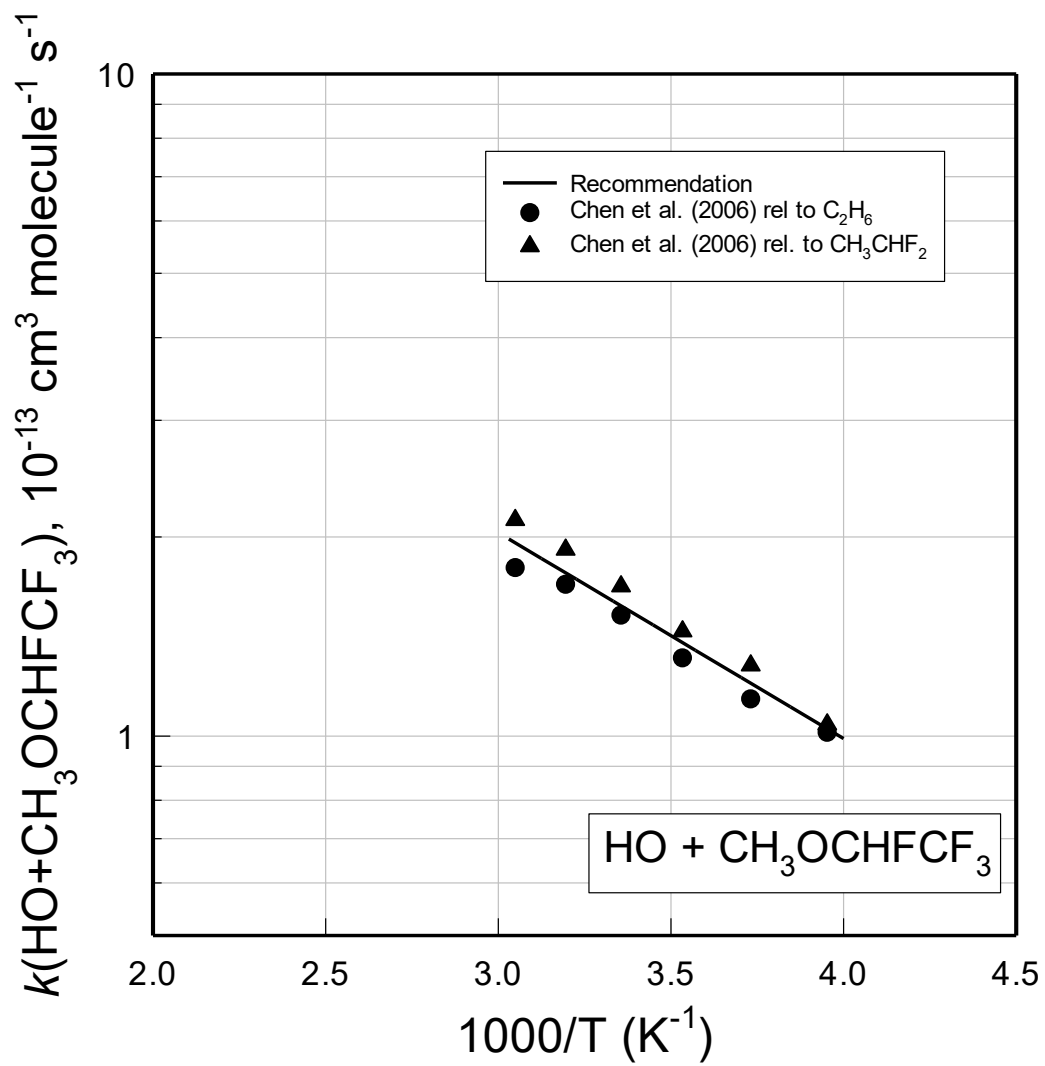
| Parameter | Value | T/K |
|--|---|----------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.57×10^{-13} $1.74 \times 10^{-12} \exp(-716/T)$ | 298 250-330 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta E/R$ | ± 100 | 250-330 |

4873 **Comments on Preferred Values**

4874 The preferred value is based on a fit to the results from the relative rate study of Chen et al.
 4875 (2006).

4876 **References**

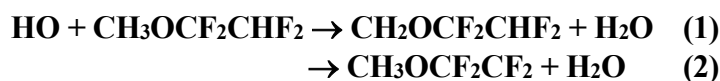
- 4877 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
 4878 Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric
 4879 Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>
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4896 **oFOx142: HO + CH₃OCF₂CHF₂**
 4897 Last evaluated: June 2025; Last change in preferred values: June 2019.

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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(1.63 \pm 0.32) \times 10^{-13}$ | 298 | Heathfield et al. (1998) | PR-UVA (a) |
| $2.60 \times 10^{-12} \exp[(-1420)/T]$ | 250-430 | Tokuhashi et al. (2000) | LP/FP/DF-LIF (b) |
| 2.56×10^{-14} | 298 | | |

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Comments

- (a) HO radicals were generated by the pulsed radiolysis of 1000 mbar of argon in the presence of 18 mbar of water vapor. The decay of HO radicals was monitored using UV absorption at 309 nm.
- (b) Three different absolute rate methods were employed by Tokuhashi et al. (2000): LP-LIF, FP-LIF, and DF-LIF. HO radicals in the LP-LIF experiments were generated by the photolysis (ArF laser) of N₂O to produce O(¹D) atoms in the presence of H₂O in 20-60 Torr (27-80 mbar) of helium diluent. HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp, $\lambda < 180 \text{ nm}$) of H₂O in 20-40 Torr (27-53 mbar) argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction of H atoms with NO₂ in 5-6 Torr (7-8 mbar) of argon diluent. There was good agreement between the results from experiments using the three different techniques. The value at 298 K cited above is the average obtained using the different techniques.

Preferred Values

| Parameter | Value | T/K |
|--|--|----------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.24×10^{-14} $2.50 \times 10^{-12} \exp(-1405/T)$ | 298 240-440 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta E/R$ | ± 100 | 240-440 |

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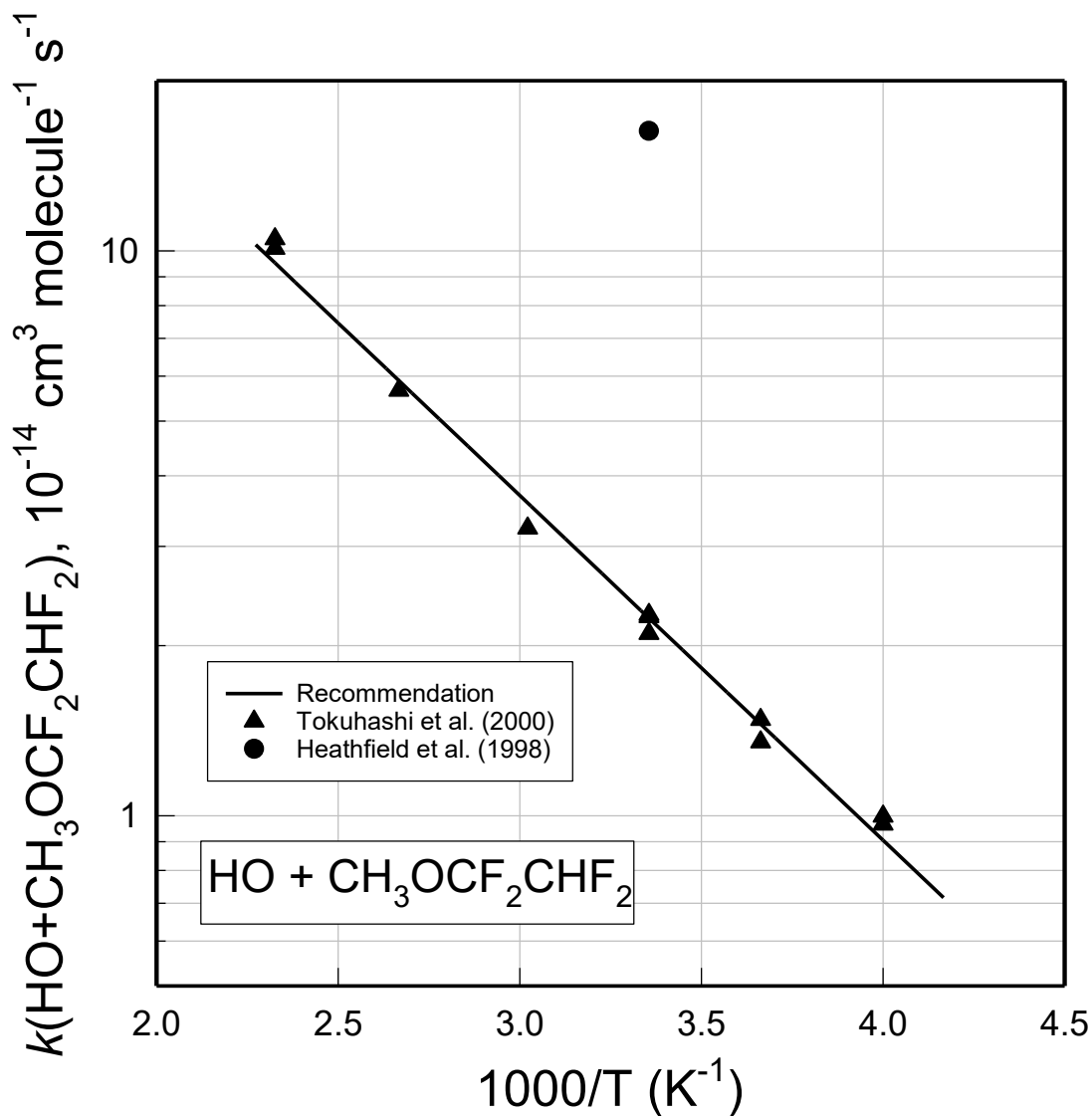
Comments on Preferred Values

The preferred values are based on a fit to the results from the comprehensive study of Tokuhashi et al. (2000) in which three different absolute rate techniques were applied and extra care was taken in purifying the samples. The results from the study by Heathfield et al. (1998) at 298 K are approximately a factor of 6 higher than from Tokuhashi et al. (2000) and probably reflect the presence of reactive impurities in the samples used.

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References

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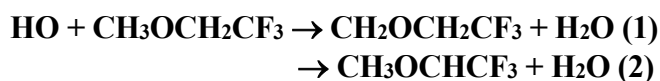


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oFOx143: HO + CH₃OCH₂CF₃

Last evaluated: February 2026; Last change in preferred values: February 2026.



Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(6.24 \pm 0.67) \times 10^{-13}$ | 296 | Zhang et al. (1992) | FP-RF (a) |
| $(3.88 \pm 0.89) \times 10^{-12} \exp[-(508 \pm 69)/T]$ | 263-353 | Blázquez et al. (2022) | PLP-LIF (b) |
| $(6.88 \pm 0.21) \times 10^{-13}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(6.4 \pm 0.5) \times 10^{-13}$ | 298 | Nolan et al. (1999) | RR (c) |
| $(6.24 \pm 0.33) \times 10^{-13}$ | 298 | Oyaro et al. (2005) | RR (d) |
| $(5.17 \pm 0.54) \times 10^{-13}$ | | | |
| $(4.71 \pm 0.37) \times 10^{-13}$ | 296 | Østerstrøm et al. (2011) | RR (e) |
| $(4.16 \pm 0.39) \times 10^{-13}$ | | | |

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Comments

- (a) HO radicals were generated by the photolysis of water vapor in 35 Torr (47 mbar) of argon diluent and monitored by resonance fluorescence.
- (b) HO radicals were generated by the photolysis of H₂O₂ at 248 nm in 50-500 Torr of helium diluent and monitored by laser induce fluorescence.
- (c) HO radicals were generated by the 254 nm photolysis of ozone in the presence of water vapor in 1 atmosphere of air diluent. The reference compound was not specified.
- (d) HO radicals were produced by the photolysis of O₃ at 254 nm in the presence of H₂ in 1013 mbar of air diluent. The loss of CH₃OCH₂CF₃ was monitored relative to those of CHCl₃ and CH₃C(O)OCH₃ by GC/MS. Rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{OCH}_2\text{CF}_3)/k(\text{HO} + \text{CHCl}_3) = 5.94 \pm 0.31$ and $k(\text{HO} + \text{CH}_3\text{OCH}_2\text{CF}_3)/k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{OCH}_3) = 2.87 \pm 0.305$ were reported. Using $k(\text{HO} + \text{CHCl}_3) = 1.05 \times 10^{-13}$ and $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{OCH}_3) = 1.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson et al., 2006, 2008) gives $k(\text{HO} + \text{CH}_3\text{OCH}_2\text{CF}_3) = (6.24 \pm 0.33) \times 10^{-13}$ and $(5.17 \pm 0.54) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (e) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr of air diluent in the presence of NO. The loss of CH₃OCH₂CF₃ was monitored indirectly by the formation of its oxidation product COF₂ and was measured relative to that of C₂H₂ and C₂H₄. Rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{OCH}_2\text{CF}_3)/k(\text{HO} + \text{C}_2\text{H}_2) = 0.63 \pm 0.05$ and $k(\text{HO} + \text{CH}_3\text{OCH}_2\text{CF}_3)/k(\text{HO} + \text{C}_2\text{H}_4) = 0.053 \pm 0.005$ were reported. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in 700 Torr of air at 296 K (Atkinson et al., 2006) gives $k(\text{HO} + \text{CH}_3\text{OCH}_2\text{CF}_3) = (4.71 \pm 0.37) \times 10^{-13}$ and $(4.16 \pm 0.39) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 6.56×10^{-13} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $3.61 \times 10^{-12} \exp(-508/T)$ | 260-360 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta E/R$ | 300 | 260-360 |

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Comments on Preferred Values

4983 The absolute rate measurements by Zhang et al. (1992) and Blázquez et al. (2022) at 298 K are in
4984 excellent agreement. Taking an average of the results from these studies gives the recommended rate
4985 coefficient at 298 K. The temperature dependence is taken from Blázquez et al. (2022) and the
4986 preexponential factor is scaled to reproduce the recommended $k(298\text{K})$ value. The results from the
4987 relative rate studies by Nolan et al. (1999) and Oyaro et al. (2005) are in good agreement while those
4988 from Østerstøm et al. (2012) are approximately 30% lower. Østerstøm et al. (2012) measured the loss
4989 of $\text{CH}_3\text{OCH}_2\text{CF}_3$ indirectly by the formation of its oxidation product COF_2 and assuming a molar yield
4990 of 45% which was determined in separate experiments. Given the good agreement of the results from
4991 the relative rate studies of Nolan et al. (1999) and Oyaro et al. (2005) with the absolute rate studies by
4992 Zhang et al. (1992) and Blázquez et al. (2022), it appears there were problems associated with the
4993 indirect method of monitoring loss of $\text{CH}_3\text{OCH}_2\text{CF}_3$ used by Østerstøm et al. (2012).
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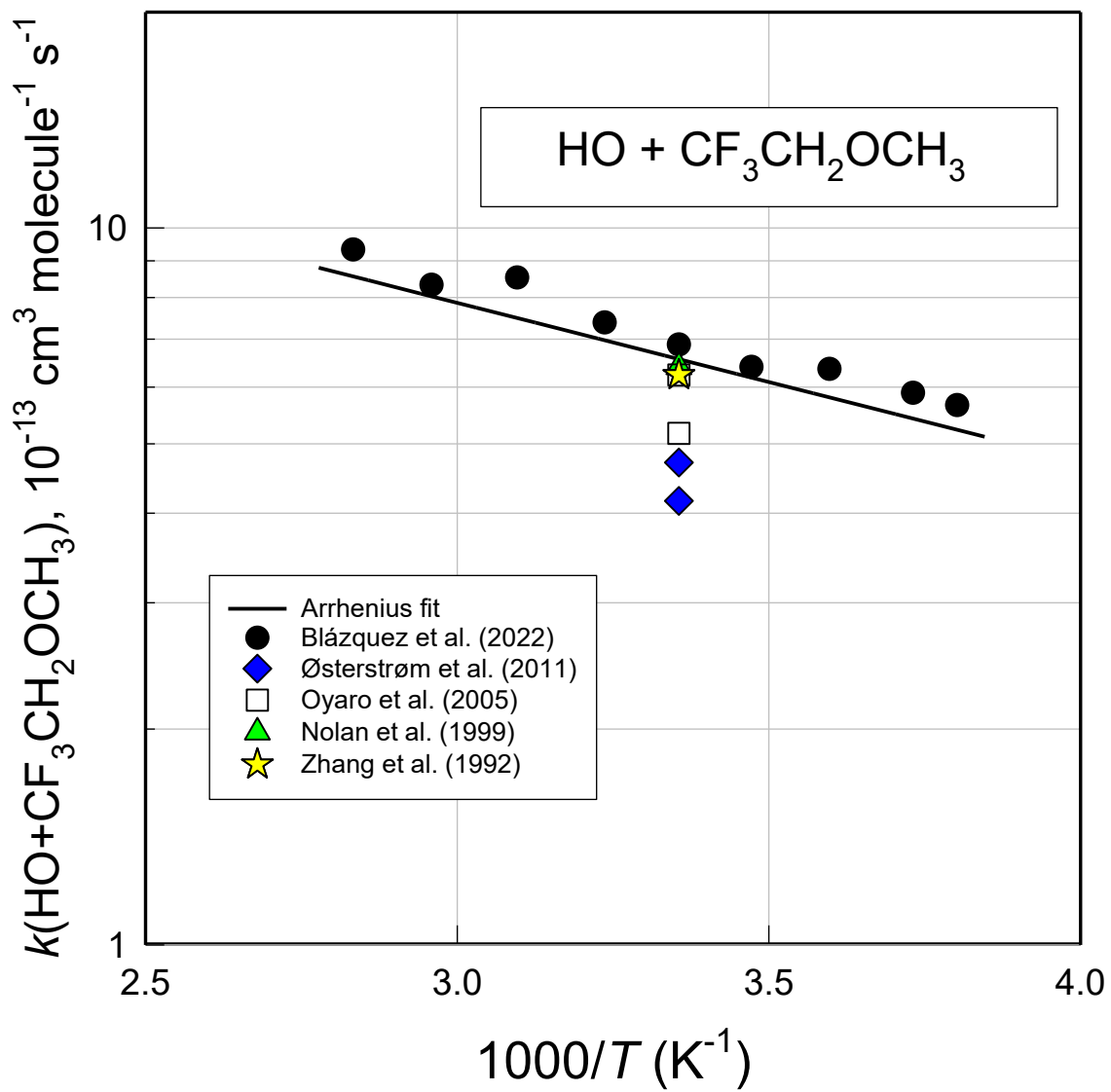
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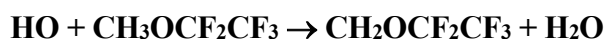
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5020 **oFOx144: HO + CH₃OCF₂CF₃**
 5021 Last evaluated: June 2025; Last change in preferred values: June 2019.



5023 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|----------------|--------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (1.90 ^{+0.90} _{-0.61} × 10 ⁻¹²) exp[(-1510±120)/T] 1.12 × 10 ⁻¹⁴ | 250-430 298 | Tokuhashi et al. (1999) | LP/FP/DF-LIF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (1.12±0.15) × 10 ⁻¹⁴ | 296 | Østerstrøm et al. (2016) | RR (b) |

5027 **Comments**

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5030 (a) Three different absolute rate methods were employed by Tokuhashi et al. (1999): LP-LIF, FP-LIF, and
 5031 DF-LIF. HO radicals in the LP-LIF experiments were generated by the photolysis (ArF laser) of N₂O
 5032 to produce O(¹D) atoms in the presence of H₂O in 20-60 Torr (27-80 mbar) of helium diluent. HO
 5033 radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp, λ < 180 nm) of
 5034 H₂O in 10-40 Torr (13-53 mbar) argon diluent. HO radicals in the DF-LIF experiments were
 5035 generated by the reaction of H atoms with NO₂ in 5-6 Torr (7-8 mbar) of argon diluent. There was
 5036 good agreement between the results from experiments using the three different techniques. The value
 5037 at 298 K cited above is the average obtained using the different techniques.
 5038 (b) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The
 5039 loss of CH₃OC₂F₅ was measured indirectly by measuring the formation of the product C₂F₅OCHO.
 5040 C₂H₂ was used as the reference and a rate coefficient ratio $k(\text{CH}_3\text{OC}_2\text{F}_5)/k(\text{C}_2\text{H}_2) = 0.015 \pm 0.002$ was
 5041 reported. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{CH}_3\text{OC}_2\text{F}_5) =$
 5042 $(1.12 \pm 0.15) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

5043 **Preferred Values**

| Parameter | Value | T/K |
|--|---|----------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.20 × 10 ⁻¹⁴ 1.84 × 10 ⁻¹² exp(-1499/T) | 298 240-440 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |
| Δ E/R | ±100 | 240-440 |

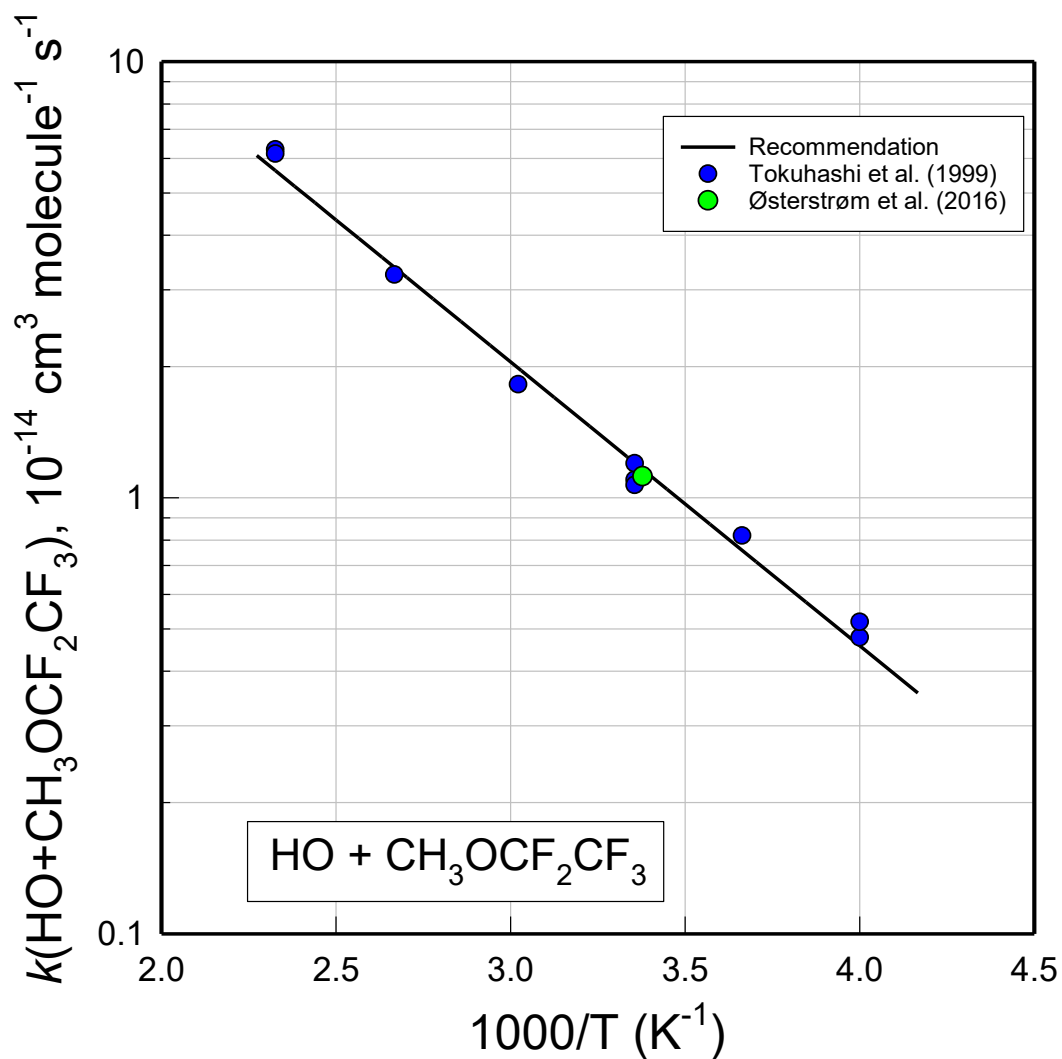
5046 **Comments on Preferred Values**

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5049 The preferred values are based on a fit to the results from the comprehensive study of
 5050 Tokuhashi et al. (2000) in which three different absolute rate techniques were applied and extra care
 5051 was taken in purifying the samples. The results reported in the relative rate study by Østerstrøm are
 5052 consistent with the preferred values.

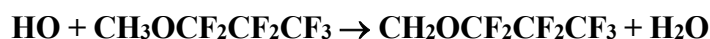
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5070 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|---|---------|-------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (2.06 ^{+0.58} _{-0.45} × 10 ⁻¹²) exp[(-1540±80)/T] | 250-430 | Tokuhashi et al. (1999) | LP/FP/DF-LIF (a) |
| 1.13 × 10 ⁻¹⁴ | 298 | | |
| (2.0 ^{+1.2} _{-0.7}) × 10 ⁻¹¹ exp [(-2130±290/T)] | 288-368 | Bravo et al. (2010) | DF-MS (b) |
| (1.54±0.05) × 10 ⁻¹⁴ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| 1.11 × 10 ⁻¹⁴ | 295 | Ninomiya et al. (2000) | RR (c) |

5073 **Comments**

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- 5076 (a) Three different absolute rate methods were employed by Tokuhashi et al. (1999): LP-LIF, FP-LIF, and
 5077 DF-LIF. HO radicals in the LP-LIF experiments were generated by the photolysis (ArF laser) of
 5078 N₂O to produce O(¹D) atoms in the presence of H₂O in 20-60 Torr (27-80 mbar) of helium diluent.
 5079 HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp, λ < 180
 5080 nm) of H₂O in 20-40 Torr (27-53 mbar) argon diluent. HO radicals in the DF-LIF experiments were
 5081 generated by the reaction of H atoms with NO₂ in 5-6 Torr (7-8 mbar) of argon diluent. There was
 5082 good agreement between the results from experiments using the three different techniques. The
 5083 value at 298 K cited above is the average obtained using the different techniques.
- 5084 (b) F atoms produced in a microwave discharge of F₂/He mixtures were reacted with H₂O to generate
 5085 HO radicals. Experiments were conducted in a flow tube at a pressure of 1 Torr of helium diluent.
 5086 HO radicals were monitored by mass spectroscopy by adding I₂ and detecting the HOI product.
- 5087 (c) HO radicals were generated by the photolysis of O₃ at 254 nm in the presence of water vapor.
 5088 Experiments were performed in approximately 200 Torr of helium diluent in the presence of 3-5
 5089 Torr of ozone and 2-3 Torr of water vapor. The loss of CH₃OC₃F₇ was measured relative to those of
 5090 CH₄ and CH₃Cl and rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{OC}_3\text{F}_7)/k(\text{HO} + \text{CH}_4) = 1.68 \pm 0.20$ and
 5091 $k(\text{HO} + \text{CH}_3\text{OC}_3\text{F}_7)/k(\text{HO} + \text{CH}_3\text{Cl}) = 0.35 \pm 0.03$ were reported. Using $k(\text{HO} + \text{CH}_4) = 6.01 \times 10^{-15}$
 5092 and $k(\text{HO} + \text{CH}_3\text{Cl}) = 3.47 \times 10^{-14}$ at 295 K (Atkinson et al., 2006) gives $k(\text{HO} + \text{CH}_3\text{OC}_3\text{F}_7) =$
 5093 $(1.01 \pm 0.12) \times 10^{-14}$ and $(1.21 \pm 0.10) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

5094 **Preferred Values**

| Parameter | Value | T/K |
|--|---------------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.18 × 10 ⁻¹⁴ | 298 |
| | 1.98 × 10 ⁻¹² exp(-1526/T) | 240-440 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |
| Δ E/R | ±100 | 240-440 |

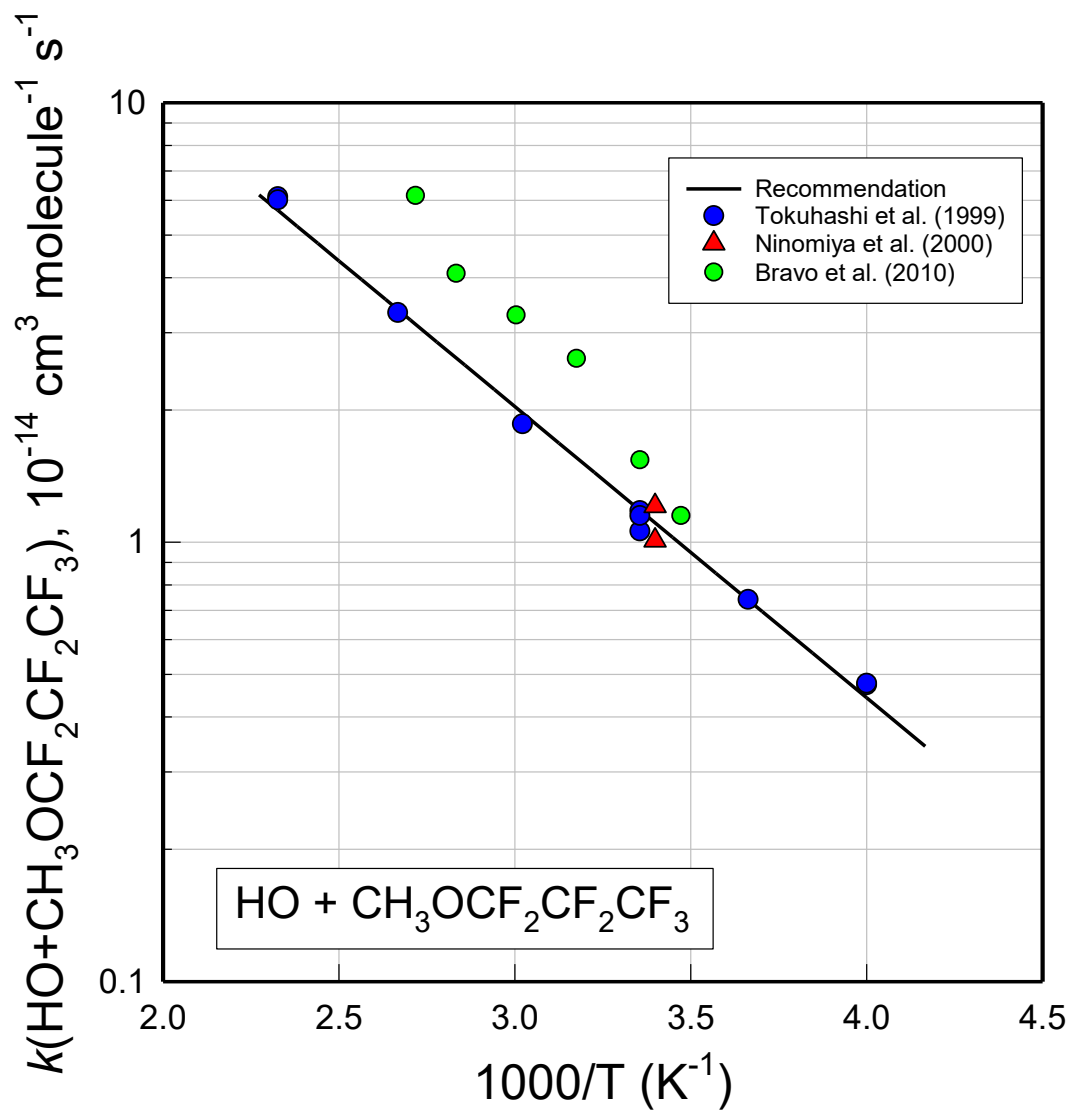
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Comments on Preferred Values

The preferred values are based on a fit to the results from the comprehensive study of Tokuhashi et al. (1999) in which three different absolute rate techniques were applied and care was taken in purifying the samples. The results from the relative rate study by Ninomiya et al. (2000) are in excellent agreement with the results from the absolute study by Tokuhashi et al. (1999). The results from the study by Bravo et al. (2010) are approximately 40-60% higher than those from Tokuhashi et al. (1999). Tokuhashi et al. (1999) showed that reactive impurities can be a complication and purified their sample of $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_3$ before use. Bravo et al. (2010) did not purify their sample and the presence of reactive impurities may explain the larger rate coefficients observed in their study.

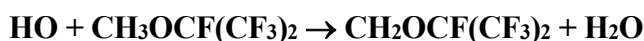
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5124 **oFOx146: HO + CH₃OCF(CF₃)₂**
 5125 Last evaluated: June 2025; Last change in preferred values: June 2019.



5127 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|---|----------------|-------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| (1.94 ^{+0.48} _{-0.38} × 10 ⁻¹²) exp[(-1450±70)/T] 1.48 × 10 ⁻¹⁴ | 250-430 298 | Tokuhashi et al. (1999) | LP/FP/DF-LIF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| (1.37 ± 0.13) × 10 ⁻¹⁴ | 296 | Andersen et al. (2014) | RR (b) |

5131 **Comments**

- 5132 (a) Three different absolute rate methods were employed by Tokuhashi et al. (1999): LP-LIF, FP-LIF, and
 5133 DF-LIF. HO radicals in the LP-LIF experiments were generated by the photolysis (ArF laser) of
 5134 N₂O to produce O(¹D) atoms in the presence of H₂O in 20-60 Torr (27-80 mbar) of helium diluent.
 5135 HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp, λ < 180
 5136 nm) of H₂O in 20-40 Torr (27-53 mbar) argon diluent. HO radicals in the DF-LIF experiments were
 5137 generated by the reaction of H atoms with NO₂ in 4-6 Torr (5-8 mbar) of argon diluent. There was
 5138 good agreement between the results from experiments using the three different techniques. The
 5139 value at 298 K cited above is the average obtained using the different techniques.
 5140 (b) HO radicals were generated by the photolysis of CH₃ONO in 700 Torr of air diluent. The loss of
 5141 CH₃OCF(CF₃)₂ was monitored indirectly by the formation of its oxidation product (CF₃)₂CFOCHO
 5142 and was measured relative to that of C₂H₂. A rate coefficient ratio of *k*(HO + CH₃OCF(CF₃)₂)/*k*(HO
 5143 + C₂H₂) = 0.0183 ± 0.0017 was reported. Using *k*(HO + C₂H₂) = 7.47 × 10⁻¹³ in 700 Torr of air
 5144 diluent at 296 K (Atkinson et al., 2006) gives *k*(HO + CH₃OCF(CF₃)₂) = (1.37±0.13) × 10⁻¹⁴ cm³
 5145 molecule⁻¹ s⁻¹.

5146 **Preferred Values**

| Parameter | Value | T/K |
|--|---|----------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 1.52 × 10 ⁻¹⁴ 1.86 × 10 ⁻¹² exp(-1432/T) | 298 240-440 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |
| Δ E/R | ±100 | 240-440 |

5151 **Comments on Preferred Values**

5152 The preferred values are based on a fit to the results from the comprehensive study of
 5153 Tokuhashi et al. (1999) in which three different absolute rate techniques were applied and care was
 5154 taken in purifying the samples. The results from the relative rate study by Andersen et al. (2014) are in
 5155

5157 excellent agreement with the results from the absolute study by Tokuhashi et al. (1999).

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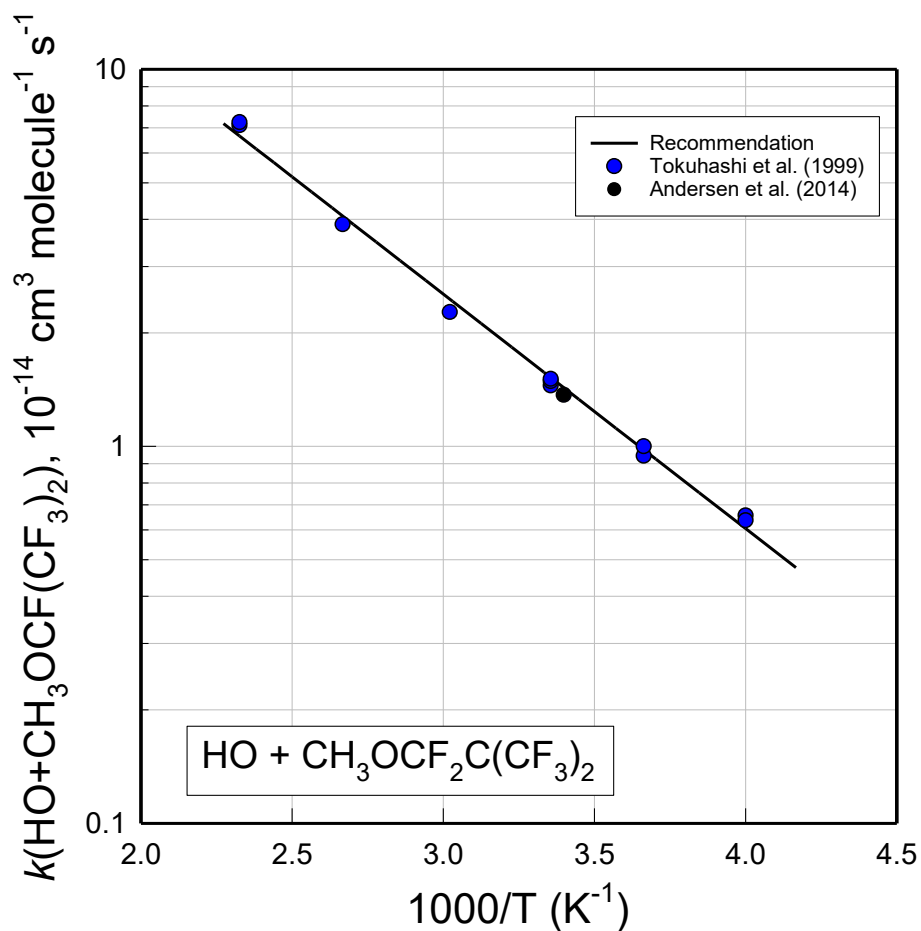
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5165 Chemical Kinetic Data Evaluation, <https://iupac.aeris-data.fr/>

5166 Tokuhashi, K., Takahashi, A., Kaise, M., Kondo, S., Sekiya, A., Yamashita, S., and Ito, H.: Int. J. Chem.
5167 Kinet., 31, 846, 1999.

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5174 **HO + CH₃OC₄F₉ (HFE-7100) → CH₂OC₄F₉ + H₂O**

5175 **Rate coefficient data**

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./ K | Reference | Technique/ Comments |
|---|-------------|---|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(2.8^{+3.2}_{-1.5}) \times 10^{-11} \exp(-2200 \pm 490/T)$ | 288-368 | Bravo et al. (2010) | DF-MS (a) |
| $(1.49 \pm 0.13) \times 10^{-14}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $\sim 1.2 \times 10^{-14}$ | 295 | Wallington et al. (1997) | RR (b) |
| $(6.9 \pm 1.5) \times 10^{-15}$ | 295 | Cavalli et al. (1998) | RR (c) |
| $(1.30 \pm 0.09) \times 10^{-14}$ | 298 | Nolan et al. (1999) | RR (d) |
| $(1.53 \pm 0.10) \times 10^{-14}$ | 298 | Oyaro and Nielsen (2003) | RR (e) |
| $1.10 \times 10^{-12} \exp(-1347/T)$ | 253-328 | Chen et al. (2011) <i>n</i> -C ₄ F ₉ OCH ₃ | RR (f) |
| $(1.19 \pm 0.12) \times 10^{-14}$ | 298 | | |
| $1.21 \times 10^{-12} \exp(-1377/T)$ | 253-328 | Chen et al. (2011) <i>i</i> -C ₄ F ₉ OCH ₃ | RR (f) |
| $(1.19 \pm 0.12) \times 10^{-14}$ | 298 | | |

5179 **Comments**

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- 5182 (a) F atoms produced in a microwave discharge of F₂/He mixtures were reacted with H₂O to generate
 5183 HO radicals. Experiments were conducted in a flow tube at a pressure of 1 Torr of helium diluent.
 5184 HO radicals were monitored by mass spectroscopy by adding I₂ and detecting the HOI product.
- 5185 (b) HO radicals were generated by the photolysis of O₃ at 254 nm in the presence of water vapor.
 5186 Experiments were performed in approximately 200 Torr of helium diluent in the presence of ~1 Torr
 5187 of ozone. The sample of CH₃OC₄F₉ was a mixture of 95% *n*-C₄F₉OCH₃ (CF₃CF₂CF₂CF₂OCH₃) and
 5188 5% *i*-C₄F₉OCH₃ ((CF₃)₂CF₂CF₂OCH₃). The loss of CH₃OC₄F₉ was measured relative to those of CH₄
 5189 and CH₃Cl. Two experiments with CH₃Cl gave rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{OC}_4\text{F}_9)/k(\text{HO} +$
 5190 $\text{CH}_3\text{Cl}) = 0.35$ and 0.32 . Using $k(\text{HO} + \text{CH}_3\text{Cl}) = 3.47 \times 10^{-14}$ at 295 K (Atkinson et al., 2006) gives
 5191 $k(\text{HO} + \text{CH}_3\text{OC}_4\text{F}_9) = 1.2 \times 10^{-14}$ and $1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Results from experiments using
 5192 CH₄ were more scattered, but consistent with, those using CH₃Cl as reference.
- 5193 (c) HO radicals were generated by the photolysis of O₃ at 254 nm in the presence of water vapor in 740
 5194 Torr (986 mbar) of air diluent. The sample of CH₃OC₄F₉ was a mixture of 25% *n*-C₄F₉OCH₃
 5195 (CF₃CF₂CF₂CF₂OCH₃) and 75% *i*-C₄F₉OCH₃ ((CF₃)₂CF₂CF₂OCH₃). The loss of CH₃OC₄F₉ was
 5196 measured relative to that of CH₄. Rescaling the result using $k(\text{HO} + \text{CH}_4) = 6.01 \times 10^{-15}$ at 295 K
 5197 (Atkinson et al., 2006) gives $k(\text{HO} + \text{CH}_3\text{OC}_4\text{F}_9) = (6.9 \pm 1.5) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 5198 (d) HO radicals were generated by the 254 nm photolysis of ozone in the presence of water vapor in 1
 5199 atmosphere of air diluent. Neither the isomeric composition of CH₃OC₄F₉, nor the reference
 5200 compound used, was specified.
- 5201 (e) HO radicals were generated by the photolysis of ozone in the presence of hydrogen in 1 atmosphere
 5202 of air diluent. The loss of CH₃OC₄F₉ was measured relative to CH₃CN and CHCl₃ using GC-MS
 5203 and rate coefficient ratios of 0.663 ± 0.009 and 0.151 ± 0.004 were reported, respectively. Using
 5204 $k(\text{HO} + \text{CH}_3\text{CN}) = 2.2 \times 10^{-14}$ and $k(\text{HO} + \text{CHCl}_3) = 1.05 \times 10^{-13}$ (IUPAC 2024) gives $k(\text{HO} +$
 5205 $\text{CH}_3\text{OC}_4\text{F}_9) = (1.46 \pm 0.02) \times 10^{-14}$ and $(1.59 \pm 0.04) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The average with

5206 uncertainties that encompass the extremes of the ranges is $k(\text{HO}+\text{CH}_3\text{OC}_4\text{F}_9) = (1.53 \pm 0.10) \times 10^{-14}$
 5207 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The commercial sample of $\text{CH}_3\text{OC}_4\text{F}_9$ used was an approximately 50:50 mixture
 5208 of the *n*- and *i*- isomers. The isomers could not be resolved, and the measured rate coefficient is for
 5209 the mixture.

5210 (f) HO radicals were produced by the 254 nm photolysis of ozone in the presence of water vapor. The
 5211 commercial sample of $\text{C}_4\text{F}_9\text{OCH}_3$ obtained for the experiments was a mixture of 36% *n*- $\text{C}_4\text{F}_9\text{OCH}_3$
 5212 and 64% *i*- $\text{C}_4\text{F}_9\text{OCH}_3$. GC-FID was used to monitor the decay of $\text{C}_4\text{F}_9\text{OCH}_3$ and the reference
 5213 compounds (CF_3OCH_3 and $\text{C}_2\text{F}_5\text{OCH}_3$). The two isomers were resolved and rate coefficient ratios
 5214 for both isomers were reported. Scaling the reported ratios using the IUPAC preferred values of
 5215 $k(\text{HO}+\text{CF}_3\text{OCH}_3) = 1.15 \times 10^{-12} \exp(-1324/T)$ and $k(\text{HO}+\text{C}_2\text{F}_5\text{OCH}_3) = 1.84 \times 10^{-12} \exp(-1499/T)$
 5216 (IUPAC, 2023) and fitting the Arrhenius expression to the results gives $k(\text{HO}+n\text{-C}_4\text{F}_9\text{OCH}_3) = 1.10 \times$
 5217 $10^{-12} \exp(-1347/T)$ and $k(\text{HO}+i\text{-C}_4\text{F}_9\text{OCH}_3) = 1.21 \times 10^{-12} \exp(-1377/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As
 5218 shown in the figure below, there is no observable difference in the reactivity of the different isomers.
 5219 A fit to the combined data set gives $k(\text{HO}+ \text{C}_4\text{F}_9\text{OCH}_3) = 1.15 \times 10^{-12} \exp(-1362/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
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Preferred Values

| Parameter | Value | T/K |
|--|--------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $1.15 \times 10^{-12} \exp(-1362/T)$ | 250-330 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 1.19×10^{-14} | 298 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.08 | 298 |
| $\Delta E/R$ | 100 | 250-330 |

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Comments on Preferred Values

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5227 Commercial samples of $\text{C}_4\text{F}_9\text{OCH}_3$ are supplied as mixtures of the *n*- and *i*- isomers. All studies
 5228 except that of Chen et al. (2011) did not resolve the reactivity of the individual isomers and hence report
 5229 results for the mixture of isomers. Chen et al. (2011) were able to distinguish the two isomers in their
 5230 relative rate study and reported separate kinetic data for each isomer; $k(\text{HO}+n\text{-C}_4\text{F}_9\text{OCH}_3) = 1.10 \times 10^{-12}$
 5231 $\exp(-1347/T)$ and $k(\text{HO}+i\text{-C}_4\text{F}_9\text{OCH}_3) = 1.21 \times 10^{-12} \exp(-1377/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. At 298 K the
 5232 isomers have the same rate coefficient; $1.19 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A fit to the combined data set
 5233 gives $k(\text{HO}+\text{C}_4\text{F}_9\text{OCH}_3) = 1.15 \times 10^{-12} \exp(-1362/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and is the preferred value. The
 5234 298 K rate coefficients reported by Wallington et al. (1997), Nolan et al. (1999), Oyaro and Nielsen
 5235 (2003), and Bravo et al. (2010) for the mixtures of *n*- and *i*-isomers used in the different studies agree,
 5236 within the likely combined experimental uncertainties, with that measured by Chen et al. (2011). For
 5237 reasons which are unclear, the rate coefficient reported by Cavalli et al. (1997) is approximately 40%
 5238 lower.

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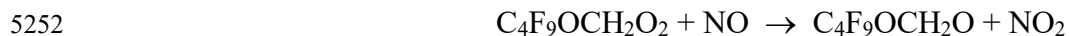
5240 Bravo et al. (2010) used an absolute rate technique to study the reaction over the temperature range
 5241 288-368 K. The rate coefficients results reported by Bravo et al. (2010) are 25-100% larger than
 5242 those from Chen et al. (2011). Tokuhashi et al. (1999) showed that the presence of reactive impurities
 5243 can be problematic in studies of HO reactions with fluorinated ethers. Bravo et al. (2010) did not
 5244 purify their sample and the presence of reactive impurities may explain the larger rate coefficients
 5245 observed in their study.

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5247 The reaction of HO with $\text{CH}_3\text{OC}_4\text{F}_9$ proceeds via H-abstraction from the CH_3 - which then leads to the

5248 formation of the formate:

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References

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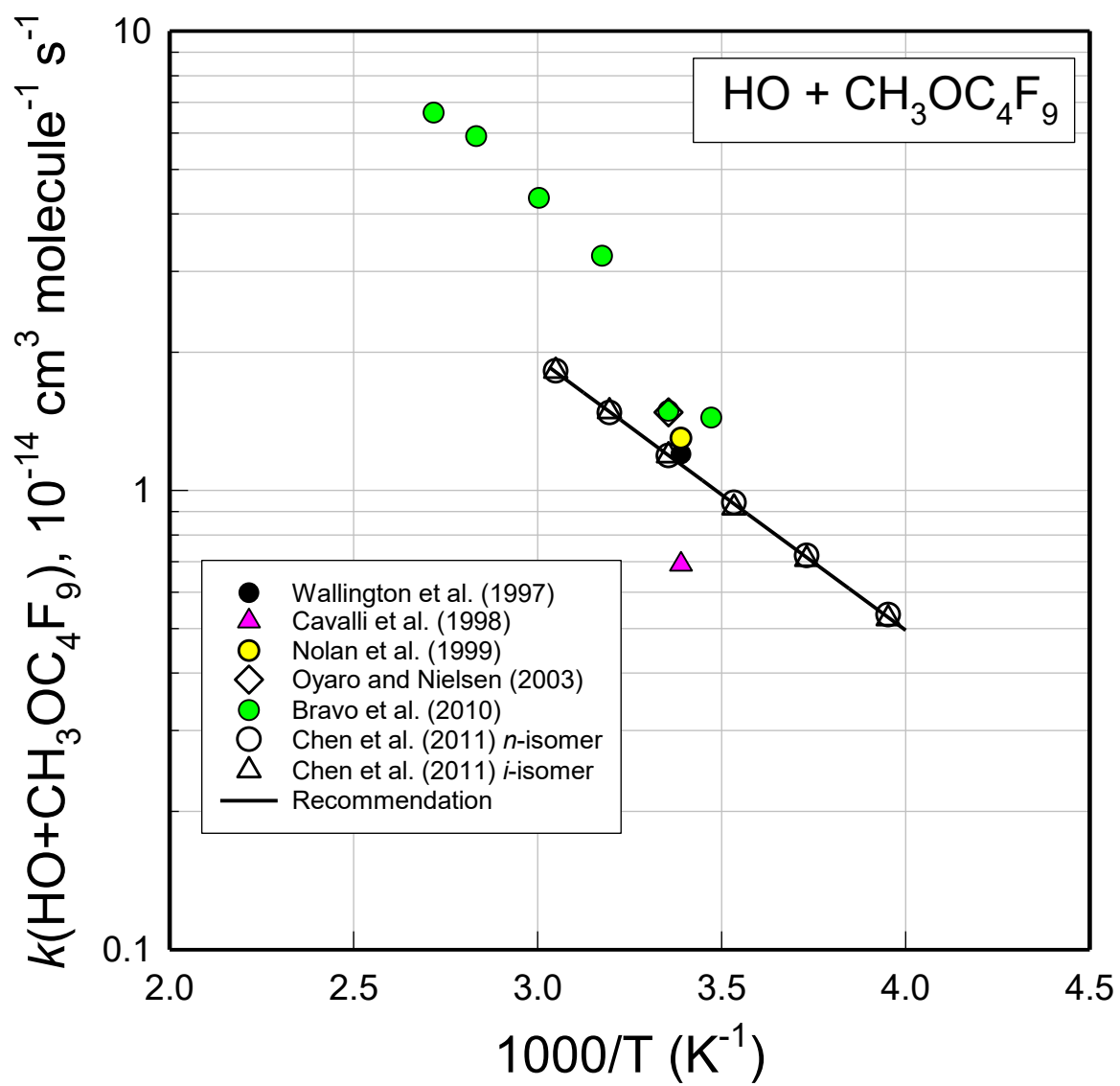
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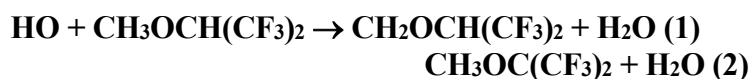
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5278 **oFOx148: HO + CH₃OCH(CF₃)₂**
 5279 Last evaluated: June 2025; Last change in preferred values: June 2023.

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Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|----------------|---------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $7.69 \times 10^{-14} \times (T/298)^{2.99} \times \exp(342/T)$ $(2.38 \pm 0.03) \times 10^{-13}$ | 230-370 | Orkin et al. (2017) | FP-RF (a) |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.40 \pm 0.28) \times 10^{-12} \exp[(-550 \pm 60/T)]$ 2.25×10^{-13} | 253-328 295 | Chen et al. (2005) | RR (b) |

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Comments

- (a) HO radicals were generated by the flash photolysis of H₂O in 4 and 13.3 kPa (30 and 100 Torr) of argon diluent and monitored by resonance fluorescence at 308 nm. The sample of CH₃OCH(CF₃)₂ was purified using a preparative scale gas chromatograph before use.
- (b) HO radicals were generated by the photolysis of O₃ at 254 nm in the presence of water vapor in 200 Torr (267 mbar) of O₂ diluent. The loss of CH₃OCH(CF₃)₂ was measured relative to those of C₂H₆ and CH₂Cl₂. The results obtained using the two different reference compounds were in excellent agreement. Using $k(\text{HO} + \text{C}_2\text{H}_6) = 6.90 \times 10^{-12} \exp(-1000/T)$ and $k(\text{HO} + \text{CH}_2\text{Cl}_2) = 1.80 \times 10^{-12} \exp(-860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006; 2008) places the reported rate coefficient ratios on an absolute basis and fitting an Arrhenius expression to the results gives $k(\text{HO} + \text{CH}_3\text{OCH}(\text{CF}_3)_2) = 1.22 \times 10^{-12} \exp(-508/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

| Parameter | Value | T/K |
|--|---|----------------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.29×10^{-13} $1.08 \times 10^{-12} \exp(-461/T)$ | 298 230-340 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta \log E/R$ | ± 100 | 250-340 |

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Comments on Preferred Values

There is excellent agreement between the results from the relative rate study by Chen et al. (2005) and the absolute study by Orkin et al. (2017). Curvature in the Arrhenius plot is evident in the data from Orkin et al. (2017). Taking an average of the values reported by Chen et al. (2005) and Orkin et al. (2017) gives the preferred value at 298 K. A fit to the combined data set from Chen et al. (2005) and Orkin et al. (2017) below 340 K and adjusting the pre-exponential factor to match the

5311 preferred rate coefficient at 298 K gives the preferred Arrhenius expression.

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References

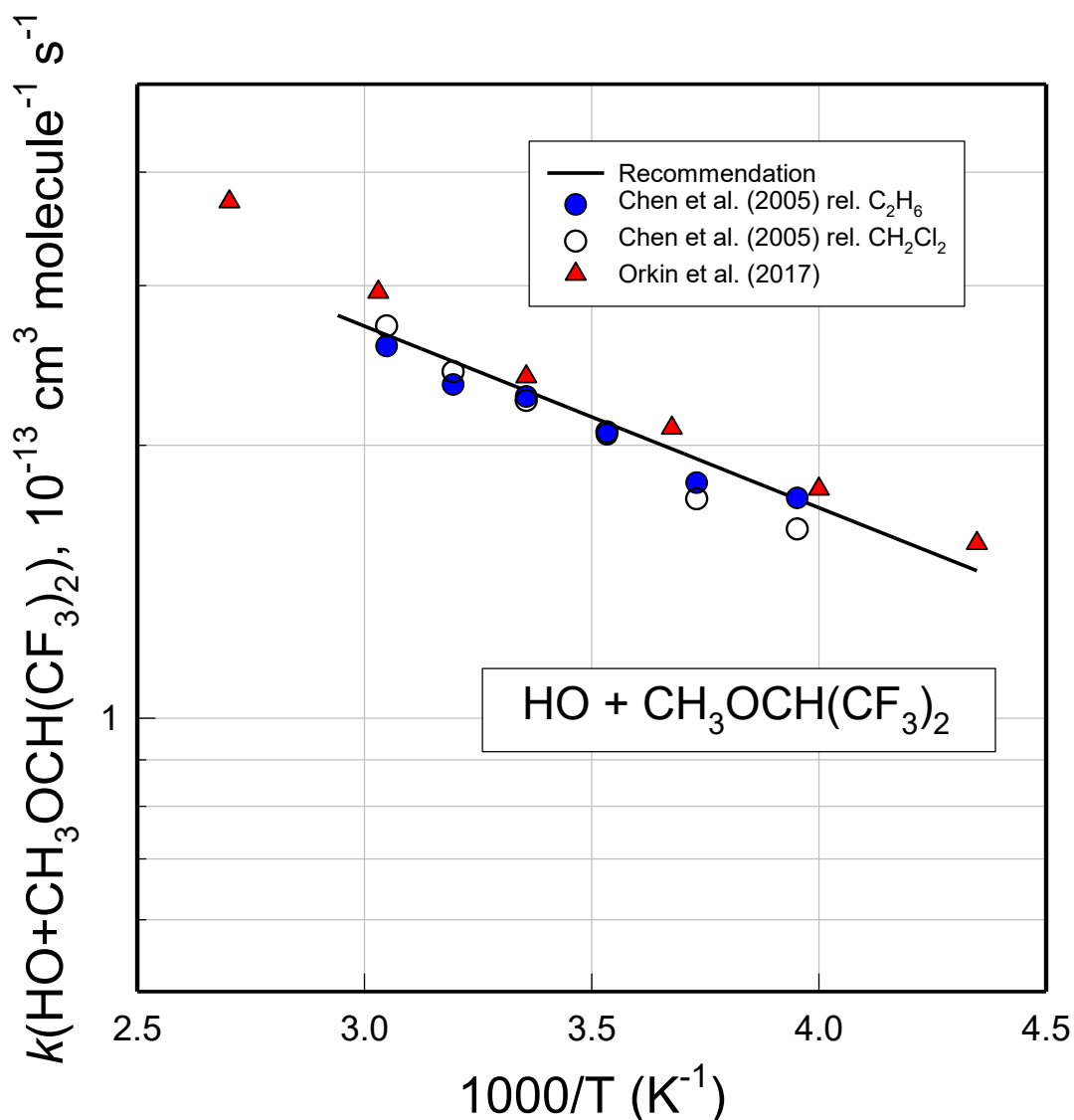
5315 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
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oFOx149: HO + CH₂FOCH(CF₃)₂ (Sevoflurane)

Last evaluated: February 2026; Last change in preferred values: February 2026.



Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---------|--------------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $1.53 \times 10^{-12} \exp(-900/T)$ | 299-422 | Brown et al. (1990) | DF-RF (a) |
| $(7.3 \pm 2.2) \times 10^{-14}$ | 299 | | |
| $(2.7 \pm 0.5) \times 10^{-14}$ | 298 | Langbein et al. (1999) | PLP-UVA (b) |
| $(9.98 \pm 3.24) \times 10^{-12} \exp[(-969 \pm 82)/T]$ | 243-298 | Sulbaek Andersen et al. (2012) | PLP-LIF (c) |
| $(3.94 \pm 0.30) \times 10^{-14}$ | 298 | | |
| $(1.6 \pm 0.7) \times 10^{-12} \exp[(-1065 \pm 138)/T]$ | 253-423 | Espinosa et al. (2025) | PLP-LIF (d) |
| $(4.25 \pm 0.86) \times 10^{-14}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(2.98 \pm 0.18) \times 10^{-14}$ | 296 | Sulbaek Andersen et al. (2012) | RR (e) |
| $(3.31 \pm 0.22) \times 10^{-14}$ | 296 | | |

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Comments

- (a) HO radicals were generated by the reaction of H atoms with NO₂ in 1-8 – 6.3 Torr of helium diluent.
- (b) HO radicals were produced by 248 nm photolysis of HNO₃ and monitored by laser long-path absorption at 308.42 nm. Experiments were performed in N₂ diluent, the total pressure was not specified, but judging from the conditions specified for the HO detection limit, it was probably 50 mbar.
- (c) HO radicals were generated by the 248 nm photolysis of O₃ to give O(¹D) atoms which react with CH₄. GC analysis of the sevoflurane sample indicated a purity of >99.98%. There was no discernable effect of total pressure over the range 111 - 300 Torr of argon diluent.
- (d) HO radicals were generated by the 248 nm photolysis of either H₂O₂ or HNO₃ in 70-80 Torr of helium diluent and monitored by laser induced fluorescence.
- (e) HO radicals were generated by the photolysis of CH₃ONO in the presence of NO in 700 Torr of air diluent. The loss of CH₂FOCH(CF₃)₂ was inferred from the formation of its oxidation product FC(O)OCH(CF₃)₂ measured using FTIR spectroscopy. C₂H₂ and C₂H₄ were used as reference compounds and rate coefficient ratios $k(\text{HO} + \text{CH}_2\text{FOCH}(\text{CF}_3)_2)/k(\text{HO} + \text{C}_2\text{H}_2) = (0.0399 \pm 0.0024)$ and $k(\text{HO} + \text{CH}_2\text{FOCH}(\text{CF}_3)_2)/k(\text{HO} + \text{C}_2\text{H}_4) = (4.22 \pm 0.28) \times 10^{-3}$ were reported. Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(\text{HO} + \text{CH}_2\text{FOCH}(\text{CF}_3)_2) = (2.98 \pm 0.18) \times 10^{-14}$ and $(3.31 \pm 0.22) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Preferred Values

| Parameter | Value | T/K |
|--|--------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 4.10×10^{-14} | 298 |
| | $1.24 \times 10^{-12} \exp(-1017/T)$ | 230-440 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta \log E/R$ | ± 200 | 230-440 |

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Comments on Preferred Values

5363 The rate coefficient reported by Brown et al. (1990) at 299 K is approximately a factor of 2-3
5364 higher than those reported by Langbein et al. (1999), Sulbaek Andersen et al. (2012), and Espinosa et
5365 al (2025). As noted elsewhere (e.g., Calvert et al. 2008), for several of the compounds investigated by
5366 Brown et al. (1990) substantially higher rate coefficients were reported than in subsequent studies. It
5367 seems likely that the presence of reactive impurities was a complicating factor in the study by
5368 Brown et al. (1990). The result from Langbein et al. (1999) at 298 K is approximately 30% lower
5369 than reported by Sulbaek Andersen et al. (2012) and Espinosa et al (2025) but consistent within the
5370 extremes of the likely uncertainties in the studies. The rate coefficients reported by Sulbaek Andersen
5371 et al. (2012) and Espinosa et al (2025) are in excellent agreement. The recommended rate coefficient
5372 at 298 K is the average of the absolute rate determinations by Sulbaek Andersen et al. (2012) and
5373 Espinosa et al (2025). The recommended temperature dependence is the average from Sulbaek
5374 Andersen et al. (2012) and Espinosa et al (2025), the pre-exponential factor A was chosen to return the
5375 recommended rate coefficient at 298 K. Results from the relative rate measurements by Sulbaek
5376 Andersen et al. (2012) at ambient temperature are consistent with the recommended data.

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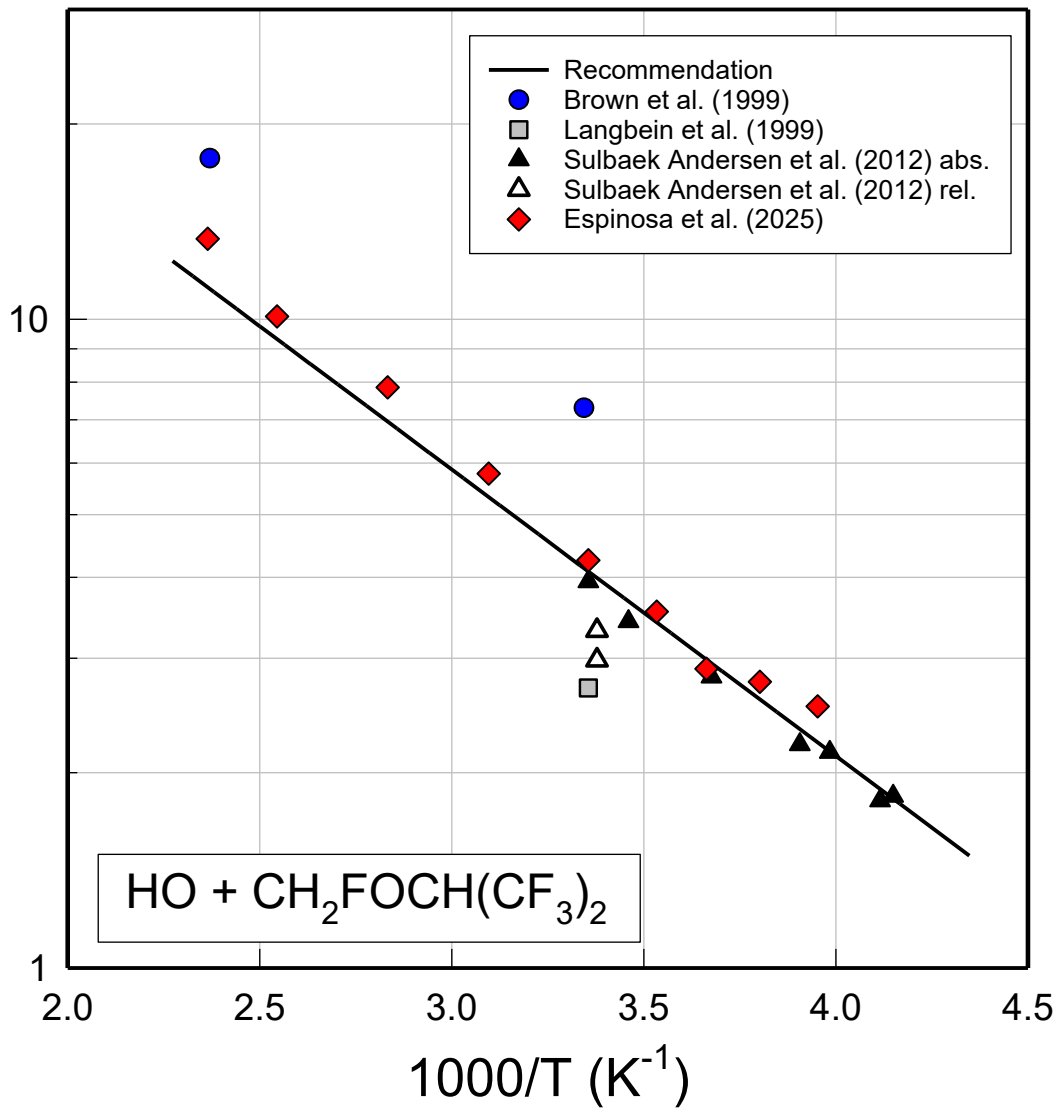
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5392 Phys. Chem. A, 116, 5806, 2012.

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$k(\text{HO} + \text{CH}_2\text{FOCH}(\text{CF}_3)_2), 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$



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oFOx150: HO + CHF₂OCHF₂CF₃ (Desflurane)

Last evaluated June 2025; Last change in preferred values: September 2019.



Rate coefficient data ($k = k_1 + k_2$)

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|--------------------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $(4.4 \pm 0.8) \times 10^{-15}$ | 298 | Langbein et al. (1999) | PLP-UVA (a) |
| $(7.05 \pm 1.80) \times 10^{-13} \exp[(-1551 \pm 72)/T]$ | 239-296 | Sulbaek Andersen et al. (2012) | PLP-LIF (b) |
| $(3.73 \pm 0.08) \times 10^{-15}$ | 296 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(6.37 \pm 0.23) \times 10^{-15}$ | 298 | Orayo et al. (2005) | RR (c) |
| $(5.40 \pm 0.17) \times 10^{-15}$ | 298 | | |

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Comments

- (a) HO radicals were produced by 248 nm photolysis of HNO₃ and monitored by laser long-path absorption at 308.42 nm. Experiments were performed in N₂ diluent, the total pressure was not specified, but judging from the conditions specified for the HO detection limit, it was probably 50 mbar.
- (b) HO radicals were generated by the 248 nm photolysis of O₃ to give O(¹D) atoms which react with CH₄. GC analysis of the desflurane sample indicated a purity of >99.998%. Experiments were conducted in 111 Torr of argon diluent.
- (c) HO radicals were produced by the photolysis of O₃ at 254 nm in the presence of H₂ in 1013 mbar of air diluent. The loss of CHF₂OCHF₂CF₃ was monitored relative to those of CH₃CCl₃ and CHF₂CH₂F by GC/MS. Rate coefficient ratios of $k(\text{HO} + \text{CHF}_2\text{OCHF}_2\text{CF}_3)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = 0.67 \pm 0.024$ and $k(\text{HO} + \text{CHF}_2\text{OCHF}_2\text{CF}_3)/k(\text{HO} + \text{CHF}_2\text{CH}_2\text{F}) = 0.36 \pm 0.04$ were reported. Using $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 9.5 \times 10^{-15}$ and $k(\text{HO} + \text{CHF}_2\text{CH}_2\text{F}) = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson et al., 2006, 2008) gives $k(\text{HO} + \text{CHF}_2\text{OCHF}_2\text{CF}_3) = (6.37 \pm 0.23) \times 10^{-15}$ and $(5.40 \pm 0.17) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

| Parameter | Value | T/K |
|--|--|----------------|
| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 4.08×10^{-15} $7.43 \times 10^{-13} \exp(-1551/T)$ | 298 230-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta \log E/R$ | ± 200 | 230-300 |

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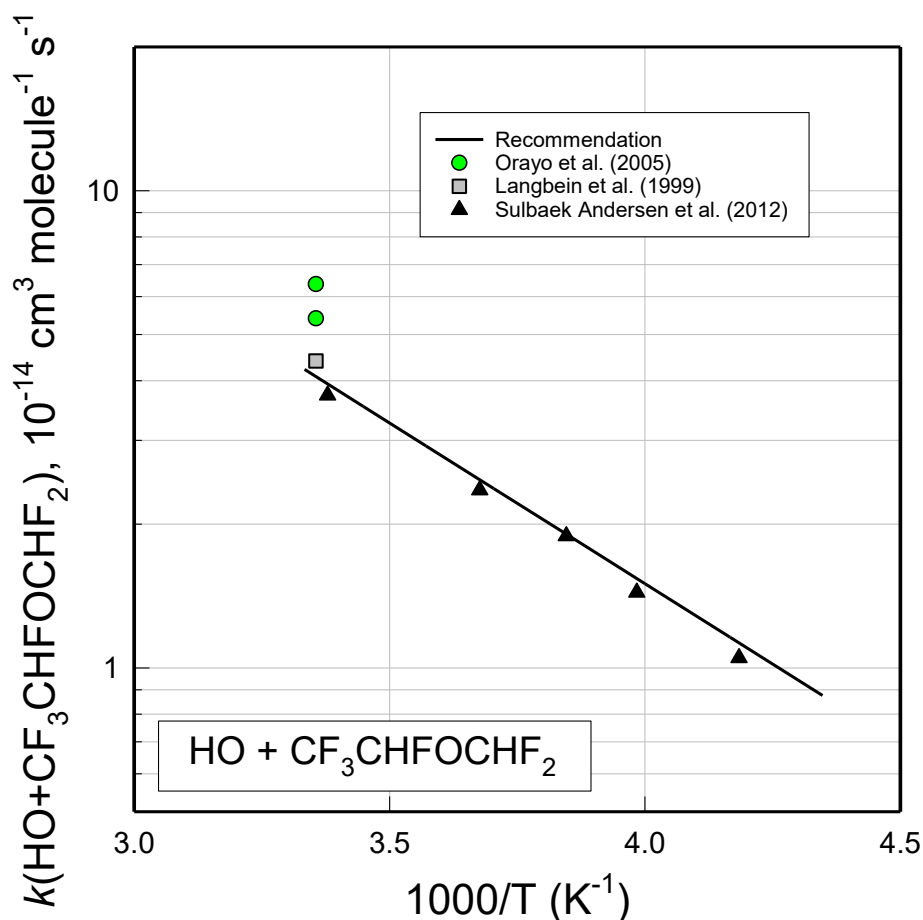
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The rate coefficients measured at 298 K in the absolute rate studies by Langbein et al. (1999) and Sulbaek Andersen et al. (2012) are in good agreement and are averaged to provide the preferred value. The preferred Arrhenius expression is based on the temperature dependence reported by Sulbaek Andersen et al. (2012) with the pre-exponential factor adjusted to return the preferred value at 298 K. The results from the relative rate study by Orayo et al. (2005) are consistent within the uncertainties with the preferred values.

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5455 **HO + CF₃OCF=CF₂ → products**

5456 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|-------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 6.41 × 10 ⁻¹¹ exp(-868/ <i>T</i>) | 253-348 | Li et al. (2000) | DF-RF (a) |
| (3.58 ± 0.42) × 10 ⁻¹² | 298 | | |
| 1.01 × 10 ⁻¹² exp(320/ <i>T</i>) | 250-430 | Tokuhashi et al. (2000) | LFP-RF (b) |
| (2.98 ± 0.03) × 10 ⁻¹² | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| (2.16 ± 0.19) × 10 ⁻¹² | 296 | Mashino et al. (2000) | RR (c) |
| (2.28 ± 0.16) × 10 ⁻¹² | | | |

5460 **Comments**

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- 5463 (a) HO radicals were produced by the reaction of F atoms with H₂O or by the reaction of H atoms with
 5464 NO₂ in 1 Torr of He diluent at 298 K.
- 5465 (b) HO radicals were produced by the pulsed xenon flash lamp photolysis of H₂O, or pulsed ArF excimer
 5466 laser photolysis of N₂O to produce O(¹D) atoms which were then reacted with either H₂O or CH₄ to
 5467 give HO radicals, or pulsed laser photolysis of H₂O₂. Experiments were conducted in 5-200 Torr of
 5468 helium, or argon, diluent. There was no discernible effect of pressure or diluent gas over the range
 5469 studied. Results from experiments using four different sources of HO radicals were
 5470 indistinguishable.
- 5471 (c) Photolysis of CH₃ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The
 5472 loss of CF₃OCF=CF₂ was measured relative to those of C₂H₂ and C₂H₄ and used to measure the rate
 5473 coefficient ratios $k(\text{CF}_3\text{OCF}=\text{CF}_2)/k(\text{C}_2\text{H}_2) = 2.89 \pm 0.25$ and $k(\text{CF}_3\text{OCF}=\text{CF}_2)/k(\text{C}_2\text{H}_4) = 0.29 \pm 0.02$.
 5474 Using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.47 \times 10^{-13}$ and $k(\text{HO} + \text{C}_2\text{H}_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives
 5475 $k(\text{HO} + \text{CF}_3\text{OCF}=\text{CF}_2) = (2.16 \pm 0.19) \times 10^{-12}$ and $(2.28 \pm 0.16) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

5476 **Preferred Values**

| Parameter | Value | <i>T</i> /K |
|--|--|-------------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 2.96 × 10 ⁻¹² | 298 |
| | 1.01 × 10 ⁻¹² exp(320/ <i>T</i>) | 250-430 |
| <i>Reliability</i> | | |
| Δ log <i>k</i> | 0.10 | 298 |
| Δ E/R | ±100 | 250-430 |

5479 **Comments on Preferred Values**

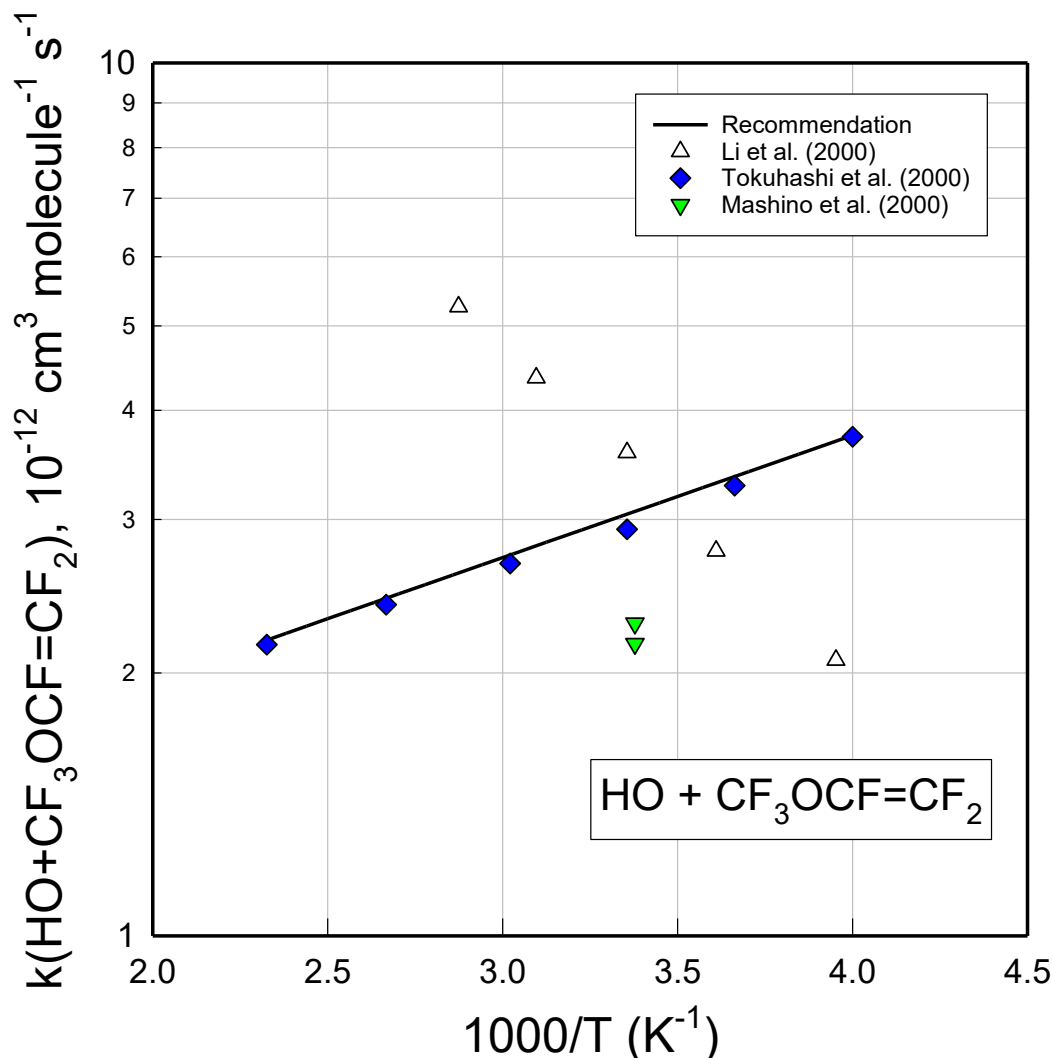
5480 While the rate coefficients measured at 298 K in the absolute rate studies by Li et al. (2000) and
 5481 Tokuhashi et al. (2000) differ by only approximately 20%, the temperature dependencies measured in
 5482 the two studies are strikingly different. It is well established that the mechanism of the reaction of HO
 5483 radicals with alkenes is addition to the >C=C< bond and the temperature dependence reported by Li et
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5486 al. (2000) is not physically plausible. The results from the relative rate study by Mashino et al. (2000)
5487 at 296 K are approximately 25% lower than the rate coefficient reported by Tokuhashi et al. (2000) at
5488 298 K. Such a difference lies at the extreme end of the likely combined experimental uncertainties
5489 from the two studies. The preferred expression is taken from Tokuhashi et al. (2000) and gives $k(\text{HO} +$
5490 $\text{CF}_3\text{OCF}=\text{CF}_2) = 2.96 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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References

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 5507 **oFOx134: HO + C₂F₅OCF=CF₂**
 5508 Last evaluated: June 2025; Last change in preferred values: June 2019.

5509 **HO + C₂F₅OCF=CF₂ → products**

5510 **Rate coefficient data**

| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | Temp./K | Reference | Technique/ Comments |
|--|---------|---------------------------|---------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $6.0 \times 10^{-13} \exp(480 \pm 38/T)$ | 207-300 | Srinivasulu et al. (2018) | PLP-LIF (a) |
| $(3.0 \pm 0.3) \times 10^{-12}$ | 298 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(3.08 \pm 0.07) \times 10^{-12}$ | 298 | Srinivasulu et al. (2018) | RR (b) |
| $(2.82 \pm 0.05) \times 10^{-12}$ | 298 | Bunkan et al. (2018) | RR (c) |

5514 **Comments**

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 5517 (a) HO radicals were produced by the photolysis of H₂O₂ or HNO₃ at 248 nm in 50 or 100 Torr of N₂
 5518 diluent. The pseudo first order loss of HO radicals was measured in the presence of an excess of
 5519 C₂F₅OCF=CF₂.
 5520 (b) HO radicals were produced by the photolysis of O₃ in the presence of H₂ in 1 atmosphere of air
 5521 diluent. The loss of C₂F₅OCF=CF₂ was measured relative to that of C₃H₈ and a rate coefficient ratio
 5522 of $k(\text{C}_2\text{F}_5\text{OCF}=\text{CF}_2)/k(\text{C}_3\text{H}_8) = 2.802 \pm 0.061$ was reported. Using $k(\text{HO} + \text{C}_3\text{H}_8) = 1.1 \times 10^{-12}$
 5523 (Atkinson et al., 2006) gives $k(\text{C}_2\text{F}_5\text{OCF}=\text{CF}_2) = (3.08 \pm 0.07) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 5524 (c) Photolysis of CH₃ON0.60 in 1 bar of air diluent was used to generate HO radicals. The loss of
 5525 C₂F₅OCF=CF₂ was measured relative to that of C₂H₄ and used to measure the rate coefficient ratio
 5526 $k(\text{C}_2\text{F}_5\text{OCF}=\text{CF}_2)/k(\text{C}_2\text{H}_4) = 0.361 \pm 0.006$. Using $k(\text{HO} + \text{C}_2\text{H}_4) = 7.8 \times 10^{-12}$ (Atkinson et al., 2006)
 5527 gives $k(\text{HO} + \text{C}_2\text{F}_5\text{OCF}=\text{CF}_2) = (2.82 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
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5530 **Preferred Values**

| Parameter | Value | T/K |
|--|-----------------------------------|---------|
| <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹ | 3.0×10^{-12} | 298 |
| | $6.0 \times 10^{-13} \exp(480/T)$ | 200-300 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | 0.10 | 298 |
| $\Delta E/R$ | ±100 | 200-300 |

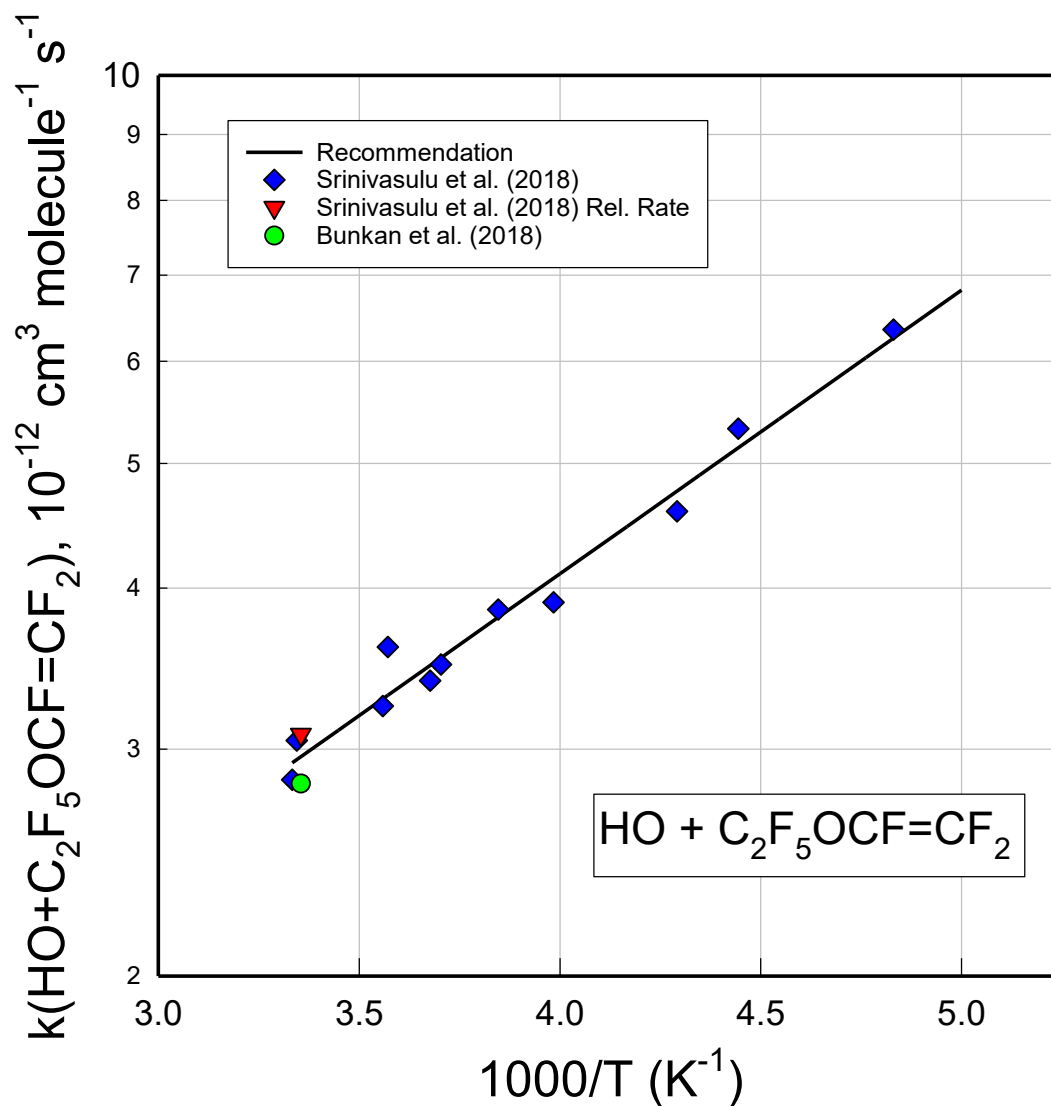
5531 *Comments on Preferred Values*

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 5534 There is excellent agreement in the results from the absolute and relative rate studies by Srinivasula et
 5535 al. (2018) and Bunkan et al. (2018) at 298-300 K. The preferred Arrhenius expression is taken from
 5536 Srinivasula et al. (2018) which gives $k(\text{HO} + \text{C}_2\text{F}_5\text{OCF}=\text{CF}_2) = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K
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oFOx160: CF₃C(O)O₂ + HO₂

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Last evaluated: June 2025; Last change in preferred values: November 2022.

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Rate coefficient data ($k = k_1 + k_2 + k_3$)

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| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|-------------|-------------------------------|------------------------|
| Branching ratios | | | |
| $k_1/k = 0.09 \pm 0.04$ | 296 ± 2 | Sulbaek Andersen et al., 2004 | S-FTIR (a) |
| $k_2/k = 0.38 \pm 0.04$ | | | |
| $k_3/k = 0.56 \pm 0.05$ | | | |

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Comments

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- (a) Experiments were carried out in a 140 L static reactor with reactants and products analysed by FTIR. CF₃C(O)O₂ and HO₂ radicals were generated by the broad-band photolysis of Cl₂ in the presence of CF₃CHO and H₂ in air or O₂. The initial relative production rate of HO₂ to CF₃C(O)O₂ was varied from 0 to ~13; at the high end of the scale all CF₃C(O)O₂ radicals are expected to react with HO₂. The loss of CF₃CHO and the formation of CF₃C(O)OOH, CF₃C(O)OH and COF₂ were used to derive branching ratios for k_1 , k_2 and k_3 respectively. O₃, (co-produced with CF₃C(O)OH) was also observed and its yield was indistinguishable from that of CF₃C(O)OH.

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Preferred Values

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| Parameter | Value | T/K |
|--|------------|-----|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2e-11 | 298 |
| k_1/k | 0.09 | 296 |
| k_2/k | 0.38 | 296 |
| k_3/k | 0.56 | 296 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.3 | 298 |
| $\Delta \log(k_1/k)$ | ± 0.2 | 298 |
| $\Delta \log(k_2/k)$ | ± 0.15 | 298 |
| $\Delta \log(k_3/k)$ | ± 0.15 | 298 |

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Comments on Preferred Values

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There is very little experimental data on the reaction between CF₃C(O)O₂ and HO₂ and the rate coefficient has not been studied. The relative importance of the three reaction pathways has been determined (at room temperature only) by Sulbaek Andersen et al., 2004, who showed that the formation of trifluoro acetic acid (CF₃C(O)OH) with a branching ratio of 0.38 ± 0.04 is preferred over the peroxide (or peroxyacid CF₃C(O)OOH) with a branching ratio 0.09 ± 0.04 . The most important pathway at room temperature is however formation of CF₃CO₂ + O₂ + HO with a branching ratio of 0.56 ± 0.05 . The initially formed CF₃CO₂ product decomposes to CF₃ + CO₂. By comparison with the larger experimental dataset on the analogous reaction of the non-fluorinated peroxy radical

5584 CH₃C(O)O₂ (see IUPAC Data-Sheet HO_x_VOC54) we may expect that the acid forming pathway (k_2)
5585 will gain in relative importance at the cost of k_1 and k_3 as the temperature decreases, but this requires
5586 experimental / theoretical confirmation.

5587 In the absence of a direct measurement of k , we list the value for the non-fluorinated analogue
5588 CH₃C(O)O₂. This value and its temperature dependence need to be determined experimentally.

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References

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5592 Sulbaek Andersen, M. P., Stenby, C., Nielsen, O. J., Hurley, M. D., Ball, J. C., Wallington, T. J.,
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Rate coefficient data

| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|-------------|-------------------------|------------------------|
| Absolute rate coefficients | | | |
| $> 9 \times 10^{-12}$ | 296 ± 2 | Wallington et al., 1994 | PR-UV (a) |
| $4.0 \times 10^{-12} \exp(563/T)$ | | Maricq et al., 1994 | FP-IR (b) |
| $2.8 \pm 0.6 \times 10^{-11}$ | 220-324 | | |

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Comments

- 5605 (a) CF₃C(O)O₂ radicals were generated in the pulsed radiolysis of SF₆/CF₃CHO/O₂ mixtures. The
 5606 conditions were chosen so that the fate of the initially formed CF₃CO radicals was reaction with
 5607 O₂ to form CF₃C(O)O₂. By adding NO to the mixture (0-1 mbar), the rate coefficient for
 5608 CF₃C(O)O₂ + NO was derived by monitoring the rate of formation of the NO₂ product via
 5609 absorption spectroscopy at 400 nm.
- 5610 (b) CF₃C(O)O₂ radicals were generated in the 351 nm flash photolysis of either Cl₂ or F₂ in the
 5611 presence of CF₃CHO/N₂/O₂/NO mixtures. The rate coefficient for CF₃C(O)O₂ + NO was derived
 5612 by monitoring the rate of loss of NO and formation of NO₂ via infra-red absorption spectroscopy.

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Preferred Values

| Parameter | Value | T/K |
|--|-----------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 2.8×10^{-11} | 298 |
| | $4.0 \times 10^{-12} \exp(560/T)$ | 220-340 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.2 | 298 |
| $\Delta \log (E/R)$ | ± 200 | 220-340 |

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Comments on Preferred Values

5619 There are two kinetic studies on the reaction between CF₃C(O)O₂ and NO which (at the
 5620 common temperature) are not in good agreement despite the use of similar methods. The rate
 5621 coefficient was derived by analysis of NO₂ formation (Wallington et al, 1994; Maricq et al., 1996) or
 5622 NO loss (Maricq et al., 1996). In both cases, the analyses were complicated by reactions of NO_x with
 5623 other radicals in the system.

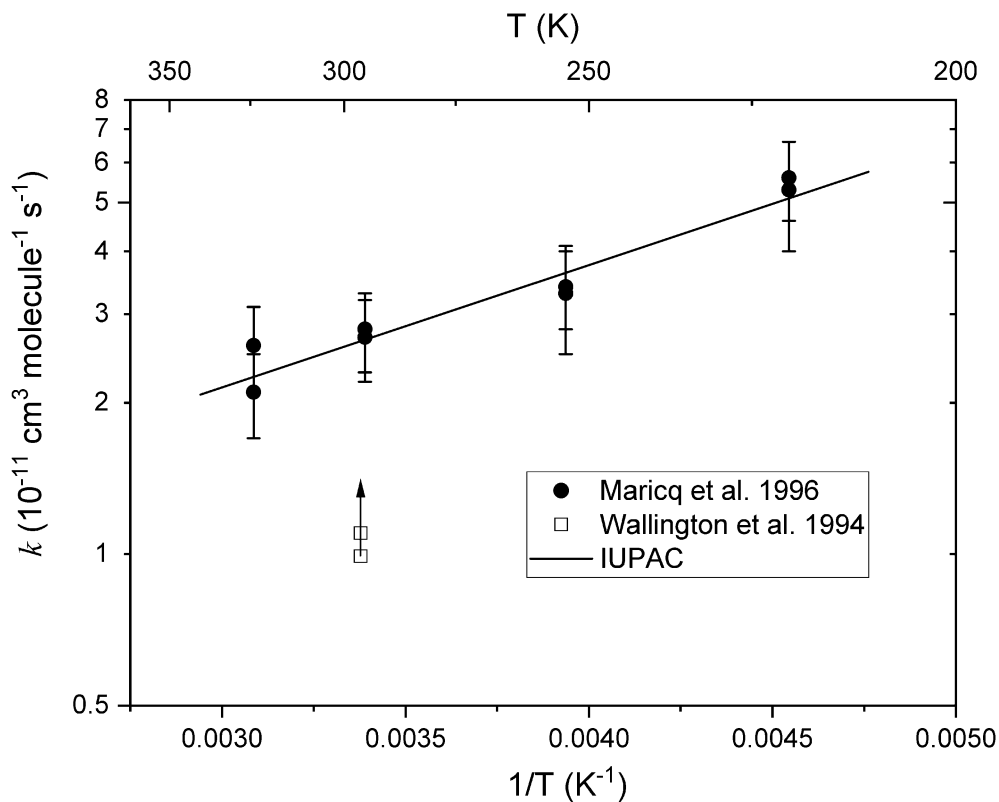
5624 Wallington et al. (1994) derived a room-temperature rate coefficient of $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 5625 from a plot of the NO₂ formation rate-constant versus NO. However a large positive intercept and a
 5626 NO₂ yield of 173 % indicated that other peroxy radicals (e.g. CF₃O₂) also converted NO to NO₂ and
 5627 the authors preferred to report a lower limit of $k > 9.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Maricq et al. (1996)
 5628 found that the time profiles of both NO and NO_x were impacted by reactions of NO with CF₃O₂ (to
 5629 form NO₂) and with CF₃CO₂ and CF₃O (to remove NO) thus complicating the kinetic analysis. They
 5630 found a much larger (factor 2.5) rate coefficient at room temperature than Wallington et al.

5631 As the result of Maricq et al. (1996) is consistent with the lower limit of Wallington et al. and is

5632 similar to the large rate coefficient for reaction of the non-fluorinated analogue ($\text{CH}_3\text{C}(\text{O})\text{O}_2$) with
5633 NO , we adopt this as our preferred value, albeit with expanded uncertainty. Maricq et al (1996)
5634 observed a negative temperature dependence, which is consistent with the kinetic data on $\text{CH}_3\text{C}(\text{O})\text{O}_2$
5635 with NO and we adopt their measurement of the temperature dependence of k .

References

5639 Maricq, M. M., Szente, J. J., Khitrov, G. A., and Francisco, J. S.: *J. Phys. Chem.*, 100, 4514, 1996.
5640 Wallington, T. J., Hurley, M. D., Nielsen, O. J., and Sehested, J.: *J. Phys. Chem.*, 98, 5686, 1994.



Rate coefficients for $\text{CF}_3\text{CO}_3 + \text{NO}$. The arrow indicates that the (lower) value of Wallington et al. is a lower limit. The upper value is their actual measurement (see text for details).

5643 **oFOx162: CF₃C(O)O₂ + NO₂ + M**
5644 Last evaluated: June 2025; Last change in preferred values: November 2022.



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Rate coefficient data

| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|-------------|-------------------------|------------------------|
| Absolute rate coefficients (6.6 ± 1.3) $\times 10^{-12}$ | 296 ± 2 | Wallington et al., 1994 | PR-UV (a) |

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Comments

(a) CF₃C(O)O₂ radicals were generated in the pulsed radiolysis of SF₆/CF₃CHO/O₂ mixtures. The conditions were chosen so that the initially formed CF₃CO radicals were converted to CF₃C(O)O₂ in < 2 μs. The rate coefficient for CF₃C(O)O₂ + NO₂ was derived by monitoring the rate of loss of NO₂ via absorption spectroscopy at 400 nm.

Preferred Values

| Parameter | Value | T/K |
|--|-----------------------|-----|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 6.6×10^{-12} | 296 |
| Reliability $\Delta \log k$ | ± 0.3 | 296 |

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Comments on Preferred Values

The pulsed radiolysis experiments of Wallington et al. (1994) represent the only kinetic study of the reaction between CF₃C(O)O₂ and NO₂ which was limited to room temperature and a total pressure of 1 bar SF₆. Although pseudo first-order kinetics appeared to be followed, the NO₂ concentration was significantly depleted during the reaction and corrections ($\leq 12\%$) were applied to take this into account. In addition, $\approx 15\%$ of the initially formed CF₃C(O) radicals decomposed to CF₃ (+ CO) with subsequent formation of CF₃O₂ which may also react with NO₂ thus complicating the analysis. The uncertainty listed in the preferred value of k reflect the fact that there is only one study of the reaction and the potential complications involving the presence of peroxy radicals other than CF₃C(O)O₂.

In line with other termolecular reactions between organic peroxy radicals NO₂, the reaction is likely to be in the high-pressure limit in the experiments of Wallington et al. (1994) at one bar SF₆.

References

Wallington, T. J., Sehested, J., and Nielsen, O. J.: Chem. Phys. Lett., 226, 563, 1994.

5677 **oFOx163: CF₃C(O)O₂NO₂ + M**
 5678 Last evaluated: June 2025; Last change in preferred values: November 2022.

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Rate coefficient data

| k / s^{-1} | Temp./K | Reference | Technique/ Comments |
|--|---------|-------------------------|------------------------|
| Absolute rate coefficients | | | |
| $1.75 \times 10^{14} \exp(-12600/T)^a$ | 285-303 | Wallington et al., 1994 | P-IR (a) |
| $6.16 \times 10^{16} \exp(-14500/T)^b$ | 314-321 | Zabel et al., 1994 | P-IR (b) |
| $1.94 \times 10^{17} \exp(-14800/T)^c$ | 315-319 | | |
| $6.0 \times 10^{16} \exp(-14325/T)^d$ | 314-321 | | |

5683 ^aExpression derived by fitting to data listed at 933 mbar, ^b Expression derived by fitting to data listed at 8
 5684 mbar, ^cExpression derived by fitting to data listed at 30 mbar, ^dValue reported at 1000 mbar.

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Comments

- 5688 (a) CF₃C(O)O₂ radicals were generated in the broad-band (300-400 nm) photolysis of Cl₂ in the
 5689 presence of CF₃CHO, O₂ and N₂ at a total pressure of 100 or 700 Torr (133 or 933 mbar) and
 5690 converted to CF₃C(O)O₂NO₂ via addition of NO₂. When the NO₂ was completely depleted, NO
 5691 was added and the first-order rate of loss of CF₃C(O)O₂NO₂ monitored via IR-absorption features.
 5692 Corrections (9-21%) were applied to the rate constants to take into account reformation of
 5693 CF₃C(O)O₂NO₂ through recombination of the CF₃C(O)O₂ and NO₂ products.
- 5694 (b) CF₃C(O)O₂ radicals were generated in the broad-band ($\lambda > 300$ nm) photolysis of Cl₂ in the
 5695 presence of CF₃CHO, O₂ and N₂ at a total pressure of 100 or 700 Torr (133 or 933 mbar) and
 5696 converted to CF₃C(O)O₂NO₂ via addition of NO₂. When the NO₂ was completely depleted, NO
 5697 was added and the first-order rate of loss of CF₃C(O)O₂NO₂ monitored via IR-absorption features.
 5698 Corrections (10-25 %) were applied to the rate constants to take into account reformation of
 5699 CF₃C(O)O₂NO₂ through recombination of the CF₃C(O)O₂ and NO₂ products.

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Preferred Values

| Parameter | Value | T/K |
|---|--------------------------------------|-----------|
| k (s ⁻¹) (1bar) | 7.95×10^{-5} | 298 |
| k_0 (cm ³ molecule ⁻¹ s ⁻¹) | $5.0 \times 10^{-20} \exp(-12350/T)$ | 290 – 330 |
| k_∞ (s ⁻¹) | $1.1 \times 10^{17} \exp(-14440/T)$ | 290 – 330 |
| F_c | 0.2 | 290 – 330 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.3 | 296 |

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Comments on Preferred Values

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5705 The two studies of the thermal decomposition of CF₃C(O)O₂NO₂ cover a limited ranges of
 5706 pressures and temperatures. While the experiments of Zabel et al. (1994) show a clear pressure
 5707 dependence (8-1000 mbar) at temperatures between ~ 314 and 320 K, the experiments of Wallington
 5708 et al. (1994) at 303 K are independent of pressure between 100 and 933 mbar. Both studies indicate a
 5709 strong dependence on temperature at all pressures (see Figure 1). In order to parameterise this

5710 termolecular reaction, rate coefficients at temperatures of exactly 303 K, 314 K and 320 K were
5711 calculated for each pressure studied using temperature dependent expressions (see parameters in the
5712 table above) derived by fitting to the individual datasets at single pressures. The results are shown in
5713 Figure 2. The solid lines are Troe-type fits to the data in which the temperature dependence of k_0 and
5714 k_∞ were taken from Zabel et al. (1994) as was the broadening factor, F_c , which they calculated using
5715 vibrational frequencies of $\text{CF}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$. The pre-exponential factor for k_0 was adjusted to best fit
5716 all datasets.

5717 While the parameterisation adequately reproduces the experimental data, extrapolation beyond the
5718 temperature range of the two studies should be performed with caution.

5720 The following text-line combines the preferred values for the high and low pressure limiting rate
5721 coefficients to generate a single, cut-and-paste expression for calculation of k :

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$$=((5e-2*\exp(-12350/T))*M*(1.1e17*\exp(-14440/T)))/((5e-2*\exp(-12350/T))*M+(1.1e17*\exp(-$$

5724 $14440/T))*10^{(\log10(0.2)/(1+(\log10((5e-2*\exp(-12350/T))*M/(1.1e17*\exp(-14440/T)))/(0.75-$
5725 $1.27*\log10(0.2)))^2))$

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5727 The molecular density, $M = 7.243 \times 10^{21} P(\text{bar})/T(\text{K})$

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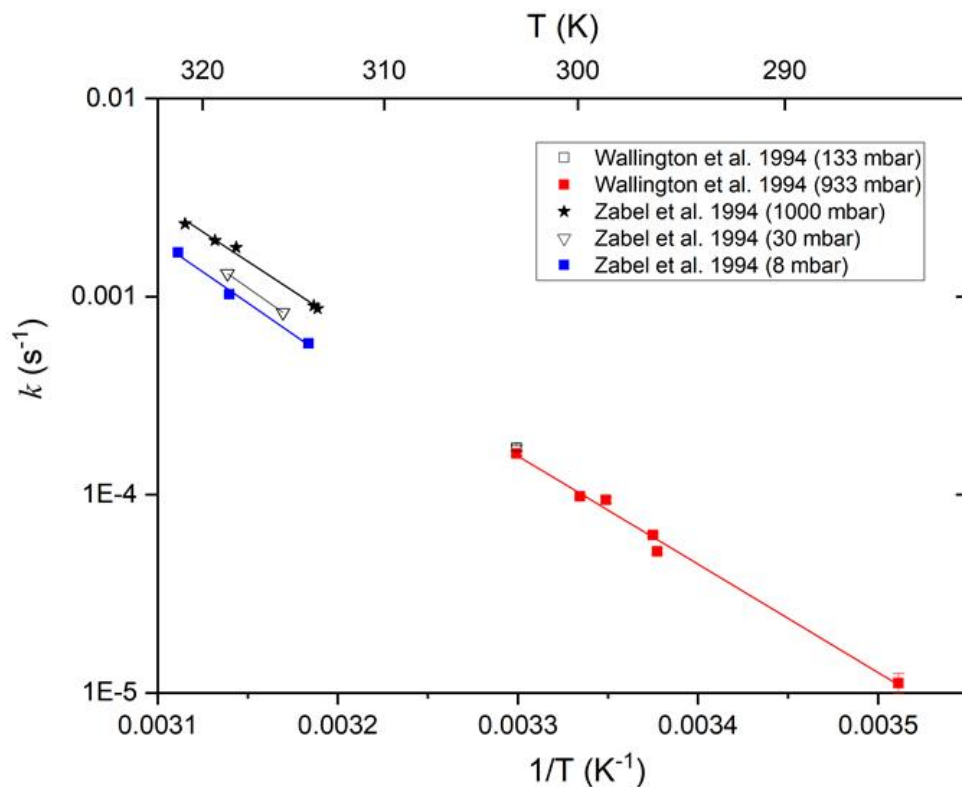
References

5731 Wallington, T. J., Hurley, M. D., Nielsen, O. J., and Sehested, J.: J. Phys. Chem., 98, 5686, 1994.

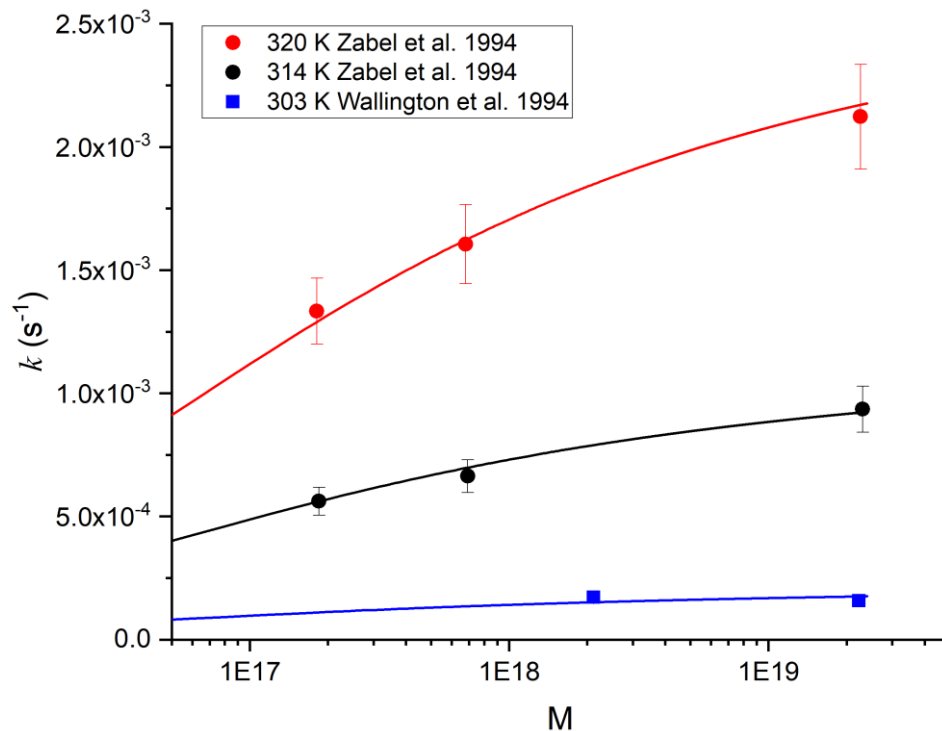
5732 Zabel, F., Kirchner, F., and Becker, K. H.: Int. J. Chem. Kinet., 26, 827, 1994.

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5736 Measurements of the rate coefficient (k) for the thermal dissociation of $\text{CF}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ at various temperatures and
 5737 pressures. The solid lines are fits to the raw data at each pressure.
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5741 Pressure dependence of $k(T)$. Data points at single temperatures were calculated from fits to the raw data as shown in
 5742 The solid lines are the IUPAC preferred values based on a fall off parameterisation.
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5746 **PF5: CHF₂CHO + hv**
5747 Last evaluated: June 2025; last change in preferred values: June 2010.
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5750 **CHF₂CHO + hv → products**

5751 **Primary photochemical transitions**

| Reaction | | |
|---------------------------|---------------------------------------|-----|
| CHF ₂ CHO + hv | → CHF ₂ + HCO | (1) |
| | → CHF ₂ CO + H | (2) |
| | → CH ₂ F ₂ + CO | (3) |

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Absorption cross-section data

| Wavelength range/nm | References | Comments |
|---------------------|------------------------|----------|
| 190-400 | Sellevåg et al. (2005) | (a) |

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Quantum yield data

| Measurement | Wavelength/nm | References | Comments |
|------------------------|---------------|-----------------------|----------|
| $\Phi = 0.30 \pm 0.05$ | 295-400 | Sellevåg et al., 2005 | (b) |

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Comments

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- (a) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of difluoroacetaldehyde shows a broad band, centered at 310 nm and extending out to approximately 355 nm. Values of σ were given at 1 nm intervals.
- (b) Photolysis of CHF₂CHO in pure dry air in the presence of an inert tracer (SF₆) added to monitor leakage from the chamber and an OH radical tracer (di-*n*-butyl ether) in the ~200 m³ EUPHORE chamber facility under natural sunlight conditions. The measured loss rate of CHF₂CHO during a ~5 hr period around solar noon was corrected for loss via leakage from the chamber and reaction with OH radicals to yield $J_{\text{obs}} = (2.91 \pm 0.09) \times 10^{-5} \text{ s}^{-1}$. This was compared to the maximum photolysis rate of $9.8 \times 10^{-5} \text{ s}^{-1}$ calculated using a unit quantum yield for photodissociation, the measured actinic flux within the chamber, and the measured UV absorption spectrum. Taking a ratio of $J_{\text{obs}}/J_{\text{calc}} = 2.9 \times 10^{-5}/9.8 \times 10^{-5}$ gives the effective photolysis quantum yield from wavelengths relevant to the troposphere of 0.30 ± 0.05 .

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Preferred Values

Absorption cross-sections of CHF₂CHO at 298 K

| λ/nm | $10^{20} \sigma/\text{cm}^2$ | λ/nm | $10^{20} \sigma/\text{cm}^2$ |
|---------------------|------------------------------|---------------------|------------------------------|
| 190 | 0.27 | 300 | 4.34 |
| 195 | 0.20 | 305 | 4.49 |
| 200 | 0.12 | 310 | 4.53 |
| 205 | 0.08 | 315 | 4.07 |
| 210 | 0.06 | 320 | 4.22 |
| 215 | 0.05 | 325 | 3.37 |
| 220 | 0.05 | 330 | 2.92 |
| 225 | 0.06 | 335 | 2.07 |
| 230 | 0.06 | 340 | 1.11 |
| 235 | 0.07 | 345 | 0.97 |
| 240 | 0.11 | 350 | 0.55 |
| 245 | 0.17 | 355 | 0.09 |
| 250 | 0.28 | 360 | 0.04 |
| 255 | 0.44 | 365 | 0.01 |
| 260 | 0.68 | 370 | 0.01 |
| 265 | 1.01 | 375 | 0.02 |
| 270 | 1.40 | 380 | 0.01 |
| 275 | 1.87 | 385 | 0.01 |
| 280 | 2.43 | 390 | 0.01 |
| 285 | 2.95 | 395 | 0.01 |
| 290 | 3.54 | 400 | 0.00 |
| 295 | 3.97 | | |

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Quantum Yields of CHF₂CHO

$\Phi_1 = 0.30$ at 295- 360 nm

Reliability

$\Delta\Phi_1 = \pm 0.10$

Comments on Preferred Values

The preferred values for the cross-sections and quantum yield are taken from the study by Sellevåg et al. (2005). The photolysis of CHF₂CHO, presumably in air diluent (although this was not specified), at 310 nm was investigated by Sellevåg et al. (2005) and the formation of COF₂ and CO products was reported. There was no observable formation of CH₂F₂ consistent with the photolysis occurring via channel (1) to give CHF₂ and HCO radicals.

Calvert et al. (2010) assumed a wavelength independent quantum yield of 0.30 and estimated a photolysis lifetime for CHF₂CHO of 6 hours for overhead sun at 40°N latitude at 500 m altitude with an ozone column of 350 DU.

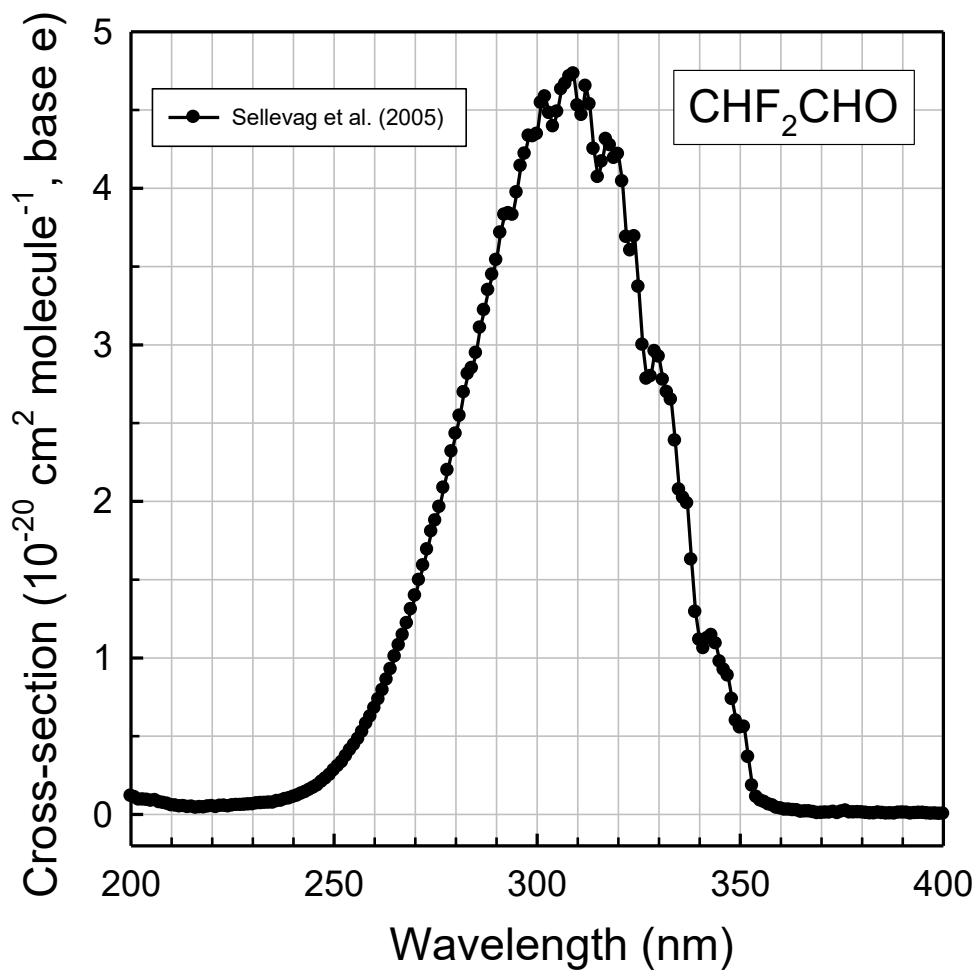
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References

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Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, in press, 2010.

Sellevåg, S. R., Stenstrom, Y., Helgaker, T., and Nielsen, C. J.: J. Phys. Chem. A, 109, 3652, 2005.



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5811 **PF6: C₂F₅CHO + hv**
 5812 Last evaluated: June 2025; last change in preferred values: June 2014.
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5814 **C₂F₅CHO + hv → products**

5815 **Primary photochemical transitions**
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| Reaction | | |
|--|--|-----|
| C ₂ F ₅ CHO + hv | → C ₂ F ₅ + HCO | (1) |
| | → C ₂ F ₅ CO + H | (2) |
| | → C ₂ F ₅ H + CO | (3) |

5819 **Absorption cross-section data**
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 5821

| Wavelength range/nm | References | Comments |
|---------------------|-------------------------------|----------|
| 265-334 | Borkowski and Ausloss, (1962) | (a) |
| 319 | Pritchard et al. (1962) | (b) |
| 185-500 | Hashikawa et al. (2004) | (c) |
| 230-400 | Chiappero et al. (2006) | (d) |
| 230-376 | Antiñolo et al. (2014) | (e) |

5822 **Quantum yield data**
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| Measurement | Wavelength/nm | References | Comments |
|----------------------------|---------------|-------------------------|----------|
| Φ ₁ = 0.38±0.08 | 254 | Chiappero et al. (2006) | (f) |
| Φ ₃ = 0.43±0.08 | 254 | Chiappero et al. (2006) | (f) |
| Φ ₁ = 0.30±0.02 | 308 | Antiñolo et al. (2014) | (g) |

5825 **Comments**
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- 5828 (a) Absolute absorption cross-sections at 334, 313, 280.4, and 265.2 nm were measured using a UV spectrometer with
 5829 the sample at 305 K.
 5830 (b) An absolute absorption cross-section at 319 nm was measured using a UV spectrometer
 5831 (c) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of
 5832 C₂F₅CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were
 5833 given at 1 nm intervals.
 5834 (d) Absolute absorption cross-sections were measured using a diode array spectrometer at 269-297 K. The UV spectrum
 5835 of C₂F₅CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were
 5836 given at 1 nm intervals. There was no discernible effect of temperature over the range 248-297 K on the UV
 5837 spectrum, however for reasons which are unclear the UV spectra at 308 K and 323 K reported in the supporting
 5838 information are approximately 10% more intense than that at 298 K.
 5839 (e) Absolute absorption cross-sections were measured using a 0.5-m spectrograph with a coupled-charge device (CCD)
 5840 detector with 0.5–9.8 Torr of C₂F₅CHO. The temperature range specified in the text of the paper is 269 – 298 K, but

5841 data in the supporting information cover the range 269 – 323 K. The spectrum had a peak at 308.13 ± 0.76 nm.
 5842 Values of σ were given at 1 nm intervals.
 5843 (f) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5
 5844 mbar of C_2F_5CHO and 20-70 mbar of NO (added as radical scavenger) were irradiated using a low-pressure ozone
 5845 free Hg lamp and the rate of loss of C_2F_5CHO was compared to that of perfluoroacetic anhydride in similar
 5846 experiments. The formation of C_2F_5NO and C_2F_5H were measured by IR spectroscopy and used to derive quantum
 5847 yields for processes (1) and (3).
 5848 (g) Photolysis quantum yield measured using acetaldehyde as a chemical actinometer with pulsed laser photolysis of
 5849 C_2F_5CHO at 308 nm in 75 – 760 Torr (100 – 1013 mbar) of air at 298 K. The quantum yield at $\lambda=308$ nm was
 5850 pressure dependent, ranging from (0.94 ± 0.28) at 75 Torr to (0.30 ± 0.02) at 760 Torr. The pressure dependence is
 5851 characterized by the Stern–Volmer expression with a Stern–Volmer constant of $(1.22 \pm 0.52) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$.
 5852 FTIR spectroscopy was used to identify the products following photolysis of C_2F_5CHO in air. From the observed
 5853 product distribution, it was concluded that photolysis at 308 nm occurs predominantly, if not exclusively, via channel
 5854 (1) to give $C_2F_5 + HCO$ radicals.
 5855

5856 Preferred Values

5857 Absorption cross-sections of C_2F_5CHO at 298 K

| λ/nm | $10^{20} \sigma/\text{cm}^2$ | λ/nm | $10^{20} \sigma/\text{cm}^2$ |
|---------------------|------------------------------|---------------------|------------------------------|
| 230 | 0.15 | 305 | 5.64 |
| 235 | 0.15 | 310 | 5.78 |
| 240 | 0.21 | 315 | 5.38 |
| 245 | 0.29 | 320 | 5.36 |
| 250 | 0.40 | 325 | 4.47 |
| 255 | 0.60 | 330 | 3.64 |
| 260 | 0.89 | 335 | 3.16 |
| 265 | 1.26 | 340 | 2.01 |
| 270 | 1.75 | 345 | 1.37 |
| 275 | 2.34 | 350 | 1.05 |
| 280 | 2.99 | 355 | 0.44 |
| 285 | 3.68 | 360 | 0.14 |
| 290 | 4.36 | 365 | 0.08 |
| 295 | 4.97 | 370 | 0.07 |
| 300 | 5.41 | 375 | 0.05 |

5860 Quantum Yields of C_2F_5CHO

5861 $\Phi_1 = 0.38$ at 254 nm
 5862 $\Phi_3 = 0.43$ at 254 nm
 5863 $\Phi_1 = 0.30$ at 308 nm

5864 Reliability

5865 $\Delta\Phi_1 = \pm 0.10$
 5866 $\Delta\Phi_3 = \pm 0.10$

5867 Comments on Preferred Values

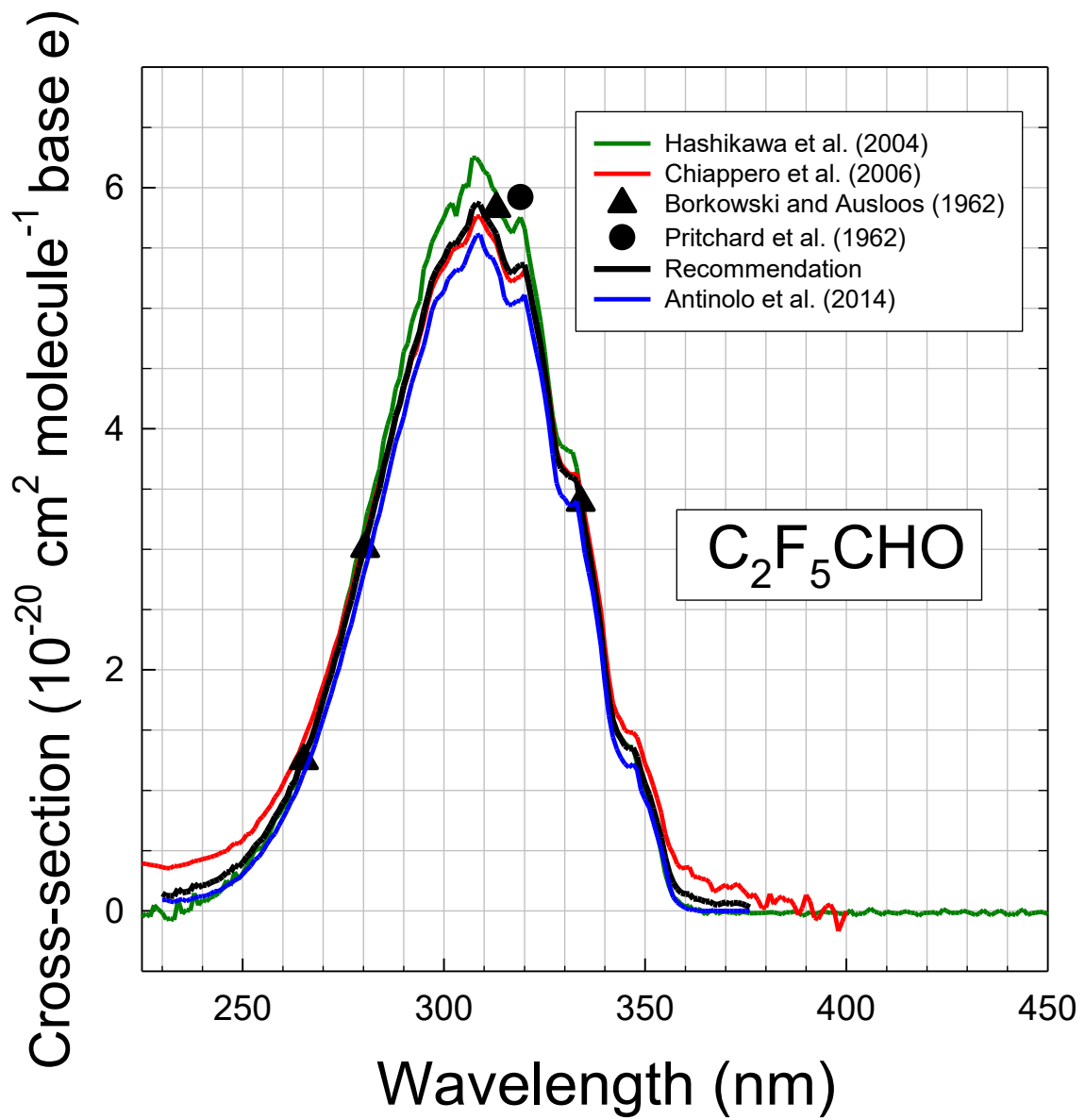
5871 There is good agreement in the absorption cross sections measured at 298 K by Borkowski and
 5872 Ausloss, (1962), Pritchard et al. (1962), Hashikawa et al. (2004), Chiappero et al. (2006), and
 5873 Antiñolo et al. (2014). Taking an average of the results from Hashikawa et al. (2004), Chiappero et
 5874 al. (2006), and Antiñolo et al. (2014) gives the recommended values. The quantum yield
 5875 measurements at 254 nm reported by Chiappero et al. (2006) and at 308 nm by Antiñolo et al. (2014)
 5876 are recommended.
 5877

5878 Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.14
 5879 for C_2F_5CHO (based upon a linear interpolation of the measured quantum yields for CF_3CHO and
 5880 C_4F_9CHO) at 308 nm and estimated the photolysis lifetimes in the summer and winter solstices and
 5881 the fall and spring equinoxes. Chiappero et al. (2006) averaged the lifetimes to give annual averages

5882 of approximately 0.9 days at 11 km altitude and 2.5 days at 0 km. Antiñolo et al. (2014) assumed an
5883 exponential decrease of photolysis quantum yield with increasing wavelength from 0.81 at 254 nm
5884 (Chiappero et al., 2006) to 0.30 at 308 nm (Antiñolo et al., 2014) and lower for wavelengths longer
5885 than 308 nm. Antiñolo et al. (2014) estimated a photolysis lifetime of 3.5 hours at an altitude of 3.5
5886 km and solar zenith angle of 16° (local noon in Ciudad Real, Spain, in summer). Photolysis is the
5887 dominant atmospheric fate of C₂F₅CHO.
5888

5889 **References**

- 5890
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5893 Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington T. J.: *The Mechanisms of*
5894 *Atmospheric Oxidation of the Oxygenates*, Oxford University Press, New York, NY, 2010.
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5896 Wallington, T. J., Waterland, R. L., and Buck, R. C.: *J. Phys. Chem. A*, 110, 11944, 2006.
5897 Hashikawa, Y., Kawasaki, M., Waterland, R. L., Sulbaek Andersen, M. P., Nielsen, O. J., Hurley, M.
5898 D.; Ball, J. C.; and Wallington, T. J.: *J. Fluorine Chem.*, 125, 1925, 2004.
5899 Pritchard, G. O., Miller, G. H., and Foote, J. K.: *Can. J. Chem.*, 40, 1830, 1962.
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5907 **PF7: *n*-C₃F₇CHO + hv**
 5908 Last evaluated: June 2025; last change in preferred values: June 2010.
 5909

5910 ***n*-C₃F₇CHO + hv → products**

5911 **Primary photochemical transitions**
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| Reaction | | |
|--|--|-----|
| C ₂ F ₅ CHO + hv | → C ₂ F ₅ + HCO | (1) |
| | → C ₂ F ₅ CO + H | (2) |
| | → C ₂ F ₅ H + CO | (3) |

5915 **Absorption cross-section data**
 5916
 5917

| Wavelength range/nm | References | Comments |
|---------------------|------------------------------|----------|
| 265-334 | Borkowski and Ausloss (1962) | (a) |
| 185-500 | Hashikawa et al. (2004) | (b) |
| 230-400 | Chiappero et al. (2006) | (c) |
| 230-390 | Solignac et al. (2007) | (d) |

5918 **Quantum yield data**
 5919
 5920

| Measurement | Wavelength/nm | References | Comments |
|----------------------------------|---------------|-------------------------|----------|
| Φ ₁ = 0.31±0.07 | 254 | Chiappero et al. (2006) | (e) |
| Φ ₃ = 0.32±0.07 | 254 | Chiappero et al. (2006) | (e) |
| Φ _{Total} = 0.023±0.012 | 290-400 | Solignac et al. (2007) | (f) |

5921 **Comments**
 5922
 5923

- 5924 (a) The absolute absorption cross-section at 319 nm was measured using a UV spectrometer.
 5925 (b) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of *n*-C₃F₇CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.
 5926
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 5928 (c) Absolute absorption cross-sections were measured using a diode array spectrometer at 248-297 K. The UV spectrum of *n*-C₃F₇CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals. There was no discernible effect of temperature on the UV spectrum.
 5929
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 5931 (d) Absolute absorption cross-sections were measured with a resolution of 0.1 nm using a diode array spectrometer for 1.4–8.0 Torr (1.9-10.7 mbar) samples of *n*-C₃F₇CHO at 298 K. The UV spectrum of *n*-C₃F₇CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.
 5932
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 5934 (e) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of *n*-C₃F₇CHO and 20-70 mbar of NO (added as radical scavenger) were irradiated using a low-pressure ozone free Hg lamp and the rate of loss of *n*-C₃F₇CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of *n*-C₃F₇NO and *n*-C₃F₇H were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).
 5935
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 5939 (f) Photolysis of *n*-C₃F₇CHO in one atmosphere of pure dry air in the presence of an OH radical tracer (di-*n*-butyl ether)

5940 in the ~200 m³ EUPHORE chamber facility under natural sunlight conditions. The measured rate of photolysis of *n*-
 5941 C₃F₇CHO was (1.3 ± 0.6) × 10⁻⁵ s⁻¹. When compared to the maximum photolysis rate calculated using unit quantum
 5942 yield for photodissociation across the atmospheric range of absorption of *n*-C₃F₇CHO a quantum yield of 0.023 ±
 5943 0.012 was derived.

5944 **Preferred Values**

5945 **Absorption cross-sections of *n*-C₃F₇CHO at 298 K**

5946

| λ/nm | 10 ²⁰ σ/cm ² | λ/nm | 10 ²⁰ σ/cm ² |
|------|------------------------------------|------|------------------------------------|
| 200 | 0.34 | 305 | 7.97 |
| 205 | 0.12 | 310 | 8.29 |
| 210 | 0.21 | 315 | 7.77 |
| 215 | 0.16 | 320 | 7.83 |
| 220 | 0.11 | 325 | 6.40 |
| 225 | 0.14 | 330 | 5.32 |
| 230 | 0.09 | 335 | 4.74 |
| 235 | 0.10 | 340 | 2.91 |
| 240 | 0.15 | 345 | 1.98 |
| 245 | 0.24 | 350 | 1.52 |
| 250 | 0.41 | 355 | 0.65 |
| 255 | 0.68 | 360 | 0.13 |
| 260 | 1.03 | 365 | 0.04 |
| 265 | 1.54 | 370 | 0.00 |
| 270 | 2.18 | | |
| 275 | 2.97 | | |
| 280 | 3.87 | | |
| 285 | 4.87 | | |
| 290 | 5.83 | | |
| 295 | 6.79 | | |
| 300 | 7.45 | | |

5949 **Quantum Yields of *n*-C₃F₇CHO**

5950
 5951
 5952 Φ₁ = 0.31 at 254 nm
 5953 Φ₃ = 0.32 at 254 nm

5954
 5955 *Reliability*

5956 ΔΦ₁ = ± 0.10
 5957 ΔΦ₃ = ± 0.10

5958
 5959 *Comments on Preferred Values*

5960 There is good agreement between the absorption cross sections measured by Borkowski and Ausloss,
 5961 (1962), Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007). Taking an
 5962 average of the results from Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al.
 5963 (2007) gives the recommended values. The quantum yield measurements at 254 nm reported by
 5964 Chiappero et al. (2006) and at 290-400 nm are recommended.

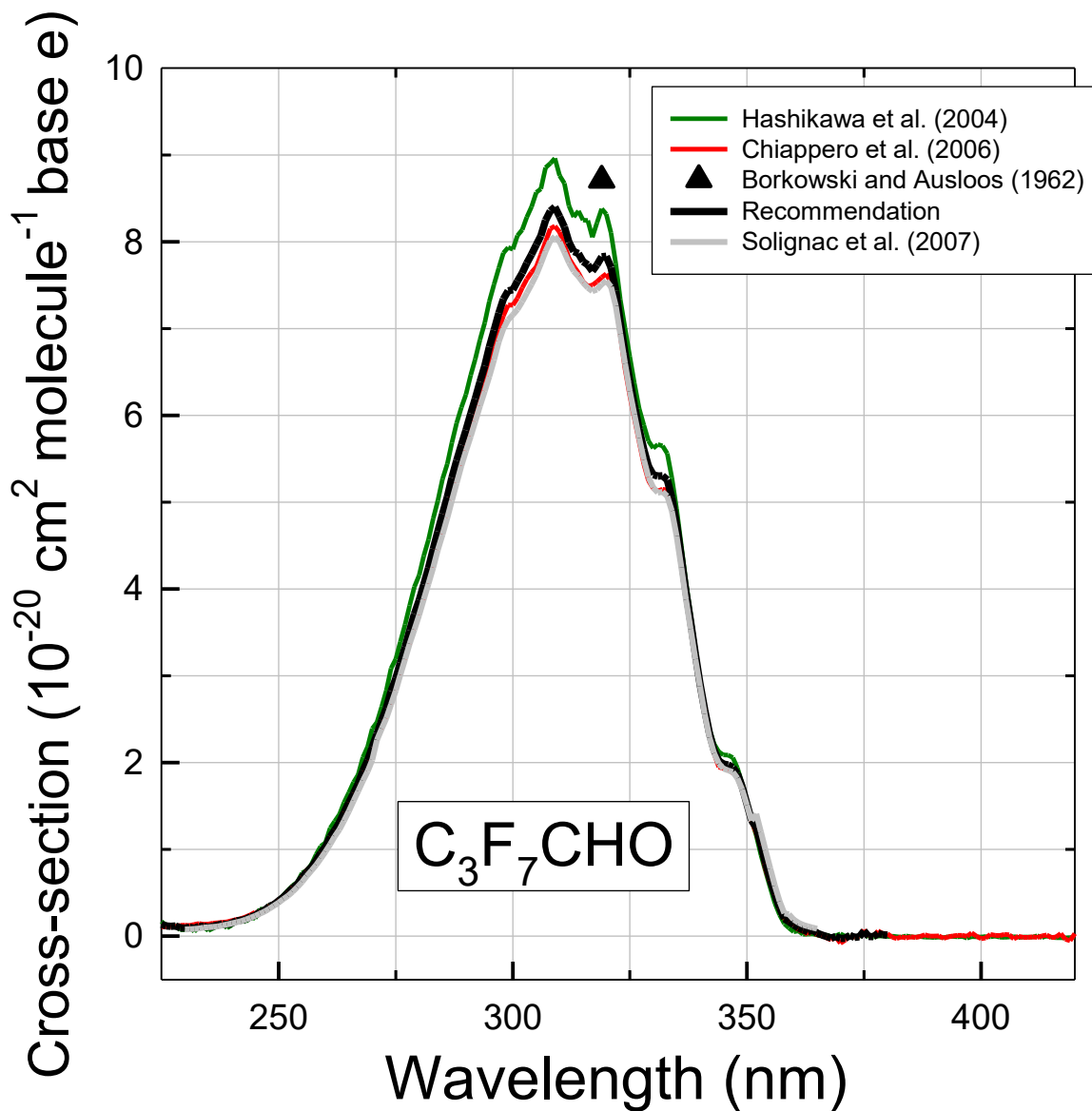
5965 Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.11
 5966 for *n*-C₃F₇CHO (based upon a linear interpolation of the measured quantum yields for CF₃CHO and
 5967 C₄F₉CHO) at 308 nm and estimated the photolysis lifetimes in the summer and winter solstices and
 5968 the fall and spring equinoxes. Chiappero et al. (2006) averaged the lifetimes to give annual averages
 5969 of approximately 0.75 days at 11 km altitude and 2 days at 0 km. Use of the recommended quantum
 5970 yield of 0.023 in place of the value of 0.11 used by Chiappero et al. (2006) will increase the photolytic
 5971 lifetimes by approximately a factor of 5. In either case, photolysis is the dominant atmospheric fate of
 5972 *n*-C₃F₇CHO.

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5988 **PF8: *n*-C₄F₉CHO + hv**
5989 Last evaluated: June 2025; last change in preferred values: June 2010.
5990

5991
5992 ***n*-C₄F₉CHO + hv → products**

5993
5994 **Primary photochemical transitions**

5995

| Reaction | |
|--|-----|
| <i>n</i> -C ₄ F ₉ CHO + hv → <i>n</i> -C ₄ F ₉ + HCO | (1) |
| → <i>n</i> -C ₄ F ₉ CO + H | (2) |
| → <i>n</i> -C ₄ F ₉ H + CO | (3) |

5996
5997 **Absorption cross-section data**

5998

| Wavelength range/nm | References | Comments |
|---------------------|-------------------------|----------|
| 185-500 | Hashikawa et al. (2004) | (a) |
| 230-400 | Chiappero et al. (2006) | (b) |
| 230-390 | Solignac et al. (2007) | (c) |

5999
6000 **Quantum yield data**

6001

| Measurement | Wavelength/nm | References | Comments |
|----------------------------------|---------------|-------------------------|----------|
| Φ ₁ = 0.31±0.08 | 254 | Chiappero et al. (2006) | (d) |
| Φ ₃ = 0.29±0.07 | 254 | Chiappero et al. (2006) | (d) |
| Φ _{Total} = 0.08±0.02 | 308 | Chiappero et al. (2006) | (e) |
| Φ _{Total} = 0.029±0.015 | 290-390 | Solignac et al. (2007) | (f) |

6002
6003
6004 **Comments**

- 6005 (a) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of *n*-
6006 C₄F₉CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were
6007 given at 1 nm intervals.
- 6008 (b) Absolute absorption cross-sections were measured using a diode array spectrometer at 248-297 K. The UV spectrum
6009 of *n*-C₄F₉CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ
6010 were given at 1 nm intervals. There was no discernable effect of temperature over the range studied on the UV
6011 spectrum.
- 6012 (c) Absolute absorption cross-sections were measured with a resolution of 0.1 nm using a diode array spectrometer for
6013 1.5–11.0 Torr (2.0-14.7 mbar) samples of *n*-C₄F₉CHO at 298 K. The UV spectrum of *n*-C₄F₉CHO shows a broad
6014 band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.
- 6015 (d) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5
6016 mbar of *n*-C₄F₉CHO and 20-70 mbar of NO (added as radical scavenger) were irradiated using a low-pressure ozone
6017 free Hg lamp and the rate of loss of *n*-C₄F₉CHO was compared to that of perfluoroacetic anhydride in similar
6018 experiments. The formation of *n*-C₄F₉NO and *n*-C₄F₉H were measured by IR spectroscopy and used to derive
6019 quantum yields for processes (1) and (3).
- 6020 (e) Photolysis quantum yield measured using CH₃CHO as a chemical actinometer. Mixtures of *n*-C₄F₉CHO and NO
6021 (added as radical scavenger) in 700 Torr of N₂ diluent were irradiated using the 308 nm output of an excimer

6022 laser. The rate of loss of $n\text{-C}_4\text{F}_9\text{CHO}$ was compared to that of CH_3CHO in back-to-back experiments. There was
 6023 no evidence for the formation of $n\text{-C}_4\text{F}_9\text{H}$ (<5% yield) following the irradiation of $n\text{-C}_4\text{F}_9\text{CHO-NO-N}_2$ mixtures
 6024 showing that process (3) is not significant.
 6025 (f) Photolysis of $n\text{-C}_4\text{F}_9\text{CHO}$ in one atmosphere of pure dry air in the presence of an OH radical tracer (di- n -butyl ether)
 6026 in the $\sim 200\text{ m}^3$ EUPHORE chamber facility under natural sunlight conditions. The measured rate of photolysis of $n\text{-C}_4\text{F}_9\text{CHO}$
 6027 was $(1.9 \pm 0.8) \times 10^{-5}\text{ s}^{-1}$. When compared to the maximum photolysis rate calculated using unit quantum
 6028 yield for photodissociation across the atmospheric range of absorption of $n\text{-C}_4\text{F}_9\text{CHO}$ a quantum yield of $0.029 \pm$
 6029 0.015 was derived.

6030 Preferred Values

6031 Absorption cross-sections of $n\text{-C}_4\text{F}_9\text{CHO}$ at 298 K

| λ/nm | $10^{20}\ \sigma/\text{cm}^2$ | λ/nm | $10^{20}\ \sigma/\text{cm}^2$ |
|---------------------|-------------------------------|---------------------|-------------------------------|
| 240 | 0.05 | 325 | 7.59 |
| 245 | 0.19 | 330 | 6.31 |
| 250 | 0.40 | 335 | 5.61 |
| 255 | 0.73 | 340 | 3.46 |
| 260 | 1.19 | 345 | 2.33 |
| 265 | 1.79 | 350 | 1.80 |
| 270 | 2.53 | 355 | 0.69 |
| 275 | 3.47 | 360 | 0.08 |
| 280 | 4.52 | 365 | 0.00 |
| 285 | 5.69 | 370 | -0.08 |
| 290 | 6.84 | 375 | -0.05 |
| 295 | 8.01 | 380 | -0.04 |
| 300 | 8.82 | 385 | -0.05 |
| 305 | 9.44 | 390 | -0.05 |
| 310 | 9.87 | 395 | -0.03 |
| 315 | 9.22 | 400 | -0.04 |
| 320 | 9.32 | | |

6035 Quantum Yields of $n\text{-C}_4\text{F}_9\text{CHO}$

6036 $\Phi_1 = 0.31$ at 254 nm
 6037 $\Phi_3 = 0.29$ at 254 nm
 6038 $\Phi_{\text{Total}} = 0.08$ at 308 nm
 6039 $\Phi_{\text{Total}} = 0.03$ at 290-390 nm

6040 Reliability

6041 $\Delta\Phi_1 = \pm 0.10$ at 254 nm
 6042 $\Delta\Phi_3 = \pm 0.10$ at 254 nm
 6043 $\Delta\Phi_{\text{Total}} = \pm 0.04$ at 308 nm
 6044 $\Delta\Phi_{\text{Total}} = 0.02$ at 290-390 nm

6045 Comments on Preferred Values

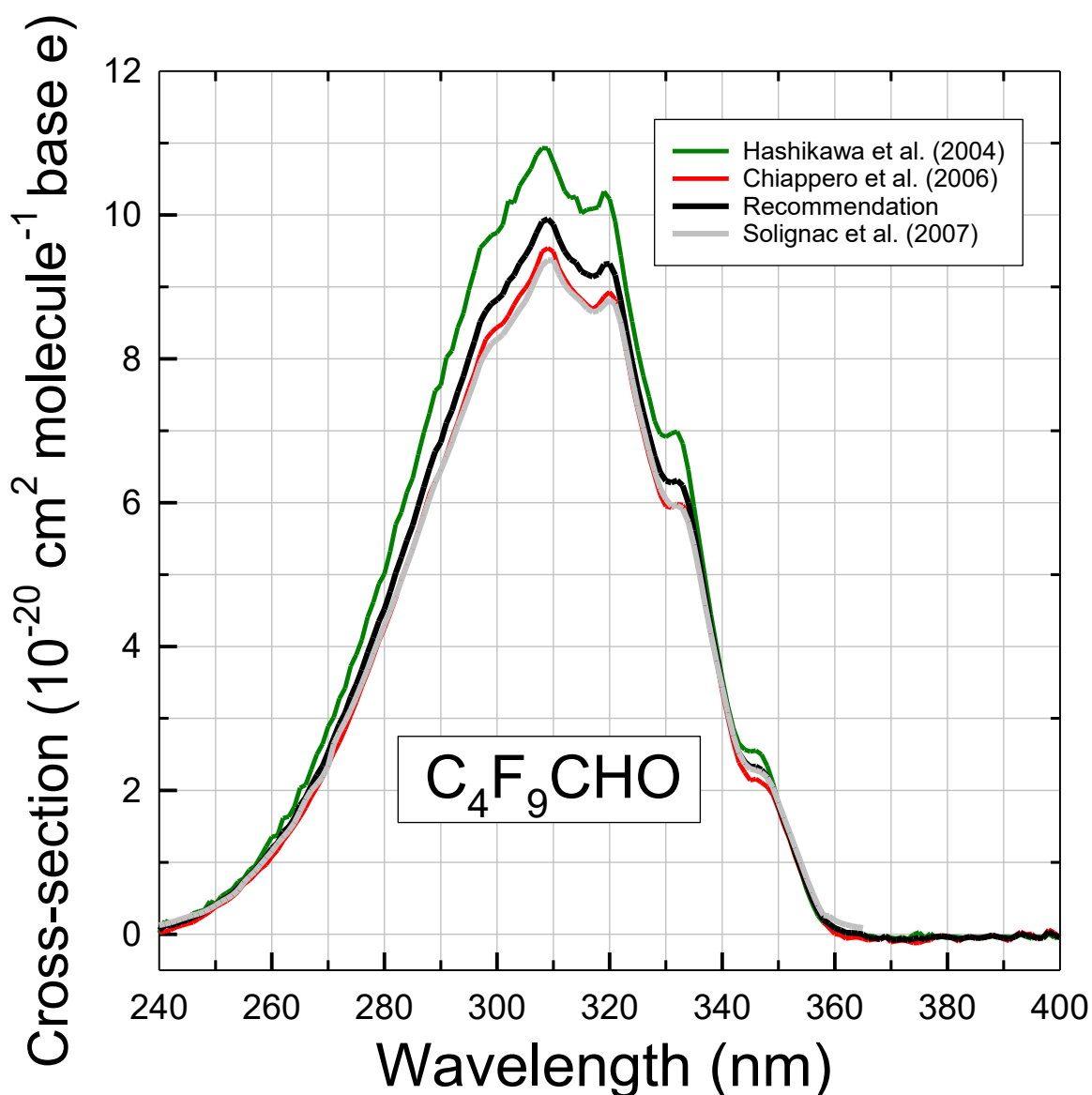
6046 There is agreement between the absorption cross sections measured by Hashikawa et al. (2004),
 6047 Chiappero et al. (2006), and Solignac et al. (2007). Taking an average of the results from Hashikawa
 6048 et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007) gives the recommended values. The
 6049 quantum yield measurements at 254 and 308 nm reported by Chiappero et al. (2006) are
 6050 recommended.

6051 Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.08
 6052 for $n\text{-C}_4\text{F}_9\text{CHO}$ (based on their data measured at 308 nm) and estimated the photolysis lifetimes in the
 6053 summer and winter solstices and the fall and spring equinoxes. Chiappero et al. (2006) averaged the

6058 lifetimes to give annual averages of approximately 0.75 days at 11 km altitude and 2 days at 0 km.
6059 Use of the recommended quantum yield of 0.03 in place of the value of 0.11 used by Chiappero et al.
6060 (2006) will increase the photolytic lifetimes by approximately a factor of 4. In either case, photolysis
6061 is the dominant atmospheric fate of *n*-C₄F₉CHO.
6062

6063 References

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6065 Chiappero M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C.,
6066 Wallington, T. J., Waterland, R. L., and Buck, R. C.: J. Phys. Chem. A, 110, 11944, 2006.
6067 Hashikawa, Y., Kawasaki, M., Waterland, R. L., Sulbaek Andersen, M. P., Nielsen, O. J., Hurley, M.
6068 D.; Ball, J. C., and Wallington, T. J.: J. Fluorine Chem., 125, 1925, 2004.
6069 Solignac, G., Mellouki, A., Le Bras, G., Yujing, M., and Sidebottom, H.: Phys. Chem. Chem. Phys., 9,
6070 4200, 2007.
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6074 **PF9: CF₃CH₂CHO + hv**
 6075 Last evaluated: June 2025; last change in preferred values: June 2014.
 6076

6077
 6078 **CF₃CH₂CHO + hv → products**

6079 **Primary photochemical transitions**
 6080
 6081

| Reaction |
|--|
| CF ₃ CH ₂ CHO + hv → CF ₃ CH ₂ + HCO (1) |
| → CF ₃ CH ₂ CO + H (2) |
| → CF ₃ CH ₃ + CO (3) |

6082
 6083 **Absorption cross-section data**
 6084

| Wavelength range/nm | References | Comments |
|---------------------|-------------------------|----------|
| 185-500 | Sellekvåg et al. (2004) | (a) |
| 230-400 | Chiappero et al. (2006) | (b) |
| 230-350 | Antiñolo et al. (2011) | (c) |

6085
 6086 **Quantum yield data**
 6087

| Measurement | Wavelength/nm | References | Comments |
|----------------------------------|---------------|-------------------------|----------|
| Φ < 0.04 | 290-400 | Sellekvåg et al. (2004) | (d) |
| Φ ₁ = 0.38±0.09 | 254 | Chiappero et al. (2006) | (e) |
| Φ ₃ = 0.36±0.07 | 254 | Chiappero et al. (2006) | (e) |
| Φ _{Total} = 0.04±0.01 | 308 | Chiappero et al. (2006) | (f) |
| Φ _{Total} = 0.023±0.012 | 308 | Antiñolo et al. (2011) | (g) |

6088
 6089
 6090 **Comments**

- 6091 (a) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K.
 6092 The UV spectrum of CF₃CH₂CHO shows a broad band, centered at 295 nm and extending out to
 6093 approximately 350 nm. Values of σ were given at 1 nm intervals.
- 6094 (b) Absolute absorption cross-sections were measured using a diode array spectrometer at 248-297
 6095 K. The UV spectrum of CF₃CH₂CHO shows a broad band, centered at 295 nm and extending out
 6096 to approximately 350 nm. Values of σ were given at 1 nm intervals. There was no discernable
 6097 effect of temperature over the range studied on the UV spectrum.
- 6098 (c) Absolute absorption cross-sections were measured using a 0.5-m spectrograph with a coupled-
 6099 charge device (CCD) detector with 1.0–7.4 Torr of CF₃CH₂CHO at 269 – 323 K. The spectrum
 6100 had a peak at 290.82 ± 0.22 nm. Values of σ were given at 1 nm intervals.
- 6101 (d) Photolysis of CF₃CH₂CHO in pure dry air in the presence of an OH radical tracer (di-*n*-butyl
 6102 ether) in the ~200 m³ EUPHORE chamber facility under natural sunlight conditions. The

6103 measured first-order loss rate of CF₃CH₂CHO during a ~3 hr period around solar noon was 7.74
6104 x 10⁻⁶ s⁻¹, essentially identical to the leak rate obtained from monitoring the decay of SF₆. After
6105 correction for the leak rate and reaction with OH radicals, the observed first-order loss rate of
6106 CF₃CH₂CHO ascribed to photolysis during this ~3 hr period was $J_{\text{obs}} < 1.5 \times 10^{-6} \text{ s}^{-1}$. This was
6107 compared to the maximum photolysis rate of $3.4 \times 10^{-5} \text{ s}^{-1}$ calculated using a unit quantum yield
6108 for photodissociation, the measured actinic flux within the chamber, and the measured UV
6109 absorption spectrum. Taking a ratio of $J_{\text{obs}}/J_{\text{calc}} = 1.5 \times 10^{-6}/3.4 \times 10^{-5}$ gives an upper limit for the
6110 photolysis quantum yield of <0.04. Solignac et al. (2007) reported quantum yields $J_{\text{obs}}/J_{\text{calc}} =$
6111 (0.023 ± 0.012) , (0.029 ± 0.015) , and (0.046 ± 0.028) for the photodissociation of C₃F₇CHO,
6112 C₄F₉CHO and CF₃(CF₂)₅CHO in the EUPHORE chamber across the atmospheric range of
6113 absorption of the aldehydes. Solignac et al. (2007) suggested that the photolytic loss of
6114 CF₃CH₂CHO may have been underestimated by Sellevåg et al. (2004).

6115 (e) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer.
6116 Mixtures of 0.5-5.5 mbar of CF₃CH₂CHO and 20-70 mbar of NO (added as radical scavenger)
6117 were irradiated using a low pressure Hg lamp and the rate of loss of CF₃CH₂CHO was compared
6118 to that of perfluoroacetic anhydride in similar experiments. The formation of CF₃CH₂NO and
6119 CF₃CH₃ were measured by IR spectroscopy and used to derive quantum yields for processes (1)
6120 and (3).

6121 (f) Photolysis quantum yield measured using CH₃CHO as a chemical actinometer. Mixtures of *n*-
6122 CF₃CH₂CHO and NO (added as radical scavenger) in 700 Torr of N₂ diluent were irradiated
6123 using the 308 nm output of an excimer laser. The rate of loss of CF₃CH₂CHO was compared to
6124 that of CH₃CHO in back-to-back experiments. There was no evidence for the formation of
6125 CF₃CH₃ (<5% yield) following the irradiation of CF₃CH₂CHO –NO–N₂ mixtures showing that
6126 process (3) is not significant.

6127 (g) Photolysis quantum yield measured using NO₂ and acetaldehyde as chemical actinometers with
6128 pulsed laser photolysis of CF₃CH₂CHO at 308 nm in 25.4 – 760 Torr (34 – 1013 mbar) of air at
6129 298 K. The quantum yield at λ=308 nm was pressure dependent, ranging from (0.142 ± 0.098) at
6130 75 Torr to (0.023 ± 0.006) at 760 Torr. The pressure dependence is characterized by the
6131 Stern–Volmer expression with a Stern-Volmer constant of $(3.25 \pm 0.48) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$.
6132 FTIR spectroscopy was used to identify the products following photolysis of CF₃CH₂CHO in air.
6133 From the observed product distribution it was concluded that photolysis at 308 nm occurs
6134 predominantly via channel (1) to give CF₃CH₂ + HCO radicals.

6135 Preferred Values

6136 Absorption cross-sections of CF₃CH₂CHO at 298 K

| λ/nm | 10 ²⁰ σ/cm ² | λ/nm | 10 ²⁰ σ/cm ² |
|------|------------------------------------|------|------------------------------------|
| 225 | 0.26 | 300 | 3.59 |
| 230 | 0.27 | 305 | 3.02 |
| 235 | 0.35 | 310 | 3.00 |
| 240 | 0.49 | 315 | 2.12 |
| 245 | 0.68 | 320 | 1.82 |
| 250 | 0.95 | 325 | 1.44 |
| 255 | 1.34 | 330 | 0.69 |
| 260 | 1.78 | 335 | 0.67 |
| 265 | 2.14 | 340 | 0.24 |
| 270 | 2.74 | 345 | 0.07 |
| 275 | 3.01 | 350 | 0.04 |
| 280 | 3.39 | 355 | 0.04 |
| 285 | 3.59 | 360 | 0.01 |
| 290 | 3.52 | 365 | 0.00 |
| 295 | 3.59 | 370 | |

6140

Quantum Yields of CF₃CH₂CHO

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$\Phi_1 = 0.38$ at 254 nm

$\Phi_3 = 0.36$ at 254 nm

$\Phi_{\text{Total}} = 0.03$ at 308 nm

Reliability

$\Delta\Phi_1 = \pm 0.10$ at 254 nm

$\Delta\Phi_3 = \pm 0.10$ at 254 nm

$\Delta\Phi_{\text{Total}} = \pm 0.01$ at 308 nm

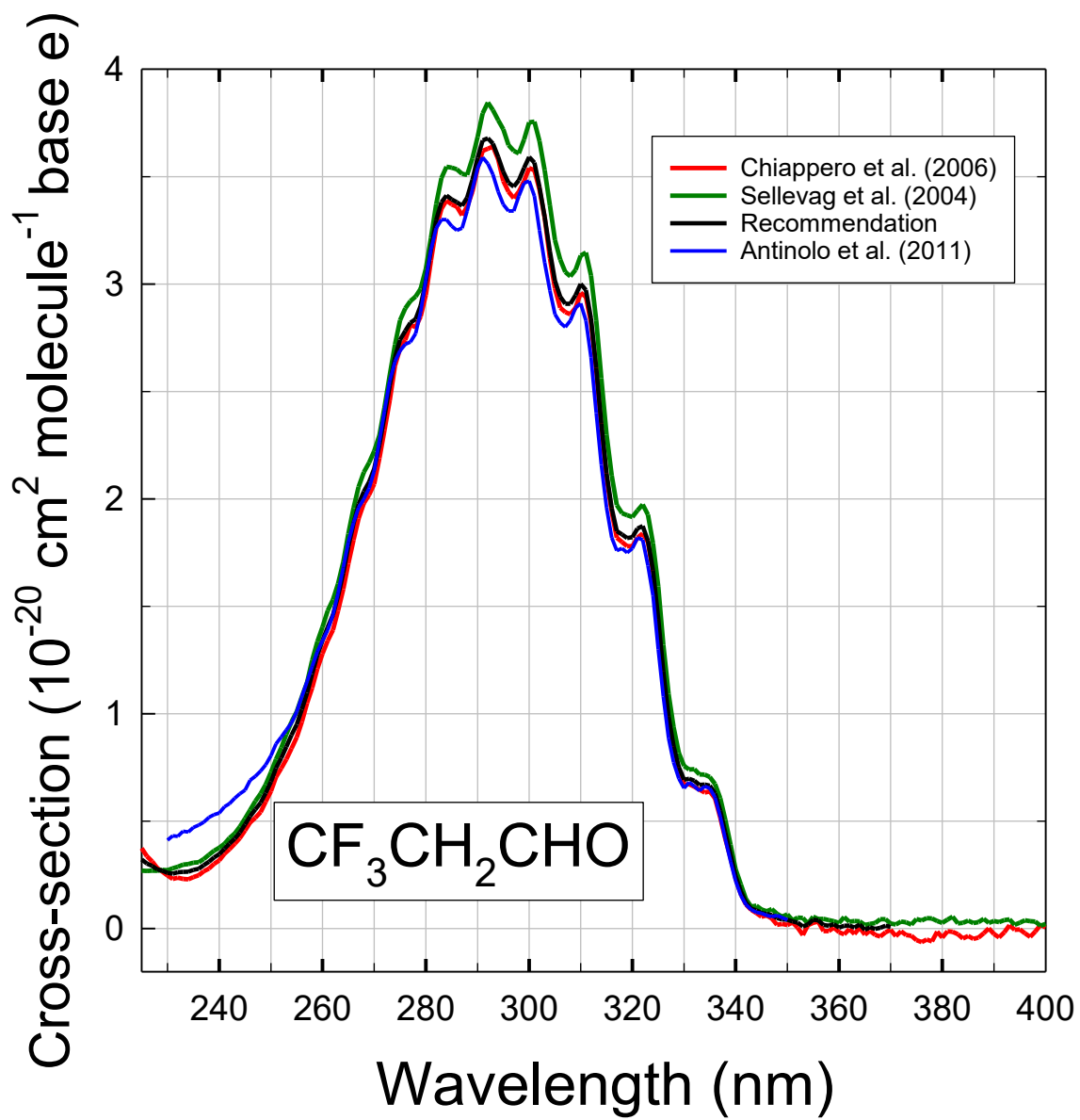
Comments on Preferred Values

There is good agreement between the absorption cross sections measured by Sellevåg et al. (2004), Chiappero et al. (2006), and Antiñolo et al. (2011) for $\lambda > 260$ nm. At wavelengths below 260 nm the absorption cross sections reported by Antiñolo et al. (2011) are substantially larger than those reported by Sellevåg et al. (2004) and Chiappero et al. (2006). Taking an average of the results from Sellevåg et al. (2004), Chiappero et al. (2006), and those from Antiñolo et al. (2011) for $\lambda > 260$ nm gives the recommended values. The quantum yield measurements at 254 nm reported by Chiappero et al. (2006) are recommended. The recommended quantum yield at 308 nm is an average of the results from Chiappero et al. (2006) and Antiñolo et al. (2011). The product identified by Antiñolo et al. (2011) indicate that photolysis at 308 nm proceeds predominately, if not exclusively, via channel (1).

Chiappero et al. (2006) assumed a wavelength and pressure independent photolysis quantum yield of 0.04 for CF₃CH₂CHO (based on their data measured at 308 nm) and estimated the photolysis lifetimes in the summer and winter solstices and the fall and spring equinoxes. Chiappero et al. (2006) averaged the lifetimes to give annual averages of approximately 11 days at 11 km altitude and 40 days at 0 km. Antiñolo et al. (2011) assumed a wavelength independent but pressure dependent photolysis quantum yield (based on their data measured at 308 nm) for CF₃CH₂CHO and reported photolysis rates of $2.83 \times 10^{-6} \text{ s}^{-1}$ and $1.0 \times 10^{-5} \text{ s}^{-1}$ at 0 km and 10 km altitude, respectively, for Ciudad Real, Spain (the solar zenith angle was unspecified, but it probably reflects noon in summer). The results from Chiappero et al. (2006) and Antiñolo et al. (2011) indicate that photolysis is an important atmospheric fate of CF₃CH₂CHO.

References

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6193 **PF10: *n*-C₆F₁₃CH₂CHO + hv**
6194 Last evaluated: June 2025; last change in preferred values: June 2010.
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6196
6197 ***n*-C₆F₁₃CH₂CHO + hv → products**

6198
6199 **Primary photochemical transitions**
6200

| Reaction | |
|--|-----|
| <i>n</i> -C ₆ F ₁₃ CH ₂ CHO + hv → <i>n</i> -C ₆ F ₁₃ CH ₂ + HCO | (1) |
| → <i>n</i> -C ₆ F ₁₃ CH ₂ CO + H | (2) |
| → <i>n</i> -C ₆ F ₁₃ CH ₃ + CO | (3) |

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6202 **Absorption cross-section data**
6203

| Wavelength range/nm | References | Comments |
|---------------------|-------------------------|----------|
| 230-400 | Chiappero et al. (2006) | (a) |
| 230-350 | Solignac et al. (2007) | (b) |

6204
6205 **Quantum yield data**
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| Measurement | Wavelength/nm | References | Comments |
|--------------------------------|---------------|-------------------------|----------|
| Φ _{Total} = 0.55±0.09 | 254 | Chiappero et al. (2006) | (c) |

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6209 **Comments**

- 6210
- 6211 (a) The UV absorption spectrum was recorded using a single sample of 1.5 mbar of *n*-
6212 C₆F₁₃CH₂CHO in a 10 cm quartz cell using a diode array spectrometer at 297 K. The reported
6213 UV spectrum of *n*-C₆F₁₃CH₂CHO shows a broad band centered at 295 nm and extending out to
6214 approximately 350 nm. Values of σ were given at 1 nm intervals.
- 6215 (b) Absolute absorption cross-sections were measured with a resolution of 0.1 nm using a diode
6216 array spectrometer for 0.6–2.0 Torr (0.8–2.7 mbar) samples of *n*-C₆F₁₃CH₂CHO in a 100 cm cell
6217 at 298 K. The UV spectrum of *n*-C₆F₁₃CH₂CHO shows a broad band centered at 285 nm and
6218 extending out to approximately 350 nm. Values of σ were given at 1 nm intervals.
- 6219 (c) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer.
6220 Mixtures of *n*-C₆F₁₃CH₂CHO and NO (added as radical scavenger) were irradiated using a low
6221 pressure Hg lamp and the rate of loss of *n*-C₆F₁₃CH₂CHO was compared to that of
6222 perfluoroacetic anhydride in similar experiments.

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6229**Preferred Values****Absorption cross-sections of *n*-C₆F₁₃CH₂CHO at 298 K**

| λ/nm | $10^{20} \sigma/\text{cm}^2$ | λ/nm | $10^{20} \sigma/\text{cm}^2$ |
|---------------------|------------------------------|---------------------|------------------------------|
| 230 | 1.27 | 290 | 5.20 |
| 235 | 1.25 | 295 | 4.79 |
| 240 | 1.59 | 300 | 4.66 |
| 245 | 1.97 | 305 | 3.90 |
| 250 | 2.43 | 310 | 3.78 |
| 255 | 2.57 | 315 | 2.67 |
| 260 | 3.12 | 320 | 2.37 |
| 265 | 3.80 | 325 | 1.79 |
| 270 | 4.39 | 330 | 1.03 |
| 275 | 5.01 | 335 | 0.75 |
| 280 | 5.27 | 340 | 0.30 |
| 285 | 5.30 | 345 | 0.18 |
| | | 350 | 0.00 |

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6231
6232**Quantum Yields of *n*-C₆F₁₃CH₂CHO**

$$\Phi_{\text{Total}} = 0.55 \text{ at } 254 \text{ nm}$$

6234

6235 *Reliability*

$$\Delta\Phi_{\text{Total}} = \pm 0.10 \text{ at } 254 \text{ nm}$$

6237

6238 *Comments on Preferred Values*

6239 The absorption spectrum reported by Chiappero et al. (2006) is based upon the measured
6240 absorption by one sample using a 10 cm pathlength and is considered less reliable than that measured
6241 by Solignac et al. (2007) using a range of sample partial pressures in a 100 cm absorption cell. The
6242 absorption spectrum from Solignac et al. (2007) is recommended.

6243 Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.01
6244 for *n*-C₆F₁₃CH₂CHO (based on an assumption that the quantum yield depends inversely on the
6245 molecular size of the fluorinated aldehyde and that the quantum yield for photolysis of *n*-
6246 C₆F₁₃CH₂CHO is approximately one quarter less than that for CF₃CH₂CHO measured at 308 nm) and
6247 estimated the photolysis lifetimes in the summer and winter solstices and the fall and spring
6248 equinoxes. Chiappero et al. (2006) averaged the lifetimes to give annual averages of approximately 8
6249 days at 11 km altitude and 20 days at 0 km. Measurements of the photolysis quantum yield at
6250 atmospherically relevant wavelengths are needed to better understand the role of photolysis in the
6251 atmospheric chemistry of this molecule.

6252

6253

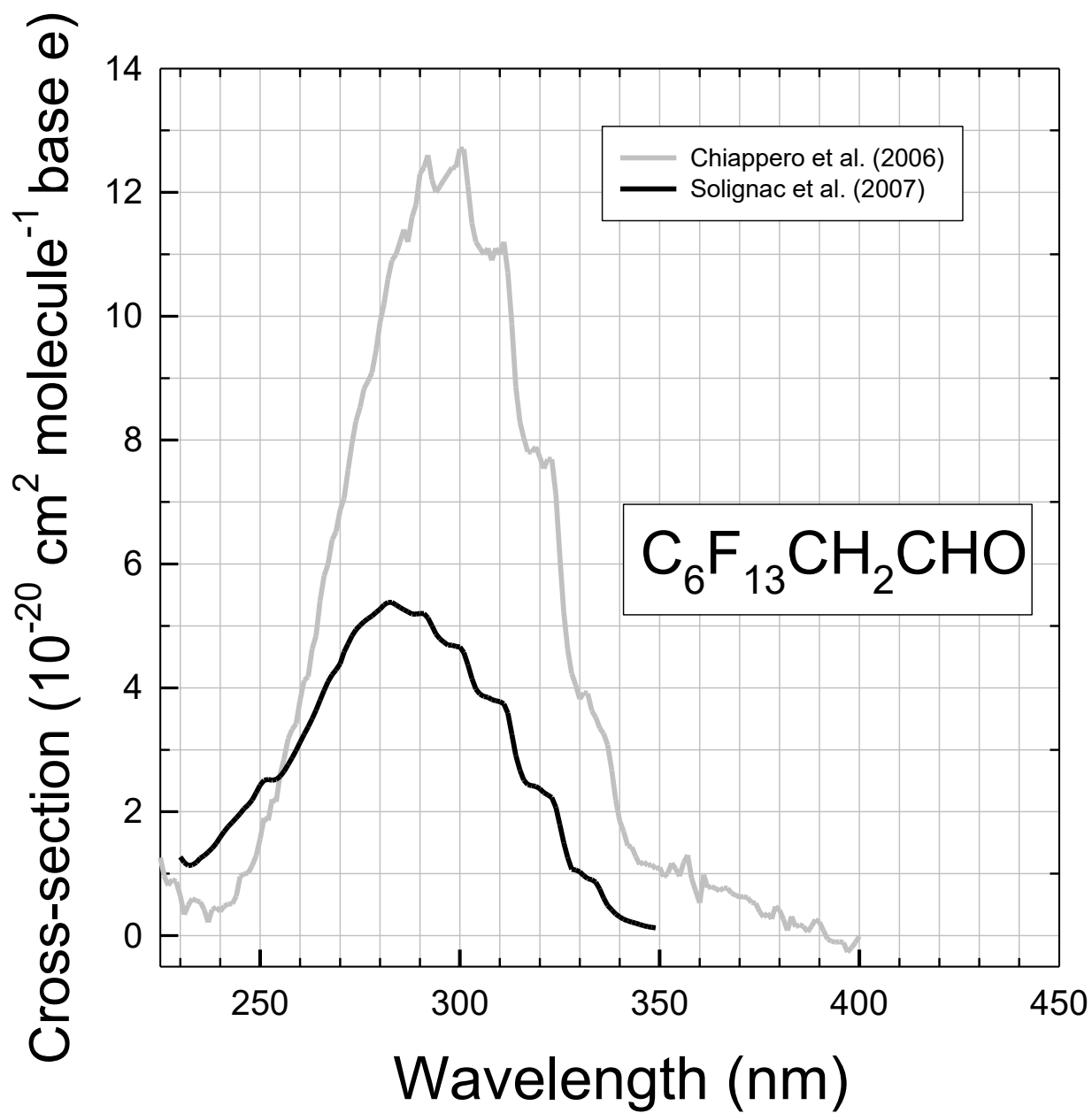
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