Supplement of Atmos. Chem. Phys., 26, 6579–6592, 2026
https://doi.org/10.5194/acp-26-6579-2026-supplement

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

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Halogenated alkanes

Halogenated alkenes

Halogenated alcohols

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Halogenated vinyl ethers

Peroxy radicals

oFOx72: HO + $CF_3CH_2CH_3$ (HFC-263fb)

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

$$\mathbf{HO + CF_3CH_2CH_3\ (HFC\text{-}263fb) \rightarrow CF_3CH_2CH_2 + H_2O \quad (1)}$$
$$\mathbf{\rightarrow CF_3CHCH_3 + H_2O \quad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4.00 \pm 0.13) \times 10^{-14}$	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		

Comments

(a) HO radicals produced via the H + NO_2 reaction. Experiments were performed in 1.1-2.0 Torr (1.5-2.7 mbar) of helium diluent.

(b) HO radicals produced by 248 nm photolysis of H_2O_2. Experiments were performed in 50-210 Torr (67-280 mbar) of helium diluent. The value given at 297 K is the average of the four determinations reported.

Preferred Values

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

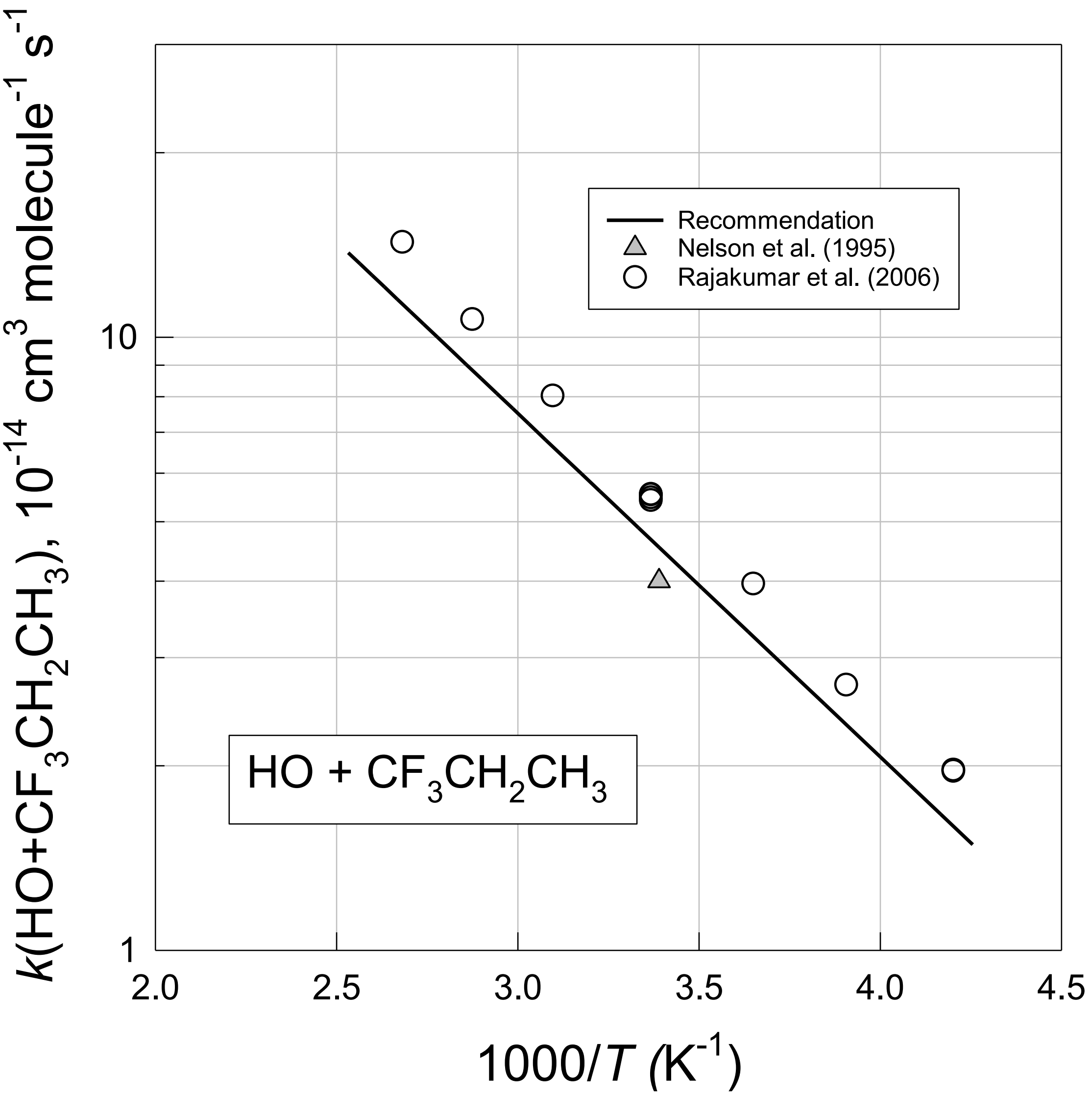
Comments on Preferred Values

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

References

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

Rajakumar, B., Portmann, R.W., Burkholder, J. B., and Ravishankara, A. R.: J. Phys. Chem. A, 110, 6724, 2006.


Recommendation
Nelson et al. (1995)
Rajakumar et al. (2006)
HO + CF3CH2CH3
k(HO+CF3CH2CH3), 10-14 cm3 molecule-1 s-1
1000/T (K-1)
1
10
2.0
2.5
3.0
3.5
4.0
4.5

oFOx73: HO + CF_3CHFCH_2F (HFC-245eb)

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

$$\text{HO} + CF_3CHFCH_2F\ (\text{HFC-245eb}) \rightarrow CF_3CHFCHF + H_2O \qquad (1)$$

$$\rightarrow CF_3CFCH_2F + H_2O \qquad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.37 \pm 0.03) \times 10^{-14}$	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		

Comments

(a) HO radicals produced via the H + NO_2 reaction. Experiments were performed in 1.4-2.9 Torr (1.9-3.9 mbar) of helium diluent.

(b) HO radicals produced by 248 nm photolysis of H_2O_2. Experiments were performed in 49-210 Torr (65-280 mbar) of helium diluent. The value given at 297 K is the average of the four determinations reported.

Preferred Values

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

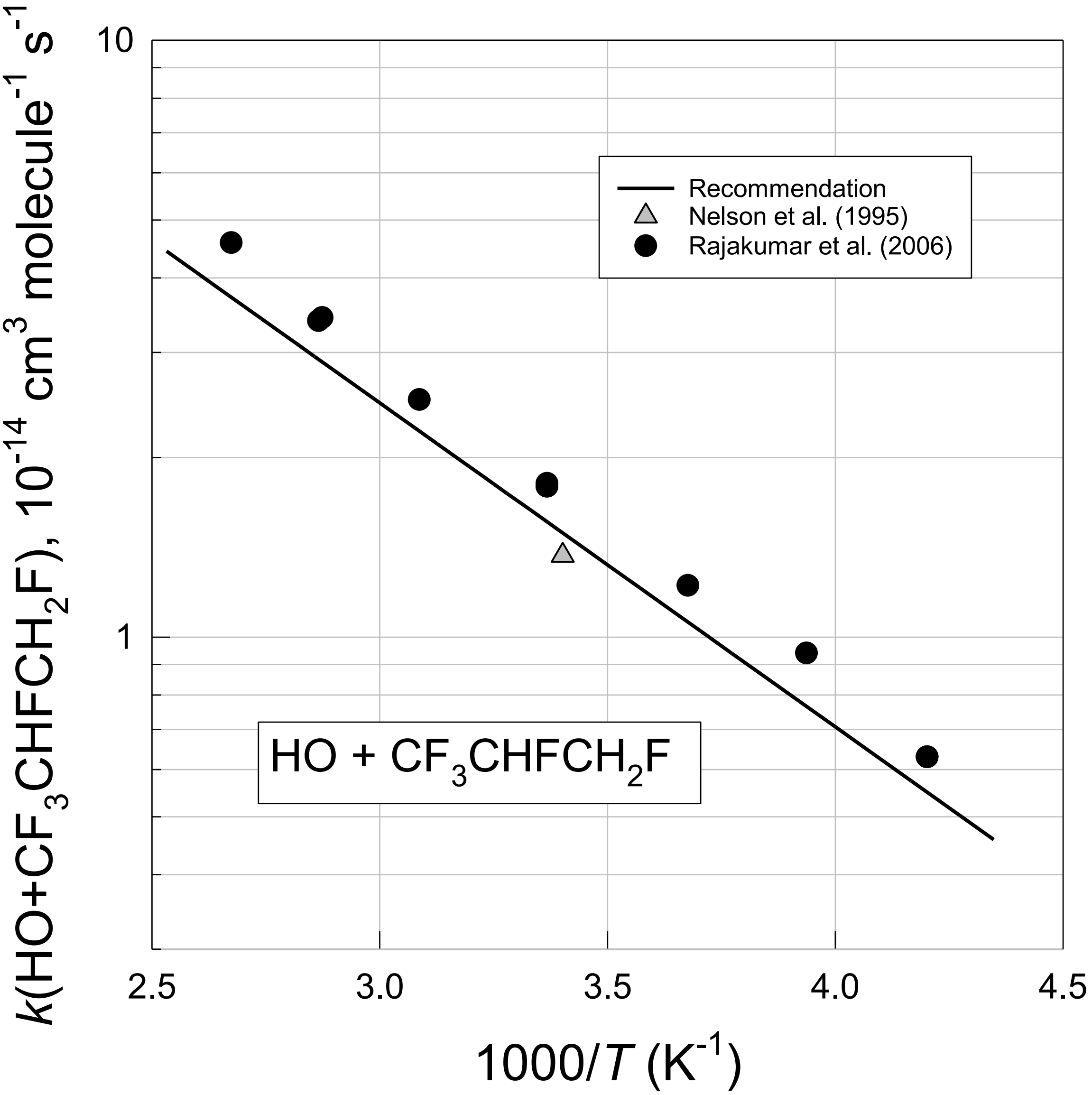
Comments on Preferred Values

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

References

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

Rajakumar, B., Portmann, R.W., Burkholder, J. B. and Ravishankara, A. R.: J. Phys. Chem. A, 110, 6724, 2006.


Recommendation
Nelson et al. (1995)
Rajakumar et al. (2006)
HO + CF_3CHFCH_2F
$k(HO+CF_3CHFCH_2F)$, 10^{-14} cm^3 $molecule^{-1}$ s^{-1}
10
1
2.5
3.0
3.5
4.0
4.5
1000/T (K^{-1})

oFOx74: HO + $CHF_2CHFCHF_2$ (HFC-245ea)

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

$$\text{HO} + CHF_2CHFCHF_2\ (\text{HFC-245ea}) \rightarrow CHF_2CHFCF_2 + H_2O \qquad (1)$$
$$\rightarrow CHF_2CFCHF_2 + H_2O \qquad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.52 \pm 0.15) \times 10^{-14}$	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		

Comments

(a) HO radicals were produced via the H + NO_2 reaction. Experiments were performed in 1.2-2.1 Torr (1.6-2.9 mbar) of helium diluent.

(b) HO radicals were produced by 248 nm photolysis of H_2O_2. Experiments were performed in 51-205 Torr (68-270 mbar) of helium diluent. The value given at 297 K is the average of the four determinations reported.

Preferred Values

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

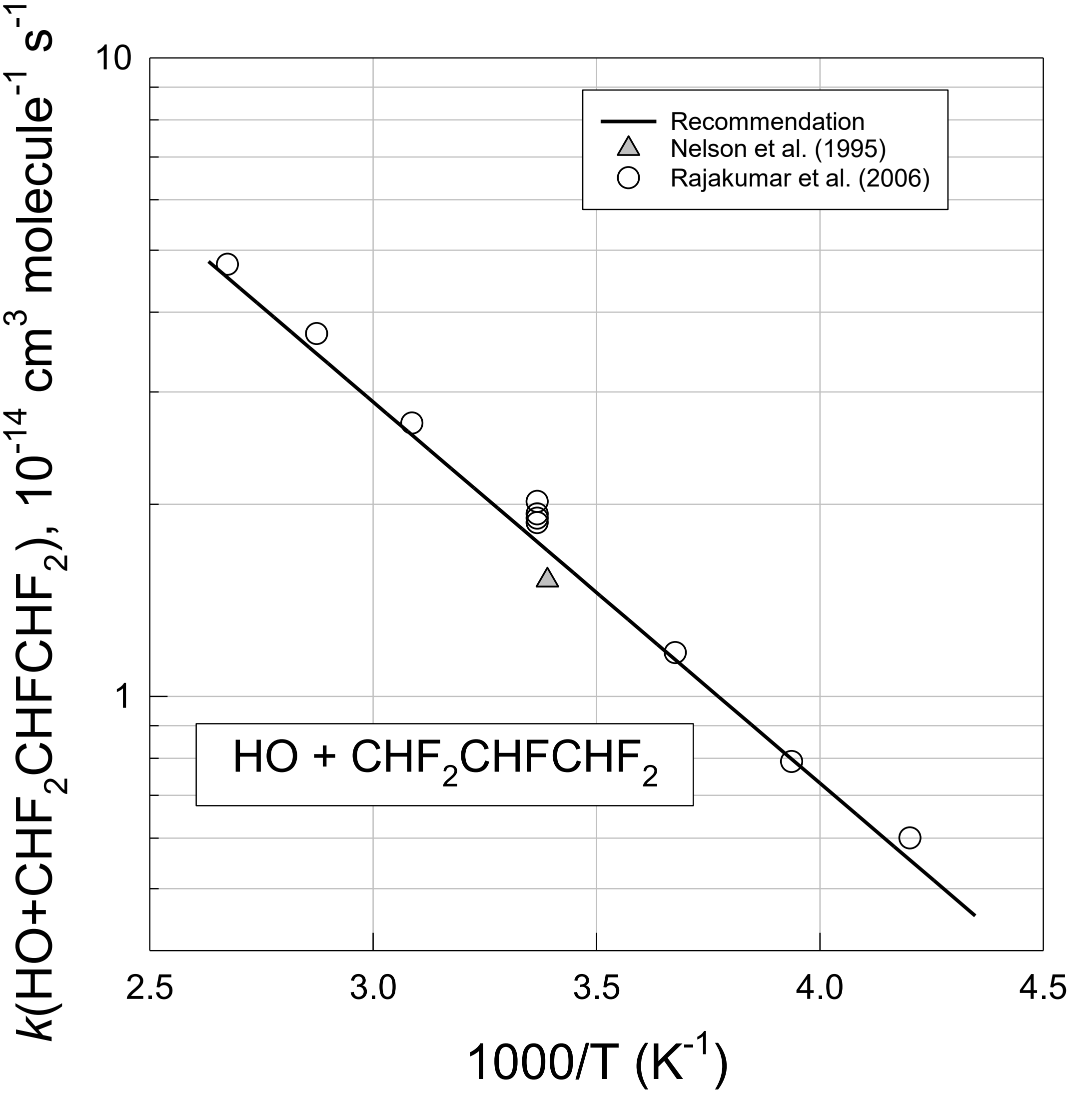
Comments on Preferred Values

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

References

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

Rajakumar, B., Portmann, R.W., Burkholder, J. B., and Ravishankara, A. R.: J. Phys. Chem. A, 110, 6724, 2006.


k(HO+CHF$_2$CHFCHF$_2$), 10^{-14} cm^3 molecule^{-1} s^{-1}
10
1
2.5
3.0
3.5
4.0
4.5
1000/T (K^{-1})
Recommendation
Nelson et al. (1995)
Rajakumar et al. (2006)
HO + CHF$_2$CHFCHF$_2$

oFOx75: HO + $CF_3CH_2CHF_2$ (HFC-245fa)

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

$$\begin{aligned} HO + CF_3CH_2CHF_2 \text{ (HFC-245fa)} &\rightarrow CF_3CH_2CF_2 + H_2O \quad (1) \\ &\rightarrow CF_3CHCHF_2 + H_2O \quad (2) \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.12 \pm 0.22) \times 10^{-15}$	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		

Comments

(a) HO radicals produced via the H + NO_2 reaction. Experiments were performed in 2.2-3.1 Torr (0.3-0.4 kPa) of helium diluent.

(b) HO radicals were produced from the photolysis of H_2O vapor using a xenon flash lamp. HO radicals were monitored by their resonance fluorescence near 308 nm using microwave discharge resonance lamp. Experiments were performed in 100 Torr (13.33 kPa) of argon diluent.

Preferred Values

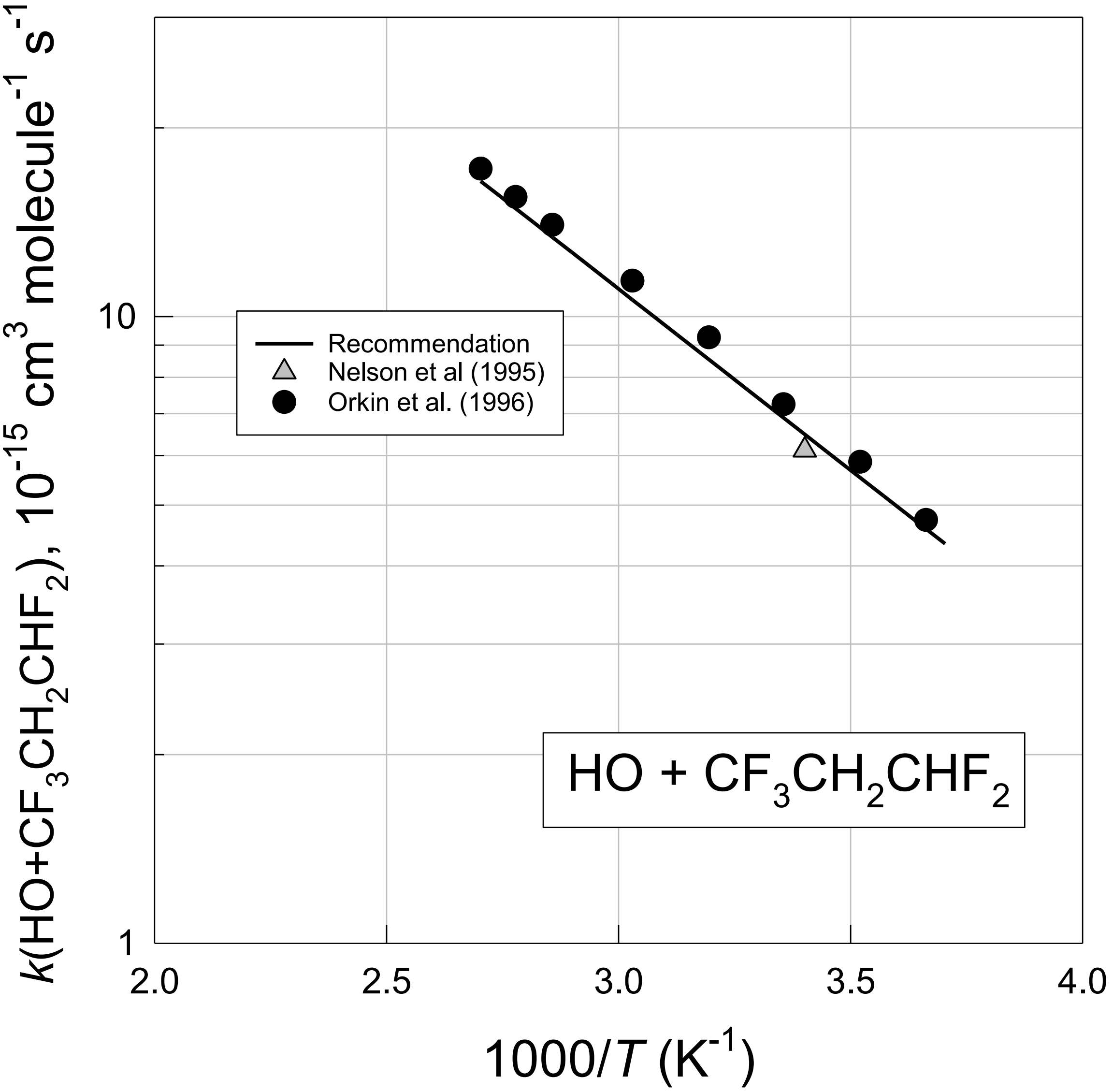
Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	6.9×10^{-15}	298
k/cm^3 molecule^{-1} s^{-1}	$6.0 \times 10^{-13} \exp(-1331/T)$	270-370
Reliability		
$\Delta \log k$	± 0.12	298
$\Delta E/R$	± 300	270-370

Comments on Preferred Values

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

References

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


$k(HO+CF_3CH_2CHF_2)$, 10^{-15} cm^3 molecule^{-1} s^{-1}
10
1
2.0
2.5
3.0
3.5
4.0
1000/T (K^{-1})
Recommendation
Nelson et al (1995)
Orkin et al. (1996)
$HO + CF_3CH_2CHF_2$

oFOx76: HO + $CF_3CH_2CF_2CH_3$ (HFC-365mfc)

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

$$HO + CF_3CH_2CF_2CH_3\ \text{(HFC-365mfc)} \rightarrow CF_3CHCF_2CH_3 + H_2O \quad (1)$$

$$\rightarrow CF_3CH_2CF_2CH_2 + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were produced by the 248 nm photolysis of H_2O_2. Experiments were performed in 100 Torr (133 mbar) of helium diluent.

(b) HO radicals were produced by the 254 nm photolysis of O_3 in the presence of H_2O. Experiments were performed in 1 bar of air diluent. Rate coefficient ratios were placed on an absolute basis using $k(OH+CH_3CCl_3) = 1.2 \times 10^{-12} \exp(-1440/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

Preferred Values

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

Comments on Preferred Values

The rate coefficient at 298 K reported in the absolute rate study by Mellouki et al. (1995) is approximately 60% greater than that measured in the relative rate study by Barry et al. (1997). A possible explanation for this discrepancy is the presence of reactive impurities in the sample used by Mellouki et al. (1995). This explanation should lead to an increasing discrepancy between the two studies with decreasing temperature, but no such trend is evident. The temperature dependencies of the rate coefficients reported in the two studies are in good agreement. There being no obvious reason to prefer either study, we prefer an average of the k(298K) values and temperature dependencies from the two studies with the pre-exponential A factor chosen for consistency with the k(298K). As discussed by Barry et al. (1997) and Inoue et al. (2008), the OH radical initiated atmospheric oxidation of $CF_3CH_2CF_2CH_3$ is expected to lead to the formation of $CF_3CH_2CF_2CHO$ as the main primary product. Oxidation of $CF_3CH_2CF_2CHO$ will generate CF_3CHO and COF_2 as secondary products. Oxidation of CF_3CHO will produce COF_2.

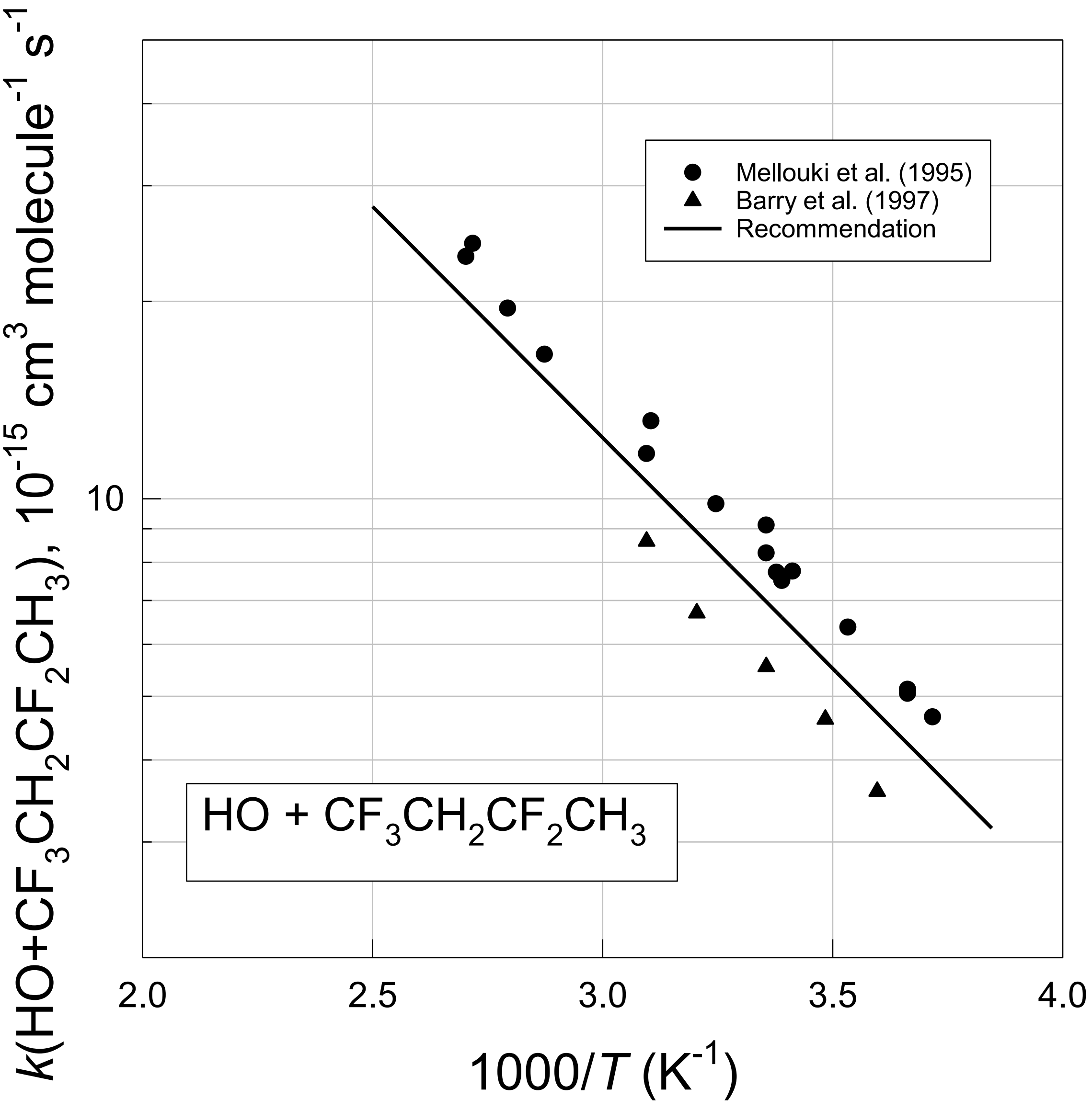
References

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.

Barry, J., Locke, G., Scollard, D., Sidebottom, H. W., Treacy, J., Clerbaux, C., Colin, R., and Franklin, J.: Int. J. Chem., 29, 607, 1997.

Inoue, Y., Kawasaki, M., Wallington, T. J., and Hurley M. D.: Chem. Phys. Lett., 462, 164, 2008.

Mellouki, A., Téton, S., and Le Bras, G.: Geophys. Res. Lett., 22, 389, 1995.



oFOx77: HO + $CF_3CH_2CH_2CF_3$ (HFC-356mff)

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

HO + $CF_3CH_2CH_2CF_3$ (HFC-356mff) → $CF_3CHCH_2CF_3$ + H_2O

Rate coefficient data (*k*)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.94 \times 10^{-12} \exp[-(1734 \pm 87)/T]$	260-365	Zhang et al. (1994)	FP-RF (a)
$(8.17 \pm 1.04) \times 10^{-15}$	296		
$(6.73 \pm 0.14) \times 10^{-15}$	296	Nelson et al. (1995)	DF-LIF (b)

Comments

(a) HO radicals were produced by photolysis of H_2O using a xenon flash lamp at λ >165 nm. Experiments were performed in 35 Torr (47 mbar) of argon diluent.

(b) HO radicals were produced by the reaction of H atoms with NO_2. Experiments were performed in 2.0 Torr (2.7 mbar) of helium diluent.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	7.8×10^{-15}	298
k/cm^3 molecule^{-1} s^{-1}	$2.6 \times 10^{-12} \exp(-1734/T)$	260-370
Reliability		
$\Delta \log k$	0.10	298
$\Delta E/R$	± 300	260-370

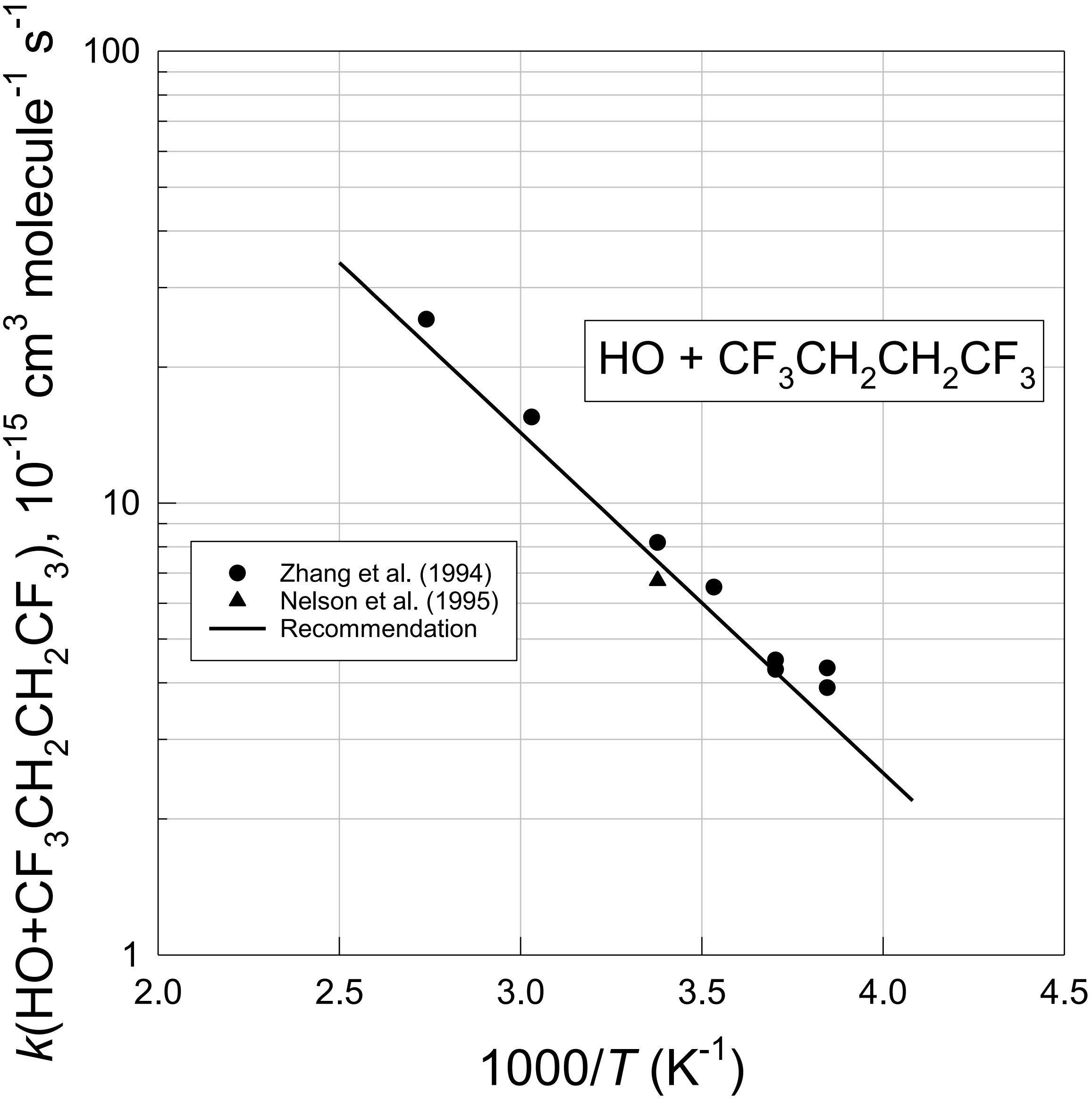
Comments on Preferred Values

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

References

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

Zhang, Z., Padmaja, S., Saini, R. D., Huie, R. E., and Kurylo, M. J.: J. Phys. Chem., 98, 4312, 1994.



HO + $CF_3CH_2CH_2CF_3$
$k(HO+CF_3CH_2CH_2CF_3)$, 10^{-15} cm^3 molecule^{-1} s^{-1}
100
10
1
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K^{-1})
● Zhang et al. (1994)
▲ Nelson et al. (1995)
Recommendation

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oFOx78: HO + $CF_3CF_2CH_2CH_2F$ (HFC-356mcf)

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

HO + $CF_3CF_2CH_2CH_2F$ (HFC-356mcf) → $CF_3CF_2CHCH_2F + H_2O$ (1)

→ $CF_3CF_2CH_2CHF + H_2O$ (2)

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

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

Comments

(a) HO radicals were produced by the reaction of H atoms with NO_2. Experiments were performed in 1.5-3.0 Torr (2-4 mbar) of helium diluent.

Preferred Values

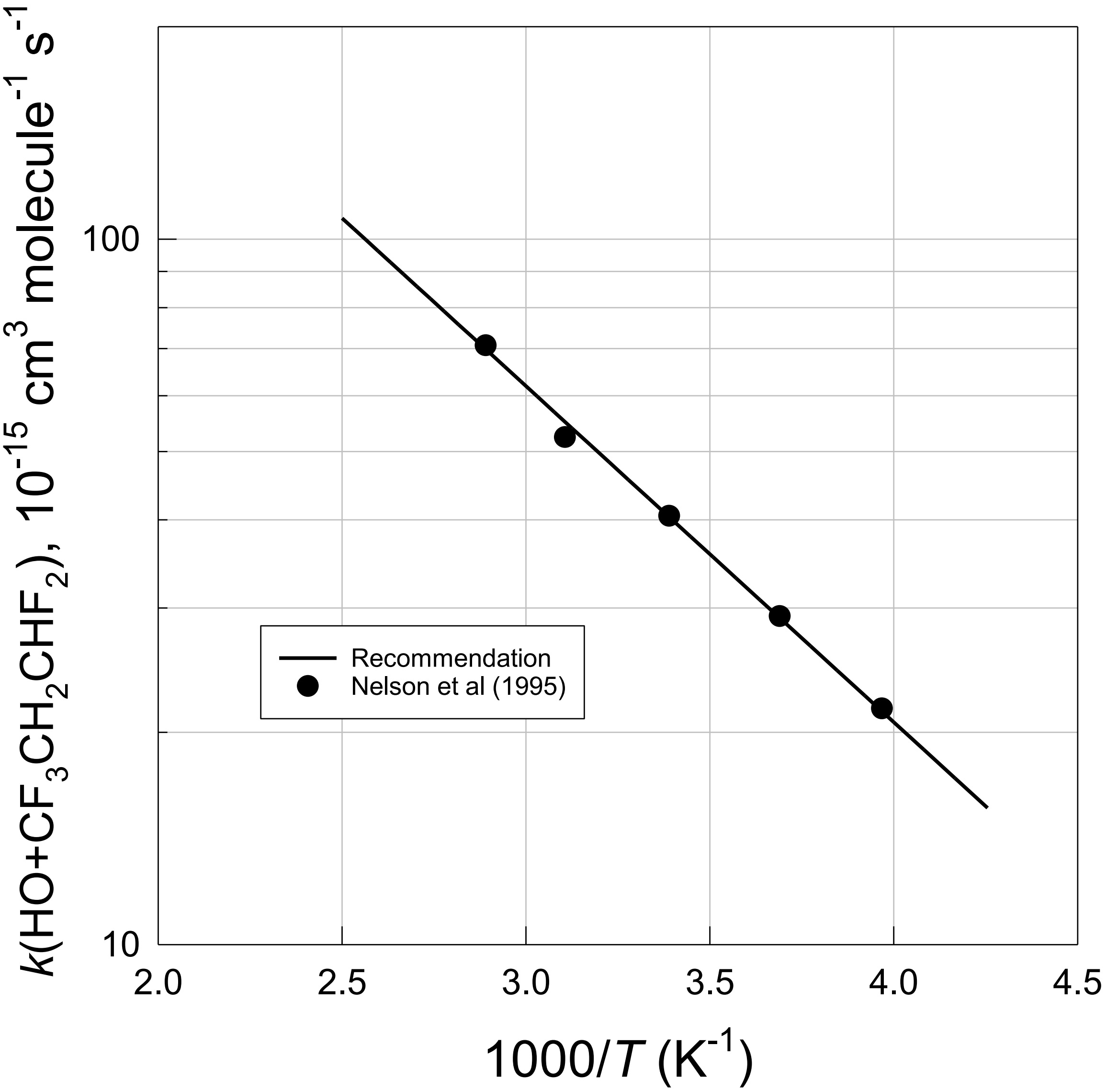
Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	4.2×10^{-14}	298
k/cm^3 molecule^{-1} s^{-1}	$1.7 \times 10^{-12} \exp(-1108/T)$	250-370
Reliability		
$\Delta \log k$	0.15	298
$\Delta E/R$	± 300	250-370

Comments on Preferred Values

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

References

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


k(HO+CF3CH2CHF2), 10-15 cm3 molecule-1 s-1
100
10
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K-1)
Recommendation
Nelson et al (1995)

oFOx79: HO + $CHF_2CF_2CF_2CHF_2$ (HFC-338pcc)

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

HO + $CHF_2CF_2CF_2CHF_2$ (HFC-338pcc) → $CF_2CF_2CF_2CHF_2$ + H_2O

Rate coefficient data (*k*)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$7.8 \times 10^{-13} \exp[-(1510\pm260)/T]$	245-419	Zhang et al. (1992)	FP-RF (a)
$(4.18 \pm 0.30) \times 10^{-15}$	296		
$7.71 \times 10^{-13} \exp[-(1550\pm60)/T]$	232-378	Schmoltner et al. (1993)	FP/PLP-LIF (b)
$(3.87 \pm 0.27) \times 10^{-15}$	297		

Comments

(a) HO radicals were produced by the flash photolysis (λ ≥ 165 nm) of H_2O in 35 Torr (47 mbar) of argon diluent.

(b) HO radicals were produced by the flash photolysis (185 nm ≥ λ ≥ 165 nm) of H_2O and pulsed laser photolysis (λ = 355 nm) of HONO.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	4.3×10^{-15}	298
	$7.82 \times 10^{-13} \exp(-1548/T)$	230-420
Reliability		
$\Delta \log k$	0.08	298
Δ E/R	± 200	230-420

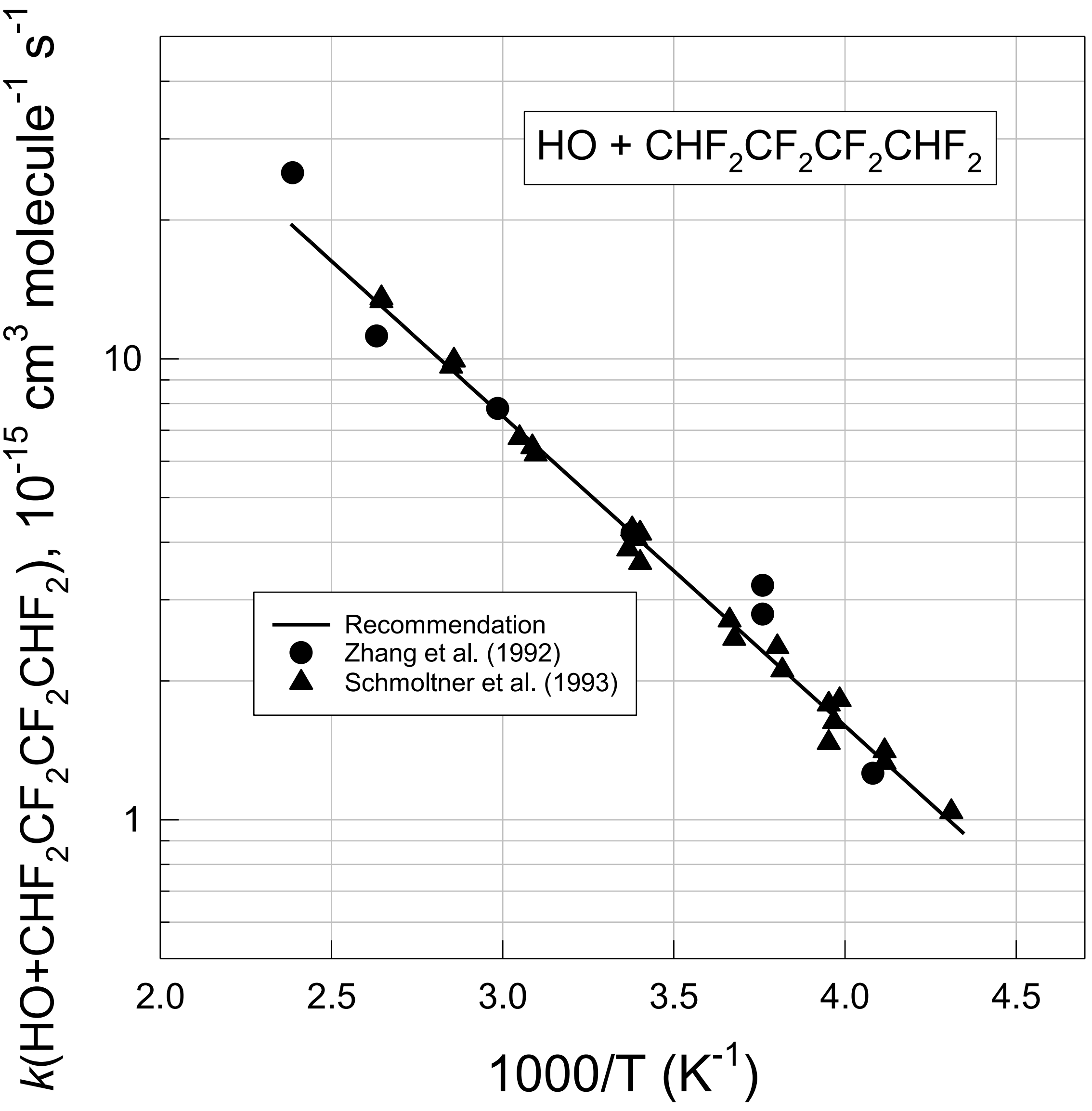
Comments on Preferred Values

The results of the two studies are in good agreement. A fit of the Arrhenius expression to the combined data set from the two studies gives $k(OH+CHF_2CF_2CF_2CHF_2) = 7.82 \times 10^{-13} \exp(-1548/T)$ cm^3 molecule^{-1} s^{-1}. This expression gives $k(OH+CHF_2CF_2CF_2CHF_2) = 4.34 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

References

Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E.: Chem. Phys. Lett., 200, 230, 1992.

Schmoltner, A. M., Talukdar, R. K., Warren, R. F., Mellouki, A., Goldfarb, L., Gierczak, T., McKeen, S. A., and Ravishankara, A. R.: J. Phys. Chem., 97, 8976, 1993.


HO + $CHF_2CF_2CF_2CHF_2$
Recommendation
Zhang et al. (1992)
Schmoltner et al. (1993)
$k(HO+CHF_2CF_2CF_2CHF_2)$, 10^{-15} cm^3 $molecule^{-1}$ s^{-1}
10
1
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K^{-1})

oFOx80: HO + $CF_3CH_2CF_2CH_2CF_3$ (HFC-458mfcf)

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

HO + $CF_3CH_2CF_2CH_2CF_3$ (HFC-458mfcf) → $CF_3CHCF_2CH_2CF_3$ + H_2O

Rate coefficient data (k)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.23 \times 10^{-12} \exp[-1833/T]$	278-354	Nelson et al. (1995)	FP-RF (a)
$(2.55 \pm 0.15) \times 10^{-15}$	298		

Comments

(a) HO radicals were produced by the reaction of H atoms with NO_2. Experiments were performed in 0.8-6.4 Torr (1.1-8.5 mbar) of helium diluent.

Preferred Values

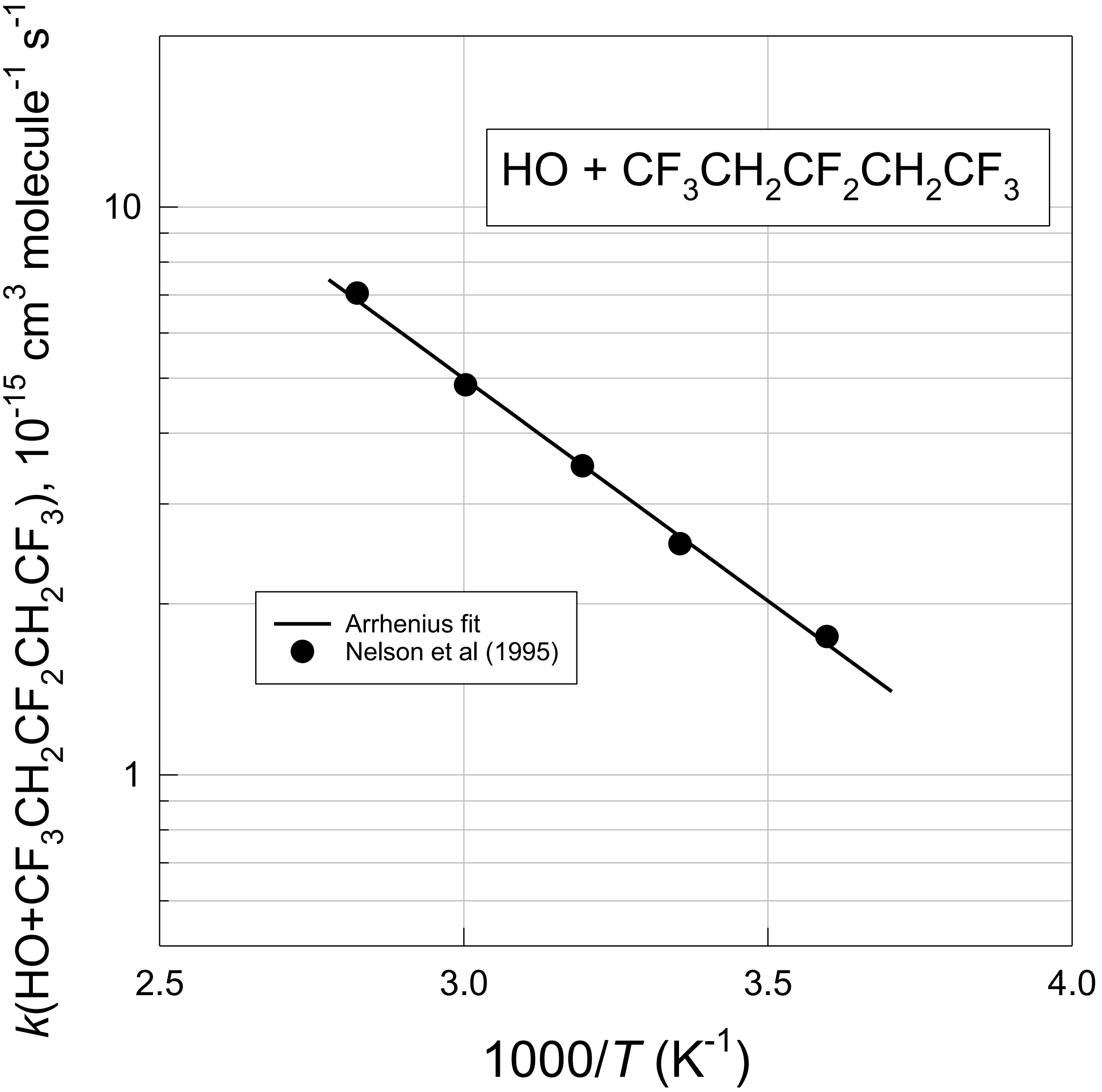
Parameter	**Value**	***T*/K**
k/cm^3 molecule^{-1} s^{-1}	2.6×10^{-15}	298
	$1.23 \times 10^{-12} \exp(-1833/T)$	270-360
Reliability		
$\Delta \log k$	0.15	298
$\Delta E/R$	± 300	270-360

Comments on Preferred Values

The Arrhenius expression from Nelson et al. (1995), $k(HO+CF_3CH_2CF_2CH_2CF_3) = 1.23 \times 10^{-12} \exp(-1833/T)$ cm^3 molecule^{-1} s^{-1} is adopted. This expression gives $k(HO+CF_3CH_2CF_2CH_2CF_3) = 2.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

References

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


HO + $CF_3CH_2CF_2CH_2CF_3$
Arrhenius fit
Nelson et al (1995)
$k(HO+CF_3CH_2CF_2CH_2CF_3)$, 10^{-15} cm^3 $molecule^{-1}$ s^{-1}
10
1
2.5
3.0
3.5
4.0
1000/T (K^{-1})

oFOx81: HO + $CF_3CHFCHFCF_2CF_3$ (HFC-43-10mee)

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

$$HO + CF_3CHFCHFCF_2CF_3\ (\text{HFC-43-10mee}) \rightarrow CF_3CFCHFCF_2CF_3 + H_2O \quad (1)$$
$$\rightarrow CF_3CHFCFCF_2CF_3 + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were produced by the flash photolysis (λ ≥ 165 nm) of H_2O in 35 Torr (47 mbar) of argon diluent.

(b) HO radicals were produced by the flash photolysis (185 nm ≥ λ ≥ 165 nm) of H_2O.

Preferred Values

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

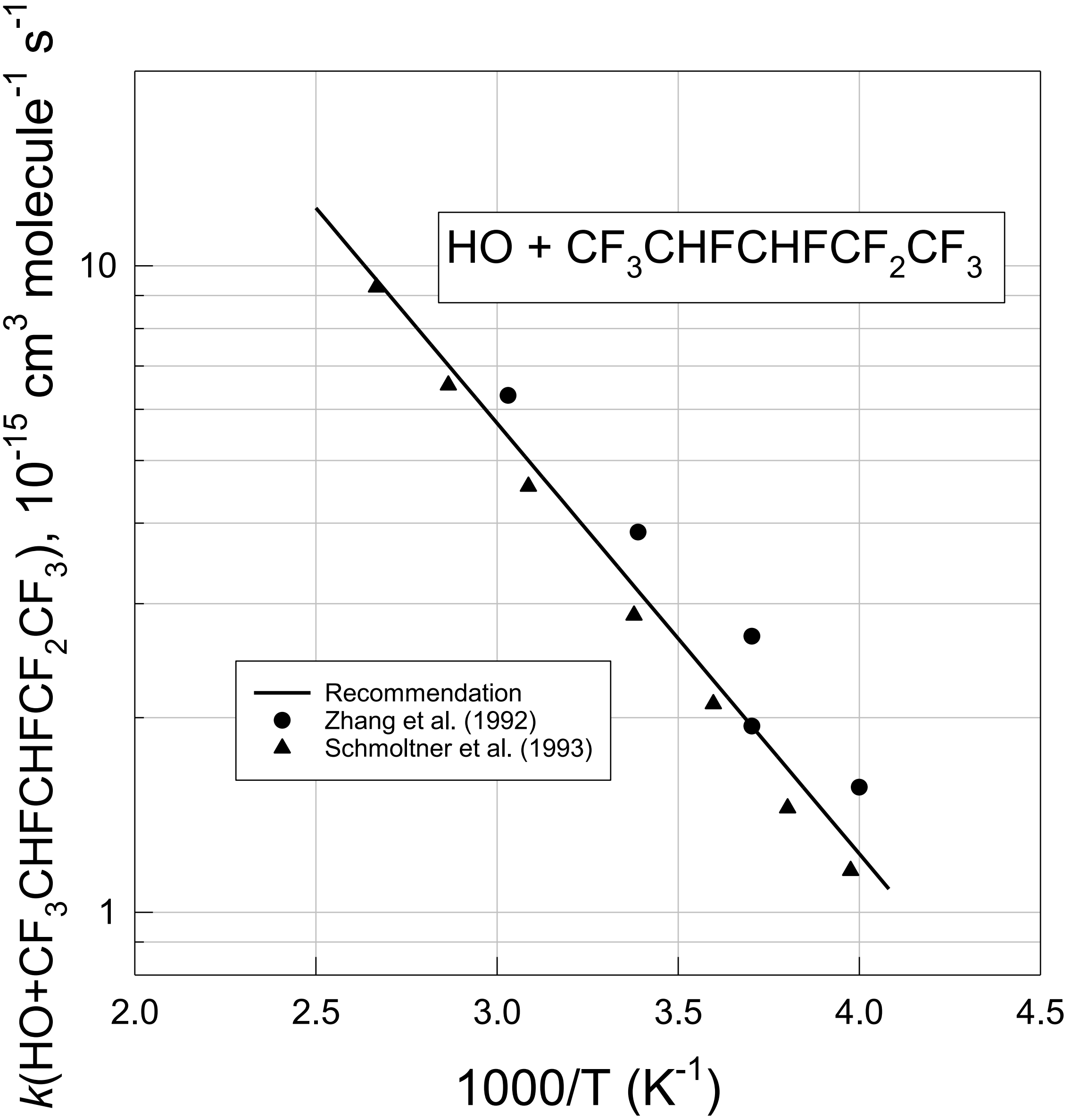
Comments on Preferred Values

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

References

Zhang, Z., Saini, R.D., Kurylo, M. J., and Huie, R. E.: Chem. Phys. Lett., 200, 230, 1992.

Schmoltner, A. M., Talukdar, R. K., Warren, R. F., Mellouki, A., Goldfarb, L., Gierczak, T., McKeen, S. A., and Ravishankara, A. R.: J. Phys. Chem., 97, 8976, 1993.


HO + CF3CHFCHFCF2CF3
Recommendation
Zhang et al. (1992)
Schmoltner et al. (1993)
k(HO+CF3CHFCHFCF2CF3), 10-15 cm3 molecule-1 s-1
10
1
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K-1)

oFOx82: HO + $CF_3CF_2CH_2CH_2CF_2CF_3$ (HFC-55-10mcff)

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

HO + $CF_3CF_2CH_2CH_2CF_2CF_3$ (HFC-55-10mcff) → $CF_3CF_2CHCH_2CF_2CF_3$+ H_2O

Rate coefficient data (*k*)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(7.87\pm0.38) \times 10^{-15}$	295	Nelson et al. (1995)	DF-LIF (a)

Comments

(a) HO radicals were produced by the reaction of H atoms with NO_2. Experiments were performed in 1.6-2.7 Torr (2.1-3.6 mbar) of helium diluent.

Preferred Values

Parameter	**Value**	**T/K**
k/cm^3 molecule^{-1} s^{-1}	8.3×10^{-15}	298
Reliability		
$\Delta \log k$	0.2	298

Comments on Preferred Values

Nelson et al. measured $k(HO+CF_3CF_2CH_2CH_2CF_2CF_3) = (7.87 \pm 0.38) \times 10^{-15}$ cm^3 molecule^{-1} 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 $k(HO+CF_3CF_2CH_2CH_2CF_2CF_3) = (8.3 \pm 0.9) \times 10^{-15}$ cm^3 molecule^{-1} 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.

oFOx83: HO + $CHF_2(CF_2)_4CF_3$ (HFC-52-13p)

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

HO + $CHF_2(CF_2)_4CF_3$ (HFC-52-13p) → $CF_2(CF_2)_4CF_3$ + H_2O

Rate coefficient data (*k*)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
7.36×10^{-12} exp[-(1820 ± 60)/T]	250-430	Chen et al. (2004)	FP-LIF/ PLP-LIF (a)
$(1.69\pm0.07) \times 10^{-15}$	298		FP-LIF (b)
$(1.72\pm0.07) \times 10^{-15}$	298		PLP-LIF (c)
Relative Rate Coefficients			
4.87×10^{-13} exp[-1661/T]	253-328	Chen et al. (2004)	RR (d)
1.87×10^{-15}	298		
2.61×10^{-13} exp[-1422/T]	253-328	Chen et al. (2004)	RR (e)
2.28×10^{-15}	298		

Comments

(a) Experiments were conducted using two different absolute rate methods. The sample of $CHF_2(CF_2)_4CF_3$ was determined to be 99.998% pure. In the FP-LIF experiments the HO radicals were produced by the photolysis of H_2O using a Xe flash lamp and experiments were performed in 20-100 Torr (27-133 mbar) of argon bath gas. In the PLP-LIF experiments the HO radicals were produced by the 193 nm photolysis of N_2O in the presence of H_2O. Experiments were performed in 20-100 Torr (27-133 mbar) of either argon or helium bath gas. The Arrhenius expression is that given by Chen et al. (2004) from a fit to the absolute rate data.

(b) Result obtained using FP-LIF technique at 298 K in 40-100 Torr (53-133 mbar) total pressure of argon bath gas.

(c) Result obtained using PLP-LIF technique at 298 K in 40-100 Torr (53-133 mbar) total pressure of argon or helium bath gas.

(d) Relative rate method with HO radicals produced by the 254 nm photolysis of O_3 in the presence of H_2O vapor in 200-500 Torr (267-665 mbar) of helium diluent. CHF_2Cl was used as a reference compound. The rate coefficient ratios $k(HO+CHF_2(CF_2)_4CF_3)/k(HO+CHF_2Cl)$ were placed on an absolute basis using $k(HO+CHF_2Cl) = 7.9 \times 10^{-13} \exp(-1530/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

(e) Relative rate method with HO radicals produced by the 254 nm photolysis of O_3 in the presence of H_2O vapor in 200-500 Torr (267-665 mbar) of helium diluent. CH_2FCF_3 was used as a reference compound. The rate coefficient ratios $k(HO+CHF_2(CF_2)_4CF_3)/k(HO+ CH_2FCF_3)$ were placed on an absolute basis using $k(HO+CH_2FCF_3) = 4.9 \times 10^{-13} \exp(-1395/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	1.8×10^{-15}	298
k /cm^3 molecule^{-1} s^{-1}	$5.76 \times 10^{-13} \exp(-1726/T)$	250-430

Reliability

Δ log *k*	0.10	298
Δ E/R	± 300	250-430

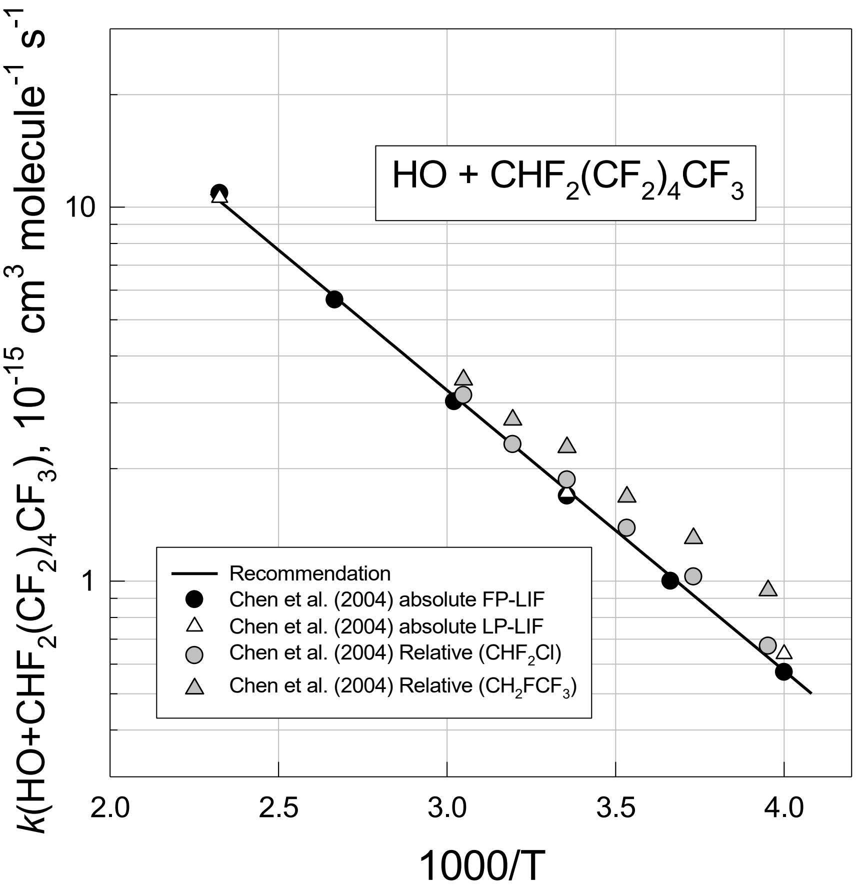
Comments on Preferred Values

The results obtained using two absolute rate methods by Chen et al. (2004) are in good agreement. An Arrhenius fit to the absolute rate data reported by Chen et al. (2004) gives $k(HO+CHF_2(CF_2)_4CF_3)$ = $5.76 \times 10^{-13} \exp(-1726/T)$ cm^3 $molecule^{-1}$ s^{-1} which is preferred. The relative rate experiments using CHF_2Cl reference are in excellent agreement with the results from the absolute rate study. The relative rate experiments using CH_2FCF_3 reference lie somewhat above but are consistent within the experimental uncertainties with the preferred values.

References

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; IUPAC Subcommittee for Gas Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Chen, L., Tokuhashi, K., Kutsuna, S., and Sekiya, A.: Int. J. Chem. Kinet., 36, 26, 2004.



oClOx86: HO + CH_3CH_2Cl

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

$$\begin{aligned} HO + CH_3CH_2Cl &\rightarrow CH_2CH_2Cl + H_2O \qquad (1)\\ &\rightarrow CH_3CHCl + H_2O \qquad (2)\end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.9\pm0.7) \times 10^{-13}$	296	Howard and Evenson (1976)	DF-LMR (a)
$(3.94\pm0.53) \times 10^{-13}$	297	Paraskevopoulos et al. (1981)	FP-RA (b)
$2.96\times10^{-13}(T/300)^{2.59} \exp[-(28\pm75/T)]$	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)
$(4.3\pm0.5) \times 10^{-13}$	295		
$1.5 \times 10^{-13}\ T^{0.5} \exp(-637/T)$	223-426	Herndon et al. (2001)	PLP-LIF (e)
$(2.92\pm0.12) \times 10^{-13}$	296		

Comments

(a) HO radicals were generated by the reaction of H atoms with NO_2 in 0.1-1.0 kPa (1-10 mbar) of helium.

(b) HO radicals produced by the flash photolysis of H_2O ($\lambda \geq 165$ nm) in 20-30 Torr (27-40 mbar) of helium.

(c) HO radicals were produced by the 193 nm (ArF excimer laser) photolysis of N_2O to produce $O(^1D)$ atoms in the presence of H_2O in 1 bar of helium.

(d) HO radicals were produced by the pulsed radiolysis of argon (1 bar) containing 15 mbar of H_2O.

(e) HO radicals were produced by either the photolysis of HONO at 355 nm (third harmonic Nd:YAG laser) or the photolysis of H_2O_2 at 248 nm (KrF excimer laser) in approximately 100 Torr (133 mbar) of helium.

Preferred Values

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

Comments on Preferred Values

The room temperature rate coefficients reported by Howard and Evenson (1976), Paraskevopoulos et al. (1981), Kasner et al. (1990), and Markert and Nielsen (1992) are in excellent agreement. However, there is disagreement between the temperature dependences reported by Kasner et al. (1990) and Markert and Nielsen (1992). The data of Markert and Nielsen (1992) are more scattered than those from Kasner et al. (1990). The rate coefficients reported by Herndon et al. (2001) lie approximately 20-30% below those from the other studies. Herdon et al. (2001) argue that the presence of reactive impurities and/or complications caused by photolysis or radiolysis of the C_2H_5Cl sample may have led to overestimation of $k(OH+ C_2H_5Cl)$ in previous studies. However, the discharge flow experiments by Howard and Evenson (1976) would not suffer from photolysis or radiolysis of the C_2H_5Cl sample. Also, the impact of an unsaturated reactive impurity such as ethene or isobutene would be reduced at the low pressures used. Averaging the results obtained by Howard and Evenson (1976), Paraskevopoulos et al. (1981), Kasner et al. (1990), and Herndon et al. (2001) gives our preferred value of $k(HO+ C_2H_5Cl) = 3.71 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. Fitting the three parameter equation $k = CT^2 \exp(-D/T)$ to the data from Herndon et al. (2001) gives $k = 5.19 \times 10^{-18}$ $T^2 \exp(-131/T)$ cm^3 molecule^{-1} s^{-1} which when centered at 298 K with $A = C\, e^2\, T^2$ and $B = D + 2T$ gives $k = 3.41 \times 10^{-12} \exp(-727/T)$ cm^3 molecule^{-1} s^{-1}. Adjusting the A factor to match the 298 K preferred value of $k(HO+ C_2H_5Cl) = 3.71 \times 10^{-13}$ gives our preferred Arrhenius expression of $k = 4.25 \times 10^{-12} \exp(-727/T)$ cm^3 molecule^{-1} s^{-1}.

References

Herndon, S. C., Gierczak, T., Talukdar, R. K., and Ravishankara, A. R.: Phys. Chem. Chem. Phys., 3 4529, 2001.

Howard, C. J., and Evenson, K. M.: J. Chem. Phys., 64, 4303, 1976.

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Markert, F., and Nielsen, O. J.: Chem. Phys. Lett., 194, 123, 1992.

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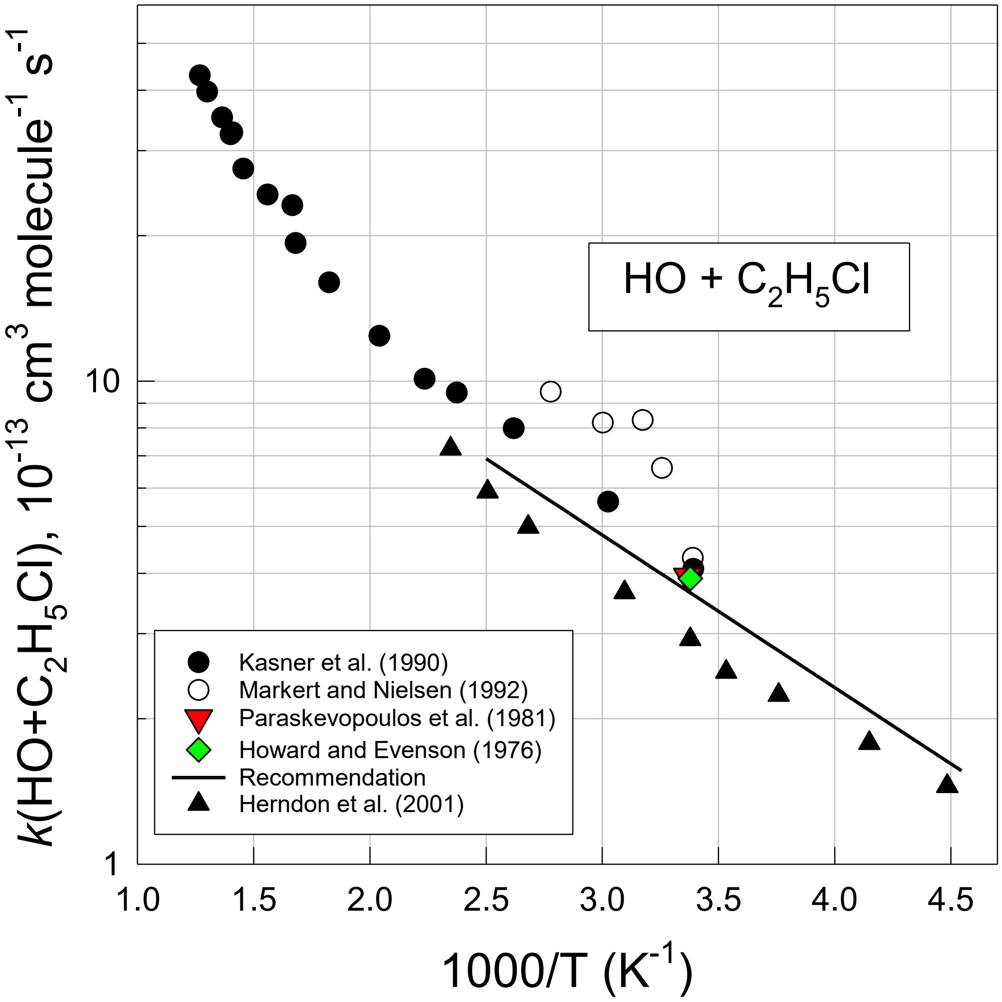

oClOx87: HO + CH_2ClCH_2Cl

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

$$HO + CH_2ClCH_2Cl \rightarrow CHClCH_2Cl + H_2O$$

Rate coefficient data (k)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.2\pm0.5) \times 10^{-13}$	296	Howard and Evenson (1976)	DF-LMR (a)
$4.08\times10^{-12}(T/300)^{1.0} \exp[-(825\pm88/T)]$	292-775	Taylor et al. (1991)	PLP-LIF (b)
$(2.48\pm0.38) \times 10^{-13}$	292		
$1.05 \times 10^{-11} \exp[-(1141\pm107)/T]$	292-363	Qiu et al. (1992)	DF-RF (c)
2.14×10^{-13}	295		
Relative Rate Coefficients			
$(2.50\pm0.54) \times 10^{-13}$	297	Arnts et al. (1989)	RR (d)

Comments

(a) HO radicals were generated by the reaction of H atoms with NO_2 in 0.1-1.0 kPa (0.7-7 Torr) of helium diluent.

(b) HO radicals were produced by the 193 nm (ArF eximer laser) photolysis of N_2O to produce $O(^1D)$ atoms in the presence of H_2O in 730-750 Torr (973-1000 mbar) of helium diluent.

(c) HO radicals were produced by the reaction of F atoms with H_2O in 2-3 Torr (2.7-4.0 mbar) of argon diluent gas.

(d) The rate coefficient ratio $k(HO+CH_2ClCH_2Cl)/k(HO+C_2H_6) = 1.02 \pm 0.22$ was placed on an absolute basis using $k(HO+C_2H_6) = 1.49 \times 10^{-17} T^2 \exp(-499/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.4×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$8.57 \times 10^{-12} \exp(-1070/T)$	290-360
Reliability		
$\Delta \log k$	0.08	298
$\Delta E/R$	± 200	290-360

Comments on Preferred Values

The rate coefficients of Howard and Evenson (1976), Arnts et al. (1989), Taylor et al. (1991), and Qiu et al. (1992) are in good agreement. Adjusting the rate coefficients reported by Howard and Evenson (1976), Taylor et al. (1991), and Qiu et al. (1992) at 292 – 296 K using the temperature dependence reported by Qiu et al. (1992) and taking an average give the preferred value of 2.4×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K. Fitting the three-parameter equation $k = CT^2 \exp(-D/T)$ to the data from Howard and Evenson (1976), Arnts et al. (1989), Taylor et al. (1991), and Qiu et al. (1992) and adjusting the C factor to reproduce the preferred value at 298 K gives $k = 1.06 \times 10^{-17} T^2 \exp(-410/T)$ cm^3 molecule^{-1} s^{-1}. Centering this expression at 330 K with $A = C e^2 T^2$ and $B = D + 2T$ gives $k = 8.57$

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

References

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

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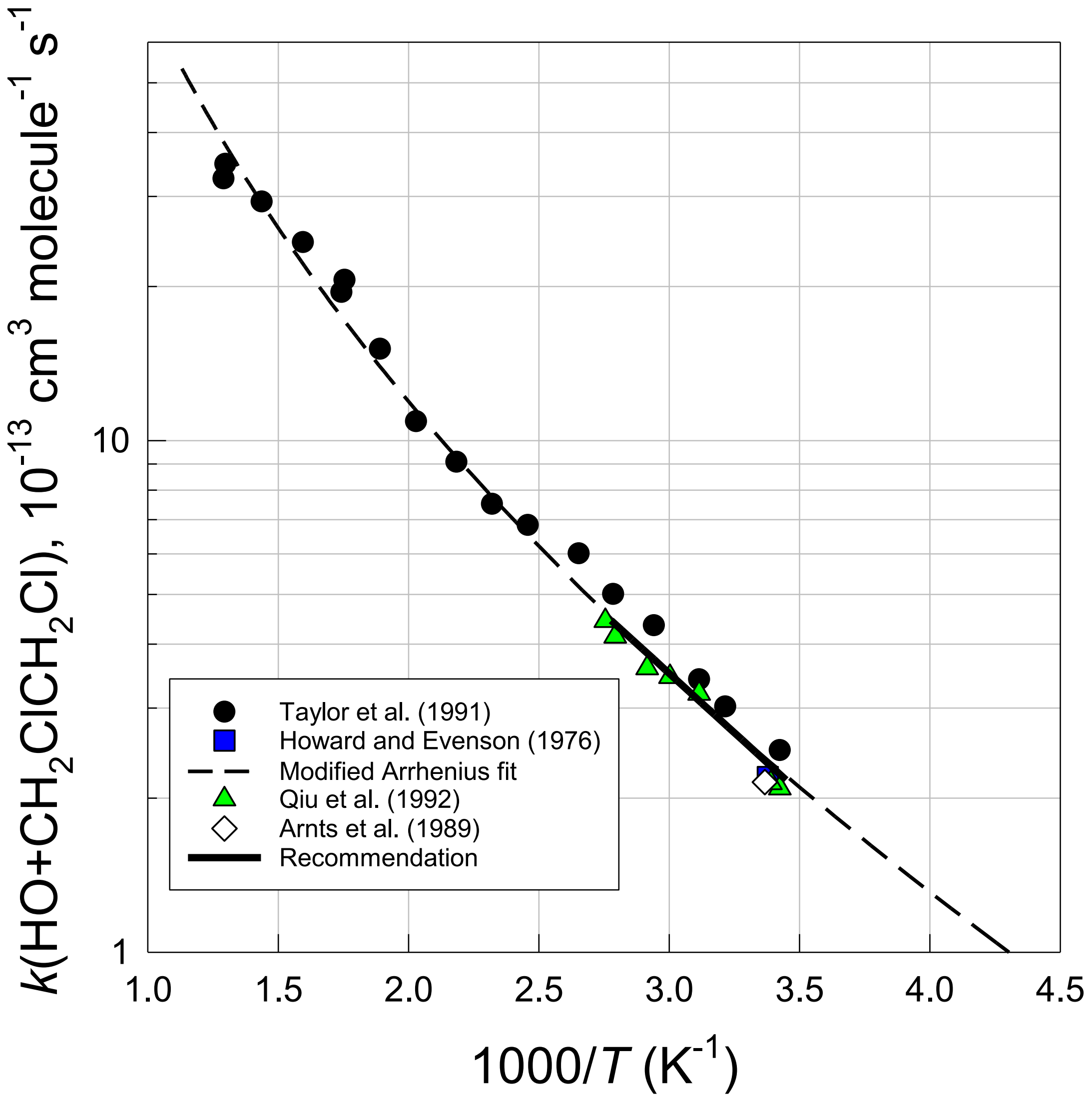
Taylor, P. H., McCarron, S., and Dellinger, B.: Chem. Phys. Lett., 177, 27, 1991.



oClOx88: HO + CH_3CHCl_2

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

$$HO + CH_3CHCl_2 \rightarrow CH_2CHCl_2 + H_2O \quad (1)$$
$$\rightarrow CH_3CCl_2 + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.6) \times 10^{-13}$	296	Howard and Evenson (1976)	DF-LMR (a)
$(8.29\pm0.36) \times 10^{-14} (T/300)^{2.67}\exp(387\pm18)/T$	294-800	Jiang et al. (1992)	PLP-LIF (b)
$(2.82 \pm 0.14) \times 10^{-13}$	294		

Comments

(a) HO radicals were generated by the reaction of H atoms with NO_2 in 0.1-1.0 kPa of helium.

(b) HO radicals were produced by the 193 nm photolysis of N_2O to give $O(^1D)$ atoms in the presence of H_2O vapor in 740 ± 10 Torr (986 ± 13 mbar) of helium.

Preferred Values

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

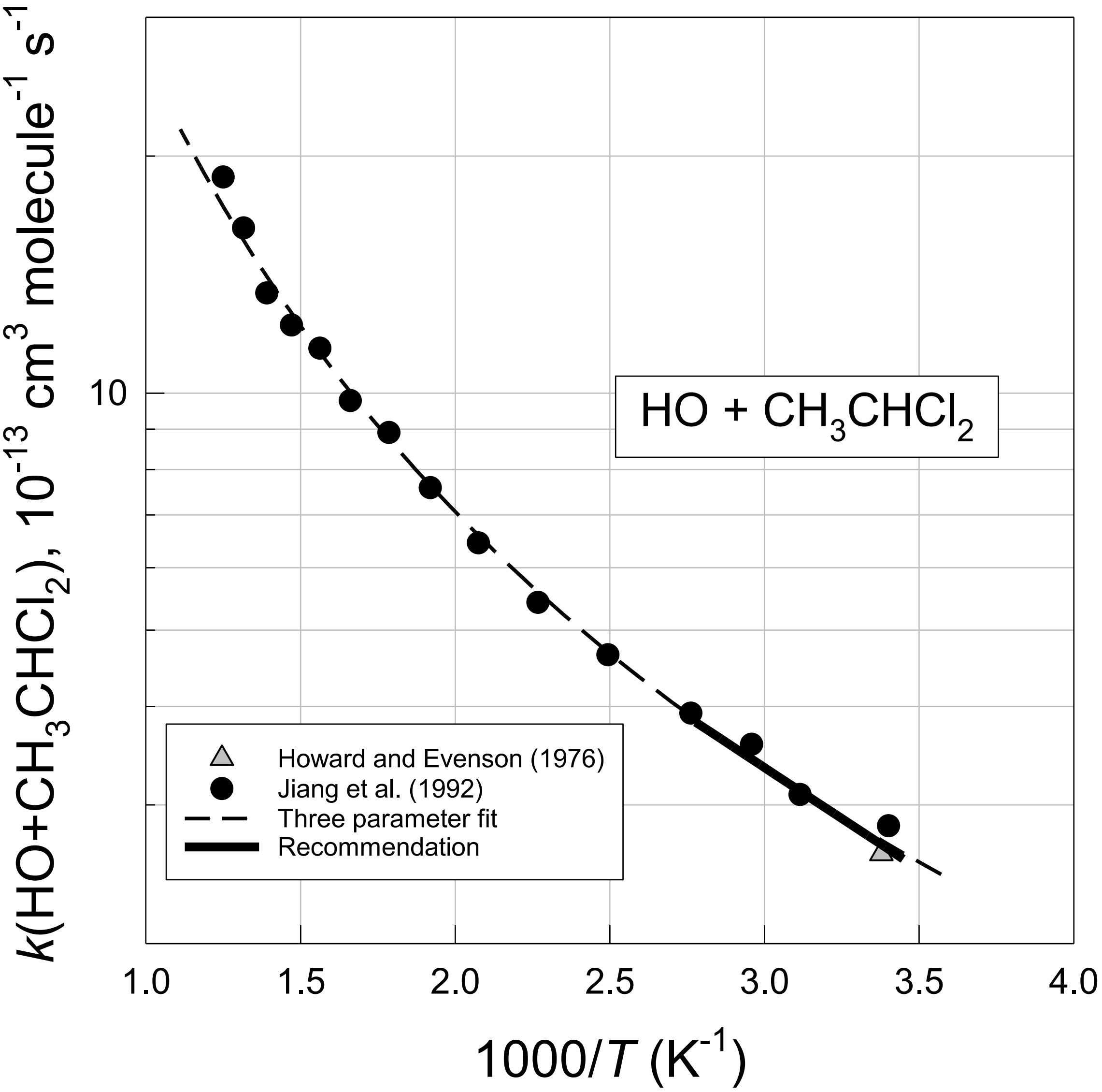
Comments on Preferred Values

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

References

Howard, C. J., and Evenson, K. M.: J. Chem. Phys., 64, 4303, 1976.

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


$k(HO+CH_3CHCl_2)$, 10^{-13} cm^3 $molecule^{-1}$ s^{-1}
10
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (K^{-1})
HO + CH_3CHCl_2
Howard and Evenson (1976)
Jiang et al. (1992)
Three parameter fit
Recommendation

oBrOx16: HO + $CHBr_3$

Last evaluated: June 2023; Last change in preferred values: June 2014.

$$HO + CHBr_3 \rightarrow CBr_3 + H_2O$$

Rate coefficient data (*k*)

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

Comments

(a) HO radicals were generated by the VUV pulsed photolysis of H_2O in 30 Torr (40 mbar) of argon. HO radicals were monitored by resonance fluorescence near 308 nm. The purity of the $CHBr_3$ sample was checked using GC-MS. Results measured using an older version of the FP-RF system with a different gas handling system and higher flash energies were consistent with those using a newer version of the experimental apparatus.

(b) HO radicals produced by photolysis of O_3 at 254 nm in the presence of H_2O vapor in argon diluent (total pressure was not specified). CH_2Cl_2 was used as the reference compound. The loss of $CHBr_3$ and CH_2Cl_2 was measured using FTIR spectroscopy. A rate coefficient ratio $k(HO+CHBr_3)/k(HO+CH_2Cl_2) = (0.73 \pm 0.16) \exp[(276 \pm 71)/T]$ was reported. Using $k(HO+CH_2Cl_2) = 1.8 \times 10^{-12} \exp(-860/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008) gives $k(HO+CHBr_3) = 1.31 \times 10^{-12} \exp(-584/T)$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.7×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$1.00 \times 10^{-12} \exp(-388/T)$	290-370
Reliability		
$\Delta \log k$	0.15	298
$\Delta E/R$	± 300	290-370

Comments on Preferred Values

There is a substantial disagreement between the results from the relative rate study by DeMore (1996) and the absolute rate study by Orkin et al. (2013). Considerable efforts were made by Orkin et al. (2013) to assure the purity of the $CHBr_3$ sample and it is unlikely that the discrepancy reflects the presence of a reactive impurity in the work of Orkin et al. (2013). Orkin et al. (2013) obtained consistent results using two different versions of their experimental system over a period of several years. DeMore (1996) used CH_2Cl_2 as a reference compound. In the presence of O_2 the degradation of CH_2Cl_2 produces chlorine atoms (Niki et al., 1980). At 298 K, the rate coefficient ratio $k(Cl+CHBr_3)/k(Cl+CH_2Cl_2) = 0.79$ (Atkinson et al., 2008; Kamboures et al, 2002) is about a factor of 3 lower than the rate coefficient ratio k(HO+$CHBr_3$)/k(HO+CH_2Cl_2) = 2.7 (present work; Atkinson et al., 2008). Additional loss of CH_2Cl_2 via reaction with chlorine atoms is a likely explanation of the discrepancy between the results from DeMore (1996) and the absolute rate study by Orkin et al. (2013). The preferred Arrhenius expression is derived from a fit to the data from Orkin et al. (2013).

References

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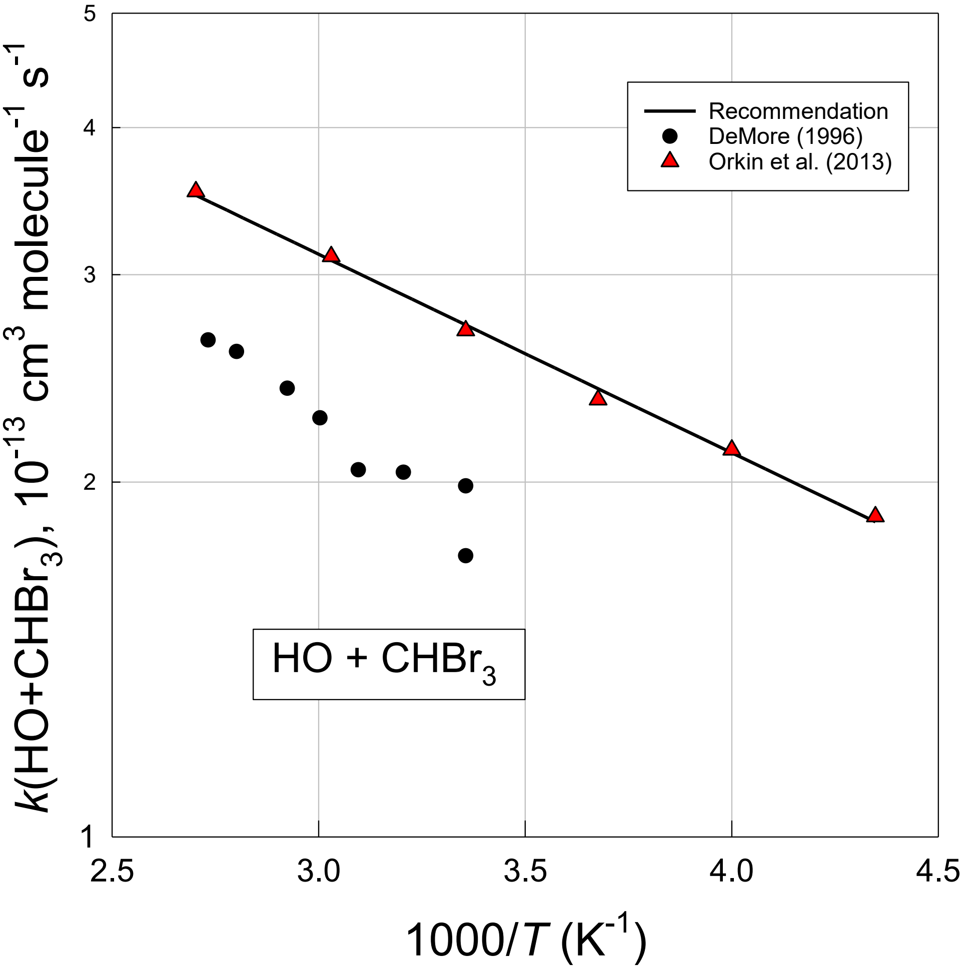

oBrOx17: HO + CH_3CH_2Br

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

$$HO + CH_3CH_2Br \rightarrow CH_2CH_2Br + H_2O \quad (1)$$
$$\rightarrow CH_3CHBr + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.77 \pm 0.34) \times 10^{-12} \exp[-(1344\pm86)/T)]$	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		
Relative Rate Coefficients			
$(2.18 \pm 0.07) \times 10^{-13}$	300	Donaghy et al. (1993)	RR (c)

Comments

(a) HO radicals were produced by the reaction of F atoms with H_2O in 2-3 Torr (2.7-4.0 mbar) of argon diluent gas. There is substantial overlap in the data set reported by Qiu et al. (1992) and Xing et al. (1992). For simplicity we refer to the combined data set published in these two papers as Qiu et al. (1992). Experiments were performed before and after pumping on, and removing a third of the sample. There was no discernable difference in the measured rate coefficients suggesting the absence of complications from volatile impurities. The value given at 298 K above is the average of the measurements reported by Qiu et al. (1992).

(b) HO radicals were produced by either the photolysis of HONO at 355 nm or the photolysis of H_2O_2 at 248 nm in approximately 100 Torr (133 mbar) of helium. The value given at 296 K above is the average of the measurements reported by Herndon et al. (2001). The C_2H_5Br sample was checked for impurities using gas chromatography; none were found.

(c) HO radicals were produced by the photolysis of CH_3ONO in one atmosphere pressure of air. Ethane was used as the reference compound and a rate coefficient ratio of $k(HO+C_2H_5Br)/k(HO+C_2H_6) = 0.885 \pm 0.030$ was reported. Using $k(HO+C_2H_6) = 6.9 \times 10^{-12} \exp(-1000/T)$ (Atkinson et al., 2006) gives $k(HO+C_2H_5Br) = (2.18 \pm 0.07) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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

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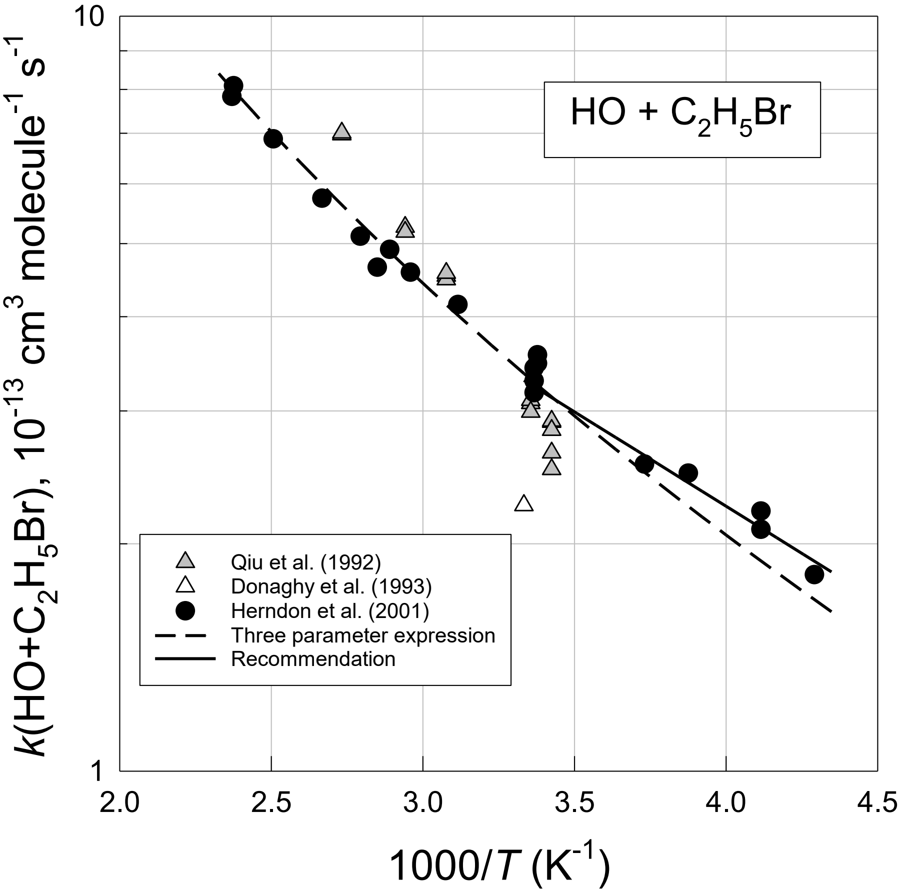

oBrOx18: HO + CH_2BrCH_2Br

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

$HO + CH_2BrCH_2Br \rightarrow CHBrCH_2Br + H_2O$

Rate coefficient data (*k*)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.50 \pm 0.55) \times 10^{-13}$	296	Howard and Evenson (1976)	DF-LMR (a)
$(1.46\pm0.26) \times 10^{-11} \exp[-(1283\pm136)/T)]$	294-365	Qiu et al. (1992)	DF-RF (b)
1.86×10^{-13}	294		
Relative Rate Coefficients			
$(2.15 \pm 0.45) \times 10^{-13}$	300	Arnts et al. (1989)	RR (c)

Comments

(a) HO radicals were generated by the reaction of H atoms with NO_2 in 0.1-1.0 kPa (1-10 mbar) of helium.

(b) HO radicals were produced by the reaction of F atoms with H_2O in 2-3 Torr (2.7-4.0 mbar) of argon. The results reported by Qiu et al. (1992) are an extension of the data set reported by Xing et al. (1992).

(c) The rate coefficient ratio $k(HO+CH_2BrCH_2Br)/k(HO+C_2H_6) = 0.88 \pm 0.18$ was placed on an absolute basis using $k(HO+C_2H_6) = 1.49 \times 10^{-17} T^2 \exp(-499/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	2.22×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$7.69 \times 10^{-12} \exp(-1056/T)$	290-370
Reliability		
$\Delta \log k$	0.1	298
$\Delta E/R$	± 300	290-370

Comments on Preferred Values

The absolute rate coefficients of Howard and Evenson (1976), Qiu et al. (1992), and Arnts et al. (1989) are in reasonable agreement at ambient temperature. Fitting the Arrhenius expression to the combined data set from the three studies gives $k = 7.69 \times 10^{-12} \exp(-1056/T)$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2010) which is preferred over the range 290-370 K.

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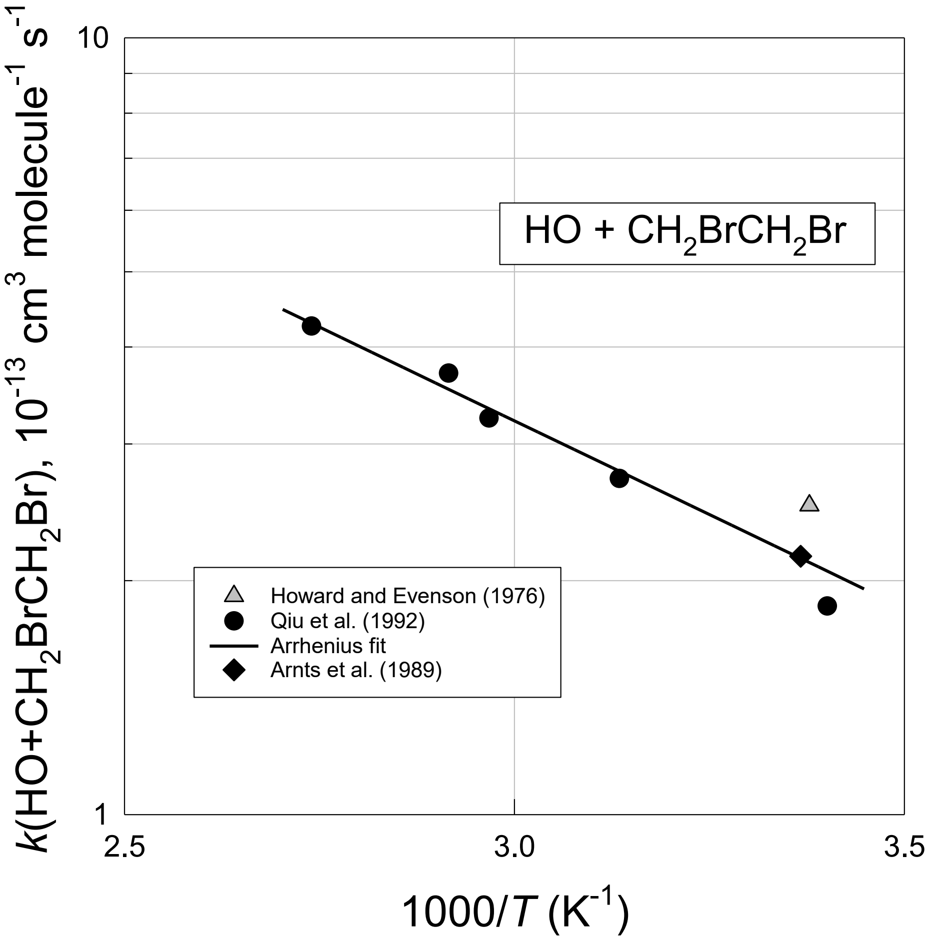

oBrOx19: HO + $CH_3CH_2CH_2Br$

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

$$\begin{aligned} HO + CH_3CH_2CH_2Br &\rightarrow CH_2CH_2CH_2Br + H_2O \qquad (1)\\ &\rightarrow CH_3CHCH_2Br + H_2O \qquad (2)\\ &\rightarrow CH_3CH_2CHBr + H_2O \qquad (3) \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(5.29\pm0.29) \times 10^{-12} \exp[-(456\pm31)/T)]$	233-372	Téton et al. (1996)	PLP-LIF (a)
1.17×10^{-12}	298		
$(5.75\pm0.90) \times 10^{-12} \exp[-(504\pm50)/T)]$	294-365	Nelson et al. (1997)	DF-LIF (b)
$(1.01\pm0.10) \times 10^{-12}$	295		
9.1×10^{-14} T$^{0.5}$ $\exp(-157/T)$	230-386	Herndon et al. (2001)	PLP-LIF (c)
$(8.8\pm0.4) \times 10^{-13}$	298		
$(6.6 \pm 0.52) \times 10^{-18}$ T^2 $\exp(154 \pm 24)$	230-360	Gilles et al. (2002)	PLP-LIF (d)
$(9.72\pm0.32) \times 10^{-13}$	297		
2.99 x 10^{-13} $(T/298)^{2.79}$ $\exp(369/T)$	210-480	Kozlov et al. (2003)	FP-RF (e)
$(1.01\pm0.15) \times 10^{-12}$	298		
1.32×10^{-17} T$^{1.95}$ $\exp(25/T)$	297-725	Brykov et al. (2007)	PLP-LIF (f)
9.51×10^{-13}	297		
Relative Rate Coefficients			
$(1.10 \pm 0.06) \times 10^{-12}$	300	Donaghy et al. (1993)	RR (g)

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 at 248 nm in approximately 100 Torr (133 mbar) of helium.

(b) HO radicals were generated by the reaction of H atoms with NO_2 in 1.1-2.3 Torr (1.5-3.1 kPa) of helium.

(c) HO radicals were produced by the photolysis of HONO at 355 nm (third harmonic Nd:YAG laser) in approximately 100 Torr (133 mbar) of helium diluent.

(d) HO radicals were generated by the photolysis of HONO at 351 nm in 50 Torr (67 kPa) of helium.

(e) HO radicals were generated by the photolysis of H_2O using a xenon flash lamp. Experiments were performed in 30 Torr (4 mbar) of argon.

(f) HO radicals were generated by either the photolysis of N_2O at 193 nm (ArF excimer laser) to make $O(^1D)$ atoms in the presence of H_2O vapor, or the photolysis of HNO_3 at 248 nm (KrF excimer laser) in 6.69-26.73 kPa of helium.

(g) The rate coefficient ratio $k(HO+C_3H_5Br)/k(HO+cyclohexane) = 0.156 \pm 0.008$ was placed on an absolute basis using k(HO+cyclohexane) = 3.26×10^{-17} T^2 $\exp(-262/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-12}	298
k /cm^3 molecule^{-1} 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	
Reliability		
$\Delta \log k$	0.1	298
Δ log E/R	± 200	210-300
$\Delta k_1/k$	0.10	
$\Delta k_2/k$	0.05	
$\Delta k_3/k$	0.10	

Comments on Preferred Values

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 $k = 8.14 \times 10^{-18}\ T^2 \exp(111/T)$ cm^3 molecule^{-1} s^{-1}. Centering this expression at 255 K with $A = C\ e^2\ T^2$ and $B = D + 2T$ gives $k = 3.91 \times 10^{-12} \exp(-399/T)$ cm^3 molecule^{-1} s^{-1} which is preferred over the range 210-300 K.

From an analysis of kinetic data for the reaction of HO radicals with $CH_3CH_2CH_2Br$, $CD_3CH_2CH_2Br$, $CD_3CH_2CD_2Br$, $CH_3CD_2CD_2Br$, and $CD_3CD_2CD_2Br$, Gilles et al. (2002) deduced branching ratios at 298 K for abstraction at the 1-, 2-, and 3- positions in $CH_3CH_2CH_2Br$ 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 $CH_3CH_2CH_2Br$ 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 ± 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 [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 CH_3CHCH_2Br radicals. Gilles et al. (2002) derived $k_{O2}/k_{diss} = (4.0 \pm 0.6) \times 10^{-18}$ cm^3 molecule^{-1}. In one atmosphere of air $k_{O2}[O_2]/k_{diss} = 21$, and reaction with O_2 dominates the atmospheric fate of CH_3CHCH_2Br radicals. Reaction of HO radicals with $CH_3CH_2CH_2Br$ at the 3– position is expected to be of minor (< 20%) importance. The major products of the HO radical initiated oxidation of $CH_3CH_2CH_2Br$ are propanal and bromoacetone.

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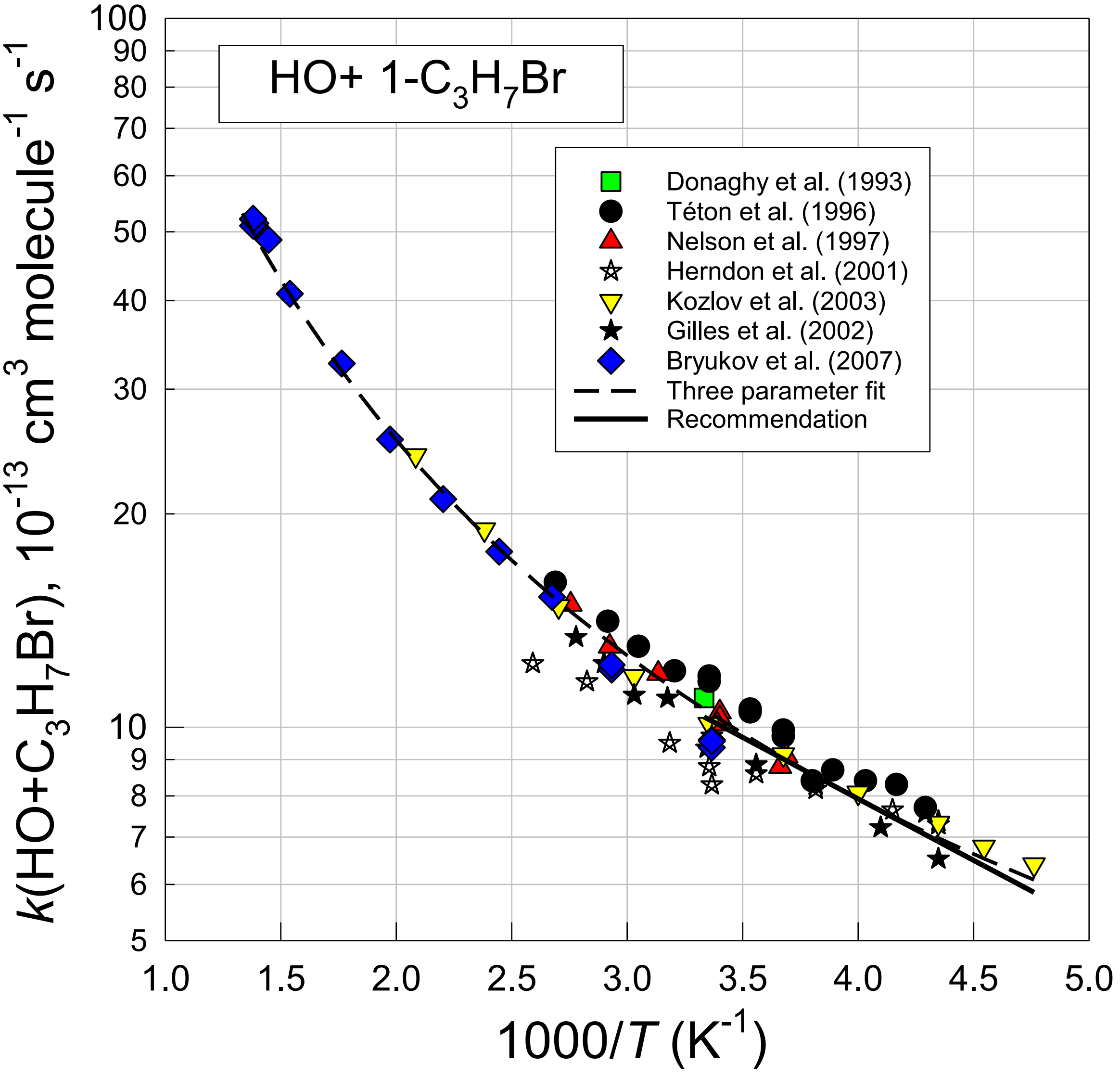

oBrOx20: HO + $CH_3CHBrCH_3$

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

$$\mathbf{HO + CH_3CHBrCH_3 \rightarrow CH_2CHBrCH_3 + H_2O \qquad (1)}$$

$$\mathbf{\rightarrow CH_3CBrCH_3 + H_2O \qquad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.58\pm0.47) \times 10^{-12} \exp[-(392\pm75)/T)]$	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)
$(7.45\pm0.15) \times 10^{-13}$	298		
$1.66 \times 10^{-13}\ (T/298)^{2.95} \exp(461/T)$	210-480	Kozlov et al. (2003)	FP-RF (c)
$(7.58\pm0.12) \times 10^{-13}$	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		
Relative Rate Coefficients			
$(8.16 \pm 0.35) \times 10^{-13}$	298	Donaghy et al. (1993)	RR (e)

Comments

(a) The value at 298 K is the average of the five determinations reported by Téton et al. (1996) at this temperature.

(b) HO radicals were produced by the photolysis of HONO at 355 nm (third harmonic Nd:YAG laser) in approximately 100 Torr (133 mbar) of helium.

(c) HO radicals were generated by the photolysis of H_2O using a xenon flash lamp. Experiments were performed in 30 Torr (4 mbar) of argon.

(d) The value at 297 K is the average of the five determinations reported by Bryukov et al. (2003) at this temperature.

(e) The rate coefficient ratio $k(HO+C_3H_5Br)/k(HO+cyclohexane) = 0.117 \pm 0.005$ was placed on an absolute basis using $k(HO+cyclohexane) = 3.26 \times 10^{-17}\ T^2 \exp(-262/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

Preferred Values

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

Comments on Preferred Values

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

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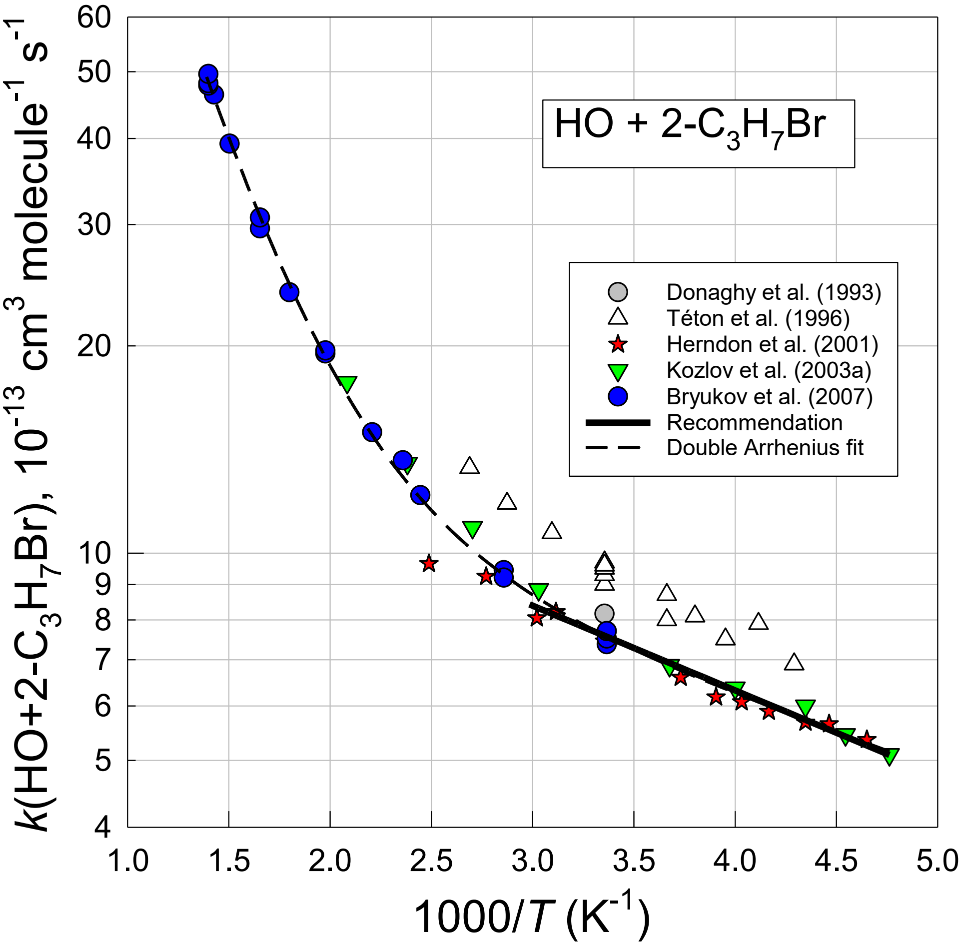

oBrOx21: HO + $CH_3CH_2CH_2CH_2Br$

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

$HO + CH_3CH_2CH_2CH_2Br \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(2.29 \pm 0.07) \times 10^{-12}$	299	Donaghy et al. (1993)	RR (a)

Comments

(a) The rate coefficient ratio $k(HO+C_4H_9Br)/k(HO+\text{cyclohexane}) = 0.327 \pm 0.010$ was placed on an absolute basis using $k(HO+\text{cyclohexane}) = 3.26 \times 10^{-17}\ T^2 \exp(-262/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.3×10^{-12}	298
Reliability		
$\Delta \log k$	0.20	298

Comments on Preferred Values

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

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Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.

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oBrOx22: HO + $CH_3CH_2CH_2CH_2CH_2Br$

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

HO + $CH_3CH_2CH_2CH_2CH_2Br \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(3.71 \pm 0.13) \times 10^{-12}$	304	Donaghy et al. (1993)	RR (a)

Comments

(a) The rate coefficient ratio $k(HO+C_5H_{11}Br)/k(HO+cyclohexane) = 0.520 \pm 0.018$ was placed on an absolute basis using $k(HO+cyclohexane) = 3.26 \times 10^{-17}\ T^2 \exp(-262/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.7×10^{-12}	298
Reliability		
$\Delta \log k$	0.20	298

Comments on Preferred Values

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

References

Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.

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

oBrOx23: HO + $CH_3CH_2CH_2CH_2CH_2CH_2Br$

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

HO + $CH_3CH_2CH_2CH_2CH_2CH_2Br$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(5.48 \pm 0.19) \times 10^{-12}$	306	Donaghy et al. (1993)	RR (a)

Comments

(a) The rate coefficient ratio $k(HO+C_6H_{13}Br)/k$(HO+cyclohexane) = 0.763 ± 0.027 was placed on an absolute basis using k(HO+cyclohexane) = 3.26×10^{-17} T^2 exp(-262/T) cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	5.5×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.20	298

Comments on Preferred Values

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

References

Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.

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

oIOx4: HO + CH_3CH_2I

Last evaluated: June 2025; Last change in preferred values: June 2014

$$HO + CH_3CH_2I \rightarrow CH_2CH_2I + H_2O \quad (1)$$
$$\rightarrow CH_3CHI + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were generated by the VUV flash photolysis of H_2O 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 NO_2 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 $k(HO+C_2H_5I) = (7.7 \pm 1.0) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} could be an overestimation because of secondary loss of HO radicals via reaction with products of the $HO+C_2H_5I$ 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 5.5×10^{-13} cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

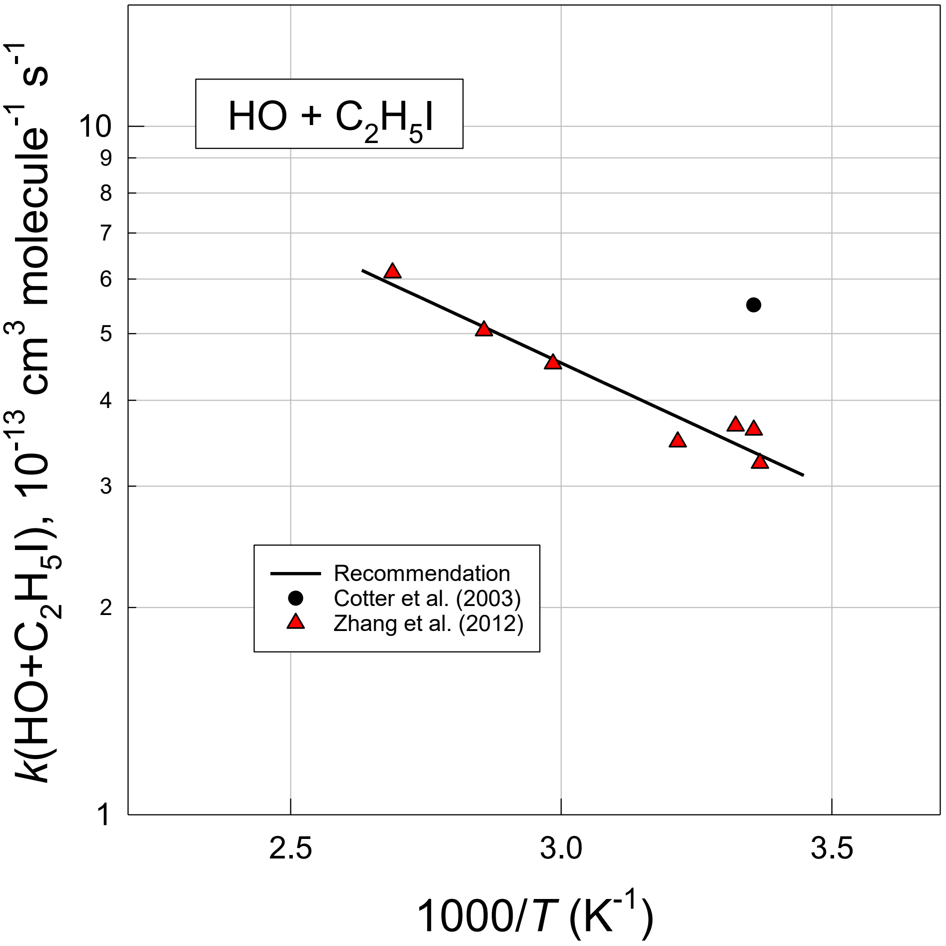
Comments on Preferred Values

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 $k(HO+C_2H_5I) = 3.43 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

References

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.



oIOx5: $HO + CH_3CH_2CH_2I$

Last evaluated: June 2025; Last change in preferred values: June 2014

$$\mathbf{HO + CH_3CH_2CH_2I \rightarrow CH_2CH_2CH_2I + H_2O} \quad (1)$$
$$\mathbf{\rightarrow CH_3CHCH_2I + H_2O} \quad (2)$$
$$\mathbf{\rightarrow CH_3CH_2CHI + H_2O} \quad (3)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.47 \pm 0.08) \times 10^{-12}$	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		
Relative Rate Coefficients			
$(2.5 \pm 0.3) \times 10^{-12}$	298	Cotter et al. (2003)	DF-RF (c)

Comments

(a) HO radicals were generated by the two photon 439.44 nm (Nd-YAG pumped dye laser) photolysis of NO_2 (generating $O(^1D)$ and $O(^3P)$ atoms) in the presence of H_2. Experiments were conducted in 20 Torr (27 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence at 308 nm.

(b) HO radicals were generated by the VUV flash photolysis of H_2O in 188 Torr (250 mbar) of helium diluent. HO radicals were monitored using resonance fluorescence at 308 nm.

(c) HO radicals were generated by the reaction of H atoms with NO_2 in 1.5 or 5.0 Torr (2.0 or 6.7 mbar) of helium diluent at 298 ± 2 K. There was no discernible effect of total pressure over the range studied. It was noted that the measured rate coefficient could be an upper limit to $k(HO+C_3H_7I)$ because of additional loss of HO radicals via reaction with products of the $HO+C_3H_7I$ reaction. Cotter et al. (2003) estimated that correction of the rate coefficient for possible additional loss of HO radicals via secondary reactions would lower the rate coefficient to 1.8×10^{-12} cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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

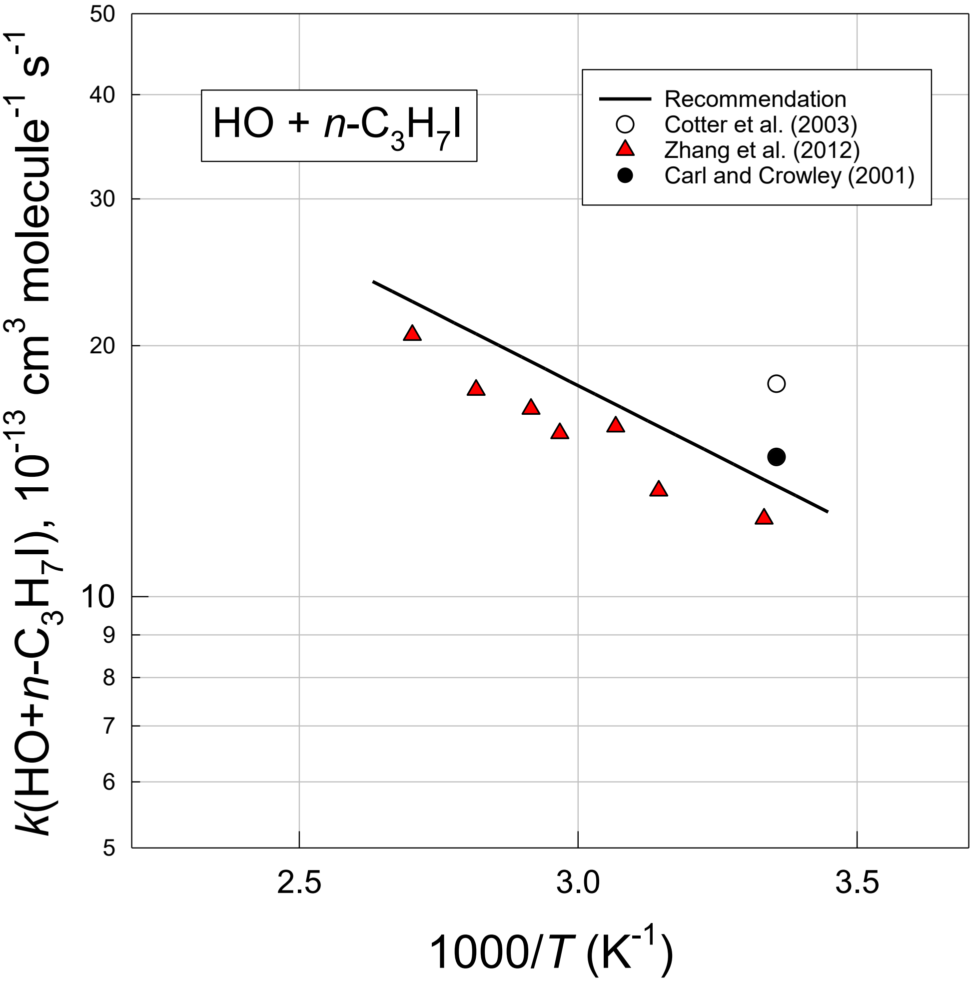
Crowley (2001) and Zhang et al. (2012) are in good agreement within the combined uncertainties. Our preferred value at 298 K is the average from Carl and Crowley (2001) and Zhang et al. (2012). The temperature dependence is taken from a fit to the work by Zhang et al. (2012) with the A-factor adjusted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

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.



oIOx6: HO + CH_3CHICH_3

Last evaluated: June 2025; Last change in preferred values: June 2014

$$HO + CH_3CHICH_3 \rightarrow CH_2CHICH_3 + H_2O \quad (1)$$
$$\rightarrow CH_3CICH_3 + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.22 \pm 0.06) \times 10^{-12}$	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		
Relative Rate Coefficients			
$(1.6 \pm 0.2) \times 10^{-12}$	298	Cotter et al. (2003)	DF-RF (c)

Comments

(a) HO radicals were generated by either the two photon 439.44 nm (Nd-YAG pumped dye laser) photolysis of NO_2 (generating $O(^1D)$ and $O(^3P)$ atoms) in the presence of H_2, or the photolysis of HNO_3 at 248 nm. Experiments were conducted in 20 Torr (27 mbar) of argon. HO radicals were monitored using resonance fluorescence.

(b) HO radicals were generated by the VUV flash photolysis of H_2O in 188 Torr (250 mbar) of helium diluent. HO radicals were monitored using resonance fluorescence at 308 nm.

(c) HO radicals were generated by the reaction of H atoms with NO_2 in 1.5 or 5.0 Torr (2.0 or 6.7 mbar) of helium diluent at 298 ± 2 K. There was no discernible effect of total pressure over the range studied. It is possible that the measured rate coefficient is an overestimation of $k(HO+i\text{-}C_3H_7I)$ because of additional loss of HO radicals via reaction with products of the $HO+i\text{-}C_3H_7I$ reaction. While secondary chemistry should manifest itself in curvature of the first order ($\ln([HO]_{to}/[HO]_t$ versus time) plots, Cotter et al. (2003) calculated that such curvature would not be discernable given the data scatter. Cotter et al. (2003) estimated that correction of the rate coefficient for possible additional loss of HO radicals via secondary reactions would lower the rate coefficient to 1.1×10^{-12} cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

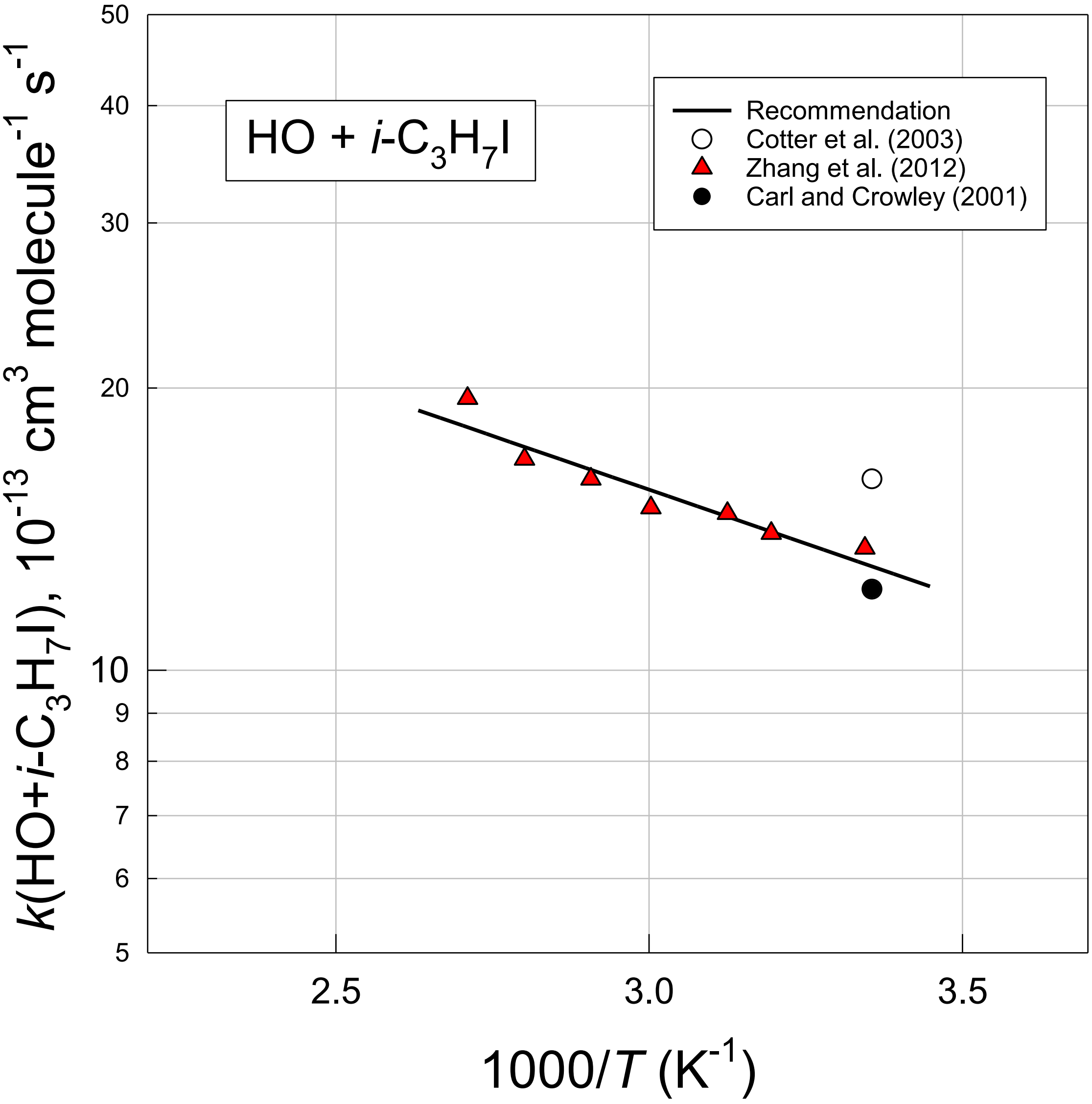
Recognizing the possible contribution of secondary loss of HO radicals, Cotter et al. (2003) considered their rate coefficient determination to be an upper limit. The value derived by Cotter et al. (2003) corrected for possible secondary reactions is consistent with those from Carl and Crowley (2001) and Zhang et al. (2012). The results from Carl and Crowley (2001) and Zhang et al. (2012) are in good agreement within the combined uncertainties. Our recommended value at 298 K is the average from Carl and Crowley (2001) and Zhang et al. (2012). The temperature dependence is taken from a fit to the work by Zhang et al. (2012) with the A-factor adjusted to reproduce the recommended value at 298 K.

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.



oFOx108: Cl + $CHF_2CH_2CF_3$ (HFC-245fa)

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

$$\text{Cl} + \text{CHF}_2\text{CH}_2\text{CF}_3 \text{ (HFC-245fa)} \rightarrow \text{CF}_2\text{CH}_2\text{CF}_3 + \text{HCl} \quad (1)$$

$$\rightarrow \text{CHF}_2\text{CHCF}_3 + \text{HCl} \quad (2)$$

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

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

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in $CHF_2CH_2CF_3/CF_3CHClF/Cl_2$ mixtures in 700 Torr (933 mbar) of N_2. The decays of $CHF_2CH_2CF_3/CF_3CHClF$ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(Cl+CHF_2CH_2CF_3)/ k(Cl+CF_3CHClF)$ = 2.55 ± 0.30 was placed on an absolute basis using $k(Cl+CF_3CHClF) = 2.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

Preferred Values

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

Comments on Preferred Values

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

References

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., 9, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Chen, J., Young, V., Niki, H., and Magid, H.: J. Phys. Chem., A, 101, 2648, 1997.

oFOx110: Cl + CF_3CHFCF_3 (HFC-227ea)

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

Cl + CF_3CHFCF_3 (HFC-227ea) → CF_3CFCF_3 + HCl

Rate coefficient data (*k*)

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(4.68 \pm 0.52) \times 10^{-16}$	296	Møgelberg et al. (1996)	(a)
$(4.10 \pm 0.63) \times 10^{-16}$	296		(b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in $CF_3CHFCF_3/CHF_2CF_3/Cl_2$ and $CF_3CHFCF_3/CHF_2CF_2CF_3/Cl_2$ mixtures in 700 Torr (933 mbar) of N_2 or air diluent. The loss of the reactant and reference compounds was measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(Cl+CF_3CHFCF_3)/k(Cl+CHF_2CF_3) = 0.18 \pm 0.02$ and $k(Cl+CF_3CHFCF_3)/k(Cl+CHF_2CF_2CF_3) = 0.13 \pm 0.02$ were placed on an absolute basis using $k(Cl+CHF_2CF_3) = 2.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008) and $k(Cl+CHF_2CF_2CF_3) = 3.15 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (Giessing et al., 1996).

(b) Using $CHF_2CF_2CF_3$ as reference.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	4.4×10^{-16}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

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

References

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., 9, 4141, 2008; IUPAC Task Group on Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Giessing, A. M. B., Feilberg, A., Møgelberg, T. E., Sehested, J., Bilde, M., Wallington, T. J., and Nielsen, O. J.: J. Phys. Chem., 100, 6572, 1996.

Møgelberg, T. E., Sehested, J., Bilde, M., Wallington, T. J., and Nielsen, O.J: J. Phys. Chem., 100, 8882, 1996.

oFOx111: Cl + CHF_3

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

$$Cl + CHF_3 \rightarrow HCl + CF_3$$

$\Delta H° = 17.9$ kJ mol^{-1}

Rate coefficient data

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

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 Cl_2 at 366 nm (mercury lamp). The expression in the table above was derived from the measured ratios k_{CH4}/k_{C2F5H} =12.4 exp[(1450±40)/RT] and k_{C2F5H}/k_{CHF3} = 1.16 exp[(3080±70)/RT]) which leads to k_{CH4}/k_{CHF3} = 14.4 exp[(4530±80)/RT]) = 14.4 exp[(2280±40)/T]). Using $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(Cl + CHF_3) = 4.6 \times 10^{-13} \exp(-3520/T)$ cm^3 molecule^{-1} s^{-1}. At 298 K this expression gives $k(Cl + CHF_3) = 3.4 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

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 (Ea/R = 2150) which combined with an estimate of 1×10^{-12} for the A factor gives an upper limit of $k(Cl + CHF_3) < 7 \times 10^{-16}$ cm^3 molecule^{-1} 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 $k(Cl + CH_4)/k(Cl + C_2HF_5) = 144$ which is approximately a factor of two lower than the ratio of the preferred rate coefficients $k(Cl + CH_4)/k(Cl + C_2HF_5) = 385$ (Atkinson et al., 2006; 2008). The preferred value of $k(Cl + CHF_3) = 3.4 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K is based on the results from Coomber and Whittle and has substantial uncertainty.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

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oBrOx24: Cl + CH3Br

Last evaluated: June 2023; Last change in preferred values: June 2014.

$Cl + CH_3Br \rightarrow HCl + CH_2Br$

Rate coefficient data

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

Comments

(a) The reaction rate coefficients were measured by generating Cl atoms via 308 nm laser photolysis of Cl_2 and measuring their temporal profiles via resonance fluorescence detection. Experiments were performed in approximately 50 Torr (66.7 mbar) of helium.

(b) The reaction rate coefficients were measured using a very low pressure reactor, employing a microwave discharge in Cl_2 for the generation of Cl atoms with mass spectrometric detection of reactants and products. Experiments were performed in approximately 1 mTorr (1.33 mbar) of helium.

(c) The reaction rate coefficients were measured by generating Cl atoms via 266 nm laser photolysis of Cl_2CO (or Cl_2 at 355 nm in a few experiments) and measuring their temporal profiles via resonance fluorescence detection. Experiments were performed at 161 – 697 K in 20 - 250 Torr (27 - 270 mbar) of nitrogen. At temperatures in the range 161 – 177 K reversible addition of Cl atoms to give the CH_3BrCl adduct was observed. For $T \geq 213$ K where hydrogen abstraction is the dominant reaction pathway the Arrhenius expression given in the table above was obtained.

(d) Cl atoms generated by microwave discharge of Cl_2 in helium diluent. Cl atoms were detected using resonance fluorescence at 118.9 nm.

(e) Cl atoms were generated by the photolysis of Cl_2 at 424 nm, and the concentrations of the reactions products CH_2ClBr and CH_3Cl measured by GC. The measured rate coefficient ratio of $k(Cl + CH_3Br)/k(Cl + CH_4) = (1.91 \pm 0.09) \exp[-(325 \pm 10)/T]$ is placed on an absolute basis using $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(f) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. Experiments were performed in approximately 700 Torr (933 mbar) of N_2. The measured rate coefficient was placed on an absolute basis using $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(g) The decays of the reactant and reference (CH_4) organic were measured by GC. The measured rate coefficient ratios were placed on an absolute basis using $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

Preferred Values

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

Comments on Preferred Values

The preferred value at 298 K is an average of the results reported by Gierczak et al. (1994), Kambanis et al. (1997), Piety et al. (1998), Orlando et al. (1996), and Gola et al. (2010). The expression for the temperature dependence listed in the Table of preferred values is derived from the fit to the data of these studies below 300 K. The values reported by Tschuikow-Roux et al. are not used because they seem to be systematically higher than the results of the other measurements. The results reported by Larin et al. (2018) are consistent with the preferred value. At temperatures of 161 – 177 K the reaction leads to the reversible formation of the adduct CH_3BrCl. For temperatures above 213 K there is no experimental evidence for formation of the adduct and reaction proceeds via hydrogen abstraction (Piety et al., 1998; Enami et al., 2005). For temperatures above 298 K there is some disagreement between the results from Piety et al. (1998) and Gola et al. (2010). A fit of the modified Arrhenius expression to the entire data set from Gierczak et al., Kambanis et al., Piety et al., Orlando et al., and Gola et al. gives $k = 1.78 \times 10^{-17} T^2 \exp(-396/T)$ cm^3 molecule^{-1} s^{-1} and is preferred for 550 K > T > 298 K.

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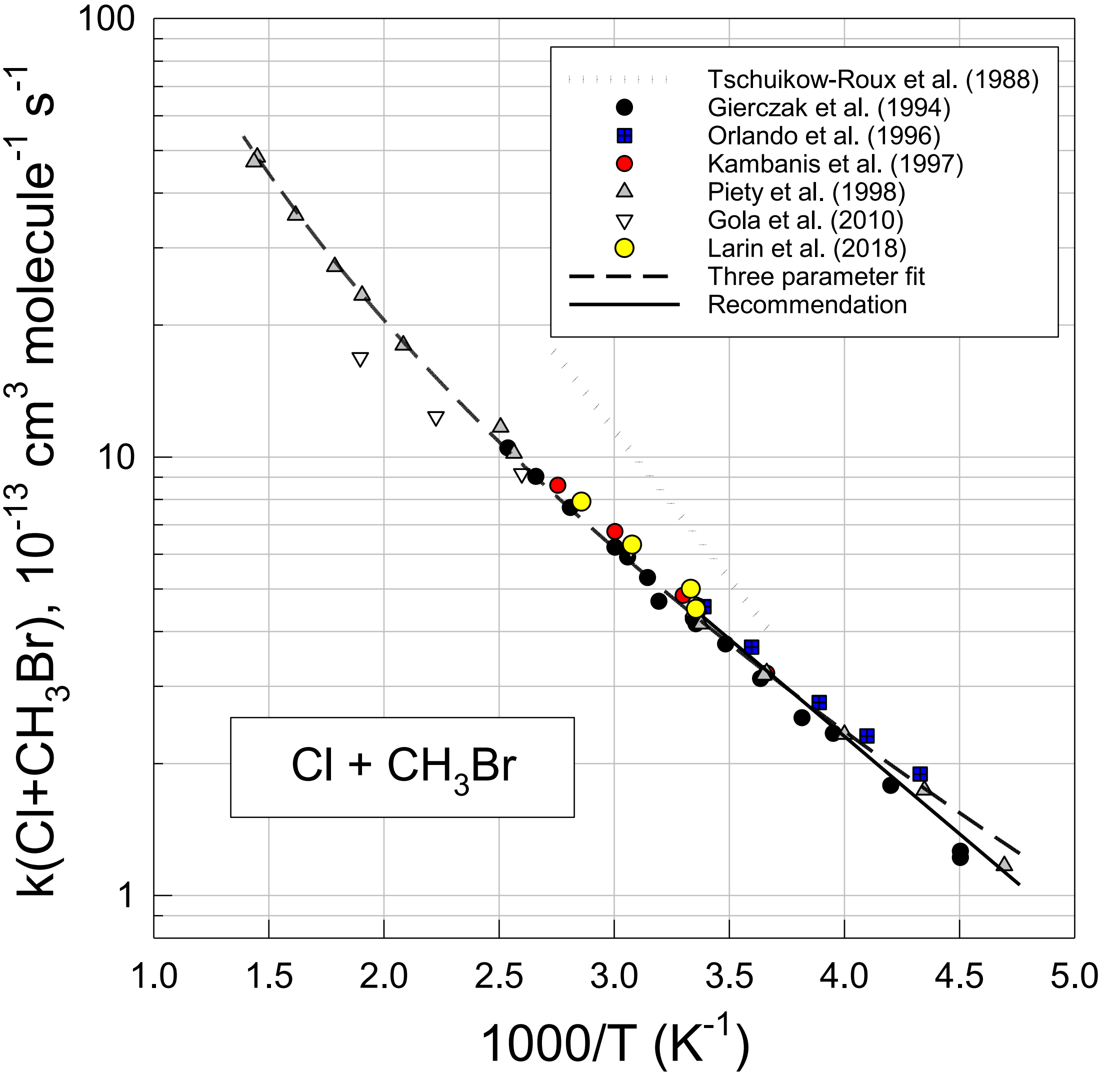
1427



1428
1429

oFOx112: HO + CF_2=CF_2

Last evaluated: June 2025; Last change in preferred values: June 2017.

HO + CF_2=CF_2 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.02 \pm 0.05) \times 10^{-11}$	298	Orkin et al., 1997	FP-RF (a)
$3.39 \times 10^{-12} \exp[(323\pm11)/T]$	250-370	Orkin et al., 2002	FP-RF (a)
$(1.00 \pm 0.015) \times 10^{-11}$	298		
$(8.0 \pm 0.3) \times 10^{-12}$	370	Orkin et al., 2011	FP-RF (a)
$(7.09 \pm 0.02) \times 10^{-12}$	480		
Relative Rate Coefficients			
$(1.07 \pm 0.34) \times 10^{-11}$	298	Acerboni et al., 1999	RR (b)
$(1.07 \pm 0.15) \times 10^{-11}$	298		

Comments

(a) HO radicals were generated by the photolysis of H_2O by a xenon flash lamp in 100 Torr (133 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence.

(b) Photolysis of CH_3ONO in C_2F_4-C_3H_6-NO and C_2F_4-cyclohexane-NO mixtures in 740 Torr (986 mbar) of air diluent was used to generate HO radicals and measure $k(C_2F_4)/k(C_3H_6) = 0.375\pm0.118$ and $k(C_2F_4)/k(\text{cyclohexane}) = 1.566\pm0.226$. Using $k(HO + C_3H_6) = 2.85 \times 10^{-11}$ (Atkinson et al., 2006) and $k(HO + \text{cyclohexane}) = 6.85 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2015) gives $k(HO + C_2F_4) = (1.07\pm0.34) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(1.07\pm0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.04×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$3.84 \times 10^{-12} \exp(297/T)$	250-500
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 100	250-500

Comments on Preferred Values

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

The reaction proceeds via addition to the >C=C< double bond. Based upon the behavior of the reaction of HO radicals with similar halogenated alkenes such as CH_2=CF_2 (Howard, 1976) it is expected that the kinetics of the reaction will be at the high pressure limit for total pressures above approximately 5 Torr (7 mbar). Consistent with this expectation there is no discernable difference between the rate coefficient measured in 100 Torr of argon diluent by Orkin et al. (1997, 2002) and that measured in 740 Torr of air by Acerboni et al. (1999). The HO radical initiated oxidation of $CF_2{=}CF_2$ will give COF_2 as the major product.

$$HO + CF_2{=}CF_2 \rightarrow HOCF_2CF_2$$
$$HOCF_2CF_2 + O_2 \rightarrow HOCF_2CF_2O_2$$
$$HOCF_2CF_2O_2 + NO/RO_2 \rightarrow HOCF_2CF_2O + NO_2/RO + O_2$$
$$HOCF_2CF_2O \rightarrow HOCF_2 + COF_2$$
$$HOCF_2 + O_2 \rightarrow HO_2 + COF_2$$

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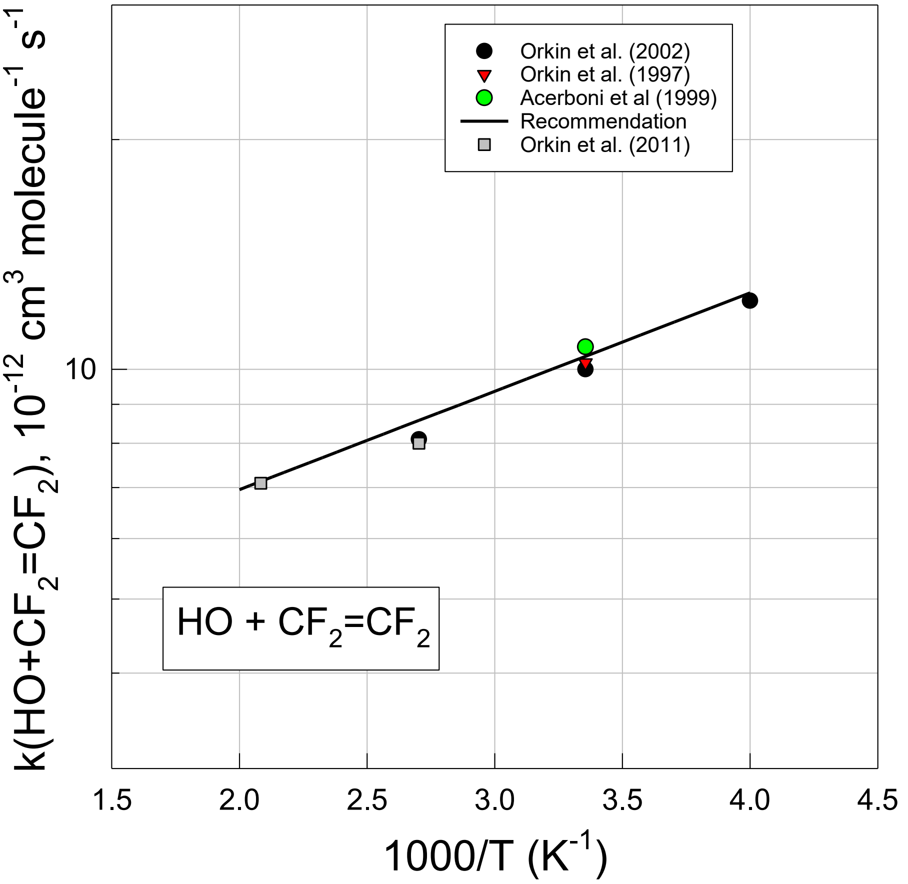

oFOx114: HO + $CF_3CF=CH_2$ (HFO-1234yf)

Last evaluated: June 2025; Last change in preferred values: June 2017.

HO + $CF_3CF=CH_2$ (HFO-1234yf) → products

Rate coefficient data

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

Comments

(a) HO radicals were generated by the photolysis of H_2O by a xenon flash lamp in 100 Torr (133 mbar) of argon diluent.

(b) HO radicals were produced using the pulsed laser photolysis of either H_2O_2 or HNO_3 at 248 nm. Experiments at 296K were conducted in a total pressure of 25-600 Torr (33-800 mbar) using helium, nitrogen, or SF_6 diluent. There was no discernable effect of total pressure or diluent on the kinetics of the reaction.

(c) HO radicals were generated by the photolysis of H_2O by a xenon flash lamp in 30-300 Torr (40-400 mbar) of argon diluent.

(d) HO radicals were generated by either flash photolysis or pulsed laser photolysis. In the flash photolysis experiments one chemical system (photolysis of water vapor) was employed while in the laser photolysis experiments three different chemical systems were used to generate HO radicals. There was no discernible difference in results obtained using the different methods. Experiments were performed in 5-200 Torr of argon or helium diluent, there was no discernible effect of pressure or diluent gas. The $CF_3CF=CH_2$ sample was purified before use and determined to be 99.99% pure.

(e) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of $CF_3CF=CH_2$ was measured relative to those of C_2H_2 and C_2H_4 and used to measure the rate coefficient ratios $k(CF_3CF=CH_2)/k(C_2H_2) = 1.21 \pm 0.09$ and $k(CF_3CF=CH_2)/k(C_2H_2) = 0.125 \pm 0.007$. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + CF_3CF=CH_2) = (9.04 \pm 0.67) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $(9.82 \pm 0.55) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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 $k = 0.545 \times (T/298)^{0.882} \exp(212/T)$ cm^3 molecule^{-1} 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 $k = 1.16 \times 10^{-12} \exp(-10/T)$ cm^3 molecule^{-1} 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 $CF_3CF{=}CH_2$ gives $CF_3C(O)F$ and HCHO as products (Hurley et al., 2008). The atmospheric fate of $CF_3C(O)F$ is hydrolysis to give $CF_3C(O)OH$ (trifluoroacetic acid).

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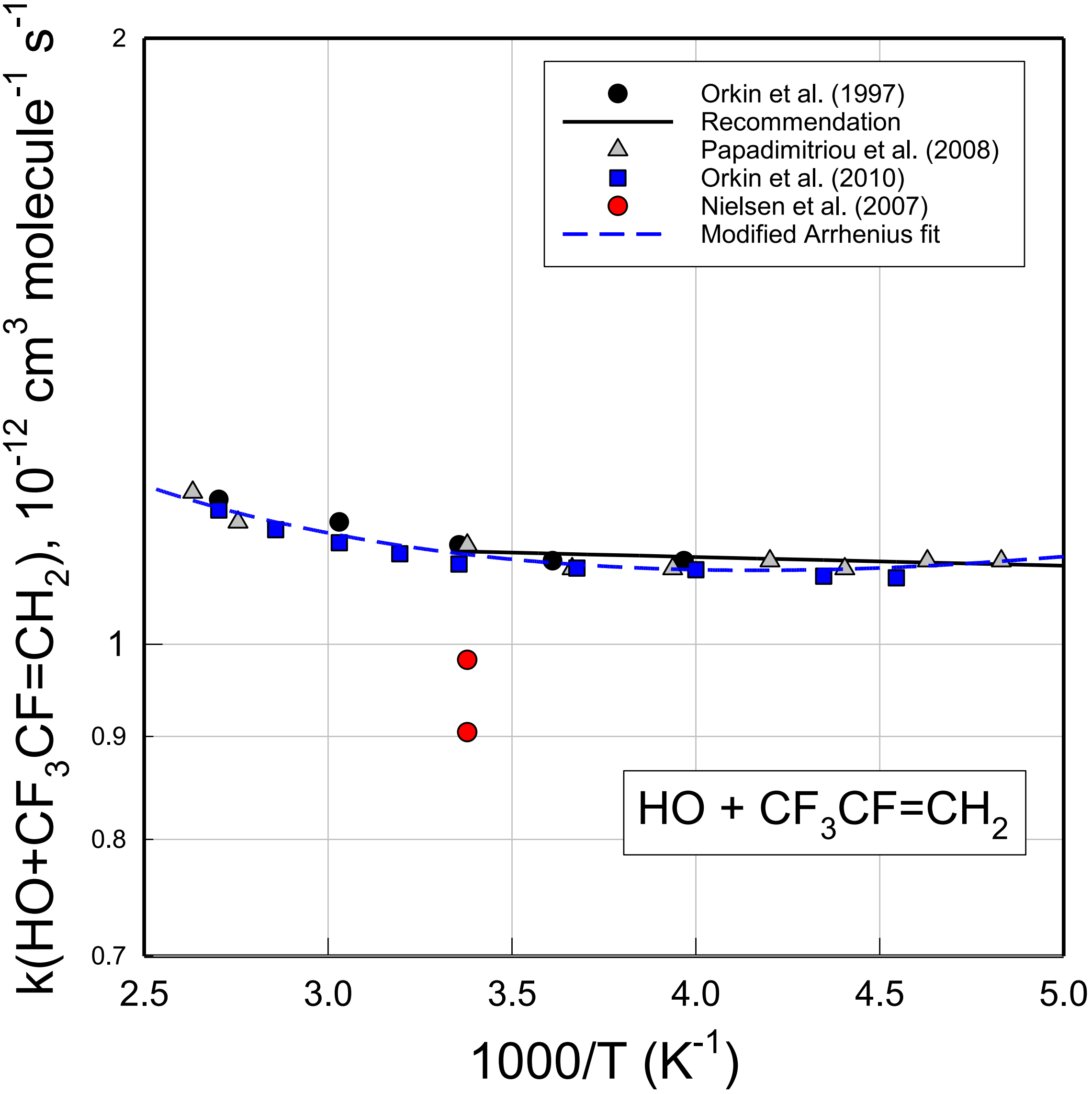
k(HO+CF3CF=CH2), 10-12 cm3 molecule-1 s-1
2
1
0.9
0.8
0.7
2.5
3.0
3.5
4.0
4.5
5.0
1000/T (K-1)
Orkin et al. (1997)
Recommendation
Papadimitriou et al. (2008)
Orkin et al. (2010)
Nielsen et al. (2007)
Modified Arrhenius fit
HO + CF3CF=CH2

oFOx115: HO + *E*-$CF_3CH{=}CHF$ (HFO-1234ze(E))

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

HO + *E*-$CF_3CH{=}CHF$ (HFO-1234ze(E)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
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		
Relative Rate Coefficients			
$(8.00 \pm 0.82) \times 10^{-13}$	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		

Comments

(a) HO radicals were generated by the photolysis of H_2O by a xenon flash lamp in 30-200 Torr (40-267 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence. There was no discernable (<5%) effect of total pressure over the range studied on the rate of reaction. A small but distinct curvature was evident in the Arrhenius plot and a modified Arrhenius expression, $k = 1.115 \times 10^{-13} (T/298)^{2.03} \exp(552/T)$ cm^3 molecule^{-1} s^{-1} was used to best represent the data.

(b) HO radicals were generated by the pulsed laser photolysis of H_2O_2 or HNO_3 and monitored using laser induced fluorescence in 45-300 Torr of helium diluent. There was no discernable effect of total pressure over the range studied.

(c) HO radicals were generated by either flash photolysis or laser photolysis and were monitored using laser induced fluorescence. In the flash photolysis experiments photolysis of water vapor was employed while in the laser photolysis experiments photolysis of N_2O to produce $O(^1D)$ atoms in the presence of either water vapor or CH_4 were used to generate HO radicals. There was no discernible difference in results obtained using the different methods. Experiments were performed in 5-200 Torr of argon or helium diluent, there was no discernible effect of pressure or diluent gas. The $CF_3CH{=}CHF$ sample was purified before use and the purity of the purified sample was determined to be 99.99%.

(d) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of *E*-$CF_3CH{=}CHF$ was measured relative to C_2H_2 and C_2H_4 and used to measure the rate coefficient ratios $k(CF_3CH{=}CHF)/k(C_2H_2) = 1.07 \pm 0.11$ and $k(E\text{-}CF_3CH{=}CHF)/\mathrm{k}(C_2H_2) = 0.111 \pm 0.006$. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + E\text{-}CF_3CH{=}CHF) = (8.00 \pm 0.82) \times 10^{-13}$ and $(8.72 \pm 0.47) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(e) Photolysis of O_3 in the presence of water vapor in 200 Torr of helium diluent was used to generate HO radicals. The loss of *E*-$CF_3CH{=}CHF$ was measured relative to n-C_4H_{10} and n-C_5H_{12} and used to measure rate coefficient ratios $k(E\text{-}CF_3CH{=}CHF)/k(n\text{-}C_4H_{10})$ and $k(E\text{-}CF_3CH{=}CHF)/k(n\text{-}C_5H_{12})$ over the temperature range 253-328 K. Rate coefficient ratios at 298 K were $k(E\text{-}CF_3CH{=}CHF)/k(n\text{-}C_4H_{10}) = 0.291 \pm 0.011$ and $k(E\text{-}CF_3CH{=}CHF)/k(n\text{-}C_5H_{12}) = 0.187 \pm 0.009$. Using $k(HO + n\text{-}C_4H_{10}) =$

$9.80 \times 10^{-12} \exp(-425/T)$ (Atkinson et al., 2006) and $k(\mathrm{HO} + n\text{-}C_5H_{12}) = 1.81 \times 10^{-11} \exp(-452/T)$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2008) gives $k(\mathrm{HO} + E\text{-}CF_3CH{=}CHF) = (7.42 \pm 0.28) \times 10^{-13}$ and $(7.14 \pm 0.34) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

There is good agreement between the rate coefficients measured in the absolute rate studies by Orkin et al. (2010), Antiñolo et al. (2017), and Tokuhashi et al. (2021) and the relative rate study by Zhang et al. (2015). The results of the relative rate study by Søndergaard et al. (2007) lie approximately 15% higher. There was no discernible effect of total pressure over the range 5-200 Torr in the studies by Orkin et al. (2010), Antiñolo et al. (2017), and Tokuhashi et al. (2021) indicating that the reaction is at, or near, the high-pressure limit for pressures above 5 Torr. The measurements by Orkin et al. (2010) and Antiñolo et al. (2017) indicate a slight curvature in the Arrhenius plot which is however not apparent in the results from Zhang et al. (2015) and Tokuhashi et al. (2021). A fit of a modified Arrhenius expression to the combined data set from Orkin et al. (2010) and Antiñolo et al. (2017) gives $k = 1.30 \times 10^{-18} T^2 \exp(551/T)$ cm^3 molecule^{-1} s^{-1}. Taking an average of the rate coefficients reported by Orkin et al. (2010), Antiñolo et al. (2017), and Tokuhashi et al. (2021) gives our preferred value at 298 K. A fit of the Arrhenius expression to the data from all studies below 300 K, except from Søndergaard et al. (2007), and adjusting the A factor to match the preferred value at 298 K gives $k = 6.91 \times 10^{-13} \exp(7/T)$ cm^3 molecule^{-1} s^{-1}. For simplicity and consistency within the IUPAC database we prefer the simple Arrhenius expression. The HO radical initiated oxidation of $CF_3CH{=}CHF$ in air gives $CF_3C(O)H$ and $HC(O)F$ as products (Javadi et al., 2008).

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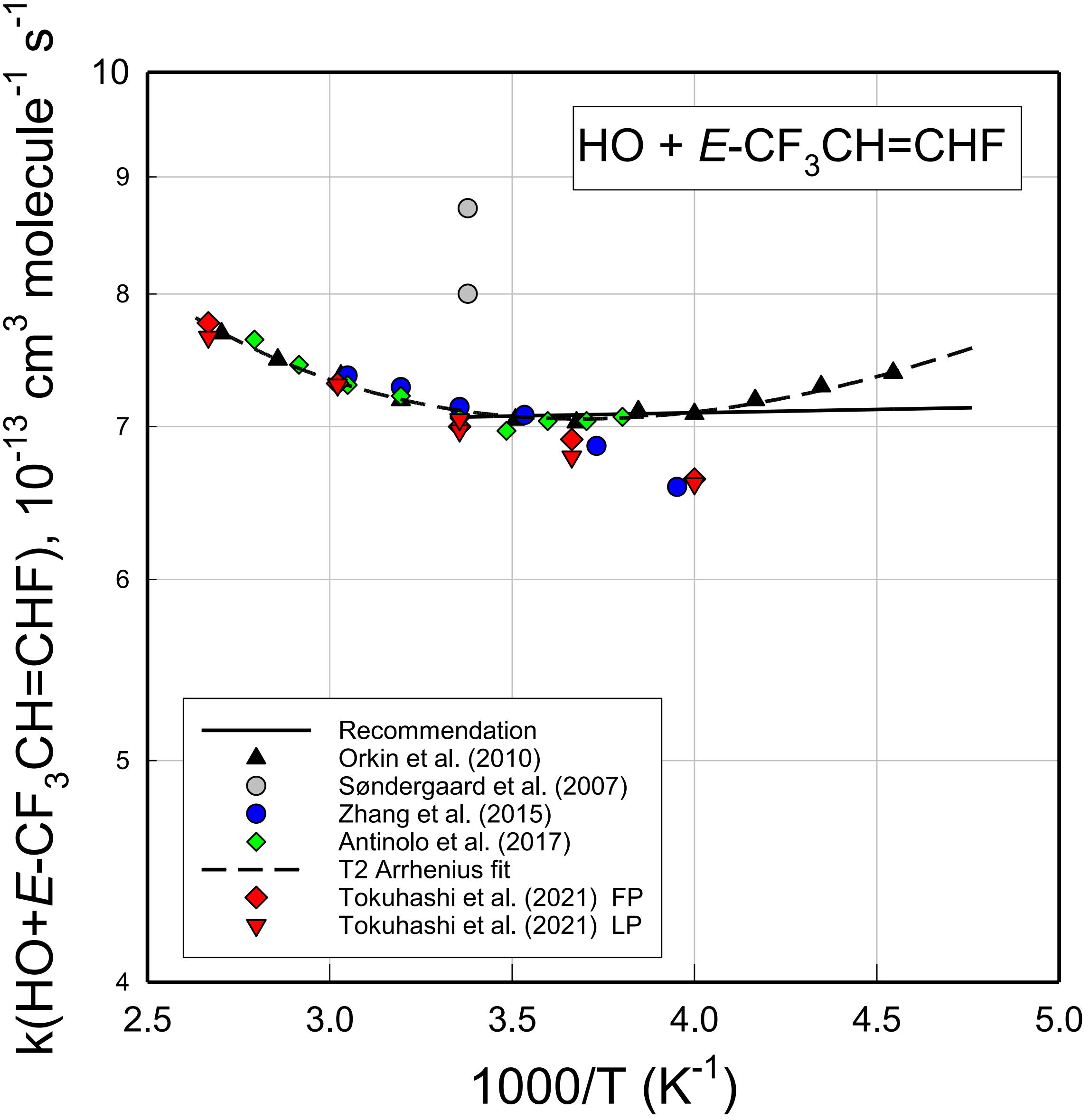
HO + *E*-$CF_3CH=CHF$
k(HO+*E*-$CF_3CH=CHF$), 10^{-13} cm^3 $molecule^{-1}$ s^{-1}
1000/T (K^{-1})
10
9
8
7
6
5
4
2.5
3.0
3.5
4.0
4.5
5.0
Recommendation
Orkin et al. (2010)
Søndergaard et al. (2007)
Zhang et al. (2015)
Antinolo et al. (2017)
T2 Arrhenius fit
Tokuhashi et al. (2021) FP
Tokuhashi et al. (2021) LP

oFOx117: HO + *Z*-CF_3CH=CHF (HFO-1234ze(Z))

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

HO + *Z*-CF_3CH=CHF (HFO-1234ze(Z)) → products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.4 \times 10^{-13} (T/298)^{1.91} \exp(640/T)$	263-358	Antiñolo et al. (2017)	PLP-LIF (a)
$(1.21 \pm 0.03) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.02 \pm 0.06) \times 10^{-12}$	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		

Comments

(a) HO radicals were generated by the pulsed laser photolysis of H_2O_2 or HNO_3 and monitored using laser induced fluorescence in 45-300 Torr of helium diluent. There was no discernible effect of total pressure on the rate coefficient over the range studied.

(b) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of *Z*-CF_3CH=CHF was measured relative to C_2H_2 and C_2H_4 and used to measure the rate coefficient ratios *k*(*Z*-CF_3CH=CHF)/*k*(C_2H_2) = 1.37±0.11 and *k*(*Z*-CF_3CH=CHF)/k(C_2H_2) = 0.146±0.012. Using *k*(HO + C_2H_2) = 7.47×10^{-13} and *k*(HO + C_2H_4) = 7.85×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006) gives *k*(HO + *Z*-CF_3CH=CHF) = (1.02±0.06) x 10^{-12} and (1.15±0.10) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

(c) Photolysis of O_3 in the presence of water vapor in 200 Torr of helium diluent was used to generate HO radicals. The loss of *E*-CF_3CH=CHF was measured relative to *n*-C_4H_{10} and *n*-C_5H_{12} to derive rate coefficient ratios *k*(*Z*-CF_3CH=CHF)/*k*(*n*-C_4H_{10}) and *k*(*Z*-CF_3CH=CHF)/*k*(*n*-C_5H_{12}) over the temperature range 253-328 K. Rate coefficient ratios at 298 K were *k*(*Z*-CF_3CH=CHF)/*k*(*n*-C_4H_{10}) = 0.585±0.009 and *k*(*Z*-CF_3CH=CHF)/*k*(*n*-C_5H_{12}) = 0.358±0.007. Using *k*(HO + *n*-C_4H_{10}) = $9.80 \times 10^{-12} \exp(-425/T)$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006) and *k*(HO + *n*-C_5H_{12}) = $1.81 \times 10^{-11} \exp(-452/T)$ cm^3 $molecule^{-1}$ s^{-1} (Calvert et al., 2008) gives *k*(HO + *Z*-CF_3CH=CHF) = $(1.38 \pm 0.02) \times 10^{-12}$ and $(1.42 \pm 0.03) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

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

Comments on Preferred Values

There is good agreement between the rate coefficients measured in the absolute rate study by Antiñolo et al. (2017) and the relative rate studies by Nilsson et al. (2009) and Zhang et al. (2015). There was no discernible effect of total pressure over the range 45-300 Torr in the study by Antiñolo et al. (2017) indicating that the reaction is at, or near, the high-pressure limit for pressures above 45 Torr. The preferred rate coefficient at 298 K is taken from the study by Antiñolo et al. (2017). The absolute rate measurements reveals a small curvature in the Arrhenius plot. A fit of a modified Arrhenius expression to the data set from Antiñolo et al. (2017) gives $k = 1.46 \times 10^{-18}\ T^2 \exp(666/T)$ cm^3 molecule^{-1} s^{-1}. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 280 K and is derived from the three-parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$.
The HO radical initiated oxidation of $CF_3CH{=}CHF$ in air yields $CF_3C(O)H$ and HC(O)F as products (Javadi et al., 2008).

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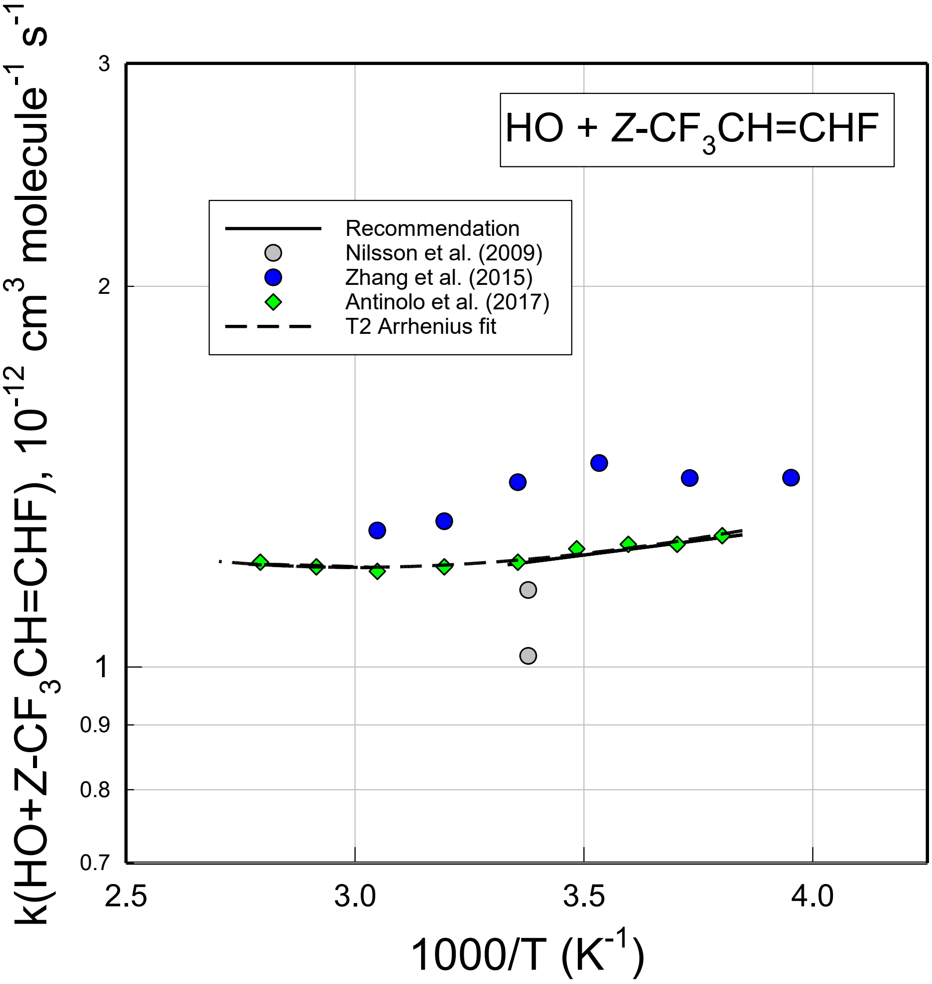
HO + Z-CF3CH=CHF
Recommendation
Nilsson et al. (2009)
Zhang et al. (2015)
Antinolo et al. (2017)
T2 Arrhenius fit
k(HO+Z-CF3CH=CHF), 10-12 cm3 molecule-1 s-1
3
2
1
0.9
0.8
0.7
2.5
3.0
3.5
4.0
1000/T (K-1)

oFOx118: HO + *E*-$CF_3CF=CHF$

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

HO + *E*-$CF_3CF=CHF \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(2.05 \pm 0.20) \times 10^{-12}$	296	Hurley et al. (2007)	RR (a)
$(2.12 \pm 0.23) \times 10^{-12}$	296		

Comments

(a) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of *E*-$CF_3CF=CHF$ was measured relative to those of C_2H_2 and C_2H_4 and used to measure the rate coefficient ratios $k(E\text{-}CF_3CF=CHF)/k(C_2H_2)$ = 2.74±0.27 and $k(E\text{-}CF_3CF=CHF)/k(C_2H_4)$ = 0.27±0.03. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + E\text{-}CF_3CF=CHF) = (2.05\pm0.20) \times 10^{-12}$ and $(2.12\pm0.23) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	2.2×10^{-12}	298
Reliability		
$\Delta \log k$	0.15	298

Comments on Preferred Values

The preferred rate coefficient at 298 K is based on the results from the study by Hurley et al. (2007). Tovar et al. (2014) and Rivela et al. (2019) reported the results of a relative rate study of the reaction of a mixture of the two isomers *E*- and *Z*-$CF_3CF=CHF$ over the temperature range 287-313 K. The isomeric composition of the sample was not measured and the IR feature(s) used to follow the loss of (*E/Z*)-$CF_3CF=CHF$ were not stated so it is unclear which isomer(s) was being studied. However, judging from the similarity of the reported rate coefficient at 298 K with that for *E*-$CF_3CF=CHF$ reported by Hurley et al. (2007) it appears that Tovar et al. (2014) and Rivela et al. (2019) were mainly measuring the kinetics of the *E*-$CF_3CF=CHF$ isomer. The rate coefficients reported by Tovar et al. (2014) and Rivela et al. (2019) at 298 K were $(2.62 \pm 0.76) \times 10^{-12}$ and $(2.85 \pm 0.78) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and are consistent within the combined uncertainties with the preferred value for the *E*-$CF_3CF=CHF$ isomer.

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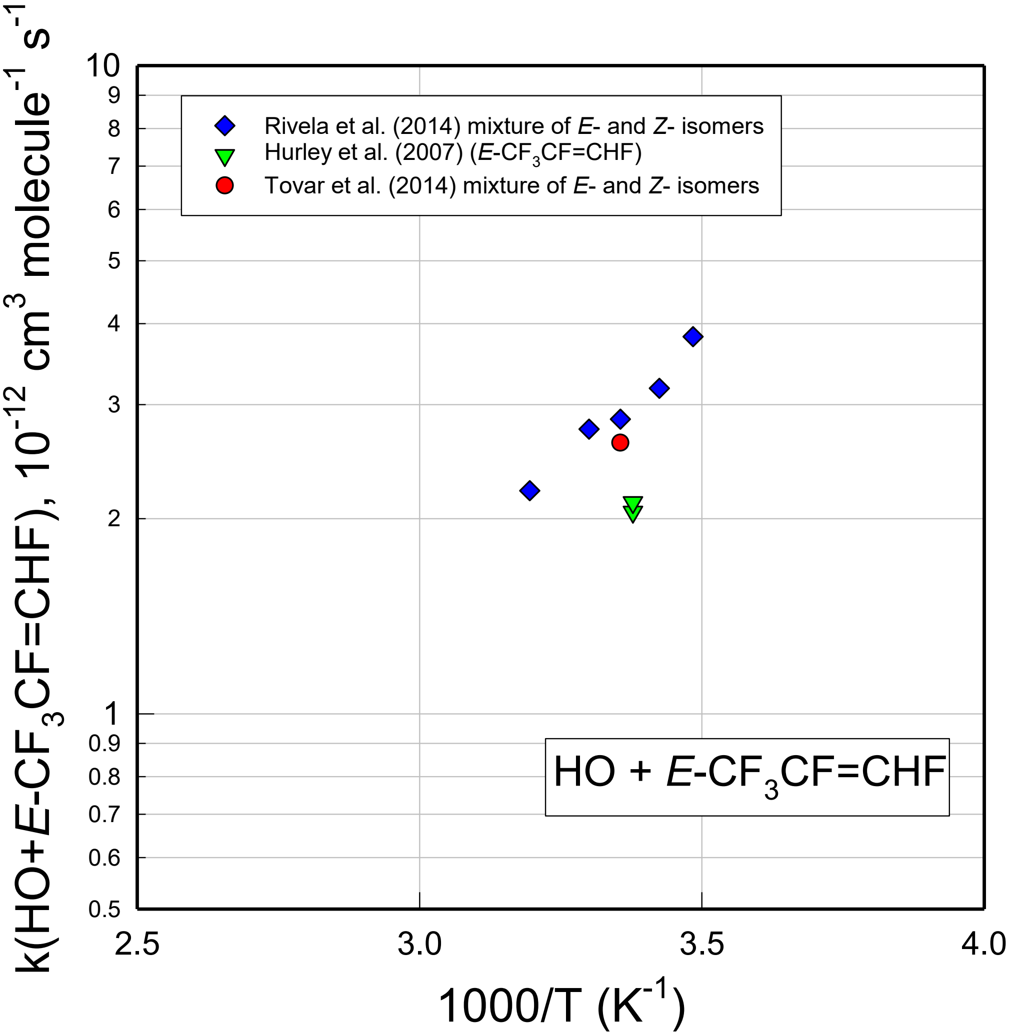

oFOx119: HO + *Z*-$CF_3CF=CHF$ (HFO-1225ye(Z))

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

HO + *Z*-$CF_3CF=CHF$ (HFO-1225ye(Z)) → products

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.6 \times 10^{-18}\ T^2 \exp(655/T)$	206-380	Papadimitriou et al. (2008)	PLP-LIF (a)
1.28×10^{-12}	298		
Relative Rate Coefficients			
$(1.15 \pm 0.11) \times 10^{-12}$	296	Hurley et al. (2007)	RR (b)
$(1.26 \pm 0.08) \times 10^{-12}$	296		

Comments

(a) HO radicals were produced using the pulsed laser photolysis of either H_2O_2 or HNO_3 at 248 nm. Experiments at 296K were conducted in a total pressure of 25-600 Torr (33-800 mbar) using helium, nitrogen, or SF_6 diluent. There was no discernable effect of total pressure or diluent on the kinetics of the reaction.

(b) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of *Z*-$CF_3CF=CHF$ was measured relative to those of C_2H_2 and C_2H_4 and used to derive rate coefficient ratios $k(Z\text{-}CF_3CF{=}CHF)/k(C_2H_2) = 1.54\pm0.15$ and $k(Z\text{-}CF_3CF{=}CHF)/k(C_2H_4) = 0.16\pm0.01$. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + Z\text{-}CF_3CF{=}CHF) = (1.15\pm0.11) \times 10^{-12}$ and $(1.26\pm0.08) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 $molecule^{-1}$ s^{-1}	1.2×10^{-12}	298
	$7.60 \times 10^{-13} \exp(155/T)$	200-300
Reliability		
$\Delta \log k$	0.10	298
Δ E/R	±100	200-300

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 $k(HO + Z\text{-}CF_3CF{=}CHF) = 1.62 \times 10^{-18}\ T^2 \exp(655/T)$ cm^3 $molecule^{-1}$ 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 parameter expression should be used.

Tovar et al. (2014) and Rivela et al. (2019) have reported the results of a relative rate study of the reaction of a mixture of the two isomers *E*- and *Z*-$CF_3CF=CHF$ over the temperature range 287-313 K. The isomeric composition of the sample was not measured and the IR feature(s) used to follow the loss of (*E/Z*)-$CF_3CF=CHF$ were not stated. However, judging from the similarity of the reported rate coefficients at 298 K of $(2.62 \pm 0.76) \times 10^{-12}$ and $(2.85 \pm 0.78) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} with the values for k(HO + *E*-$CF_3CF=CHF$) = $(2.05\pm0.20) \times 10^{-12}$ and $(2.12\pm0.23) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} reported by Hurley et al. (2008) it appears that Tovar et al. (2014) and Rivela et al. (2019) were mainly measuring the kinetics of the *E*-$CF_3CF=CHF$ isomer.

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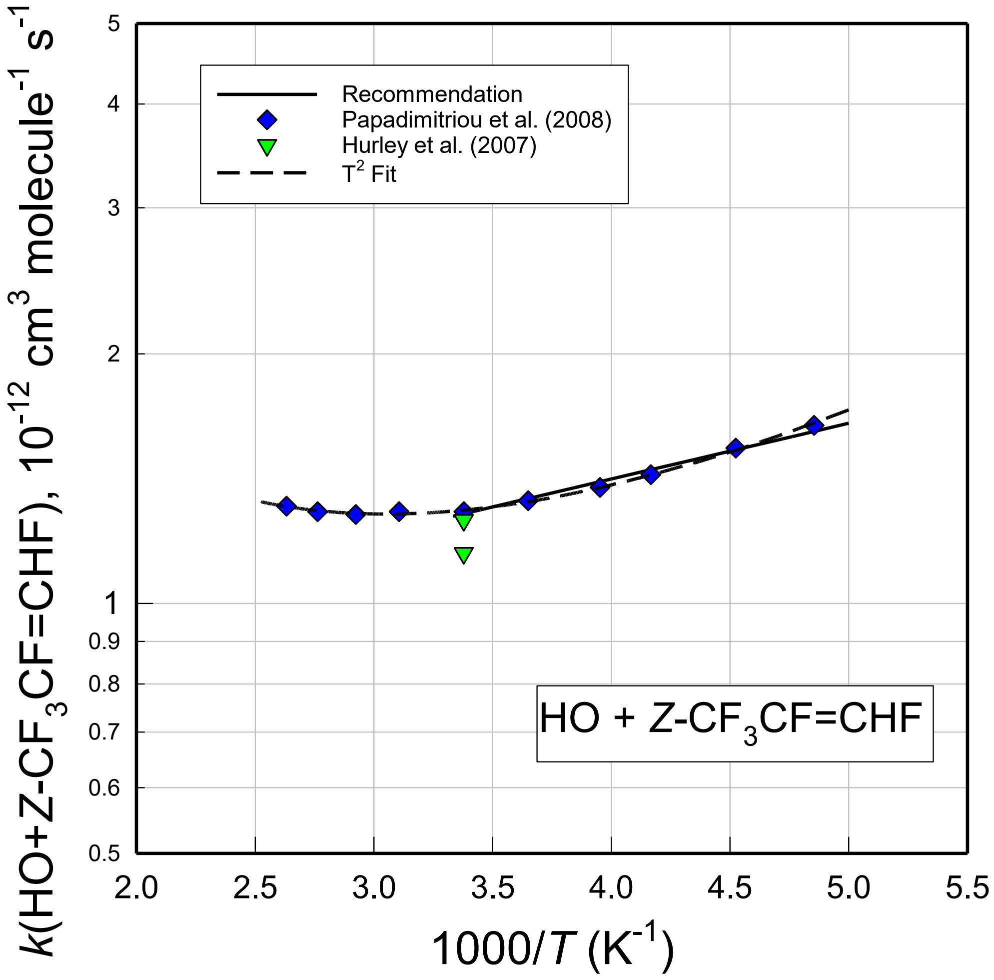

oFOx116: HO + $CF_3CF=CF_2$ (FO-1216)

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

HO + $CF_3CF=CF_2$ (FO-1216) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
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		
Relative Rate Coefficients			
$(2.28 \pm 0.16) \times 10^{-12}$	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		

Comments

(a) HO radicals were generated by the photolysis of H_2O by a xenon flash lamp in 75-750 Torr (76-760 mbar) of argon diluent. Single-exponential decays were observed over the temperature ranges 293-489 K and 656-831 K while bi-exponential decays were observed for the intermediate temperature range 528-641 K. There was no discernable effect of total pressure over the range studied on the rate of reaction at 293 K. Fitting the Arrhenius expression to the data from 293-489 K gave $k = (9.95 \pm 0.64) \times 10^{-13} \exp[(486 \pm 44 \text{ cal})/RT]$ cm^3 molecule^{-1} s^{-1}. A small but distinct curvature was evident in the Arrhenius plot and a modified Arrhenius expression, $k = 1.115 \times 10^{-13} (T/298)^{2.03} \exp(552/T)$ cm^3 molecule^{-1} s^{-1} was used to best represent the data.

(b) HO radicals were produced by the photolysis of H_2O by a xenon flash lamp in 100 Torr (133 mbar) of argon diluent.

(c) HO radicals were produced by the xenon flash lamp photolysis of H_2O, or pulsed ArF eximer laser photolysis of N_2O to produce O(^{1}D) atoms which were then reacted with either H_2O or CH_4 to give HO radicals, or pulsed laser photolysis of H_2O_2. HO radicals were monitored by laser induced fluorescence. Experiments were conducted in 5-200 Torr of helium, or argon, diluent. There was no discernible effect of pressure or diluent gas over the range studied. Results from experiments using four different sources of HO radicals were indistinguishable.

(d) HO radicals were produced by the photolysis of H_2O by a xenon flash lamp in 30-100 Torr (40-133 mbar) of argon diluent.

(e) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of $CF_3CF=CF_2$ was measured relative to C_2H_2 and C_2H_4 and used to measure the rate coefficient ratios $k(CF_3CF=CF_2)/k(C_2H_2) = 2.65\pm0.15$ and $k(CF_3CF=CF_2)/k(C_2H_4) = 0.29\pm0.02$. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + CF_3CF=CF_2) = (2.28\pm0.16) \times 10^{-13}$ and $(1.98\pm0.11) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(f) Photolysis of CH_3ONO in 740 Torr (986 mbar) of air diluent was used to generate HO radicals. The loss of $CF_3CF=CF_2$ was measured relative to C_2H_4 and C_3H_6 and used to measure the rate coefficient ratios $k(CF_3CF{=}CF_2)/k(C_2H_4)$ = 0.3151±0.0552 and $k(CF_3CF{=}CF_2)/k(C_3H_6)$ = 0.1153±0.0321. Using $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k(HO + C_3H_6) = 2.85 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO + CF_3CF{=}CF_2) = (2.47 \pm 0.43) \times 10^{-12}$ and $(3.29 \pm 0.91) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The results from the absolute rate studies of McIlroy et al. (1993), Orkin et al (1997, 2011) and Tokuhashi et al. (2000) and the relative rate studies of Aceboni et al. (2001) and Mashino et al. (2000) are in good agreement within the experimental uncertainties. There is excellent agreement in the reported rate coefficients from the absolute rate studies at 298 K. The preferred value at 298 K is the average of the measurements by McIlroy et al. (1993), Orkin et al (1997, 2011) and Tokuhashi et al. (2000). There is significant curvature in the Arrhenius plot. Fitting the expression $k = CT^2 \exp(-D/T)$ to the 240K < T < 500 K data from McIlroy et al. (1993), Orkin et al (1997, 2011) and Tokuhashi et al. (2000) and adjusting the pre-exponential A-factor to return the preferred value at 298 K gives $k(HO + CF_3CF{=}CF_2) = 1.11 \times 10^{-18}\ T^2 \exp(922/T)$ cm^3 molecule^{-1} s^{-1}. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 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 should not be used outside the specified temperature range (240-340 K); rather, the modified expression should be used.

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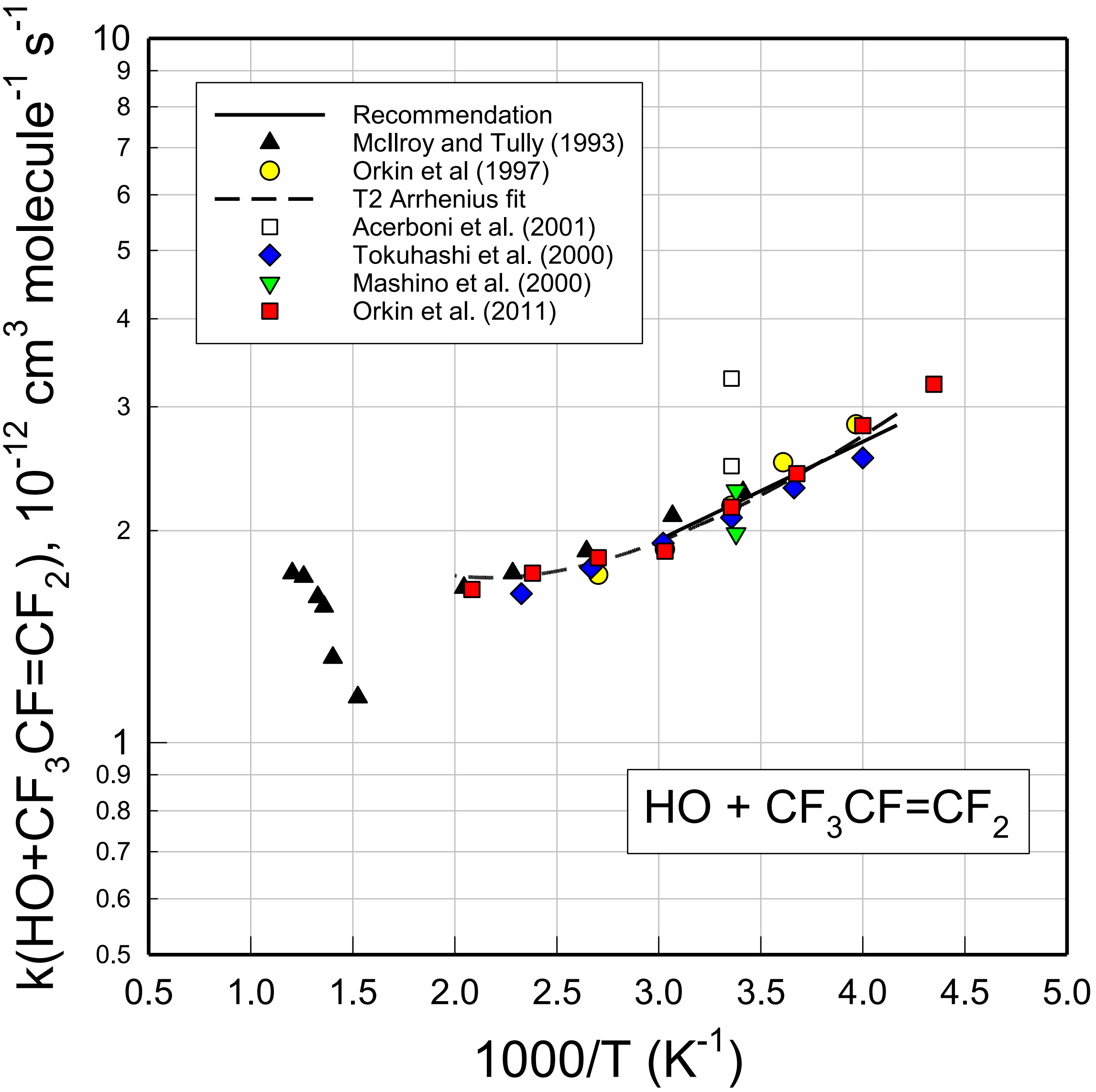

1903
1904

oFOx135: HO + *E*-$CF_3CH=CHCF_3$ (HFO-1336mzz(E))

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

HO + *E*-$CF_3CH=CHCF_3$ (HFO-1336mzz(E)) → products

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.94\pm0.80) \times 10^{-13} \exp(-(496\pm10)/T)$	211-374	Baasandorj et al. (2018)	LP-LIF (a)
$(1.31 \pm 0.15) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(1.47 \pm 0.21) \times 10^{-13}$	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		

Comments

(a) HO radicals were generated by 248 nm laser photolysis of H_2O_2 or $(CH_3)_3COOH$ in 2.5-200 Torr of He or N_2 and were monitored using laser induced fluorescence. There was no discernible effect of pressure or diluent gas on the rate coefficient.

(b) HO radicals were generated by the photolysis of $(CH_3)_2CHONO$ or CH_3ONO in 700 Torr air/N_2/O_2 in the presence of NO. The loss of *E*-$CF_3CH=CHCF_3$ was monitored relative to C_3H_8 and C_2H_6 using FTIR spectroscopy. Rate coefficient ratios of $k(E\text{-}CF_3CH=CHCF_3)/k(C_3H_8) = 0.14\pm0.02$ and $k(E\text{-}CF_3CH=CHCF_3)/k(C_2H_6) = 0.80\pm0.10$ were measured. Using $k(HO + C_3H_8) = 1.05 \times 10^{-12}$ and $k(HO + C_2H_6) = 2.35 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 2006) at 296 K gives $k(HO + E\text{-}CF_3CH=CHCF_3) = (1.47\pm0.21) \times 10^{-13}$ and $(1.88\pm0.24) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.

(c) HO radicals were generated by the pulsed laser photolysis of O_3 in the presence of H_2O in 100 Torr of He at 296-375 K. The loss of *E*-$CF_3CH=CHCF_3$ was monitored relative to that of C_2H_6 by FTIR spectroscopy. At 296 K a rate coefficient ratio of $k(E\text{-}CF_3CH=CHCF_3)/k(C_2H_6) = 0.50\pm0.04$ was measured. Using $k(C_2H_6) = 6.9 \times 10^{-13} \exp(-1000/T)$ cm³ molecule⁻¹ s⁻¹ (IUPAC, 2024) gives $k(E\text{-}CF_3CH=CHCF_3) = (1.21\pm0.10) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. Rate coefficient ratios at 296-375 K were scaled to $k(C_2H_6) = 6.9 \times 10^{-13} \exp(-1000/T)$ cm³ molecule⁻¹ s⁻¹ (IUPAC, 2024) and an Arrhenius fit to the results gives $k(E\text{-}CF_3CH=CHCF_3) = 1.18 \times 10^{-12} \exp(-668/T)$ cm³ molecule⁻¹ s⁻¹.

(d) Photolysis of O_3 in the presence of water vapor in 200 Torr of helium was used to generate HO radicals. The loss of *E*-$CF_3CH=CHCF_3$ was measured relative to C_2H_6 over the temperature range 253-328 K. A rate coefficient ratio of $k(E\text{-}CF_3CH=CHCF_3)/k(C_2H_6) = 0.458\pm0.002$ was reported at 298 K. Using $k(C_2H_6) = 6.9 \times 10^{-13} \exp(-1000/T)$ (IUPAC, 2024) gives $k(E\text{-}CF_3CH=CHCF_3) = (1.21\pm0.10) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. Rate coefficient ratios at 253-328 K were scaled to $k(C_2H_6) = 6.9 \times 10^{-13} \exp(-1000/T)$ cm³ molecule⁻¹ s⁻¹ (IUPAC, 2024) and an Arrhenius fit to the results gives $k(E\text{-}CF_3CH=CHCF_3) = 5.91 \times 10^{-13} \exp(-515/T)$ cm³ molecule⁻¹ s⁻¹.

(e) Photolysis of O_3 in the presence of water vapor in 200 Torr of helium was used to generate HO radicals. The loss of *E*-$CF_3CH=CHCF_3$ was measured relative to CH_2FCH_2F over the temperature range 253-328 K. A rate coefficient ratio of $k(E\text{-}CF_3CH=CHCF_3)/k(CH_2FCH_2F) = 1.08\pm0.02$ was reported at 298 K. Using $k(CH_2FCH_2F) = 1.5 \times 10^{-12} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2024) gives $k(E\text{-}CF_3CH{=}CHCF_3) = (1.21\pm0.10) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Rate coefficient ratios at 253-328 K were scaled to $k(CH_2FCH_2F) = 1.5 \times 10^{-12} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2024) and an Arrhenius fit to the results gives $k(HO{+}E\text{-}CF_3CH{=}CHCF_3) = 4.62 \times 10^{-13} \exp(-423/T)$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.31×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$6.94 \times 10^{-13} \exp(-496/T)$	210-380
Reliability		
$\Delta \log k$	$\pm$ 0.06	298
Δ E/R	$\pm$ 100	210-380

Comments on Preferred Values

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

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

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

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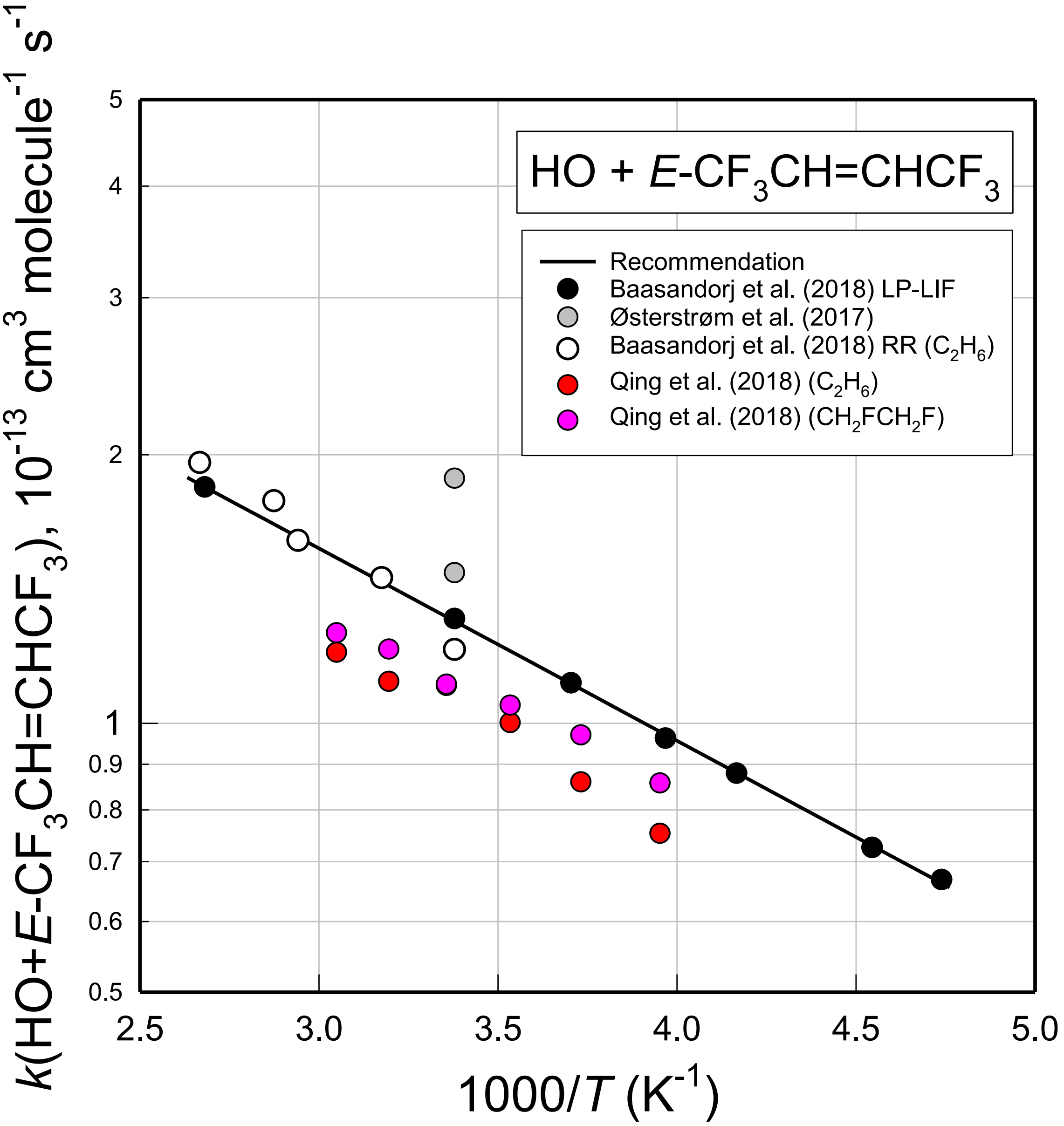

HO + E-$CF_3CH=CHCF_3$
Recommendation
Baasandorj et al. (2018) LP-LIF
Østerstrøm et al. (2017)
Baasandorj et al. (2018) RR (C_2H_6)
Qing et al. (2018) (C_2H_6)
Qing et al. (2018) (CH_2FCH_2F)
k(HO+E-$CF_3CH=CHCF_3$), 10^{-13} cm^3 $molecule^{-1}$ s^{-1}
5
4
3
2
1
0.9
0.8
0.7
0.6
0.5
2.5
3.0
3.5
4.0
4.5
5.0
1000/T (K^{-1})

oFOx136: HO + *Z*-$CF_3CH=CHCF_3$ (HFO-1336mzz(Z))

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

HO + *Z*-$CF_3CH=CHCF_3$ (HFO-1336mzz(Z)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$5.73 \times 10^{-19}\ T^2 \exp(-678/T)$	212-374	Baasandorj et al. (2011)	LP-LIF (a)
$(4.91 \pm 0.50) \times 10^{-13}$	296		
Relative Rate Coefficients			
$(3.99 \pm 0.63) \times 10^{-13}$	296	Østerstrøm et al. (2017)	RR (b)
$(4.18 \pm 0.42) \times 10^{-13}$	296		
See comment (c)	296-375	Baasandorj et al. (2018)	RR (c)
$(4.94 \pm 0.09) \times 10^{-13}$	296		

Comments

(a) HO radicals were generated by 248 nm laser photolysis of H_2O_2 or $(CH_3)_3COOH$ in 2.5-200 Torr of He or N_2. There was no discernible effect of pressure or diluent gas on the rate coefficient.

(b) HO radicals were generated by the photolysis of $(CH_3)_2CHONO$ or CH_3ONO in 700 Torr air/N_2/O_2 in the presence of NO. The loss of *Z*-$CF_3CH=CHCF_3$ was monitored relative to C_3H_8 and C_2H_6 using FTIR spectroscopy. Rate coefficient ratios of k(*Z*-$CF_3CH=CHCF_3$)/k(C_3H_8) = 0.38±0.06 and k(*Z*-$CF_3CH=CHCF_3$)/k(C_2H_6) = 1.78±0.18 were measured. Using k(HO + C_3H_8) = 1.05×10^{-12} cm^3 molecule^{-1} s^{-1} and k(HO + C_2H_6) = 2.35×10^{-13} cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) at 296 K gives k(HO + *Z*-$CF_3CH=CHCF_3$) = $(3.99 \pm 0.63) \times 10^{-13}$ and $(4.18 \pm 0.42) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(c) HO radicals were generated by the 248 nm pulsed laser photolysis of O_3 in the presence of H_2O in 100-200 Torr of He at 296-375 K. The loss of *Z*-$CF_3CH=CHCF_3$ was monitored relative to that of C_2H_6 by FTIR spectroscopy. At 296, 345, and 375 K rate coefficient ratios of k(*Z*-$CF_3CH=CHCF_3$)/k(C_2H_6) = 2.10±0.04, 1.24±0.02, and 1.02±0.02 were measured. Using k(C_2H_6) = $6.9 \times 10^{-13} \exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2024) gives k(*Z*-$CF_3CH=CHCF_3$) = (4.94±0.09), (4.71±0.08), and (4.89±0.10) × 10^{-13} cm^3 molecule^{-1} s^{-1} at 296, 345, and 375 K, respectively.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	4.80×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$2.46 \times 10^{-13} \exp(199/T)$	210-300
Reliability		
$\Delta \log k$	± 0.06	298
$\Delta E/R$	± 100	210-300

Comments on Preferred Values

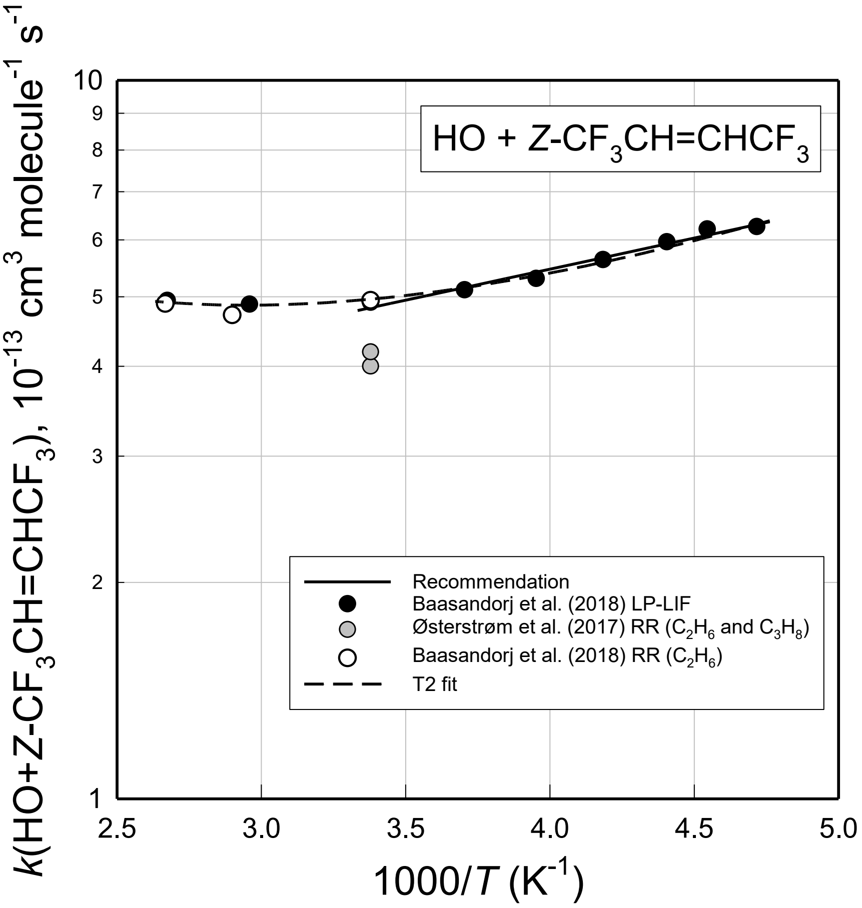
There rate coefficients measured in the absolute and relative rate studies by Baasandorj et al. (2011) and the relative rate study by Østerstrøm et al. (2017) are consistent. Distinct curvature in the Arrhenius plot is evident over temperature range studied by Baasandorj et al. (2011) and the data are well described by the modified Arrhenius expression $k = (5.73\pm0.60) \times 10^{-19}\ T^2 \exp(-(678\pm10)/T)$ cm^3 molecule^{-1} s^{-1}. A fit of the Arrhenius expression to the absolute rate data from Baasandorj et al. (2011) below 300 K gives $k = 2.46 \times 10^{-13} \exp(199/T)$ which gives $k = 4.80 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. For simplicity and consistency within the IUPAC database we prefer the simple Arrhenius expression.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

Baasandorj, M., Marshall, P., Waterland, R. L., Ravishankara, A. R., and Burkholder, J. B.: J. Phys. Chem. A, 122, 4635-4646, 2018.

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



oClOx95: HO + CH_2=CHCl

Last evaluated: June 2025; Last change in preferred values: June 2017.

HO + CH_2=CHCl → products

Rate coefficient data

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

Comments

(a) HO radicals were produced by the reaction of H atoms with NO_2 in 0.7-7.0 Torr (0.9-9.3 mbar) of helium. The rate coefficient was dependent on total pressure increasing from approximately 2×10^{-12} to 5×10^{-12} cm^3 molecule^{-1} s^{-1} over the total pressure range 0.7-7.0 Torr.

(b) Flash photolysis of H_2O in 50 or 100 Torr of argon was used as a source of HO radicals. The decay of HO radicals was monitored using resonance fluorescence. There was no discernable effect (<5%) of total pressure over the range studied.

(c) Pulse radiolysis of one atmosphere of argon containing approximately 6 Torr of water vapor was used as a source of HO radicals. Resonance absorption at 308 nm was used to monitor the decay of HO radicals in the presence of vinyl chloride. It was deduced that the predominant reaction channel changes from an addition-initiated reaction at temperatures below 588 K to a hydrogen abstraction reaction for temperatures above 723 K. The rate coefficient for the addition reaction was described by the Arrhenius expression $k = 2.14 \times 10^{-12}$ exp[(700±120)/T] while that for the H-abstraction reaction was described by $k = 2.98 \times 10^{-11}$ exp[-(4020±700)/T] cm^3 molecule^{-1} s^{-1}.

(d) Photolysis of HONO at 351 nm in 740 Torr of helium was used as a source of HO radicals.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	7.55×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	2.54×10^{-12} exp(325/T)	280-600
Reliability		
Δ log k	± 0.08	298
Δ E/R	± 100	280-600

Comments on Preferred Values

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

The reaction proceeds via addition of HO to the >C=C< double bond to give $HOCH_2CHCl$ and $CH_2CHClOH$ radicals with the former expected to predominate. Elimination of a Cl atom from the $CH_2CHClOH$ radical will give the enol $CH_2=CHOH$. Addition of O_2 followed by reaction with NO is expected to give a variety of products including $HOCH_2CHO$, HCHO, and HC(O)Cl.

References

Howard, C. J.: J. Chem. Phys., 65, 4771, 1976.

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Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., J. Chem. Phys., 67, 458, 1977.

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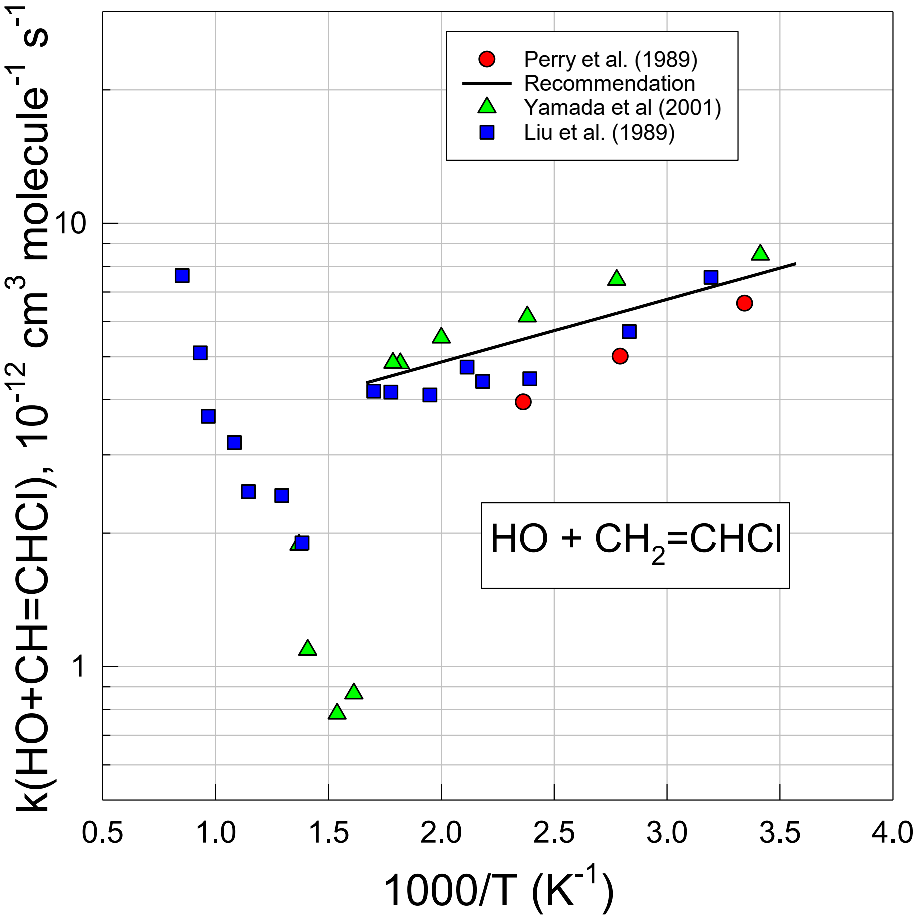

oFOx120: HO + *E*-$CF_3CH{=}CHCl$ (HCFO-1233zd(E))

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

HO + *E*-$CF_3CH{=}CHCl$ (HCFO-1233zd(E)) → products

Rate coefficient data

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

Comments

(a) HO radicals were produced by the pulsed photolysis of H_2O by a xenon flash lamp in 100 Torr (133 mbar) of argon diluent.

(b) HO radicals were generated by the photolysis of H_2O_2, HNO_3, or $(CH_3)_3COOH$ 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 CH_3ONO in 700 Torr (933 mbar) of air. The loss of *E*-$CF_3CH{=}CHCl$ was monitored relative to those of C_2H_4 and C_2H_2. In the initial work by Sulbaek Andersen et al. (2008) the loss of *E*-$CF_3CH{=}CHCl$ via reaction with Cl atoms produced during the oxidation of *E*-$CF_3CH{=}CHCl$ 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 $k(E\text{-}CF_3CH{=}CHCl)/k(C_2H_4) = 0.042 \pm 0.004$ and $k(E\text{-}CF_3CH{=}CHCl)/k(C_2H_2) = 0.430 \pm 0.034$. 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 $k(E\text{-}CF_3CH{=}CHCl) = (3.30 \pm 0.30) \times 10^{-13}$ and $(3.21 \pm 0.25) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.53×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$8.79 \times 10^{-13} \exp(-272/T)$	220-300
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 100	220-300

Comments on Preferred Values

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 is evidence in the combined data set from Orkin et al. (2014) and Gierczak et al. (2014) for a slight curvature in the Arrhenius plot. Fitting the three parameter equation, $k = CT^2 \exp(-D/T)$ to the data from Orkin et al. (2014) and Gierczak et al. (2014) gives $k(\mathrm{HO} + E\text{-}\mathrm{CF_3CH{=}CHCl}) = 1.70 \times 10^{-18}\ T^2 \exp(248/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-380 K. 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 $B = D + 2T$ with the pre-exponential factor adjusted to reproduce the preferred k(298K) value, $k(\mathrm{HO} + E\text{-}\mathrm{CF_3CH{=}CHCl}) = 8.79 \times 10^{-13} \exp(-272/T)$ cm^3 molecule^{-1} s^{-1}.

References

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

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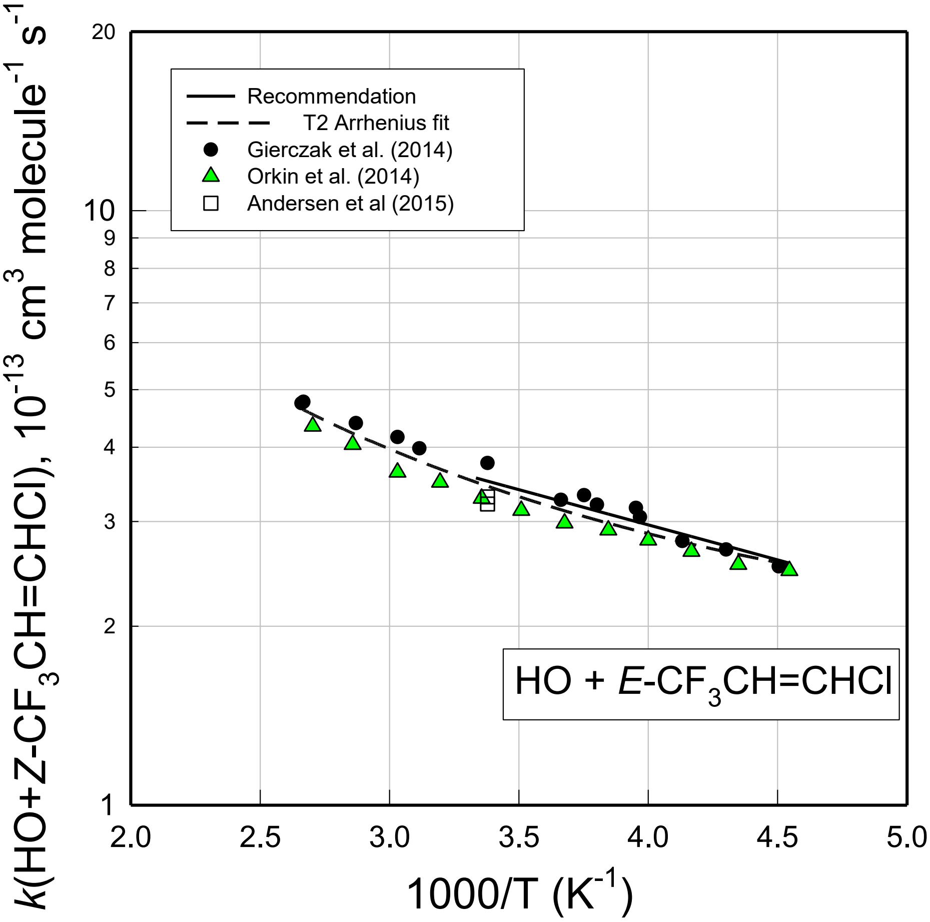
Sulbaek Andersen, M. P., Sølling, T. I., Andersen, L. L., Volkova, A., Hovanessian, D., Britzman, C., Nielsen, O. J., and Wallington, T. J.: Phys. Chem. Chem. Phys., 44, 27949, 2018.



oFOx121: HO + *Z*-$CF_3CH=CHCl$ (HCFO-1233zd(Z))

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

HO + *Z*-$CF_3CH=CHCl$ (HCFO-1233zd(Z)) → products

Rate coefficient data

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

Comments

(a) HO radicals were generated by the photolysis of H_2O_2, HNO_3, or $(CH_3)_3COOH$ 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 CH_3ONO in 700 Torr (933 mbar) of air. The loss of *Z*-$CF_3CH=CHCl$ was monitored relative to C_2H_4 and C_2H_2. Corrections for the loss of *Z*-$CF_3CH=CHCl$ via reaction with Cl atoms produced during the oxidation of *Z*-$CF_3CH=CHCl$ were computed and applied. Rate coefficient ratios of $k(Z\text{-}CF_3CH=CHCl)/k(C_2H_4) = 0.103\pm0.014$ and $k(Z\text{-}CF_3CH=CHCl)/k(C_2H_2) = 0.960\pm0.082$ were reported. 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 $k(Z\text{-}CF_3CH=CHCl) = (8.09\pm1.10) \times 10^{-13}$ and $(7.17\pm0.61) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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 $k(HO + Z\text{-}CF_3CH=CHCl) = 7.22 \times 10^{-19}\ T^2 \exp(800/T)$ cm^3 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, $k(HO + CF_3CH=CHCl) = 3.61 \times 10^{-13} \exp(280/T)$

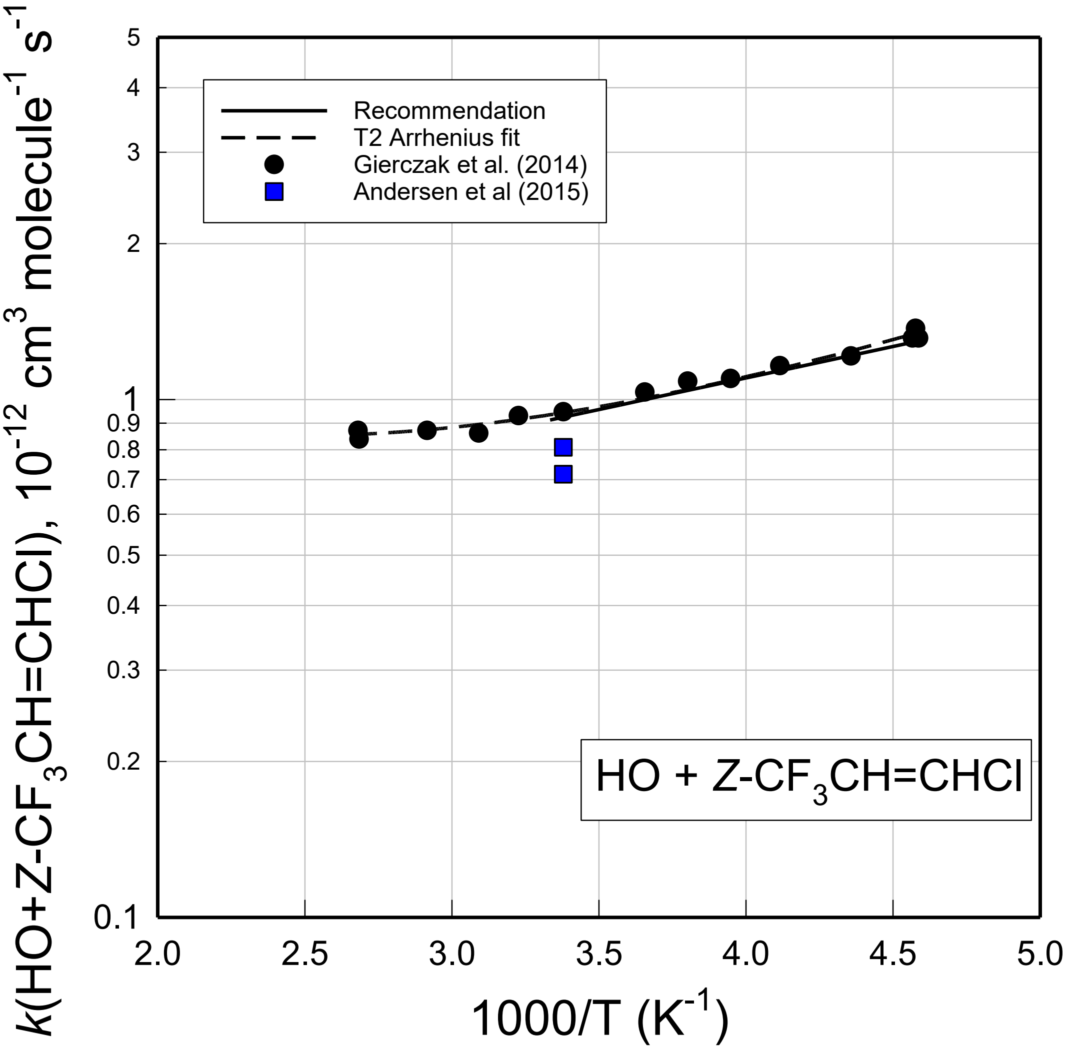
cm^3 molecule^{-1} s^{-1} should not be used outside the specified temperature range (220-300 K); rather, the full three parameter expression should be used.

References

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

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

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



oFOx165: HO + *E*-$CF_3CF=CHCl$ (HCFO-1224yd(E))

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

HO + *E*-$CF_3CF=CHCl$ (HCFO-1224yd(E)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.09 \pm 0.03) \times 10^{-12}$ exp((50±10/T)	250-430	Tokuhashi et al. (2018)	FP, LP-LIF (a)
$(1.30 \pm 0.01) \times 10^{-12}$	298		

Comments

(a) HO radicals were generated by either flash photolysis or laser photolysis and were monitored using laser induced fluorescence. In the flash photolysis experiments photolysis of water vapor using a was employed as the source of HO radicals. In the laser photolysis experiments two photolysis of N_2O using an ArF eximer laser to produce $O(^1D)$ atoms in the presence of either water vapor or CH_4 were used to generate HO radicals. There was no discernible difference in results obtained using the different methods. Experiments were performed in 5-200 Torr of argon or helium diluent, there was no discernible effect of pressure or diluent gas. The *E*-$CF_3CF=CHCl$ sample was purified before use and the purity of the purified sample was determined to be 99.4%.

Preferred Values

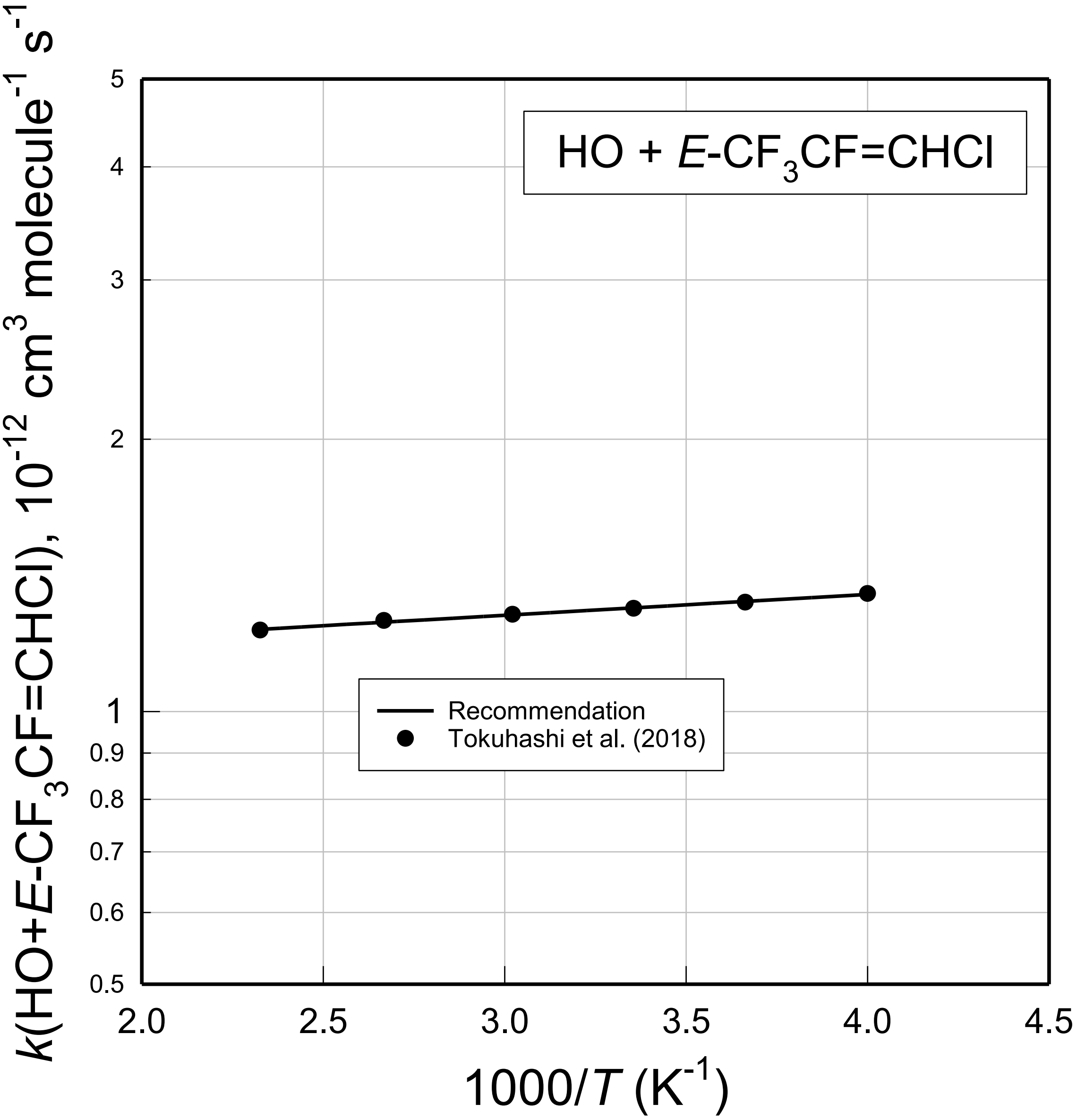
Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.30×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	1.09×10^{-12} exp(53/T)	250-430
Reliability		
Δ log k	± 0.08	298
Δ E/R	± 100	250-430

Comments on Preferred Values

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

References

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


HO + *E*-CF3CF=CHCl
Recommendation
Tokuhashi et al. (2018)
k(HO+E-CF3CF=CHCl), 10-12 cm3 molecule-1 s-1
5
4
3
2
1
0.9
0.8
0.7
0.6
0.5
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K-1)

oFOx166: HO + *Z*-$CF_3CF=CHCl$ (HCFO-1224yd(Z))

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

HO + *Z*-$CF_3CF=CHCl$ (HCFO-1224yd(Z)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(8.02\pm0.19) \times 10^{-13} \exp(-(100\pm10/T)$	250-430	Tokuhashi et al. (2018a,b)	FP, LP-LIF (a)
$(5.84 \pm 0.03) \times 10^{-13}$	298		

Comments

(a) HO radicals were generated by either flash photolysis or laser photolysis and were monitored using laser induced fluorescence. In the flash photolysis experiments photolysis of water vapor was employed as the source of HO radicals. In the laser photolysis experiments photolysis of N_2O to produce $O(^1D)$ atoms in the presence of either water vapor or CH_4 were used to generate HO radicals. There was no discernible difference in results obtained using the different methods. Experiments were performed in 5-200 Torr of argon or helium diluent, there was no discernible effect of pressure or diluent gas. The *Z*-$CF_3CF=CHCl$ sample was purified before use and the purity of the purified sample was determined to be 99.92%.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	5.83×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$8.03 \times 10^{-13} \exp -(95/T)$	250-430
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 100	250-430

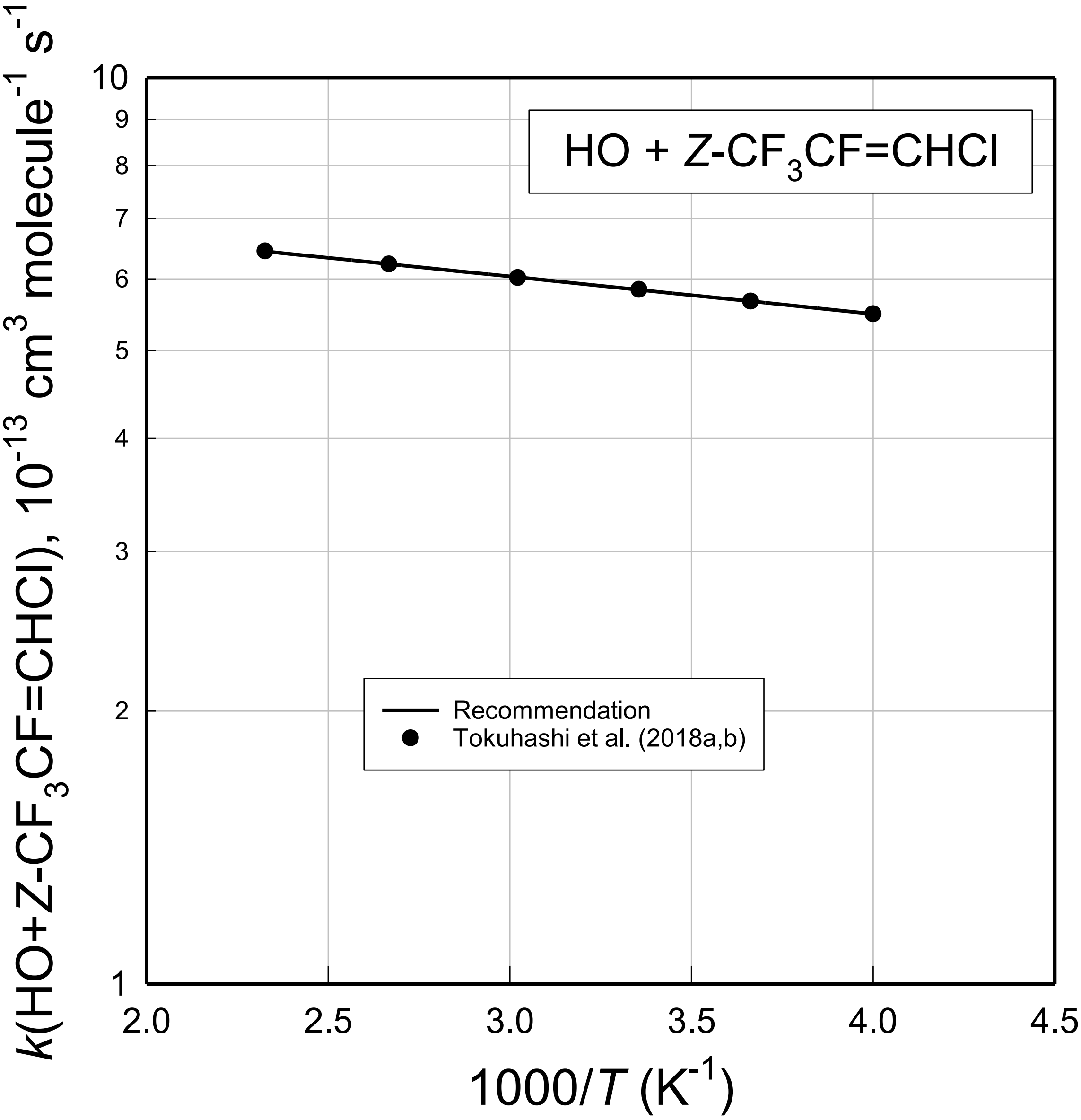
Comments on Preferred Values

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

References

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

Tokuhashi, K., Uchimaru, T., Takizawa, K., and Kondo, S.: J. Phys. Chem. A., 122, 9922-9922, 2018b.


HO + Z-CF$_3$CF=CHCl
Recommendation
Tokuhashi et al. (2018a,b)
k(HO+Z-CF$_3$CF=CHCl), 10^{-13} cm^3 molecule^{-1} s^{-1}
1000/T (K^{-1})
10
9
8
7
6
5
4
3
2
1
2.0
2.5
3.0
3.5
4.0
4.5

oFOx164: HO + $CF_3CBr=CH_2$ (HBFO-1233xfB)

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

HO + $CF_3CBr=CH_2$ (HBFO-1233xfB) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.36\pm0.16) \times 10^{-13} \exp((317\pm34)/T)$	250-370	Orkin et al. (2002)	FP-RF (a)
$(3.88 \pm 0.15) \times 10^{-12}$	298		
$4.85 \times 10^{-13} (T/298)^{0.92} \exp(613/T)$	220-370	Patten et al. (2011)	FP-RF (b)
$(3.79 \pm 0.02) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(3.61\pm0.28) \times 10^{-12}$	296	Sulbaek Andersen et al. (2009)	RR (c)
$(3.99\pm0.24) \times 10^{-12}$	296		

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 CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of $CF_3CBr=CH_2$ was measured relative to C_2H_2 and C_2H_4 and used to measure the rate coefficient ratios $k(CF_3CBr=CH_2)/k(C_2H_2) = 4.829 \pm 0.374$ and $k(CF_3CBr=CH_2)/k(C_2H_2) = 0.508\pm0.031$. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO + CF_3CBr=CH_2) = (3.61\pm0.28) \times 10^{-12}$ and $(3.99\pm0.24) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.84×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	$1.11 \times 10^{-12} \exp(370/T)$	250-430
Reliability		
$\Delta \log k$	± 0.06	298
$\Delta E/R$	± 100	250-430

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 $k = 3.84 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. Patten et al.

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

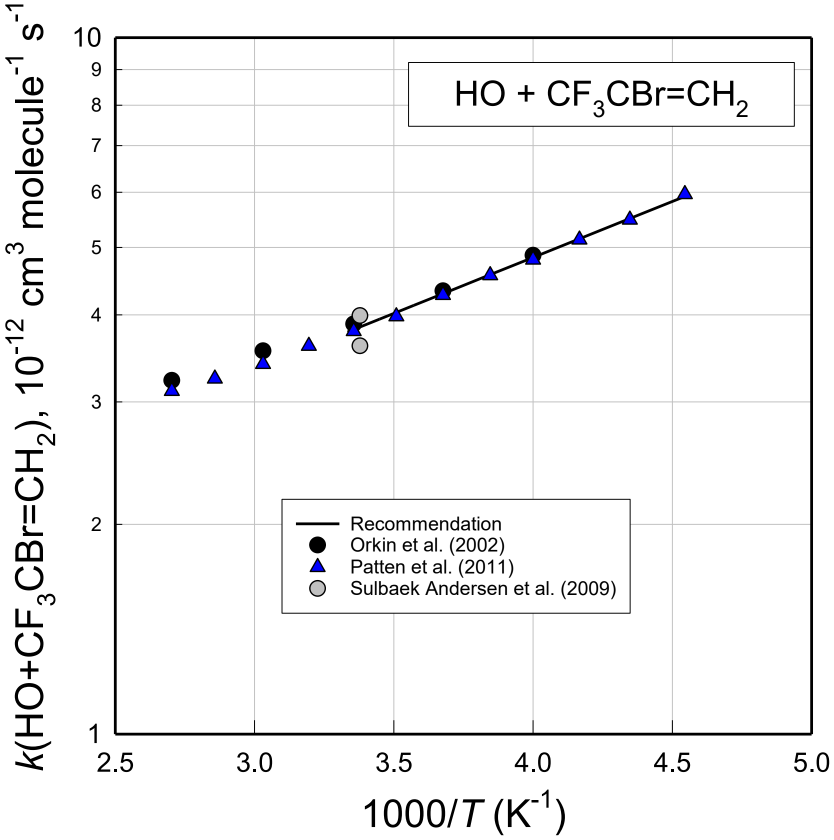
References

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

Orkin, V.L., Louis, F., Huie, R.E., Kurylo, M.J.: J. Phys. Chem. A, 106, 10195-10199, 2002.

Patten, K.O., Khamaganov, V.G., Orkin, V.L., Baughcum, S.L., Wuebbles, D.J.: J. Geophys. Res. Atmos. 116, D24307, 2011.

Sulbaek Andersen, M.P., Hurley, M.D., and Wallington, T.J.: Chem. Phys. Lett., 482, 20-23, 2009.



oFOx154: $NO_3 + CF_2{=}CF_2$

Last evaluated: June 2025; Last change in preferred values: June 2017.

$NO_3 + CF_2{=}CF_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$< 3 \times 10^{-15}$	298	Acerboni et al., 1999	RR (a)

Comments

(a) NO_3 radicals were produced by mixing O_3 with an excess of NO_2, to establish an equilibrium between NO_2, NO_3, and N_2O_5 in 740 Torr (986 mbar) of air diluent. The decay of C_2F_4 was monitored relative to that of C_3H_6 and a rate coefficient ratio $k(NO_3 + C_2F_4)/k(NO_3 + C_3H_6) = 0.159$ was measured. Using $k(NO_3 + C_3H_6) = 9.5 \times 10^{-15}$ (Atkinson et al., 2006) gives $k(NO_3 + C_2F_4) = 1.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. The authors noted a "relatively large random error" in the determination of the rate coefficient ratio, although they did not quantify the uncertainty, and chose to report an upper limit for $k(NO_3 + C_2F_4) < 3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	$<3 \times 10^{-15}$	298

Comments on Preferred Values

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

References

Acerboni, G., Jensen, N. R., Rindone, B., and Hjorth, J.: Chem. Phys. Lett., 309, 364, 1999.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

oFOx153: $NO_3 + CF_3CF{=}CH_2$ (HFO-1234yf)

Last evaluated: June 2025; Last change in preferred values: June 2017.

$NO_3 + CF_3CF{=}CH_2$ (HFO-1234yf) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$< 2 \times 10^{-16}$	233-353	Papadimitriou et al. (2011)	FT-MS (a)
Relative Rate Coefficients			
$(2.6 \pm 0.25) \times 10^{-17}$	296	Papadimitriou et al. (2011)	RR (b)

Comments

(a) NO_3 radicals were produced by thermal decomposition of N_2O_5 in a 400 K oven attached to a low-pressure flow tube reactor. NO_3 radicals were detected using a chemical ionization mass spectrometer. Experiments were performed in 2-6 Torr of helium diluent at 233-353 K. The addition of $CF_3CF{=}CH_2$ led to a barely discernable, < 2 s^{-1}, loss of NO_3 radicals from which an upper limit of $k(NO_3{+}CF_3CF{=}CH_2) < 2 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} was derived.

(b) NO_3 radicals were produced by thermal decomposition of N_2O_5 in 630 Torr (840 mbar) of air diluent at 296 K. The decay of $CF_3CF{=}CH_2$ was monitored relative to that of C_2H_4 and a rate coefficient ratio $k(NO_3 + CF_3CF{=}CH_2)/k(NO_3 + C_2H_4) = 0.124 \pm 0.012$ was measured. Using $k(NO_3 + C_3H_6) = 2.1 \times 10^{-16}$ (Atkinson et al., 2006) gives $k(NO_3 + CF_3CF{=}CH_2) = (2.6 \pm 0.25) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	2.6×10^{-17}	298
Reliability		
$\Delta \log k$	0.15	298

Comments on Preferred Values

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

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

Papadimitriou, V. C., Lazarou, Y. G., Talukdar, R. K., and Burkholder, J. B.: J. Phys. Chem. A, 115, 167, 2011.

oFOx122: $NO_3 + Z\text{-}CF_3CF{=}CHF$ (HFO-1225ye(Z))

Last evaluated: June 2025; Last change in preferred values: June 2018.

$NO_3 + Z\text{-}CF_3CF{=}CHF$ (HFO-1225ye(Z)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$< 2 \times 10^{-16}$	233-353	Papadimitriou et al. (2011)	FT-MS (a)
Relative Rate Coefficients			
$(4.2 \pm 0.5) \times 10^{-18}$	296	Papadimitriou et al. (2011)	RR (b)

Comments

(a) NO_3 radicals were produced by thermal decomposition of N_2O_5 in a 400 K oven attached to a low-pressure flow tube reactor. NO_3 radicals were detected using a chemical ionization mass spectrometer. Experiments were performed in 2-6 Torr of helium diluent at 233-353 K. The addition of $CF_3CF{=}CHF$ led to a barely discernible, < 2 s^{-1}, loss of NO_3 radicals from which an upper limit of $k(NO_3{+}CF_3CF{=}CHF) < 2 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} was derived.

(b) NO_3 radicals were produced by thermal decomposition of N_2O_5 in 630 Torr (840 mbar) of air diluent at 296 K. The decay of $CF_3CF{=}CHF$ was monitored relative to that of C_2H_4 and a rate coefficient ratio $k(NO_3 + CF_3CF{=}CHF)/k(NO_3 + C_2H_4) = 0.019 \pm 0.002$ was measured. Using $k(NO_3 + C_3H_6) = 2.1 \times 10^{-16}$ (Atkinson et al., 2006) gives $k(NO_3 + CF_3CF{=}CHF) = (4.2 \pm 0.5) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	4.2×10^{-18}	298
Reliability		
$\Delta \log k$	0.20	298

Comments on Preferred Values

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

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Papadimitriou, V. C., Lazarou, Y. G., Talukdar, R. K., and Burkholder, J. B.: J. Phys. Chem. A, 115, 167, 2011.

oFOx123: $NO_3 + CF_3CF{=}CF_2$ (FO-1216)

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

$NO_3 + CF_3CF{=}CF_2$ (FO-1216) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$< 3 \times 10^{-15}$	298	Acerboni et al., 2001	RR (a)

Comments

(a) NO_3 radicals were produced by mixing O_3 with an excess of NO_2, to establish an equilibrium between NO_2, NO_3, and N_2O_5 in 740 Torr (986 mbar) of air diluent. The authors specify that a relative rate method was employed, but do not specify the reference used on rate coefficient ratio result. The authors noted that the reaction was very slow and only an upper limit for the rate coefficient $k(NO_3 + C_3F_6) < 3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} was derived.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	$<3 \times 10^{-15}$	298

Comments on Preferred Values

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

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.

oFOx155: $NO_3 + CF_2{=}CFCF{=}CF_2$

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

$NO_3 + CF_2{=}CFCF{=}CF_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$< 3 \times 10^{-15}$	298	Acerboni et al., 2001	RR (a)
$(1.56 \pm 0.16) \times 10^{-15}$	298	Chen et al., 2005	RR (b)

Comments

(a) NO_3 radicals were produced by mixing O_3 with an excess of NO_2, to establish an equilibrium between NO_2, NO_3, and N_2O_5 in 740 Torr (986 mbar) of air diluent. The authors specify that a relative rate method was employed, but do not specify the reference used or rate coefficient ratio result. The authors noted that the reaction was very slow and only an upper limit for the rate coefficient $k(NO_3 + C_3F_6) < 3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} was derived.

(b) NO_3 radicals were produced by the thermal decomposition of N_2O_5. The loss of $CF_2{=}CFCF{=}CF_2$ was monitored relative to that of C_3H_6 using GC-FID in 720 Torr of air diluent following the addition of N_2O_5. A rate coefficient ratio of $k(NO_3 + CF_2{=}CFCF{=}CF_2)/k(NO_3 + C_3H_6) = 0.164 \pm 0.017$ was measured. Placing this result on an absolute basis using $k(NO_3 + C_3H_6) = 9.5 \times 10^{-15}$ (Atkinson et al., 2006) gives $k(NO_3 + CF_2{=}CFCF{=}CF_2) = (1.56 \pm 0.16) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.56×10^{-15}	298
Reliability		
$\Delta \log k$	0.15 ± 0.04	298 298

Comments on Preferred Values

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

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.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Chen, L., Kutsuna, S., Tokuhashi, K., Uchimaru, T., and Sekiya, A.: Chem. Phys. Lett., 416, 187, 2005.

oClOx96: $NO_3 + CH_2{=}CHCl$

Last evaluated: June 2025; Last change in preferred values: June 2018.

$NO_3 + CH_2{=}CHCl \rightarrow$ products

Rate coefficient data

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

Comments

(a) NO_3 radicals were produced by the reaction of F atoms with HNO_3 and monitored by absorption at 662 nm.

(b) NO_3 radicals were produced by the thermal decomposition of N_2O_5 in 740 Torr (986 mbar) of air at 298 K. The loss of $CH_2{=}CHCl$ was monitored using GC-FID relative to that of C_2H_4 and a rate coefficient ratio of $k(NO_3 + CH_2{=}CHCl)/k(NO_3 + C_2H_4) = 2.08 \pm 0.09$ was measured. Using $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ (Atkinson et al., 2006) gives $k(NO_3 + CH_2{=}CHCl) = (4.37 \pm 0.19) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

(c) NO_3 radicals were produced by reacting NO_2 with O_3 in one atmosphere pressure of N_2 to establish an equilibrium between NO_2, NO_3, and N_2O_5 at 296 K. The decay of N_2O_5 and $CH_2{=}CHCl$ was monitored by FTIR spectroscopy. A complex chemical mechanism was used with $k(NO_3 + CH_2{=}CHCl)$ varied to give the best fit of the decay of N_2O_5 and $CH_2{=}CHCl$. This work is superceded by the studies by Noremsaune et al. (1995, 1997) and not considered further.

(d) NO_3 radicals were produced by the thermal decomposition of N_2O_5 which was synthesized in situ by mixing O_3 with excess NO_2 in 760 Torr (1 bar) of air. Experiments were performed at 295 K and kinetic data were obtained by monitoring the decay of $CH_2{=}CHCl$ in the chamber over a period of 10-60 minutes and simulating the decay using analytical and numerical methods. The rate coefficient $k(NO_3 + CH_2{=}CHCl)$ derived in the experiments is dependent on the $NO_2 + NO_3 = N_2O_5$ equilibrium constant assumed in the calculations. Unfortunately, it is unclear what equilibrium constant was used. In the paper it is stated several times that the temperature of the experiments was 295 K, but it then stated that a value of $K_{eq} = 3.77 \times 10^{-11}$ cm^3 molecule^{-1} at 298 K (Wayne et al. 1991) was used to derive $k(NO_3 + CH_2{=}CHCl)$. K_{eq} is very sensitive to temperature and increases from 2.78×10^{-11} to 4.06×10^{-11} cm^3 molecule^{-1} over the temperature range 298 to 295 K (IUPAC, 2018). Given the uncertainty in value of K_{eq} used by Noremsaune et al. (1995) we are not able to scale their result to the latest preferred equilibrium coefficient of K_{eq}. The value in the table above is that reported by Noremsaune et al. (1995).

(e) NO_3 radicals were produced by mixing O_3 with an excess of NO_2, to establish an equilibrium between NO_2, NO_3, and N_2O_5 in 740 Torr (986 mbar) of air. The decay of $CH_2{=}CHCl$ was monitored relative to that of C_2H_4 and a rate coefficient ratio $k(NO_3 + CH_2{=}CHCl)/k(NO_3 + C_2H_4) = 1.78 \pm 0.27$ was measured. Using $k(NO_3 + C_2H_4) = 2.1 \times 10^{-16}$ (Atkinson et al., 2006) gives $k(NO_3 + CH_2{=}CHCl) = (3.74 \pm 0.57) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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

References

Andersson, Y., and Ljungstrom, E.: Atmos. Environ., 23, 1153, 1989.

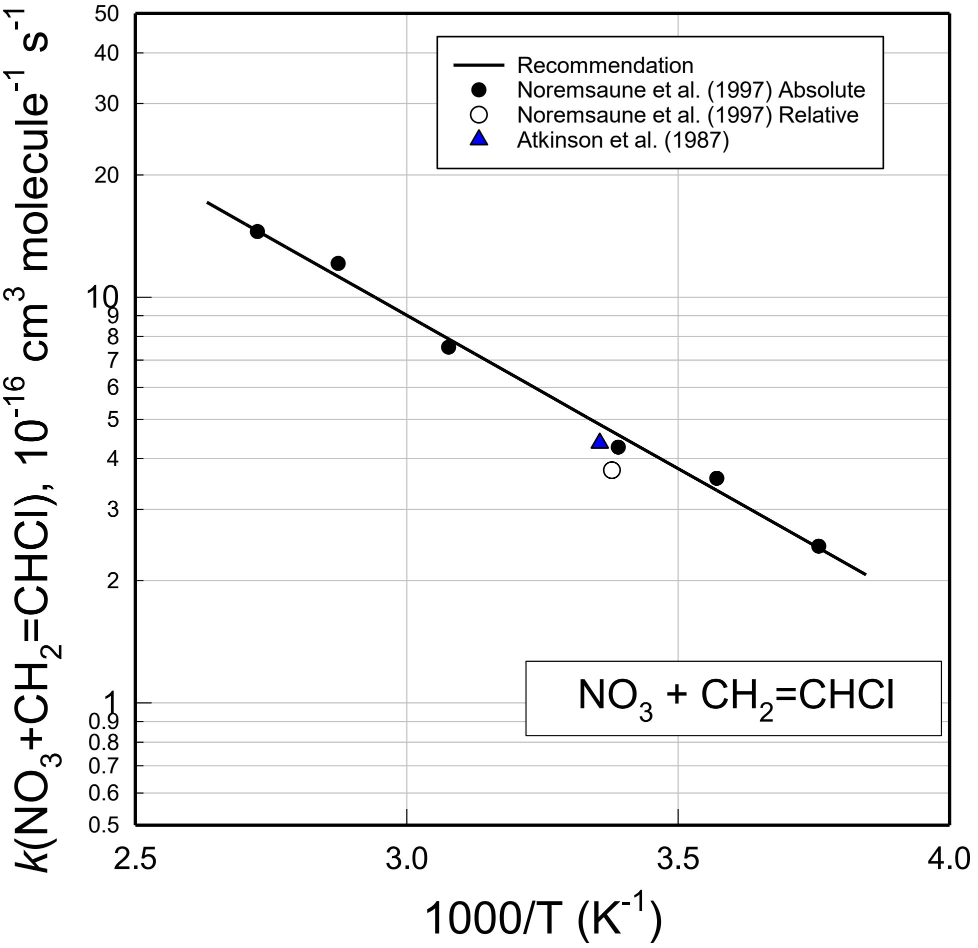
Atkinson, R., Aschmann, S. M., and Goodman, M. A.: Int. J. Chem. Kinet., 19, 299, 1987.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Noremsaune, I. M. W., Hjorth, J.; and Nielsen, C. J.: J. Atmos. Chem., 21, 223, 1995.

Noremsaune, I. M. W., Langer, S., Ljungström, E., and Nielsen, C. J.: J. Chem. Soc., Faraday Trans., 93, 525, 1997.

Wayne, R. P., Barnes, I., Biggs, P., Burrows, J. B., Canosa-Mas, C. E., Hjorth, J., LeBras, G., Moortgat, G., Perner, D., Poulet, G., Restelli, G., and Sidebottom, H.: Atmos. Environ. 25A, 1, 1991.


$k(NO_3+CH_2=CHCl)$, 10^{-16} cm^3 molecule^{-1} s^{-1}
1000/T (K^{-1})
Recommendation
Noremsaune et al. (1997) Absolute
Noremsaune et al. (1997) Relative
Atkinson et al. (1987)
$NO_3 + CH_2=CHCl$
50
40
30
20
10
9
8
7
6
5
4
3
2
1
0.9
0.8
0.7
0.6
0.5
2.5
3.0
3.5
4.0

oFOx126: $O_3 + CF_2{=}CF_2$

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

$O_3 + CF_2{=}CF_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
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		
$(4.80 \pm 0.62) \times 10^{-21}$	298	Acerboni et al., 1999	S-FTIR (c)

Comments

(a) Kinetic data were derived by following the initial rate of formation of the reaction product COF_2 using IR spectroscopy following the mixing of 0.7-24 Torr of O_3 with 0.2-5.7 Torr of C_2F_4.

(b) UV absorption at 254 nm was used to follow the loss of ozone in the presence of an excess of C_2F_4 following mixing 0.06-0.1 Torr of O_3 with 3.0-7.9 Torr of C_2F_4.

(c) FTIR spectroscopy was used to follow the loss of C_2F_4 (2-4 ppmv) in the presence of a large excess of O_3 (25-600 ppmv) in 740 Torr (986 mbar) of air at 298 K. Cyclohexane (20-60 ppmv) was added to scavenge radical products of the reaction of O_3 with C_2F_4 which could lead to unwanted secondary loss of C_2F_4. First order decay of C_2F_4 was observed and the pseudo-first order loss rates were linearly dependent on [O_3].

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	4.8×10^{-21}	298
Reliability		
$\Delta \log k$	0.15	298

Comments on Preferred Values

The chemical systems used by Heicklen (1966) and Toby and Toby (1976) in which high concentrations (of the order of Torr) of O_3 and C_2F_4 were mixed in the absence of diluent gas and kinetic data were obtained by monitoring the rate of formation of either COF_2 product (Heicklen, 1966) or O_3 reactant (Toby and Toby, 1976). The kinetic behaviour observed was complex indicating the presence of substantial complications from secondary chemistry, and hence the rate coefficients derived are likely upper limits. The study by Acerboni et al. (1999) employed lower concentrations of reactants in 740 Torr of air diluent and derived kinetic data by monitoring the loss of C_2F_4 in the presence of excess O_3. The loss of C_2F_4 followed first order kinetics and the pseudo first order rate coefficients increased linearly with [O_3]. The preferred value is based on the result from Acerboni et al. (1999) with uncertainties increased to reflect the fact that it is based on a single study.

References

Acerboni, G., Jensen, N. R., Rindone, B., Hjorth, J.: Chem. Phys. Lett., 309, 364, 1999.
Heicklen, J.: J. Phys. Chem., 70, 477, 1966.
Toby, F.S.; Toby, S.: J. Phys. Chem., 80, 2313, 1976.

oFOx113: $O_3 + CF_3CH{=}CH_2$ (HFO-1243zf)

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

$O_3 + CF_3CH{=}CH_2$ (HFO-1243zf) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.5 \pm 0.3) \times 10^{-19}$	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		
Relative Rate Coefficients			
$(3.0 \pm 0.4) \times 10^{-19}$	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)

Comments

(a) The decay of $CF_3CH{=}CH_2$ was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of $CF_3CH{=}CH_2$, cyclohexane, and O_3 in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of $CF_3CH{=}CH_2$ via reaction with OH radicals formed in the reaction system. The loss of $CF_3CH{=}CH_2$ followed first order kinetics and the pseudo first-order rate coefficients increased linearly with $[O_3]$.

(b) The decay of ozone was monitored with a commercial ozone analyser (using UV absorption) in the presence of an excess of $CF_3CH{=}CH_2$ 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 O_3 followed first order kinetics and the pseudo first-order rate coefficients increased linearly with $[CF_3CH{=}CH_2]$.

(c) The loss of $CF_3CH{=}CH_2$ was measured relative to that of acrolein ($CH_2{=}CHCHO$) in 720 Torr of synthetic air. Cyclohexane was added to avoid potential problems associated with the loss of $CF_3CH{=}CH_2$ via reaction with OH radicals formed in the reaction system. A rate constant ratio of $k(O_3{+}CF_3CH{=}CH_2)/k(O_3{+}CH_2{=}CHCHO) = 0.99 \pm 0.01$ was measured which can be combined with $k(O_3{+}CH_2{=}CHCHO) = (3.0 \pm 0.4) \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} (Treacy et al. 1992) to give $k(O_3{+}CF_3CH{=}CH_2) = (3.0 \pm 0.4) \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}.

(d) The decay of $CF_3CH{=}CH_2$ was measured relative to that of HCFO-1233xf ($CF_3CCl{=}CH_2$) 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 $k(O_3{+}CF_3CH{=}CH_2)/k(O_3{+}CF_3CCl{=}CH_2) = 3.257$ was measured and was combined with $k(O_3{+}CF_3CCl{=}CH_2) = 3.54 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} (McGillen et al. 2023) to give $k(O_3{+}CF_3CH{=}CH_2) = (1.15 \pm 0.23) \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}.

(e) The decay of $CF_3CH{=}CH_2$ was measured relative to that of HFO-1234yf ($CF_3CF{=}CH_2$) 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 $k(O_3{+}CF_3CH{=}CH_2)/k(O_3{+}CF_3CF{=}CH_2) = 4.885$ was measured and was combined with $k(O_3{+}CF_3CCl{=}CH_2) = 2.56 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} [McGillen et al. 2023] to give $k(O_3{+}CF_3CH{=}CH_2) = (1.25 \pm 0.26) \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred expression is taken from a fit to the absolute rate data from McGillen et al. (2023). The value at 298K is evaluated from the preferred Arrhenius expression. The relative rate and absolute rate results reported by McGillen et al. (2023) are in good agreement but are substantially lower than the results reported by Sulbaek Andersen et al. (2005) and Soto et al. (2018). As discussed by McGillen et al. (2023), the cyclohexane scavenger used by Sulbaek Andersen et al. (2005) and Soto et al. (2018) would be effective for HO radicals but not for Criegee intermediates. Hence, the larger rate constants reported by Sulbaek Andersen et al. (2005) and Soto et al. (2018) presumably reflect secondary loss of $CF_3CH=CH_2$ by reaction with Criegee intermediates. McGillen et al. (2023) showed that CF_3H is formed in a yield of (0.37 ± 0.02) % in a “hot acid” reaction channel.

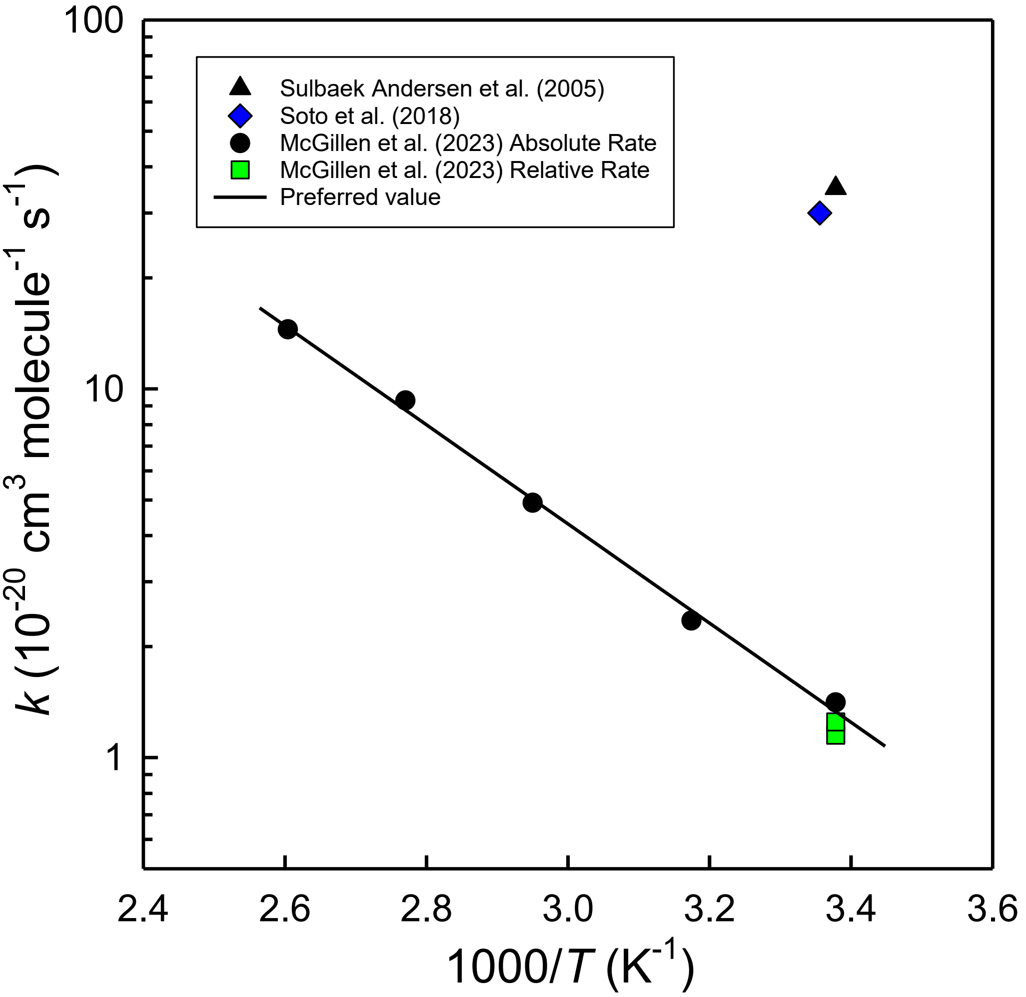
References

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.

Soto, A.; Ballesteros, B.; Jiménez, E.; Antinõlo, M.; Martínez, E.; and Albaladejo, J.: Chemosphere 201, 318–327, 2018.

Sulbæk Andersen, M. P.; Nielsen, O. J.; Toft, A.; Nakayama, T.; Matsumi, Y.; Waterland, R. L.; Buck, R. C.; Hurley, M. D.; and Wallington, T. J.: J. Photoch. Photobio. A 176, 124–128, 2005.

Treacy, J.; Elhag, M.; O’Farrell, D.; Sidebottom, H.: Ber. Bunsen-Ges. Phys. Chem., 96, 422–427, 1992.


100
10
1
k (10⁻²⁰ cm³ molecule⁻¹ s⁻¹)
2.4
2.6
2.8
3.0
3.2
3.4
3.6
1000/T (K⁻¹)
Sulbaek Andersen et al. (2005)
Soto et al. (2018)
McGillen et al. (2023) Absolute Rate
McGillen et al. (2023) Relative Rate
Preferred value

2674
2675

oFOx128: $O_3 + CF_3CF=CH_2$ (HFO-1234yf)

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

$O_3 + CF_3CF=CH_2$ (HFO-1234yf) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.77 \pm 0.21) \times 10^{-21}$	296	Nielsen et al. (2007)	S-FTIR (a)
$(2.56 \pm 1.42) \times 10^{-21}$	296	McGillen et al. (2023)	S-UV (b)
Relative Rate Coefficients			
$(2.37 \pm 0.47) \times 10^{-21}$	296	McGillen et al. (2023)	RR (c)
$(2.58 \pm 0.53) \times 10^{-21}$	296		RR (d)

Comments

(a) The decay of $CF_3CF=CH_2$ was monitored by FTIR spectroscopy when exposed to ozone in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of $CF_3CF=CH_2$ via reaction with OH radicals formed in the reaction system. The loss of $CF_3CF=CH_2$ followed first order kinetics and the pseudo first order rate coefficients increased linearly with $[O_3]$.

(b) The decay of ozone was monitored via UV absorption in the presence of an excess of $CF_3CF=CH_2$. 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 O_3 followed first order kinetics and the pseudo first order rate coefficients increased linearly with $[CF_3CF=CH_2]$.

(c) The decay of $CF_3CF=CH_2$ was measured relative to that of HCFO-1233xf ($CF_3CCl=CH_2$) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(O_3+CF_3CF=CH_2)/k(O_3+CF_3CCl=CH_2) = (0.669 \pm 0.133)$ was measured and combined with $k(O_3+CF_3CCl=CH_2) = 3.54 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} (McGillen et al., 2023) to give $k(O_3+CF_3CF=CH_2) = (2.37 \pm 0.47) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}.

(d) The decay of $CF_3CF=CH_2$ was measured relative to that of HFO-1243zf ($CF_3CH=CH_2$) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(O_3+CF_3CF=CH_2)/k(O_3+CF_3CH=CH_2) = (0.205 \pm 0.042)$ was measured and combined with $k(O_3+CF_3CH=CH_2) = 1.26 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} to give $k(O_3+CF_3CF=CH_2) = (2.58 \pm 0.53) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	2.67×10^{-21}	298
Reliability		
$\Delta \log k$	0.08	298

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 CF_4 and CF_3H 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.

oFOx129: O_3 + *E*-$CF_3CH=CHF$ (HFO-1234ze(*E*))

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

O_3 + *E*-$CF_3CH=CHF$ (HFO-1234ze(*E*)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.81 \pm 0.21) \times 10^{-21}$	296	Søndergaard et al. (2007)	S-FTIR (a)
Relative Rate Coefficients			
$(2.19 \pm 0.43) \times 10^{-21}$	296	McGillen et al. (2023)	RR (b)

Comments

(a) The decay of *E*-$CF_3CH=CHF$ was monitored by FTIR spectroscopy when exposed to ozone in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of *E*-$CF_3CH=CHF$ via reaction with OH radicals formed in the reaction system. The loss of *E*-$CF_3CH=CHF$ followed first-order kinetics and the pseudo first-order rate coefficients increased linearly with $[O_3]$.

(b) The decay of *E*-$CF_3CH=CHF$ was measured relative to that of HCFO-1233xf ($CF_3CCl=CH_2$) in the presence of a large excess of ozone in 1 bar of air. To avoid unwanted secondary chemistry isopropanol was added to scavenge HO radicals and stabilized Criegee intermediates which are formed in the system. A rate constant ratio of $k(O_3+E\text{-}CF_3CH=CHF)/k(O_3+CF_3CCl=CH_2) = 0.617 \pm 0.121$ was measured. Combining this with $k(O_3+CF_3CCl=CH_2) = 3.54 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} (McGillen et al., 2023) gives $k(O_3+ E\text{-}CF_3CH=CHF) = (2.19 \pm 0.43) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	2.50×10^{-21}	298
Reliability		
$\Delta \log k$	0.10	298

Comments on Preferred Values

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 CF_3H is formed in a yield of (3.11 ± 0.05) % in a “hot acid” reaction channel.

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.

Søndergaard, R., Nielsen, O. J., Hurley, M. D., Wallington, T. J., Singh, R.: Chem. Phys. Lett, 443, 199, 2007.

oFOx156: O_3 + *Z*-$CF_3CH=CHF$ (HFO-1234(Z))

Last evaluated: June 2023; Last change in preferred values: June 2019.

O_3 + *Z*-$CF_3CH=CHF$ (HFO-1234(Z)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.65 \pm 0.16) \times 10^{-21}$	296	Nilsson et al. (2009)	S-FTIR (a)

Comments

(a) The decay of *Z*-$CF_3CH=CHF$ was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of 14.7-16.2 mTorr *Z*-$CF_3CH=CHF$, 21-65 mTorr cyclohexane, and 950–2260 mTorr O_3 in 700 Torr (933 mbar) of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of *Z*-$CF_3CH=CHF$ via reaction with OH radicals formed in the reaction system. The loss of *Z*-$CF_3CH=CHF$ followed first order kinetics and the pseudo first order rate coefficients increased linearly with $[O_3]$.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.7×10^{-21}	298
Reliability		
$\Delta \log k$	0.30	298

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*-$CF_3CH=CHF$ 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.

oFOx130: $O_3 + CF_3CF{=}CF_2$ (FO-1216))

Last evaluated: June 2025; Last change in preferred values: June 2018.

$O_3 + CF_3CF{=}CF_2$ (FO-1216)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
2.2×10^{-17}	298	Heicklen (1966)	S-IR (a)
$< 3 \times 10^{-21}$	296	Mashino et al. (2000)	S-FTIR (b)
$(6.2 \pm 1.5) \times 10^{-22}$	298	Acerboni et al. (2001)	S-FTIR (c)

Comments

(a) Kinetic data were derived by following the initial rate of formation of the reaction product COF_2 using IR spectroscopy following the mixing of 1.9-14.8 Torr of O_3 with 0.22-7.0 Torr of $CF_3CF{=}CF_2$.

(b) The decay of $CF_3CF{=}CF_2$ was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of 1.5-8.1 mTorr $CF_3CF{=}CF_2$ and 899–963 mTorr O_3 in 700 Torr of O_2 diluent. There was no scavenger, such as cyclohexane, added to suppress unwanted radical chemistry in the system. The loss of $CF_3CF{=}CF_2$ followed first order kinetics but there was a systematic increase in the pseudo first order loss rates with increasing $[CF_3CF{=}CF_2]$. The simplest explanation of this observation is loss of $CF_3CF{=}CF_2$ via reaction with products of the $O_3 + CF_3CF{=}CF_2$ reaction. Mashino et al. (2000) chose to quote an upper limit based on the lowest value of $k(O_3 + CF_3CF{=}CF_2)$ measured in their study.

(c) FTIR spectroscopy was used to follow the loss of $CF_3CF{=}CF_2$ (2-5 ppmv) in the presence of a large excess of O_3 (25-600 ppmv) in 740 Torr (986 mbar) of air at 298 K. Cyclohexane was added as a scavenge to suppress potential complications from unwanted radical reactions. First order decay of $CF_3CF{=}CF_2$ was observed and the pseudo first order loss rates were linearly dependent on $[O_3]$.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	6.2×10^{-22}	298
Reliability		
$\Delta \log k$	0.15	298

Comments on Preferred Values

The preferred value is based on the measurements by Acerboni et al. (2001) which were conducted using cyclohexane to suppress radical chemistry in the system leading to additional loss of $CF_3CF{=}CF_2$. Mashino et al. (2000) showed that in the absence of a radical scavenger such as cyclohexane there is additional unwanted loss of $CF_3CF{=}CF_2$ and that the severity of this complication increases with the $[CF_3CF{=}CF_2]$ used in the experiment. The early experiments by Heicklen (1966) used particularly high $[CF_3CF{=}CF_2]$ and secondary losses of $CF_3CF{=}CF_2$ by radical chain reactions presumably explains the overestimation of the rate coefficient by more than a factor of 10^4 in the early studies.

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.

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

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

oFOx157: $O_3 + CF_2{=}CFCF{=}CF_2$

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

$O_3 + CF_2{=}CFCF{=}CF_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.5 \pm 0.2) \times 10^{-21}$	298	Acerboni et al. (2001)	S-FTIR (a)
$(1.14\pm0.94) \times 10^{-16} \exp[-(2800\pm225)/T]$	225-308	Chen et al. (2005)	S-FTIR (b)
$(9.37\pm0.70) \times 10^{-21}$	298		

Comments

(a) FTIR spectroscopy was used to follow the loss of $CF_2{=}CFCF{=}CF_2$ (3-5 ppmv) in the presence of a large excess of O_3 (25-600 ppmv) in 740 Torr (986 mbar) of air at 298 K. Cyclohexane (20-60 ppmv) was added as a scavenger to suppress potential complications from unwanted radical reactions. First order decay of $CF_2{=}CFCF{=}CF_2$ was observed and the pseudo first order loss rates were linearly dependent on $[O_3]$.

(b) The decay of $CF_2{=}CFCF{=}CF_2$ was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of 1.2×10^{14} molecule cm^{-3} $CF_2{=}CFCF{=}CF_2$ (5 ppmv) and $1.26\text{-}6.94 \times 10^{15}$ molecule cm^{-3} O_3 in 720 Torr of air diluent. Cyclohexane (5.6×10^{15} molecule cm^{-3}) was added as a scavenger to suppress unwanted radical chemistry in the system. The loss of $CF_2{=}CFCF{=}CF_2$ followed first order kinetics.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	7.9×10^{-21}	298
k /cm^3 molecule^{-1} s^{-1}	$9.51 \times 10^{-17} \exp(-2800/T)$	220-320
Reliability		
$\Delta \log k$	0.20	298
$\Delta E/R$	± 300	

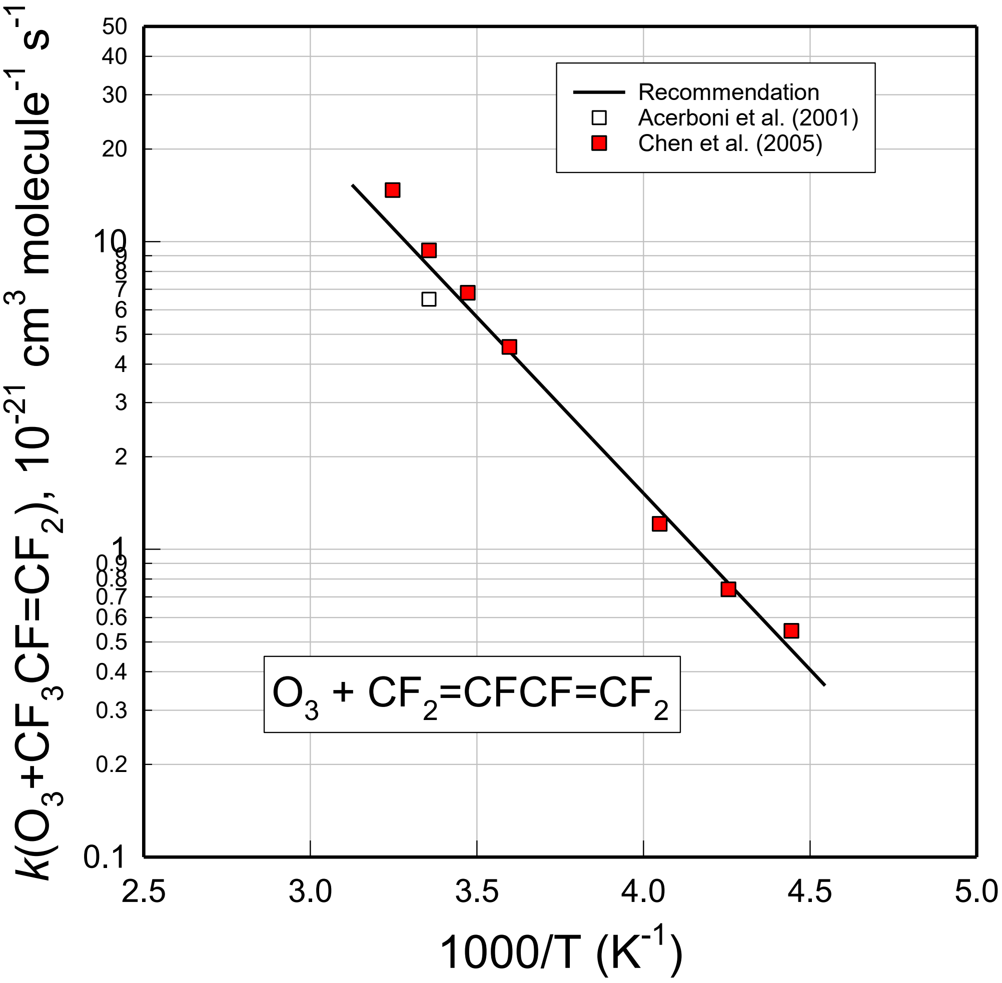
Comments on Preferred Values

The k(298 K) values reported by Acerboni et al. (2001) and Chen et al. (2005) differ by approximately 30%. However, given the comment by Chen et al. that there was “a systematic uncertainty of 20% in the measurement of O_3 concentration” in their experiments the results from the two studies are probably consistent within the combined experimental uncertainties. The preferred value at 298 K is an average of the results from Acerboni et al. (2001) and Chen et al. (2005). Taking the temperature dependence from Chen et al. (2005) and adjusting the pre-exponential factor to reproduce the preferred value at 298 K gives the preferred Arrhenius expression of $k = 9.51 \times 10^{-17} \exp(-2800/T)$ cm^3 molecule^{-1} s^{-1}.

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.



oFOx127: O_3 + *E*-$CF_3CH=CHCF_3$ (HFO-1336mzz(*E*))

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

O_3 + *E*-$CF_3CH=CHCF_3$ (HFO-1336mzz(*E*)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4.14 \pm 0.42) \times 10^{-22}$	296	Østerstrøm et al. (2017)	S-FTIR (a)
$(5.16 \pm 0.40) \times 10^{-22}$	296	Baasandorj et al. (2018)	S-FTIR (b)

Comments

(a) The decay of *E*-$CF_3CH=CHCF_3$ was monitored by FTIR spectroscopy when exposed to ozone in 700 Torr of air or N_2/O_2 diluent. Cyclohexane was added to avoid the loss of *E*-$CF_3CH=CHCF_3$ via reaction with HO radicals formed in the reaction system. The loss of *E*-$CF_3CH=CHCF_3$ followed first order kinetics and the pseudo first order rate coefficients increased linearly with [O_3].

(b) The decay of *E*-$CF_3CH=CHCF_3$ was monitored by FTIR spectroscopy when exposed to ozone in 10-250 Torr of He diluent. The loss of *E*-$CF_3CH=CHCF_3$ followed first order kinetics and the pseudo first order rate coefficients increased linearly with [O_3].

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	4.14×10^{-22}	298
Reliability		
$\Delta \log k$	0.10	298

Comments on Preferred Values

The preferred value is taken from the absolute rate study by Østerstrøm et al. (2017) in which cyclohexane was added to avoid the loss of *E*-$CF_3CH=CHCF_3$ via reaction with HO radicals formed in the reaction system. The result from the study by Baasandorj et al. (2018) is approximately 25% higher than that from Østerstrøm et al. (2017) and probably reflects additional loss of *E*-$CF_3CH=CHCF_3$ from reaction with HO radicals.

References

Baasandorj, M., Marshall, P., Waterland, R. L., Ravishankara, A. R., Burkholder, J. B.: J. Phys. Chem. A, 122, 4635-4646, 2018.

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

oFOx124: O_3 + *Z*-$CF_3CH=CHCF_3$ (HFO-1336mzz(*Z*))

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

O_3 + *Z*-$CF_3CH=CHCF_3$ (HFO-1336mzz(*Z*)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.55 \pm 0.70) \times 10^{-22}$	296	Østerstrøm et al. (2017)	S-FTIR (a)
Relative Rate Coefficients			
$(7.63 \pm 1.53) \times 10^{-22}$	296	McGillen et al. (2023)	RR (b)

Comments

(a) The decay of *Z*-$CF_3CH=CHCF_3$ was monitored by FTIR spectroscopy when exposed to ozone. Cyclohexane was added to avoid potential problems associated with the loss of *Z*-$CF_3CH=CHCF_3$ via reaction with OH radicals formed in the reaction system. The loss of *Z*-$CF_3CH=CHCF_3$ was found to be approximately 15% greater in the absence of cyclohexane than in the presence of cyclohexane. The loss of *Z*-$CF_3CH=CHCF_3$ followed first order kinetics and the pseudo first order rate coefficients increased linearly with $[O_3]$.

(b) The decay of *Z*-$CF_3CH=CHCF_3$ was measured relative to that of HCFO-1233xf ($CF_3CCl=CH_2$) 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 $k(O_3+Z\text{-}CF_3CH=CHCF_3)/k(O_3+CF_3CCl=CH_2) = 0.043$ was measured and was combined with $k(O_3+CF_3CCl=CH_2) = 3.54 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} (McGillen et al. 2023) to give $k(O_3+Z\text{-}CF_3CH=CHCF_3) = (7.63 \pm 1.53) \times 10^{-22}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	7.09×10^{-22}	298
Reliability		
$\Delta \log k$	0.08	298

Comments on Preferred Values

The results from the absolute rate study by Østerstrøm et al. (2017) and the relative rate study by McGillen et al. (2023) are in good agreement. The preferred value is an average from the two studies. The upper limit of $k < 6 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} reported by Baasandorj et al. (2011) is consistent with the preferred value. McGillen et al. (2023) observed the formation of CF_3H in a yield of 0.42 ± 0.02 % and showed that this is formed via the hot acid mechanism.

References

Baasandorj, M.; Ravishankara, A. R.; and Burkholder, J. B.: J. Phys. Chem. A, 115, 10539–10549, 2011.

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.: Proc. Nat. Acad. Sci., 120, e2312714120, 2023.

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

oClOx97: $O_3 + CH_2{=}CHCl$

Last evaluated: June 2025; Last change in preferred values: June 2017.

$O_3 + CH_2{=}CHCl \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$\sim 2.3 \times 10^{-19}$	305	Gay et al. (1976)	S-FTIR (a)
$(2.45 \pm 0.45) \times 10^{-19}$	298	Zhang et al. (1983)	S-FTIR (b)

Comments

(a) A mixture of approximately 5 ppm of O_3 and 3 ppm of $CH_2{=}CHCl$ in 1 atmosphere of air at 305 K was prepared and monitored for 4 hours. A rate coefficient of $k(O_3 + CH_2{=}CHCl) = 0.34$ ppm^{-1} min^{-1} was estimated from the rate of loss of $CH_2{=}CHCl$.

(b) The loss of $CH_2{=}CHCl$ in the presence of O_3 in 1 atmosphere of N_2 or air diluent was monitored by FTIR spectroscopy. CH_3CHO was added as a scavenger for Cl atoms formed in the oxidation of $CH_2{=}CHCl$. Initial concentrations of $CH_2{=}CHCl$ were 12-14 mTorr and O_3 were 12-71 mTorr.

Preferred Values

Parameter	Value	*T*/K
k/cm^3 molecule^{-1} s^{-1}	2.5×10^{-19}	298
Reliability		
$\Delta \log k$	0.2	298

Comments on Preferred Values

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

References

Gay, B. W., Hanst, P. L., and Noonan, R. C.: Environ. Sci. Technol., 10, 58, 1976.
Zhang, J., Hatakeyama, S., and Akimoto, H.: Int. J. Chem. Kinet., 15 655, 1983.

oFOx132: O_3 + *E*-$CF_3CH=CHCl$ (HCFO-1233zd(E))

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

O_3 + *E*-$CF_3CH=CHCl$ (HCFO-1233zd(E)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.46 \pm 0.12) \times 10^{-21}$	296	Sulbaek Andersen et al. (2008)	S-FTIR (a)

Comments

(a) The decay of *E*-$CF_3CH=CHCl$ was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of 5.9-14.2 mTorr *E*-$CF_3CH=CHCl$, 14.0-30.6 mTorr cyclohexane, and 414–4360 mTorr O_3 in 700 Torr (933 mbar) of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of *E*-$CF_3CH=CHCl$ via reaction with OH radicals formed in the reaction system. The loss of *E*-$CF_3CH=CHCl$ followed first order kinetics and the pseudo first order rate coefficients increased linearly with [O_3].

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.5×10^{-21}	298
Reliability		
$\Delta \log k$	0.15	298

Comments on Preferred Values

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

References

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

oFOx131: O_3 + *Z*-$CF_3CH=CHCl$ (HCFO-1233zd(Z))

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

O_3 + *Z*-$CF_3CH=CHCl$ (HCFO-1233zd(Z)) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.53 \pm 0.12) \times 10^{-21}$	296	Andersen et al. (2015)	S-FTIR (a)

Comments

(a) The decay of *Z*-$CF_3CH=CHCl$ was monitored by FTIR spectroscopy when exposed to ozone. Reaction mixtures consisted of 4.07-4.17 mTorr *Z*-$CF_3CH=CHCl$, 3.96-31.79 mTorr cyclohexane, and 610–2820 mTorr O_3 in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of *Z*-$CF_3CH=CHCl$ via reaction with OH radicals formed in the reaction system. The loss of *Z*-$CF_3CH=CHCl$ followed first order kinetics and the pseudo first order rate coefficients increased linearly with $[O_3]$.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.53×10^{-21}	298
Reliability		
$\Delta \log k$	0.15	298

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.

oFOx125: $O_3 + CF_3CCl=CH_2$ (HCFO-1233xf)

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

$O_3 + CF_3CCl=CH_2$ (HCFO-1233xf) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.00 \pm 0.74) \times 10^{-21}$	296	McGillen et al. (2023)	S-UV (a)
Relative Rate Coefficients			
$(3.86 \pm 0.79) \times 10^{-21}$	296	McGillen et al. (2023)	RR (b)
$(3.82 \pm 0.78) \times 10^{-21}$	296	McGillen et al. (2023)	RR (c)
$(3.95 \pm 0.87) \times 10^{-21}$	296	McGillen et al. (2023)	RR (d)
$(3.15 \pm 0.87) \times 10^{-21}$	296	McGillen et al. (2023)	RR (e)

Comments

(a) The decay of ozone was monitored via UV absorption in the presence of an excess of $CF_3CCl=CH_2$ 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 O_3 followed first-order kinetics and the pseudo first-order rate coefficients increased linearly with $[CF_3CCl=CH_2]$.

(b) The decay of $CF_3CCl=CH_2$ was measured relative to that of HFO-1243zf ($CF_3CH=CH_2$) 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 $k(O_3+CF_3CCl=CH_2)/k(O_3+CF_3CH=CH_2)$ = 0.307 was measured and was combined with $k(O_3+CF_3CH=CH_2) = 1.26 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} (McGillen et al. 2023) to give $k(O_3+CF_3CCl=CH_2) = (3.86 \pm 0.79) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}.

(c) The decay of $CF_3CCl=CH_2$ was measured relative to that of HFO-1234yf ($CF_3CF=CH_2$) 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 $k(O_3+CF_3CCl=CH_2)/k(O_3+CF_3CF=CH_2)$ = 1.495 was measured and was combined with $k(O_3+CF_3CF=CH_2) = 2.56 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} (McGillen et al. 2023) to give $k(O_3+CF_3CCl=CH_2) = (3.82 \pm 0.78) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}.

(d) The decay of $CF_3CCl=CH_2$ was measured relative to that of HFO-1243ze(*E*) (*E*-$CF_3CH=CHF$) 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 $k(O_3+CF_3CCl=CH_2)/k(O_3+E\text{-}CF_3CH=CHF)$ = 1.619 was measured and was combined with $k(O_3+ E\text{-}CF_3CH=CHF) = 2.44 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} (McGillen et al. 2023) to give $k(O_3+CF_3CCl=CH_2) = (3.95 \pm 0.87) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}.

(e) The decay of $CF_3CCl=CH_2$ was measured relative to that of HFO-1336mzz(*Z*) (*Z*-$CF_3CH=CHCF_3$) 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 $k(O_3+CF_3CCl=CH_2)/k(O_3+$ $Z\text{-}CF_3CH=CHCF_3) = 4.624$ was measured and was combined with $k(O_3+$ $Z\text{-}CF_3CH=CHCF_3) = 6.81 \times 10^{-22}$ cm^3 molecule^{-1} s^{-1} (McGillen et al. 2023) to give $k(O_3+CF_3CCl=CH_2) = (3.15 \pm 0.87) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	3.00×10^{-21}	298
Reliability		
$\Delta \log k$	0.08	298

Comments on Preferred Values

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

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.: Proc. Soc. Nat. Acad., 120, e2312714120, 2023.

oFOx84: HO + CH_2FCH_2OH

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

$$\begin{aligned} HO + CH_2FCH_2OH &\rightarrow CHFCH_2OH + H_2O \qquad (1)\\ &\rightarrow CH_2FCHOH + H_2O \qquad (2)\\ &\rightarrow CH_2FCH_2O + H_2O \qquad (3)\end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(5.15\pm0.88) \times 10^{-12} \exp[-(330\pm45)/T]$	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)
$(9.29\pm0.18) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(1.39 \pm 0.05) \times 10^{-12}$	298	Sellevåg et al. (2004)	RR (c)

Comments

(a) HO radicals were generated by the 248 nm photolysis of H_2O_2 in 60-100 Torr (80-133 mbar) of helium diluent. Additional experiments were performed at 355 K using DO radicals (formed via O_3 photolysis in the presence of D_2O). The rate coefficients for the reactions of DO and HO radicals with CH_2FCH_2OH were indistinguishable. There was no evidence for the formation of HO radicals following reaction of DO radicals with CH_2FCH_2OH.

(b) HO radicals were generated by the flash photolysis of H_2O in 1.33-26.7 kPa (10-200 Torr) of argon diluent. The rate coefficients were independent of the H_2O 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 O_3 in the presence of H_2O in 1013 mbar of air diluent at 298 K. A rate coefficient ratio of $k(HO+CH_2FCH_2OH)/k(HO+C_2H_6) = 5.81 \pm 0.19$ was measured. Placing this on an absolute basis using $k(HO+C_2H_6) = 2.4 \times 10^{-13}$ (Atkinson et al., 2006) gives $k(HO+CH_2FCH_2OH) = (1.39 \pm 0.05) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The results from the relative rate study by Sellevåg et al. (2004) and the absolute rate study of Rajakumar et al. (2005) at ambient temperature are indistinguishable within the likely combined experimental uncertainties. The results from the absolute rate study by Orkin et al. (2011) are approximately a factor of 2 lower. The concentration of CH_2FCH_2OH in the study by Rajakumar et al.

was measured using absorption at 184.9 nm. Orkin et al. remeasured the absorption spectrum of CH_2FCH_2OH and determined an absorption cross section at 184.9 nm that was 1.82 times smaller than used by Rajakumar et al. (2005). Correction of the rate coefficients reported by Rajakumar et al. by a factor of 1.82 brings them into good agreement with those from Orkin et al. (2011). A fit of the modified Arrhenius expression $k = CT^2 \exp(-D/T)$, to the combined data set from Orkin et al. (2011) and the corrected data from Rajakumar et al. (2005) gives $k = 4.28 \times 10^{-18} T^2 \exp(264/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-370 K. The preferred Arrhenius expression $k = 2.23 \times 10^{-12} \exp(-266/T)$, is centered at 265 K and is derived from the three-parameter equation with $A = C\ e^2\ T^2$ and $B = D + 2T$.

References

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

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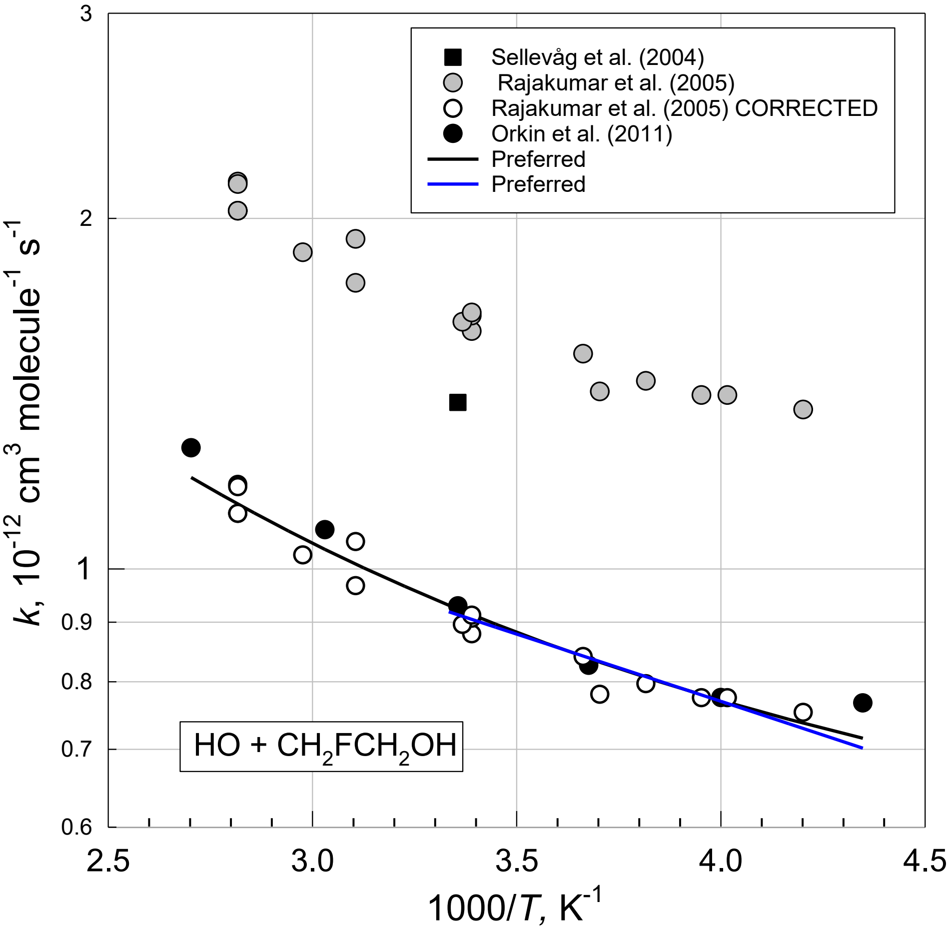
Rajakumar, B., Burkholder, J. B., Portmann, R. W., and Ravishankara, A.R.: Phys. Chem. Chem. Phys., 7, 2498, 2005.

Sellevåg, S. R., Nielsen, C. J., Søvde, O. A., Myhre, G., Sundet, J. K., Stordal, F., and Isaksen, I. S. A.: Atmos. Environ., 38, 6725, 2004.



oFOx85: $HO + CHF_2CH_2OH$

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

$$\begin{aligned} HO + CHF_2CH_2OH &\rightarrow CF_2CH_2OH + H_2O &\quad (1)\\ &\rightarrow CHF_2CHOH + H_2O &\quad (2)\\ &\rightarrow CHF_2CH_2O + H_2O &\quad (3)\end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.52 \pm 0.44) \times 10^{-13}$	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		
Relative Rate Coefficients			
$(4.57 \pm 0.38) \times 10^{-13}$	298	Sellevåg et al. (2004)	RR (c)

Comments

(a) HO radicals were produced by the photolysis of HNO_3 at 248 nm in 105 ± 5 mbar of helium diluent.

(b) HO radicals were generated by the flash photolysis of H_2O in 1.33-26.7 kPa (10-200 Torr) of argon. The rate coefficient was independent of the H_2O 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 O_3 in the presence of H_2O in 1013 mbar of air diluent at 298 K. A rate coefficient ratio of $k(HO+CHF_2CH_2OH)/k(HO+C_2H_6) = 1.903 \pm 0.016$ was measured. Placing this on an absolute basis using $k(HO+C_2H_6) = 2.4 \times 10^{-13}$ (Atkinson et al., 2006) gives $k(HO+CHF_2CH_2OH) = (4.57 \pm 0.38) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

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 $k = 2.61 \times 10^{-13}$ cm^3 molecule^{-1} 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 $k = 3.44 \text{ x } 10^{-18} T^2 \exp(-35/T)$ cm^3 molecule^{-1} 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 derived using B = D + 2*T* with the value of A adjusted to give the preferred *k*(298K) value; $k = 1.63 \times 10^{-12} \exp(-545/T)$ cm^3 molecule^{-1} s^{-1}.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

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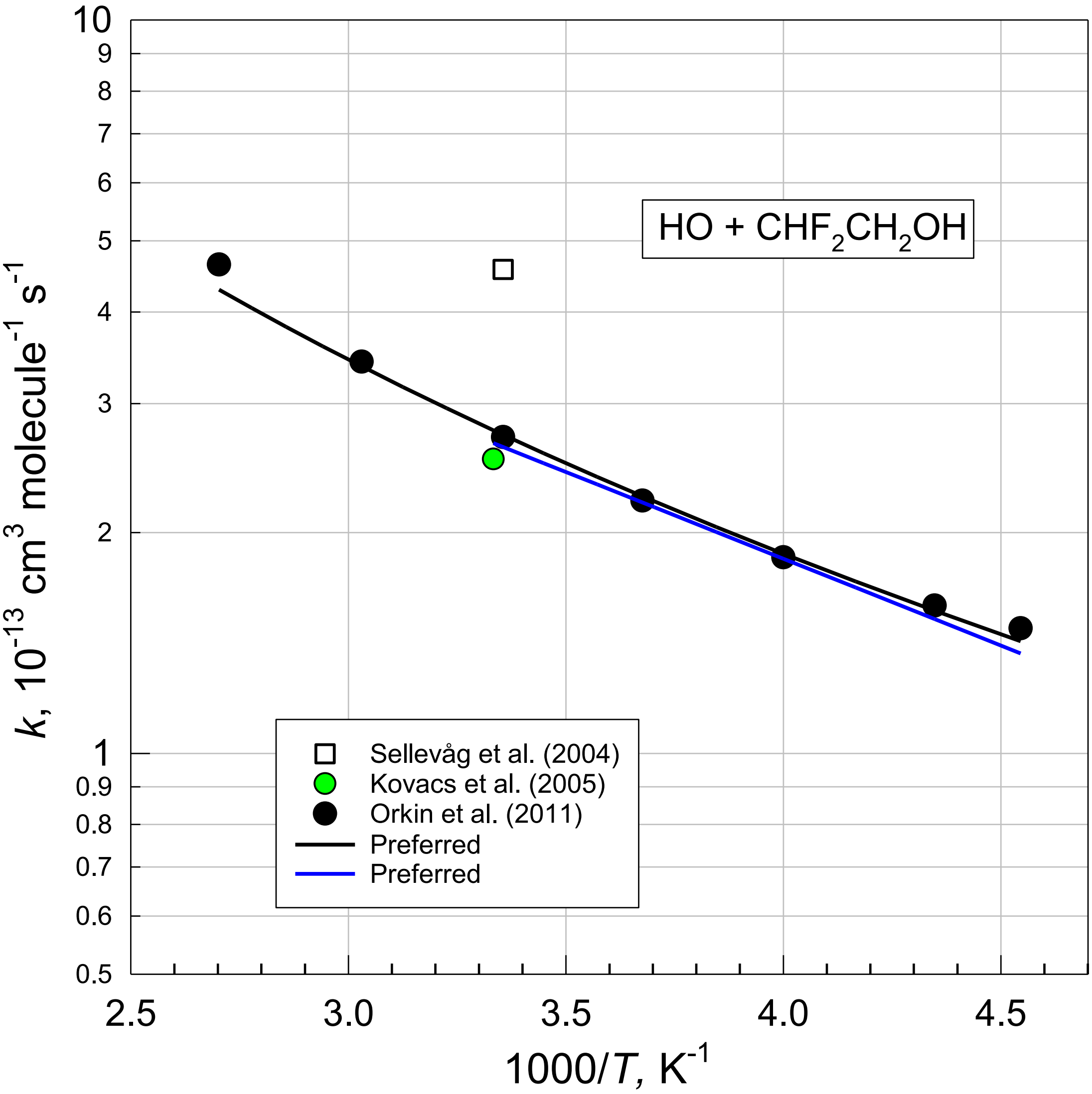
Orkin, V. L., Khamaganov, V. G., Martynova, L. E., and Kurylo, M. J.: J. Phys. Chem. A, 115, 8556, 2011.

Sellevåg, S. R., Nielsen, C. J., Søvde, O. A., Myhre, G., Sundet, J. K., Stordal, F., and Isaksen, I. S. A.: Atmos. Environ., 38, 6725, 2004.



oFOx86: HO + CF_3CH_2OH

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

$$\begin{aligned} \mathbf{HO + CF_3CH_2OH} &\rightarrow \mathbf{CF_3CHOH + H_2O} \qquad \mathbf{(1)} \\ &\rightarrow \mathbf{CF_3CH_2O + H_2O} \qquad \mathbf{(2)} \end{aligned}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(9.55 \pm 0.71) \times 10^{-14}$	298	Wallington et al. (1988)	FP-RF (a)
$(2.00\pm0.37) \times 10^{-12} \exp[-(890\pm60)/T]$	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)
$(1.23 \times 10^{-12} \exp[-(760\pm340)/T]$	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)
$(1.01\pm0.01) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(1.31 \pm 0.05) \times 10^{-13}$	298	Sellevåg et al. (2004)	RR (f)
$(9.4 \pm 0.8) \times 10^{-14}$	296	Hurley et al. (2004)	RR (g)

Comments

(a) HO radicals were generated by the photolysis ($\lambda \geq 165$ nm) of H_2O in 25-50 Torr (33-67 mbar) of argon diluent at 298 K.

(b) 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 N_2O to produce $O(^1D)$ atoms in the presence of H_2O 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, $\lambda < 180$ nm) of H_2O in argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction of H atoms with NO_2 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.

(c) HO radicals were produced by the photolysis of HNO_3 at 248 nm in 105 ± 5 mbar of helium diluent.

(d) HO radicals were produced by the photolysis of H_2O_2 at 248 nm.

(e) HO radicals were generated by the flash photolysis of H_2O in 1.33-26.7 kPa (10-200 Torr) of argon diluent. The rate coefficient was independent of the H_2O 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.

(f) HO radicals were generated by the photolysis of O_3 in the presence of H_2O in 1013 mbar of air diluent at 298 K. A rate coefficient ratio of $k(HO+CF_3CH_2OH)/k(HO+C_2H_6) = 0.547 \pm 0.019$ was measured. Placing this on an absolute basis using $k(HO+C_2H_6) = 2.4 \times 10^{-13}$ (Atkinson et al., 2006) gives $k(HO+CF_3CH_2OH) = (1.31 \pm 0.05) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(g) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. A rate coefficient ratio of $k(HO+CF_3CH_2OH)/k(HO+C_2H_2) = 0.12 \pm 0.01$ was reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+CF_3CH_2OH) = (9.4 \pm 0.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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 or 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 $k = 2.41 \times 10^{-18} T^2 \exp(-224/T)$ cm^3 molecule^{-1} 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(298K) value; $k = 1.25 \times 10^{-12} \exp(-754/T)$ cm^3 molecule^{-1} s^{-1}. Hurley et al. (2004) have reported the formation of CF_3CHO in a molar yield of 97 ± 3% following the chlorine-atom-initiated oxidation of CF_3CH_2OH in 700 Torr of air. HO and chlorine atom reaction with CF_3CH_2OH are expected to proceed via the same mechanism; hydrogen abstraction from the $–CH_2–$ group. The HO radical initiated oxidation of CF_3CH_2OH is expected to lead to quantitative conversion of CF_3CH_2OH into CF_3CHO (Calvert et al., 2011).

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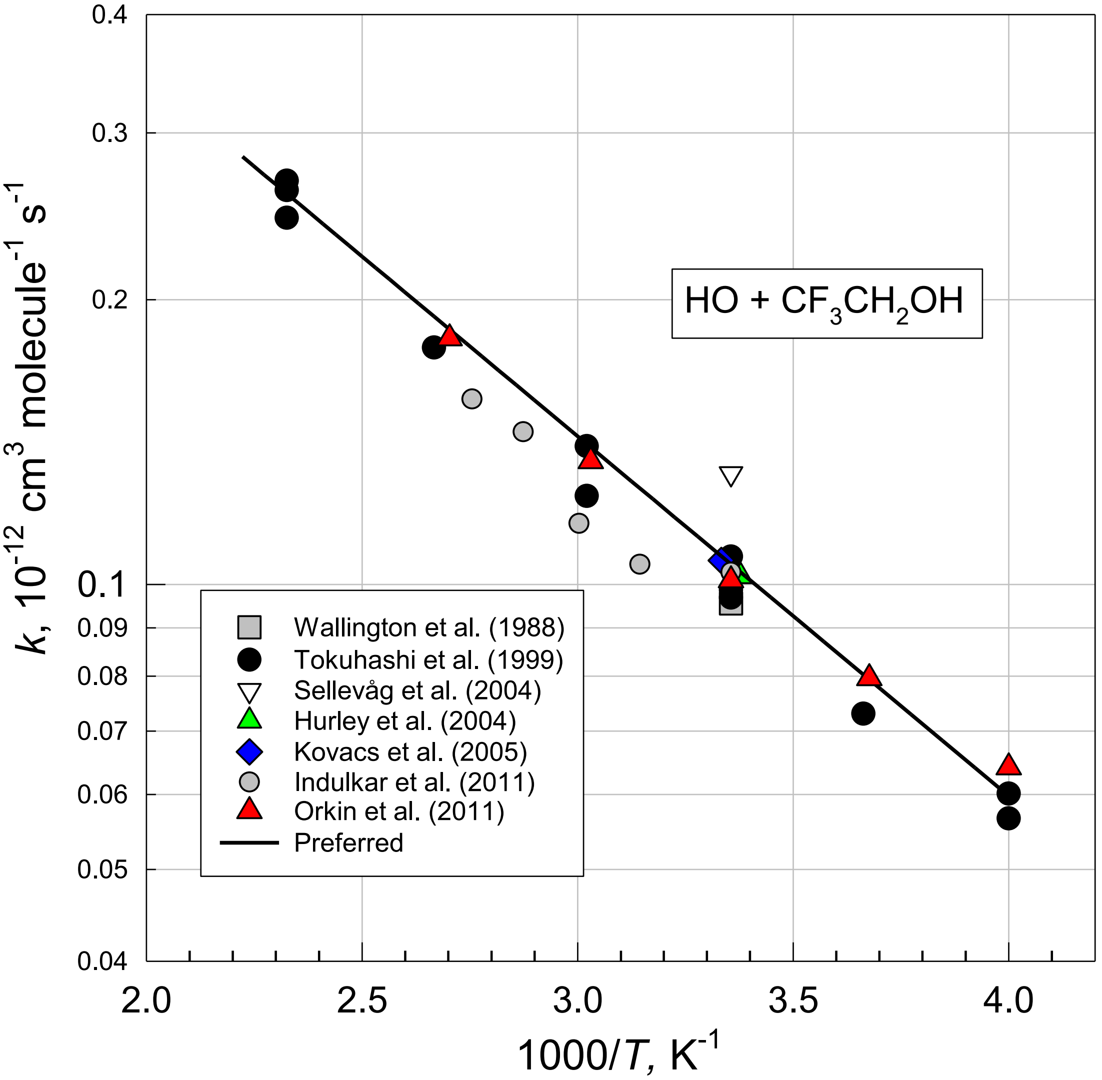

oFOx87: HO + $CF_3CH_2CH_2OH$

Last evaluated: June 2025; Last change in preferred values: June 2014.

$$\mathbf{HO + CF_3CH_2CH_2OH} \rightarrow \mathbf{CF_3CHCH_2OH + H_2O} \qquad \mathbf{(1)}$$
$$\rightarrow \mathbf{CF_3CH_2CHOH + H_2O} \qquad \mathbf{(2)}$$
$$\rightarrow \mathbf{CF_3CH_2CH_2O + H_2O} \qquad \mathbf{(2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(0.89 \pm 0.03) \times 10^{-12}$	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		
Relative Rate Coefficients			
$(1.06 \pm 0.04) \times 10^{-12}$	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)

Comments

(a) HO radicals were generated by the 248 nm photolysis of H_2O_2 in 100 Torr (133 mbar) of helium diluent at 298 K.

(b) HO radicals were produced by 248 nm photolysis of H_2O_2 in 47-211 Torr (63-281 mbar) of helium diluent at 298 K.

(c) HO radicals were produced by 248 nm photolysis of H_2O_2 in 46-95 Torr (61-127 mbar) of helium diluent at 263-358 K.

(d) HO radicals were generated by the 254 nm (Hg lamp) photolysis of either H_2O_2 or O_3 (in the presence of H_2O vapor) in one atmosphere of air. Rate coefficient ratios of $k(HO+CF_3CH_2CH_2OH)/k(HO+HC(O)OC_4H_9) = 0.30 \pm 0.01$, $k(HO+CF_3CH_2CH_2OH)$ /k(HO+n-hexane) = 0.20 ± 0.01, and $k(HO+CF_3CH_2CH_2OH)/k(HO+CF_3CH_2OH) = 0.95 \pm 0.02$ were determined. Placing these ratios on an absolute basis using $k(HO+HC(O)OC_4H_9) = 3.54 \times 10^{-12}$ (Le Calvé et al., 1997), k(HO+n-hexane) = 5.27×10^{-12} (Calvert et al., 2008), and $k(HO+CF_3CH_2OH) = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (present recommendation) gives $k(HO+CF_3CH_2CH_2OH) = (1.06 \pm 0.04) \times 10^{-12}$, $(1.05 \pm 0.05) \times 10^{-12}$, and $(1.43 \pm 0.03) \times 10^{-12}$, respectively.

(e) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. Rate coefficient ratios of $k(HO+CF_3CH_2CH_2OH)/k(HO+C_2H_2) = 0.87 \pm 0.09$ and $k(HO+CF_3CH_2CH_2OH)/k(HO+C_2H_4) = 0.089 \pm 0.010$ were reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO+CF_3CH_2CH_2OH) = (6.79 \pm 0.70) \times 10^{-13}$ and $(7.03 \pm 0.79) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

k /cm^3 molecule^{-1} s^{-1}	2.72×10^{-12} exp(-305/T)	260-360
Reliability		
Δ log k	0.10	298
Δ E/R	± 200	260-360

Comments on Preferred Values

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 $–CH_2–$ group bearing the alcohol functionality (Calvert et al., 2010). Subsequent reaction of the CF_3CH_2CHOH with O_2 will give CF_3CH_2CHO. The HO radical initiated oxidation of $CF_3CH_2CH_2OH$ is expected to give CF_3CH_2CHO in a yield close to 100%. Consistent with this expectation, Hurley et al. (2005) observed the formation of CF_3CH_2CHO as the sole product of the chlorine-atom-initiated oxidation of $CF_3CH_2CH_2OH$ in one atmosphere of air.

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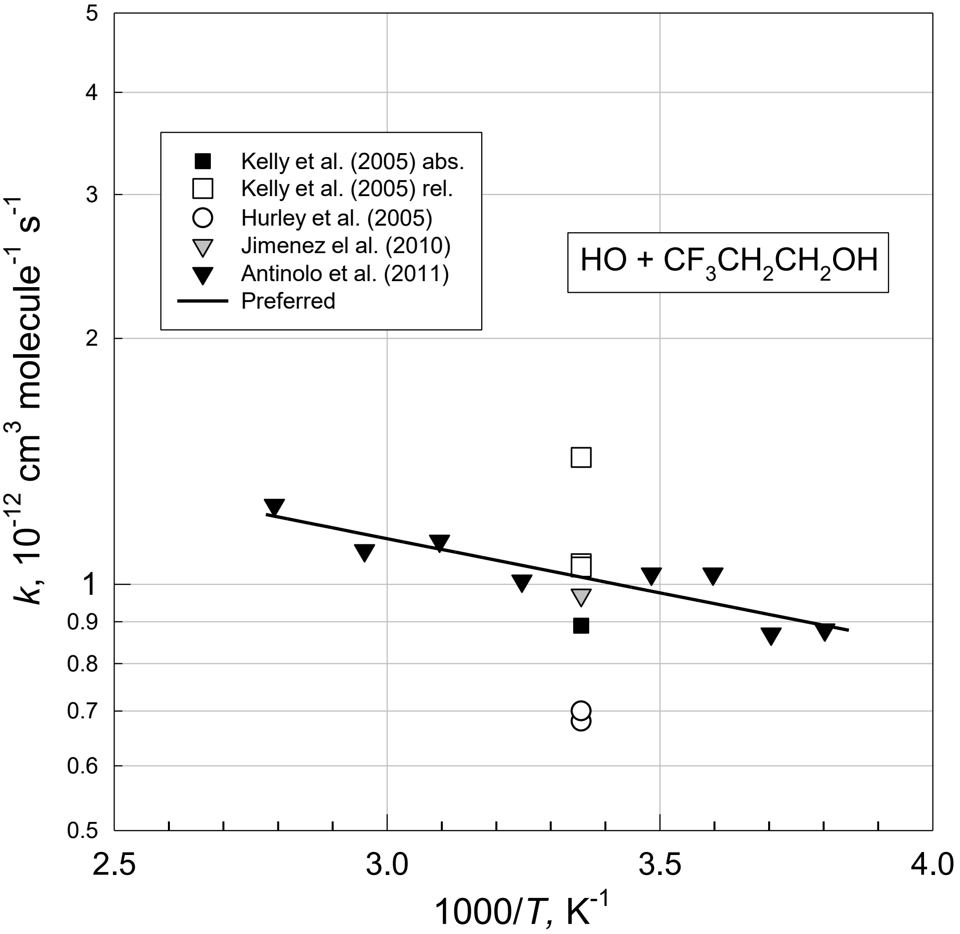

HO + CF3CH2CH2OH
Kelly et al. (2005) abs.
Kelly et al. (2005) rel.
Hurley et al. (2005)
Jimenez el al. (2010)
Antinolo et al. (2011)
Preferred
k, 10-12 cm3 molecule-1 s-1
1000/T, K-1
5
4
3
2
1
0.9
0.8
0.7
0.6
0.5
2.5
3.0
3.5
4.0

3406
3407

oFOx88: HO + $C_2F_5CH_2OH$

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

$$HO + C_2F_5CH_2OH \rightarrow C_2F_5CHOH + H_2O \quad (1)$$
$$\rightarrow C_2F_5CH_2O + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.40\pm0.27) \times 10^{-12} \exp[-(780\pm60)/T]$	250-430	Tokuhashi et al. (1999)	LP-LIF (a)
1.00×10^{-13}	298		FP-LIF (a) DF-LIF (a)
$1.36 \times 10^{-12} \exp[-(730\pm43)/T]$	263-358	Antiñolo et al. (2012)	PLP-LIF (b)
$(1.19 \pm 0.03) \times 10^{-13}$	287		
Relative Rate Coefficients			
$1.5 \times 10^{-12} \exp[-(818)/T]$	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)

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 N_2O to produce $O(^1D)$ atoms in the presence of H_2O 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 H_2O in argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction of H atoms with NO_2 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 produced by 248 nm photolysis of H_2O_2 in 43-214 Torr (57-285 mbar) of helium diluent at 263-358 K. No effect of total pressure was reported over the range studied.

(c) HO radicals were generated by the photolysis of O_3 in the presence of water vapor in 1 bar of O_2 diluent. The decay of $C_2F_5CH_2OH$ was monitored relative to that of CH_2Cl_2. Chen et al. (2000) used the expression $k(HO+CH_2Cl_2) = 3.8 \times 10^{-12} \exp(-1050/T)$ to place their results on an absolute basis. Rescaling using $k(HO+CH_2Cl_2) = 1.8 \times 10^{-12} \exp(-860/T)$ (Atkinson et al., 2008) and fitting an Arrhenius expression to the results gives $k(HO+ C_2F_5CH_2OH) = 1.5 \times 10^{-12} \exp(-818/T)$ cm^3 molecule^{-1} s^{-1}.

(d) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. A rate coefficient ratio of $k(HO+C_2F_5CH_2OH)/k(HO+C_2H_2) = 0.12 \pm 0.01$ was reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+ C_2F_5CH_2OH) = (9.4 \pm 0.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

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(HO+ $C_2F_5CH_2OH$) = 1.05×10^{-13} cm^3 molecule^{-1} 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(HO+ $C_2F_5CH_2OH$) = $1.28 \times 10^{-12} \exp(-748/T)$ cm^3 molecule^{-1} s^{-1}. The HO radical initiated oxidation of $C_2F_5CH_2OH$ is expected to lead to quantitative conversion into C_2F_5CHO (Calvert et al., 2011).

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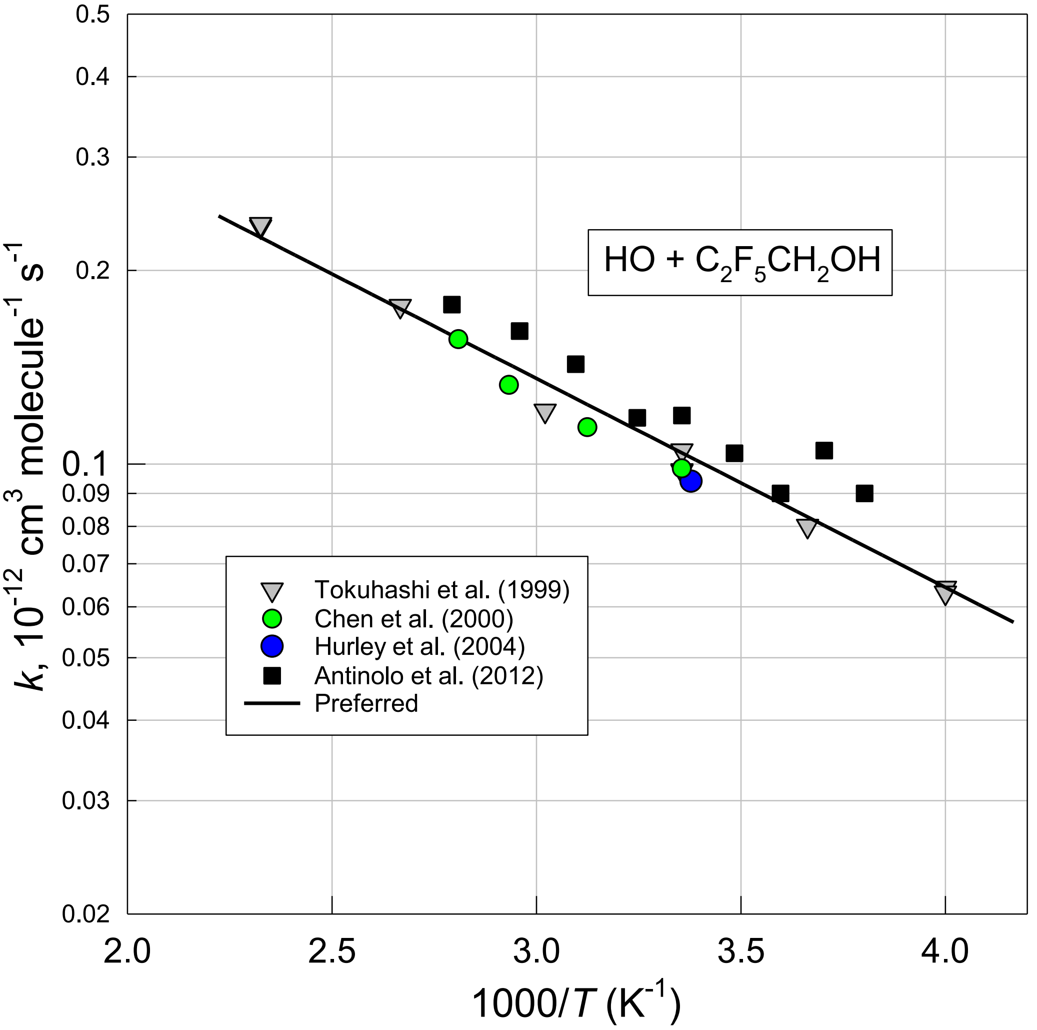
HO + $C_2F_5CH_2OH$
k, 10^{-12} cm^3 $molecule^{-1}$ s^{-1}
1000/T (K^{-1})
0.5
0.4
0.3
0.2
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
2.0
2.5
3.0
3.5
4.0
Tokuhashi et al. (1999)
Chen et al. (2000)
Hurley et al. (2004)
Antinolo et al. (2012)
Preferred

oFOx89: HO + $CF_3CH(OH)CF_3$

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

$$\mathbf{HO + CF_3CH(OH)CF_3 \rightarrow CF_3C(OH)CF_3 + H_2O} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow CF_3CH(O)CF_3 + H_2O} \quad \mathbf{(2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.99\pm1.56) \times 10^{-13} \exp[-(990\pm70)/T]$	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		

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 N_2O to produce $O(^1D)$ atoms in the presence of H_2O 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 H_2O in argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction of H atoms with NO_2 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 H_2O vapor in 30 Torr (40 mbar) of argon.

Preferred Values

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

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 $k(\mathrm{HO+ CF_3CH(OH)CF_3}) = 3.94 \times 10^{-15} (T/298)^{4.57} \exp(542/T)$ cm^3 molecule^{-1} s^{-1} which fits the data over the temperature range 220-430 K.

The HO radical initiated oxidation of $CF_3CH(OH)CF_3$ is expected to lead to quantitative conversion into $CF_3C(O)CF_3$ (Calvert et al., 2011).

$$HO + CF_3CH(OH)CF_3 \rightarrow CF_3C(OH)CF_3 + H_2O$$
$$CF_3C(OH)CF_3 + O_2 \rightarrow CF_3C(O)CF_3 + HO_2$$

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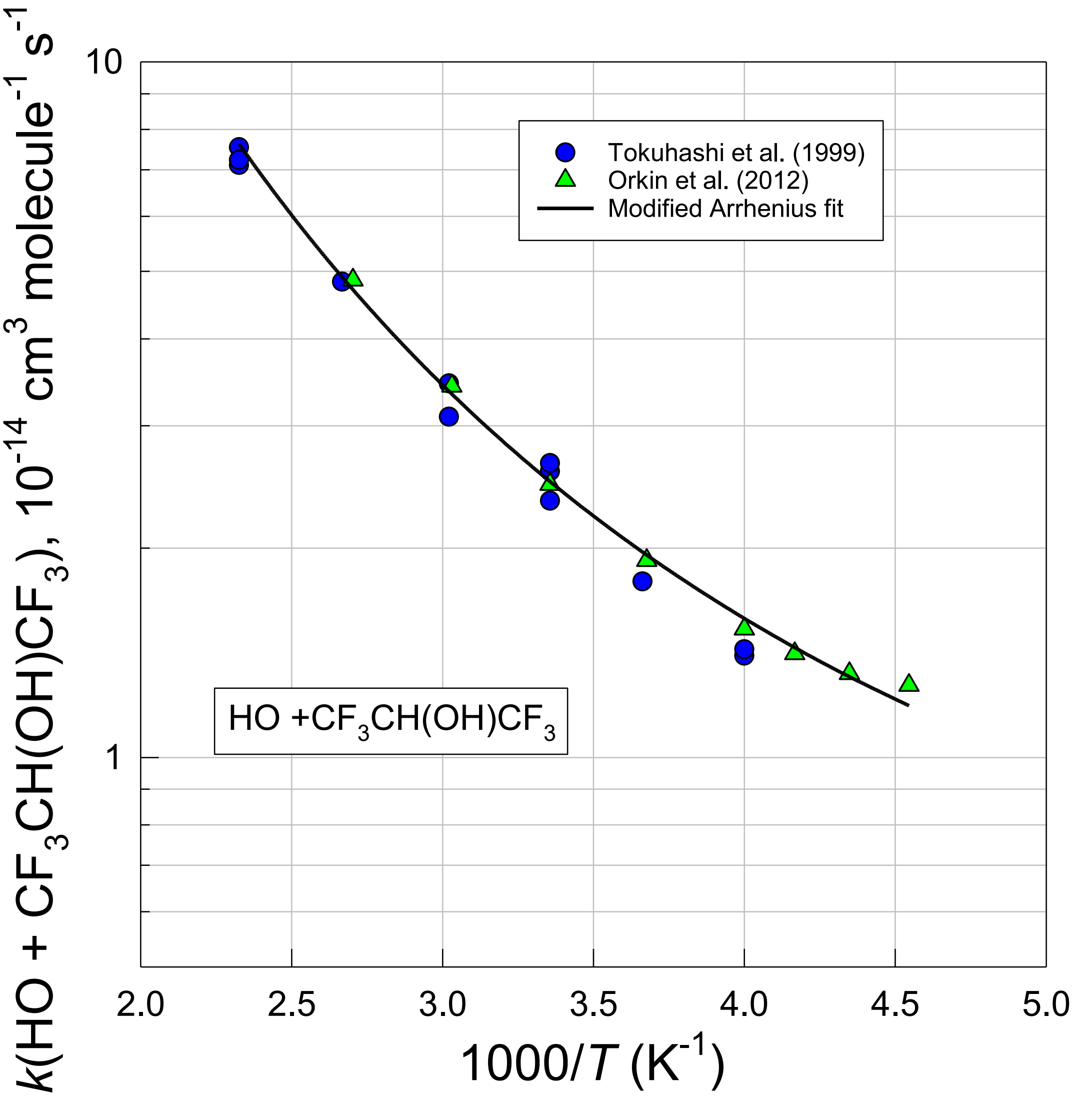

oFOx158: HO + $(CF_3)_2C(OH)CH_3$

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

$$HO + (CF_3)_2C(OH)CH_3 \rightarrow (CF_3)_2C(OH)CH_2 + H_2O \quad (1)$$
$$\rightarrow (CF_3)_2CH(O)CH_3 + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were generated using the flash photolysis of H_2O vapor in 30 Torr (40 mbar) of argon diluent and monitored using resonance fluorescence.

Preferred Values

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

Comments on Preferred Values

The preferred value at 298 K is taken from 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 data set from Orkin et al. (2012) gives $k(HO+ (CF_3)_2C(OH)CH_3) = 1.90 \times 10^{-18} (T/298)^{11.5} \exp(2476/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-370 K.

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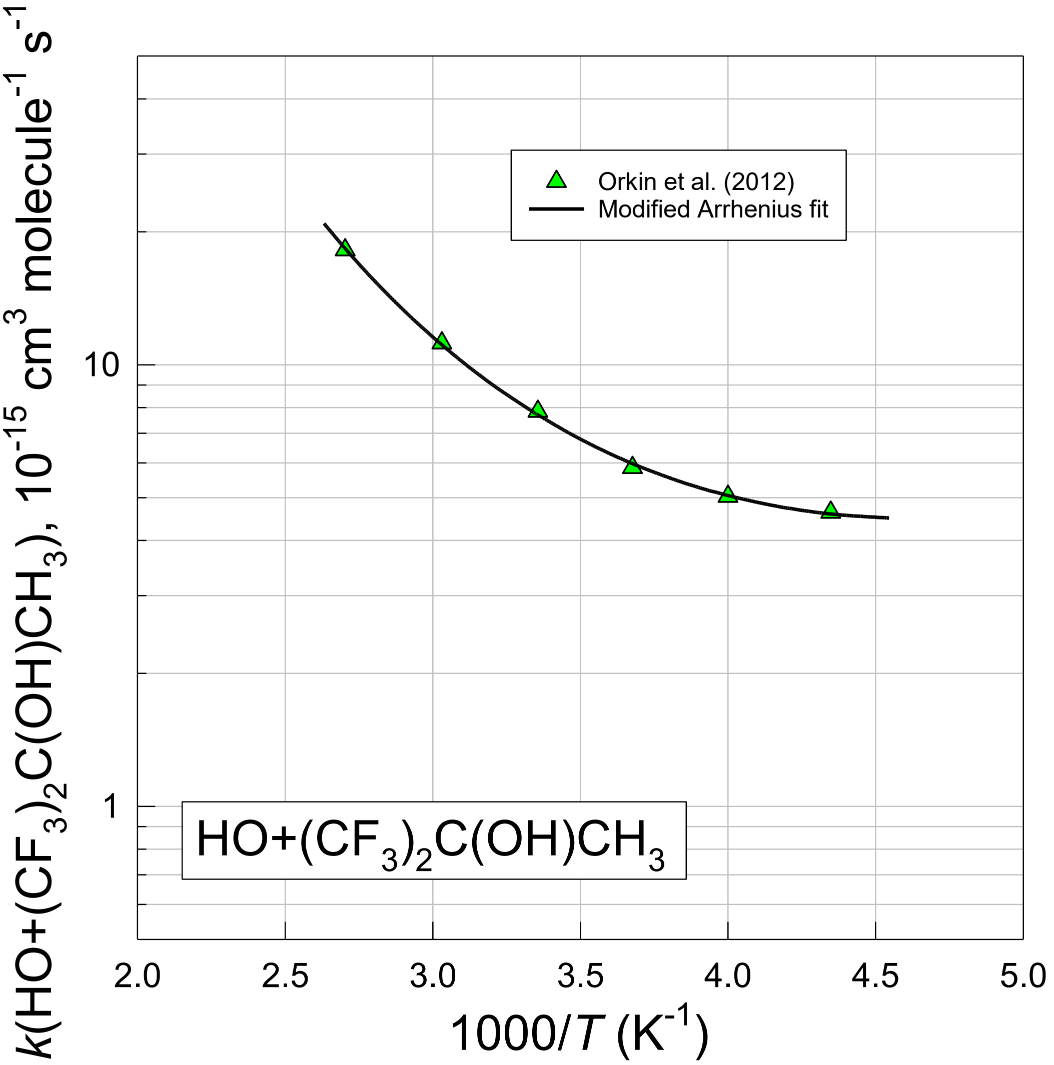

Orkin et al. (2012)
Modified Arrhenius fit
HO+(CF$_3$)$_2$C(OH)CH$_3$
k(HO+(CF$_3$)$_2$C(OH)CH$_3$), 10^{-15} cm^3 molecule^{-1} s^{-1}
10
1
2.0
2.5
3.0
3.5
4.0
4.5
5.0
1000/T (K^{-1})

oFOx159: HO + $(CF_3)_3C(OH)$

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

$$HO + (CF_3)_3C(OH) \rightarrow (CF_3)_3C(O) + H_2O \qquad (1)$$

Rate coefficient data

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

Comments

(a) HO radicals were generated using the flash photolysis of H_2O vapor in 30 Torr (40 mbar) of argon diluent and monitored using resonance fluorescence.

Preferred Values

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

Comments on Preferred Values

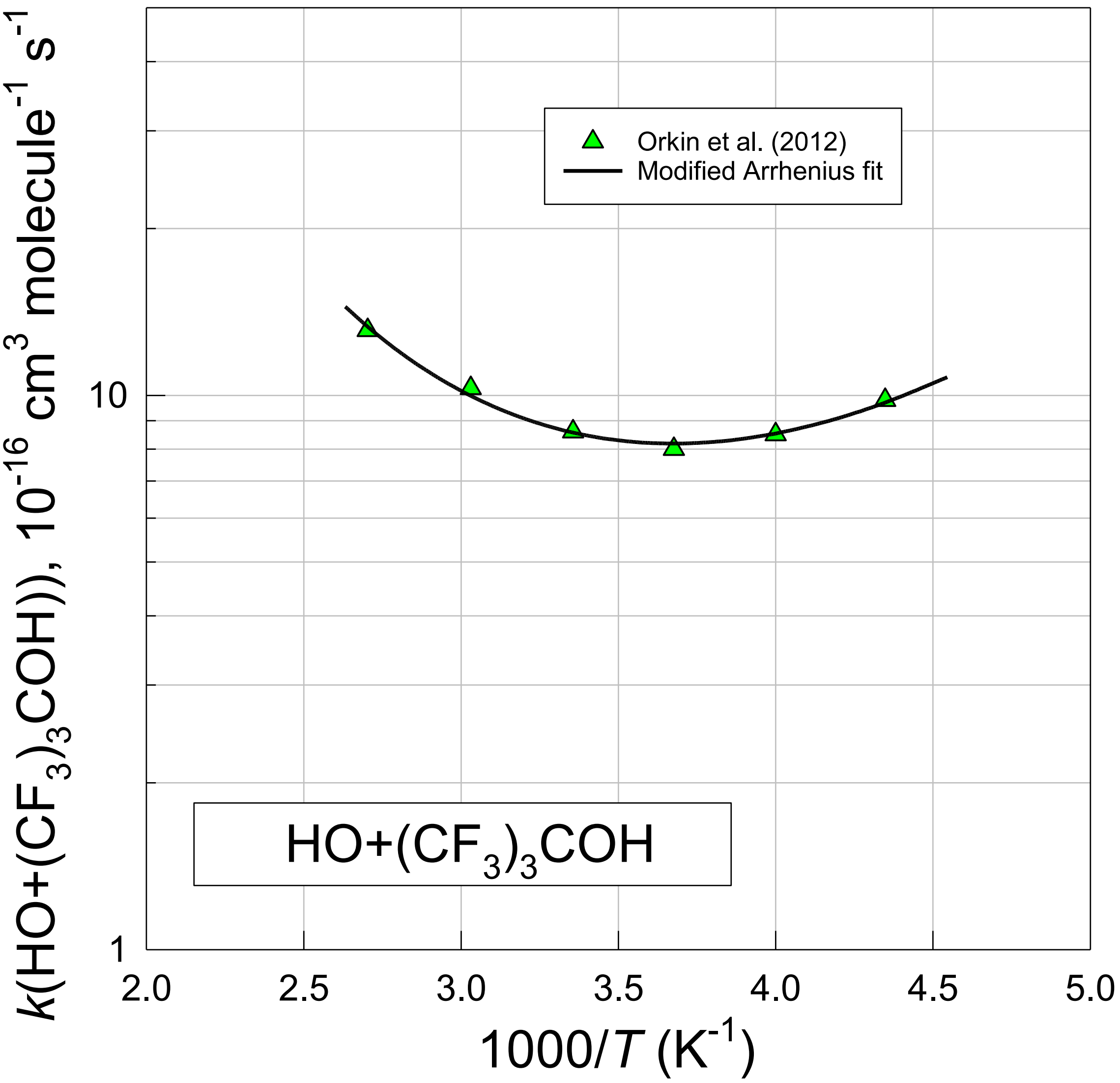
There is significant curvature in the Arrhenius plot. The k(298K) value and modified Arrhenius expression from Orkin et al. (2012) are preferred The HO radical initiated oxidation of $(CF_3)_3C(OH)$ is expected to lead to quantitative conversion into $CF_3C(O)CF_3$ (Calvert et al., 2011).

$$HO + (CF_3)_3C(OH) \rightarrow (CF_3)_3C(O) + H_2O$$
$$(CF_3)_3C(O) \rightarrow CF_3C(O)CF_3 + CF_3$$

References

Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.

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


Orkin et al. (2012)
Modified Arrhenius fit
HO+$(CF_3)_3$COH
k(HO+$(CF_3)_3$COH)), 10^{-16} cm^3 molecule^{-1} s^{-1}
10
1
2.0
2.5
3.0
3.5
4.0
4.5
5.0
1000/T (K^{-1})

oFOx90: HO + $CF_3CHFCF_2CH_2OH$

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

$$HO + CF_3CHFCF_2CH_2OH \rightarrow CF_3CFCF_2CH_2OH + H_2O \quad (1)$$
$$\rightarrow CF_3CHFCF_2CHOH + H_2O \quad (2)$$
$$\rightarrow CF_3CHFCF_2CH_2O + H_2O \quad (3)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.46\pm0.26) \times 10^{-12} \exp[-(880\pm40)/T]$	250-430	Chen et al. (2003)	LP-LIF (a)
1.3×10^{-13}	298		FP-LIF (a)
Relative Rate Coefficients			
$6.03 \times 10^{-13} \exp(-510/T)$	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		

Comments

(a) Two different absolute rate methods were employed by Chen et al. (2003): LP-LIF and FP-LIF. HO radicals in the LP-LIF experiments were generated by the 193 nm photolysis of N_2O to produce $O(^1D)$ atoms in the presence of H_2O in 20-80 Torr (27-107 mbar) of helium diluent. HO radicals in the FP-LIF experiments were generated by the photolysis (Xe flash lamp) of H_2O in 20-80 Torr (27-107 mbar) of argon diluent. There was good agreement between the results from experiments using the two different techniques. The Arrhenius expression is from a fit to the combined data set from both sets of absolute rate experiments. The value at 298 K cited above is the average obtained using the different techniques.

(b) HO radicals were generated by the photolysis of O_3 at $\lambda \geq 260$ nm using the output from Xe arc lamps in the presence of H_2O vapor in 100 Torr (133 mbar) of helium diluent. CH_2Cl_2 and $CHCl_3$ were used as reference compounds. Arrhenius fits to the rate coefficient ratios reported by Chen et al. (2003) give $k(HO+CF_3CHFCF_2CH_2OH)/k(HO+CH_2Cl_2) = 0.335 \exp(350/T)$ and $k(HO+CF_3CHFCF_2CH_2OH)/k(HO+CHCl_3) = 0.523 \exp(259/T)$. Placing these ratios on an absolute basis using $k(HO+CH_2Cl_2) = 1.8 \times 10^{-12} \exp(-860/T)$ and $k(HO+CHCl_3) = 1.8 \times 10^{-12} \exp(-850/T)$ (Atkinson et al., 2008) gives $k(HO+CF_3CHFCF_2CH_2OH) = 6.03 \times 10^{-13} \exp(-510/T)$ and $9.41 \times 10^{-13} \exp(-591/T)$ cm^3 molecule^{-1} s^{-1}, respectively. Over the temperature range where comparison is possible, the results from the relative rate studies are consistent with those from the absolute study.

Preferred Values

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

Comments on Preferred Values

The results from the absolute (two different techniques) and the relative rate experiments (two different references) of Chen et al. (2003) are in good agreement. A fit to the absolute rate data set gives $k(\mathrm{HO+CF_3CHFCF_2CH_2OH}) = 2.26 \times 10^{-12}\ \exp(-848/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. The HO radical initiated oxidation of $CF_3CHFCF_2CH_2OH$ is expected to proceed mainly via abstraction from the $–CH_2–$ group leading to essentially quantitative conversion into CF_3CHFCF_2CHO as discussed by Calvert et al. (2011).

References

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; IUPAC Subcommittee for Gas Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

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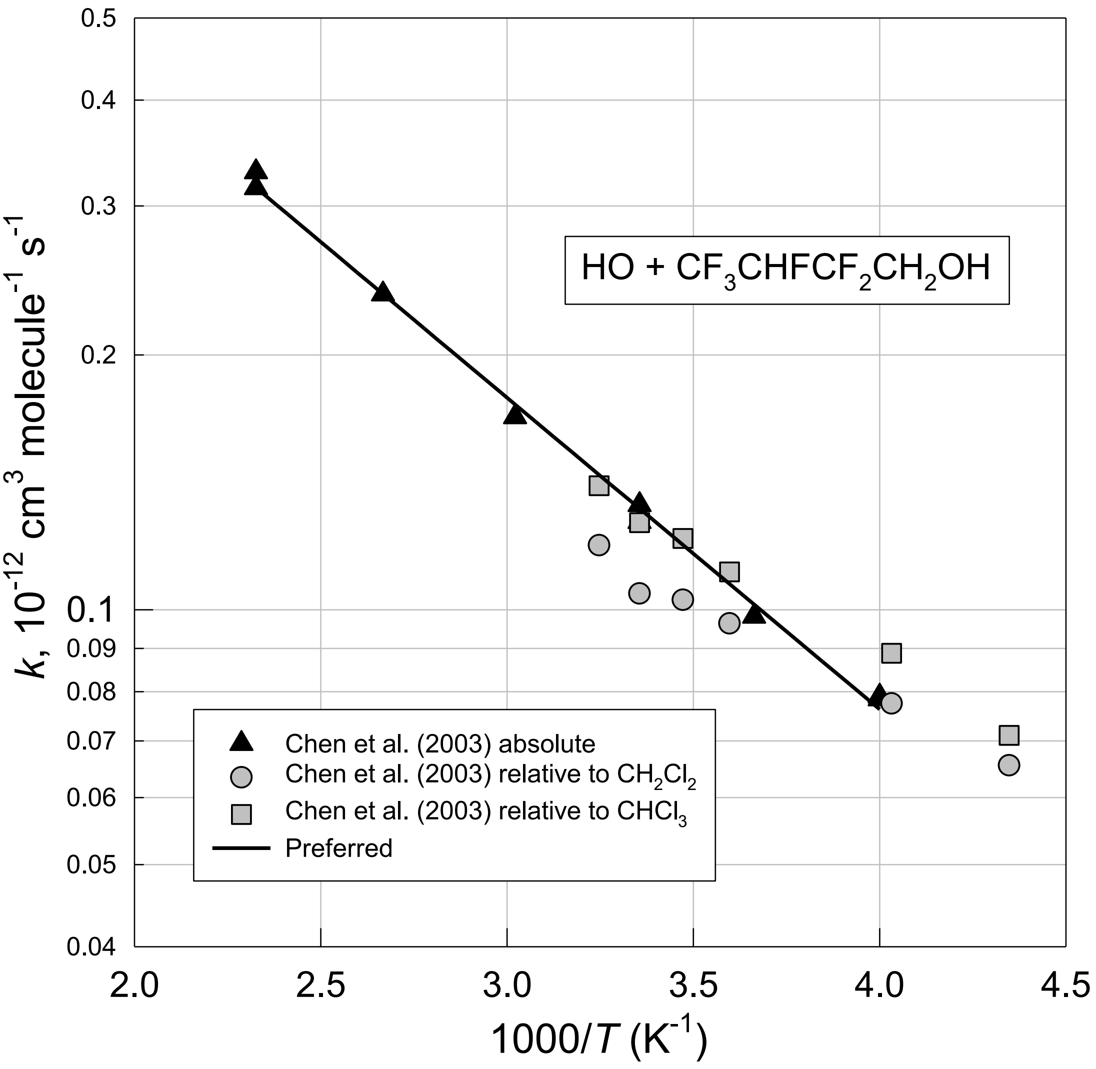

oFOx91: HO + n-$C_3F_7CH_2OH$

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

$$HO + n\text{-}C_3F_7CH_2OH \rightarrow n\text{-}C_3F_7CHOH + H_2O \quad (1)$$
$$\rightarrow n\text{-}C_3F_7CH_2O + H_2O \quad (2)$$

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

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

Comments

(a) F atoms produced in a microwave discharge of F_2/He mixtures were reacted with H_2O to generate HO radicals. Experiments were conducted in a flow tube at a pressure of 1 Torr of helium diluent. HO radicals were monitored by mass spectroscopy by adding I_2 and detecting the HOI product.

(b) HO radicals were produced by the photolysis of H_2O_2 at 248 nm and monitored by laser induced fluorescence in 55 Torr of helium diluent.

(c) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. A rate coefficient ratio of $k(HO+C_3F_7CH_2OH)/k(HO+C_2H_2) = 0.12 \pm 0.01$ was reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+C_3F_7CH_2OH) = (9.4 \pm 0.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.11×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$6.06 \times 10^{-12} \exp(-1192/T)$	280-370
Reliability		
$\Delta \log k$	± 0.10	298
$\Delta E/R$	± 200	280-370

Comments on Preferred Values

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

References

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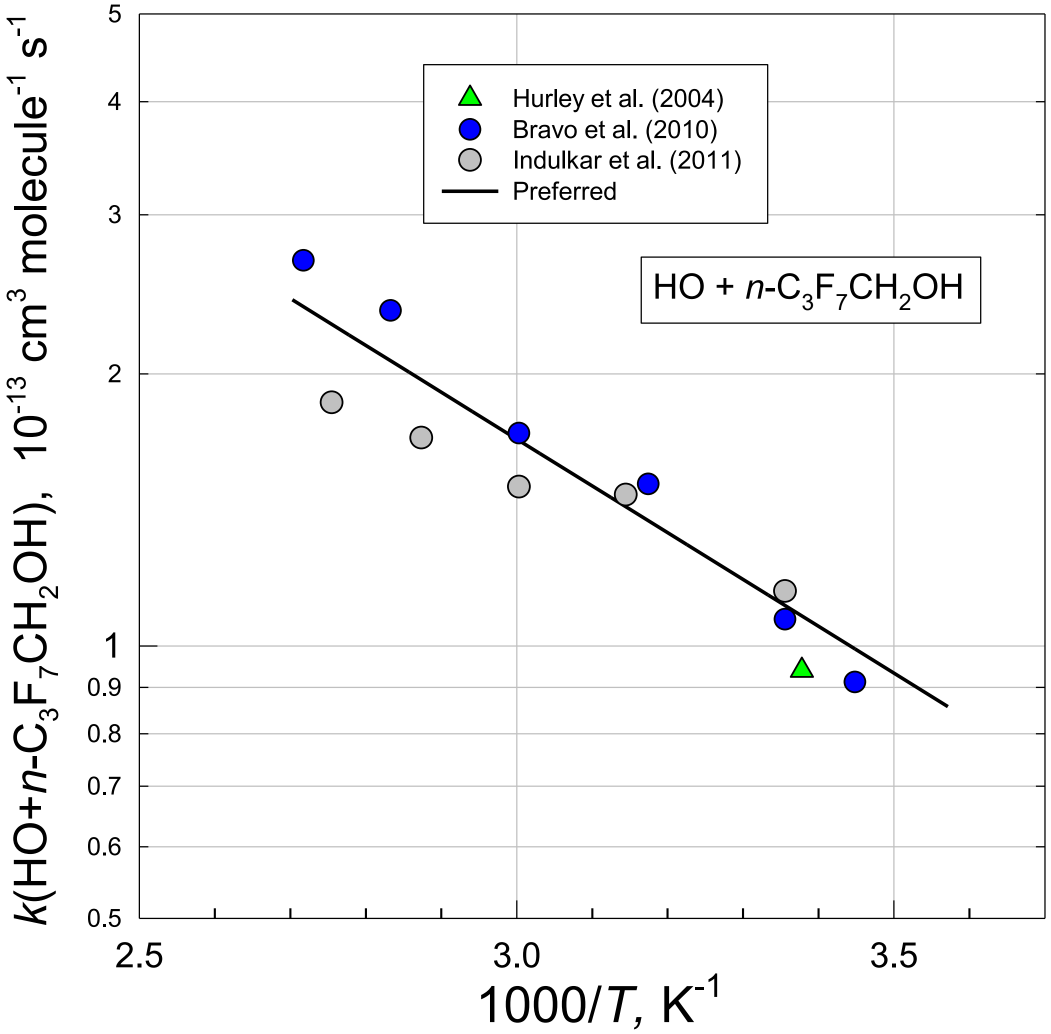

oFOx92: HO + n-$C_4F_9CH_2OH$

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

$$\mathrm{HO} + n\text{-}\mathrm{C_4F_9CH_2OH} \rightarrow n\text{-}\mathrm{C_4F_9CHOH} + \mathrm{H_2O} \quad (1)$$

$$\rightarrow n\text{-}\mathrm{C_4F_9CH_2O} + \mathrm{H_2O} \quad (2)$$

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

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. Experiments were performed with $C_xF_{2x+1}CH_2OH$ (x= 1, 2, 3, and 4). There was no discernable difference in the reactivity of $C_xF_{2x+1}CH_2OH$ molecules investigated and the composite data set was analyzed together. A rate coefficient ratio of $k(HO+C_xF_{2x+1}CH_2OH)/k(HO+C_2H_2) = 0.12 \pm 0.01$ was reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+C_4F_9CH_2OH) = (9.4 \pm 0.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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

References

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

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

oFOx93: HO + *n*-$C_4F_9CH_2CH_2OH$

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

$$\text{HO} + n\text{-}C_4F_9CH_2CH_2OH \rightarrow n\text{-}C_4F_9CHCH_2OH + H_2O \quad (1)$$
$$\rightarrow n\text{-}C_4F_9CH_2CHOH + H_2O \quad (2)$$
$$\rightarrow n\text{-}C_4F_9CH_2CH_2O + H_2O \quad (3)$$

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

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. Experiments were performed with *n*-$C_4F_9CH_2CH_2OH$, *n*-$C_6F_{13}CH_2CH_2OH$, and *n*-$C_8F_{17}CH_2CH_2OH$. There was no discernable difference in the reactivity of the three alcohols and the composite data set was analyzed together. Rate coefficient ratios of $k(HO+C_xF_{2x+1}CH_2CH_2OH)/k(HO+C_2H_2) = 1.18 \pm 0.15$ and $k(HO+C_xF_{2x+1}CH_2CH_2OH)/k(HO+C_2H_4) = 0.131 \pm 0.018$ were reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_2) = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+n\text{-}C_4F_9CH_2CH_2OH) = (0.92 \pm 0.12) \times 10^{-12}$ and $(1.03 \pm 0.14) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred value is based upon the average of the two determinations by Ellis et al. (2003). As discussed by Calvert et al. (2011), HO radicals are approximately an order of magnitude less reactive towards $C_xF_{2x+1}CH_2OH$ than towards $C_xF_{2x+1}CH_2CH_2OH$ and presumably the majority (>90%) of reaction of HO with *n*-$C_4F_9CH_2CH_2OH$ proceeds via attack on the terminal –CH_2– group. As with other α-hydroxy alkyl radicals, the atmospheric fate of *n*-$C_4F_9CH_2CHOH$ radicals will be reaction with O_2 to give the corresponding aldehyde.

$$n\text{-}C_4F_9CH_2CH_2OH + HO \rightarrow n\text{-}C_4F_9CH_2CHOH + H_2O$$
$$n\text{-}C_4F_9CH_2CHOH + O_2 \rightarrow n\text{-}C_4F_9CH_2CHO + HO_2$$

Product studies of the chlorine atom initiated oxidation of *n*-$C_4F_9CH_2CH_2OH$ in 700 Torr of air at 296 K by Hurley et al. (2004) and Andersen et al. (2005) have shown that *n*-$C_4F_9CH_2CH_2OH$ is oxidized to give *n*-$C_4F_9CH_2CHO$ in a yield which is indistinguishable from 100%.

References

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oFOx94: HO + n-$C_6F_{13}CH_2CH_2OH$

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

$$HO + n\text{-}C_6F_{13}CH_2CH_2OH \rightarrow n\text{-}C_6F_{13}CHCH_2OH + H_2O \quad (1)$$
$$\rightarrow n\text{-}C_6F_{13}CH_2CHOH + H_2O \quad (2)$$
$$\rightarrow n\text{-}C_6F_{13}CH_2CH_2O + H_2O \quad (3)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(9.2 \pm 1.2) \times 10^{-13}$	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)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. Experiments were performed with n-$C_4F_9CH_2CH_2OH$, n-$C_6F_{13}CH_2CH_2OH$, and n-$C_8F_{17}CH_2CH_2OH$. There was no discernable difference in the reactivity of the three alcohols and the composite data set was analyzed together. A rate coefficient ratio of $k(HO+C_xF_{2x+1}CH_2CH_2OH)/k(HO+C_2H_2) = 1.18 \pm 0.15$ was reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+n\text{-}C_6F_{13}CH_2CH_2OH) = (9.2 \pm 1.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(b) HO radicals were generated by the photolysis of either H_2O_2 or O_3 (in the presence of H_2O vapor) in one atmosphere of air. Experiments were performed using two different reference compounds; $HC(O)OC_4H_9$ and n-C_6H_{14}. Rate coefficient ratios of $k(HO+C_6F_{13}CH_2CH_2OH)/k(HO+HC(O)OC_4H_9) = 0.22 \pm 0.01$ and $k(HO+C_6F_{13}CH_2CH_2OH)/k(HO+n\text{-}C_6H_{14}) = 0.15 \pm 0.01$ were reported. Using $k(HO+HC(O)OC_4H_9) = 3.54 \times 10^{-12}$ (Le Calvé et al., 1997) and $k(HO+n\text{-}C_6H_{14}) = 3.27 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2008) gives $k(HO+n\text{-}C_6F_{13}CH_2CH_2OH) = (7.79 \pm 0.35) \times 10^{-13}$ and $(7.91 \pm 0.53) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The rate coefficients reported in the relative rate studies by Ellis et al. (2003) and Kelly et al. (2005) are in agreement and an average gives our preferred value. As discussed by Calvert et al. (2011), HO radicals are approximately an order of magnitude less reactive towards $C_xF_{2x+1}CH_2OH$ than towards $C_xF_{2x+1}CH_2CH_2OH$ and it seems likely that the majority (>90%) of reaction of HO with n-$C_6F_{13}CH_2CH_2OH$ proceeds via attack on the terminal –CH_2– group. As with other α-hydroxy alkyl radicals, the atmospheric fate of n-$C_6F_{13}CH_2CHOH$ radicals will be reaction with O_2 to give the corresponding aldehyde.

$$n\text{-}C_6F_{13}CH_2CH_2OH + OH \rightarrow n\text{-}C_6F_{13}CH_2CHOH + H_2O$$

$$n\text{-}C_6F_{13}CH_2CHOH + O_2 \rightarrow n\text{-}C_6F_{13}CH_2CHO + HO_2$$

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oFOx95: HO + n-$C_6F_{13}CH_2CH_2OH$

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

$$\mathbf{HO + \textit{n}\text{-}C_8F_{17}CH_2CH_2OH \rightarrow \textit{n}\text{-}C_8F_{17}CHCH_2OH + H_2O} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow \textit{n}\text{-}C_8F_{17}CH_2CHOH + H_2O} \quad \mathbf{(2)}$$
$$\mathbf{\rightarrow \textit{n}\text{-}C_8F_{17}CH_2CH_2O + H_2O} \quad \mathbf{(3)}$$

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

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. Experiments were performed with n-$C_4F_9CH_2CH_2OH$, n-$C_6F_{13}CH_2CH_2OH$, and n-$C_8F_{17}CH_2CH_2OH$. There was no discernable difference in the reactivity of the three alcohols and the composite data set was analyzed together. A rate coefficient ratio of $k(HO+C_xF_{2x+1}CH_2CH_2OH)/k(HO+C_2H_2) = 1.18 \pm 0.15$ was reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+n\text{-}C_8F_{17}CH_2CH_2OH) = (9.2 \pm 1.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The rate coefficient reported by Ellis et al. (2003) is adopted as the preferred value. As discussed by Calvert et al. (2011), HO radicals are approximately an order of magnitude less reactive towards $C_xF_{2x+1}CH_2OH$ than towards $C_xF_{2x+1}CH_2CH_2OH$ and it seems likely that the majority (>90%) of reaction of HO with n-$C_8F_{17}CH_2CH_2OH$ proceeds via attack on the terminal –CH_2– group. As with other α-hydroxy alkyl radicals, the atmospheric fate of n-$C_8F_{17}CH_2CHOH$ radicals will be reaction with O_2 to give the corresponding aldehyde.

$$n\text{-}C_8F_{17}CH_2CH_2OH + HO \rightarrow n\text{-}C_8F_{17}CH_2CHOH + H_2O$$
$$n\text{-}C_8F_{17}CH_2CHOH + O_2 \rightarrow n\text{-}C_8F_{17}CH_2CHO + HO_2$$

It is expected that the HO radical initiated oxidation of n-$C_8F_{17}CH_2CH_2OH$ will lead to the formation of n-$C_8F_{17}CH_2CHO$ in a yield of essentially 100%. Consistent with this expectation, Chiappero et al. (2008) measured a 92 ± 7% yield of n-$C_8F_{17}CH_2CHO$ in the chlorine-atom initiated oxidation of n-$C_8F_{17}CH_2CH_2OH$ (8:2 FTOH) in 700 Torr of air.

References

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

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oFOx96: HO + $CF_3CH(OH)_2$

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

$$HO + CF_3CH(OH)_2 \rightarrow CF_3C(OH)_2 + H_2O \quad (1)$$
$$\rightarrow CF_3CH(OH)O + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air. Separate experiments were performed using C_2H_2 and C_2H_4 as references. Rate coefficient ratios of $k(HO+CF_3CH(OH)_2)/k(HO+C_2H_2) = 0.146 \pm 0.015$ and $k(HO+CF_3CH(OH)_2)/ k(HO+C_2H_4) = 0.0149 \pm 0.0014$ were reported. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_2) = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+CF_3CH(OH)_2) = (1.14 \pm 0.12) \times 10^{-13}$ and $(1.18 \pm 0.11) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred value is based upon the average of the two determinations by Andersen et al. (2006). Andersen et al. (2006) reported that the chlorine atom initiated oxidation of $CF_3CH(OH)_2$ in 700 Torr (933 mbar) of air gives $CF_3C(O)OH$ in a molar yield of 101 ± 6%. The HO radical initiated of $CF_3CH(OH)_2$ is expected to give $CF_3C(O)OH$ in essentially 100% yield.

References

Andersen, M. P. S., Nielsen, O. J., Hurley, M. D., Ball, J. C., Wallington, T. J., Ellis, D. A., Martin, J. W., and Mabury, S. A.: J. Phys. Chem. A, 109, 1849, 2005.

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

oClOx90: HO + CH_2ClCH_2OH

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

$$\begin{aligned} HO + CH_2ClCH_2OH &\rightarrow CHClCH_2OH + H_2O \quad (1)\\ &\rightarrow CH_2ClCHOH + H_2O \quad (2)\\ &\rightarrow CH_2ClCH_2O + H_2O \quad (3)\end{aligned}$$

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

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

Comments

(a) HO radicals were generated by the photolysis ($\lambda \geq 165$ nm) of H_2O in 25-50 Torr (33-67 mbar) of argon at 298 K.

Preferred Values

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

Comments on Preferred Values

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

References

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

oClOx91: HO + CCl_3CH_2OH

Last evaluated: June 2023; Last change in preferred values: June 2009.

$$HO + CCl_3CH_2OH \rightarrow CCl_3CHOH + H_2O \quad (1)$$
$$\rightarrow CCl_3CH_2O + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were generated by the photolysis ($\lambda \geq 165$ nm) of H_2O in 25-50 Torr (33-67 mbar) of argon at 298 K.

Preferred Values

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

Comments on Preferred Values

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

References

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

oFOx97: HO + CHF_2CHO

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

$$HO + CHF_2CHO \rightarrow CHF_2CO + H_2O \quad (1)$$
$$\rightarrow CF_2CHO + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were generated by the 248 nm photolysis of nitric acid in argon at 15-100 Torr (20 - 133 mbar) pressure. Laser fluence was varied in the range 150-300 mJ/pulse with no discernable effect on the rate coefficient measured suggesting the absence of complications from photolysis of CHF_2CHO.

(b) HO radicals were generated by the photolysis of CH_3ONO (or C_2H_5ONO) in CH_3ONO (or C_2H_5ONO)-NO-CHF_2CHO-toluene-air mixtures at 730-750 Torr (973 - 1000 mbar) pressure. The concentrations of CHF_2CHO and toluene were measured by GC and/or FTIR spectroscopy. Scollard et al. (1993) did not report a value for the rate coefficient ratio k(HO + CHF_2CHO)/k(HO + toluene). Dividing the reported value of k(HO + CHF_2CHO) by the value of k(HO + toluene) used by Scollard et al. (1993) gives k(HO + CHF_2CHO)/k(HO + toluene) = 0.235 ± 0.005 which is placed on an absolute basis in the table above using k(HO + toluene) = 5.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Mellouki et al., 2022).

(c) HO radicals were generated by the photolysis of O_3 in the presence of H_2 in 1013 mbar of air diluent. Propane was used as the reference compound. The concentrations of CHF_2CHO and propane were measured by FTIR spectroscopy and a rate coefficient ratio of k(HO + CHF_2CHO)/k(HO + propane) = 1.626 ± 0.042 was reported. Placing this result on an absolute basis using k(HO + propane) = 1.1×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives k(HO + CHF_2CHO) = $(1.79 \pm 0.05) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The results from the relative and absolute rate studies by Scollard et al. (1993) and Sellevåg et al. (2005) are in agreement within the combined experimental uncertainties. An average of the results from Scollard et al. (1993) and Sellevåg et al. (2005) gives the preferred value of k(OH+CHF_2CHO) =

1.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K. The reaction probably proceeds predominately via abstraction of the aldehydic hydrogen (channel 1) to give $CHF_2C(O)$ radicals.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Mellouki, A., Ammann, M., Cox, R. A., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V. F., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VII - gas phase reactions of organic species with four, or more, carbon atoms (≥C4), Atmos. Chem. Phys., 21, 4797-4808, 2021; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Scollard, D. J., Treacy, J. J., Sidebottom, H. W., Balestra-Garcia, C., Laverdet, G., Le Bras, G., MacLeod, H., and Téton, S.: J. Phys. Chem., 97, 4683, 1993.

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

oFOx98: HO + C_2F_5CHO

Last evaluated: June 2025; Last change in preferred values: June 2014.

$$HO + C_2F_5CHO \rightarrow C_2F_5CO + H_2O$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
$2.56 \times 10^{-12} \exp[-(458\pm36)/T]$	263-358	Antiñolo et al. (2014)	PLP-LIF (a)
$(5.57 \pm 0.14) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(4.63 \pm 0.51) \times 10^{-13}$	296	Sulbaek Andersen et al. (2003)	RR (b)
$(5.10 \pm 0.29) \times 10^{-13}$			

Comments

(a) HO radicals were produced by 248 nm (KrF eximer laser) photolysis of HNO_3 in 50-205 Torr (67-273 mbar) of helium diluent at 263-358 K. HO radicals were monitored by LIF. No effect of total pressure was reported over the range studied

(b) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air in the presence of NO. C_2H_2 and C_2H_4 were used in separate experiments as reference compounds. The loss of C_2F_5CHO and the reference compounds were monitored using FTIR spectroscopy. Rate coefficient ratios of $k(HO+C_2F_5CHO)/k(HO+C_2H_2) = 0.593 \pm 0.065$ and $k(HO+C_2F_5CHO)/k(HO+C_2H_4) = 0.0646 \pm 0.0037$ were reported. Scaling these ratios using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO+C_2F_5CHO) = (4.63 \pm 0.51) \times 10^{-13}$ and $(5.10 \pm 0.29) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	5.2×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$2.42 \times 10^{-12} \exp(-458/T)$	250-360
Reliability		
$\Delta \log k$	0.10	298
Δ E/R	± 200	250-360

Comments on Preferred Values

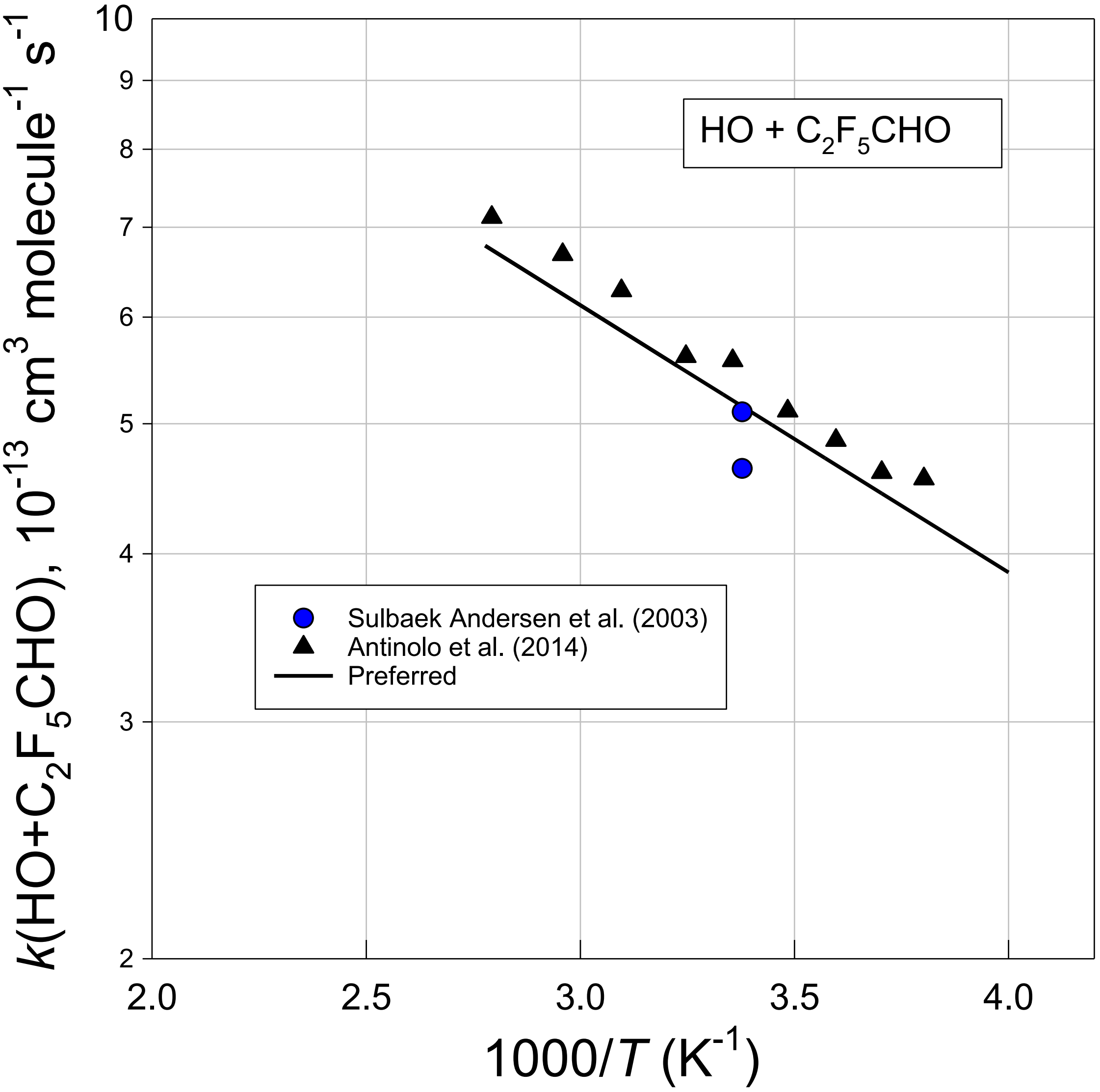
The results reported by Sulbaek Andersen et al. (2003) and Antiñolo et al. (2014) near room temperature are in agreement within the likely experimental uncertainties. Taking an average of the results from the two studies gives the preferred value of $k(OH+C_2F_5CHO) = 5.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. Taking the temperature dependence from Antiñolo et al. (2014) and adjusting the A factor to reproduce the preferred rate coefficient at 298 K gives $k(OH+C_2F_5CHO) = 2.42 \times 10^{-12} \exp(-458/T)$ cm^3 molecule^{-1} s^{-1}. The reaction proceeds via abstraction of the aldehydic hydrogen to give $C_2F_5C(O)$ radicals.

References

Antiñolo, M., Jiménez, E., Gonzalez, S., and Albaladejo, J.: J. Phys. Chem. A, 118, 178, 2014.

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

Sulbaek Andersen, M. P., Hurley, M. D., Wallington, T.J., Ball, J. C., Martin, J. W., Ellis, D.A., Mabury, S. A., and Nielsen, O. J.: Chem. Phys. Lett., 379, 28, 2003.



oFOx99: HO + *n*-C_3F_7CHO

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

$$HO + n\text{-}C_3F_7CHO \rightarrow n\text{-}C_3F_7CO + H_2O$$

Rate coefficient data

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

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 at 248 nm in the presence of C_3F_7CHO in 100 Torr (133 mbar) of helium diluent.

(b) Average of values given at 297 K

(c) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air in the presence of NO. C_2H_2 and C_2H_4 were used as reference compounds in separate experiments. The loss of C_3F_7CHO and the reference compounds were monitored using FTIR spectroscopy. Experiments were performed using CF_3CHO, C_3F_7CHO, and C_4F_9CHO. There was no discernable difference in reactivity of the three fluorinated aldehydes. An analysis of the combined data set gave rate coefficient ratios of $k(HO+ C_xF_{2x+1}CHO)/k(HO+C_2H_2) = 0.73 \pm 0.10$ and $k(HO+ C_xF_{2x+1}CHO)/k(HO+C_2H_4) = 0.0813 \pm 0.0095$. Scaling these ratios using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO+ C_xF_{2x+1}CHO) = (5.68 \pm 0.74) \times 10^{-13}$ and $(6.42 \pm 0.75) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	5.8×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$2.0 \times 10^{-12} \exp(-369/T)$	250-380
Reliability		
$\Delta \log k$	0.08	298
$\Delta E/R$	± 200	250-380

Comments on Preferred Values

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 $k(HO+C_3F_7CHO) = 2.0 \times 10^{-12} \exp(-369/T)$ from Solignac et al. (2007) is preferred and gives 5.8×10^{-13} cm^3 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 $C_3F_7C(O)$ radicals.

References

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

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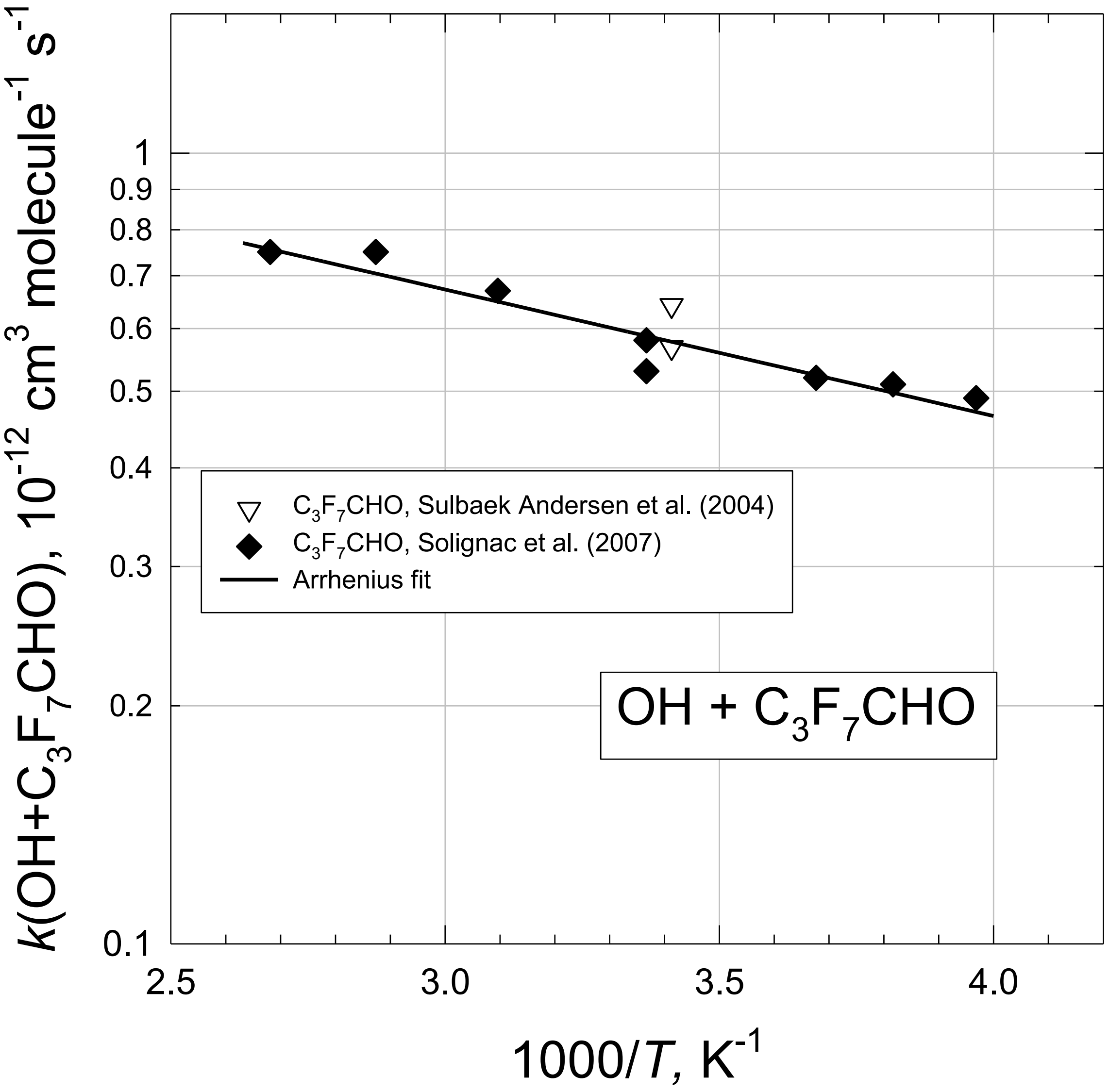


oFOx100: HO + *n*-C_4F_9CHO

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

$$HO + n\text{-}C_4F_9CHO \rightarrow n\text{-}C_4F_9CO + H_2O$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.5) \times 10^{-12} \exp[-(356 \pm 70)/T]$	253 – 373	Solignac et al. (2007)	PLP-LIF (a)
$(6.4 \pm 0.3) \times 10^{-13}$	299		
Relative Rate Coefficients			
$(5.68 \pm 0.74) \times 10^{-13}$	296	Sulbaek Andersen et al. (2004)	RR (b)
$(6.42 \pm 0.75) \times 10^{-13}$			

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 at 248 nm in the presence of C_4F_9CHO in 100 Torr (133 mbar) of helium diluent.

(b) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air in the presence of NO. In separate experiments C_2H_2 and C_2H_4 were used as reference compounds. The loss of C_4F_9CHO and the reference compounds were monitored using FTIR spectroscopy. Experiments were performed using CF_3CHO, C_3F_7CHO, and C_4F_9CHO. There was no discernable difference in reactivity of the three fluorinated aldehydes. An analysis of the combined data set gave rate coefficient ratios of $k(HO+ C_xF_{2x+1}CHO)/k(HO+C_2H_2) = 0.73 \pm 0.10$ and $k(HO+C_xF_{2x+1}CHO)/k(HO+C_2H_4) = 0.0813 \pm 0.0095$. Scaling these ratios using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO+C_xF_{2x+1}CHO) = (5.68 \pm 0.74) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $(6.42 \pm 0.75) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	6.1×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$2.0 \times 10^{-12} \exp(-356/T)$	250-380
Reliability		
$\Delta \log k$	0.08	298
$\Delta E/R$	± 150	250-380

Comments on Preferred Values

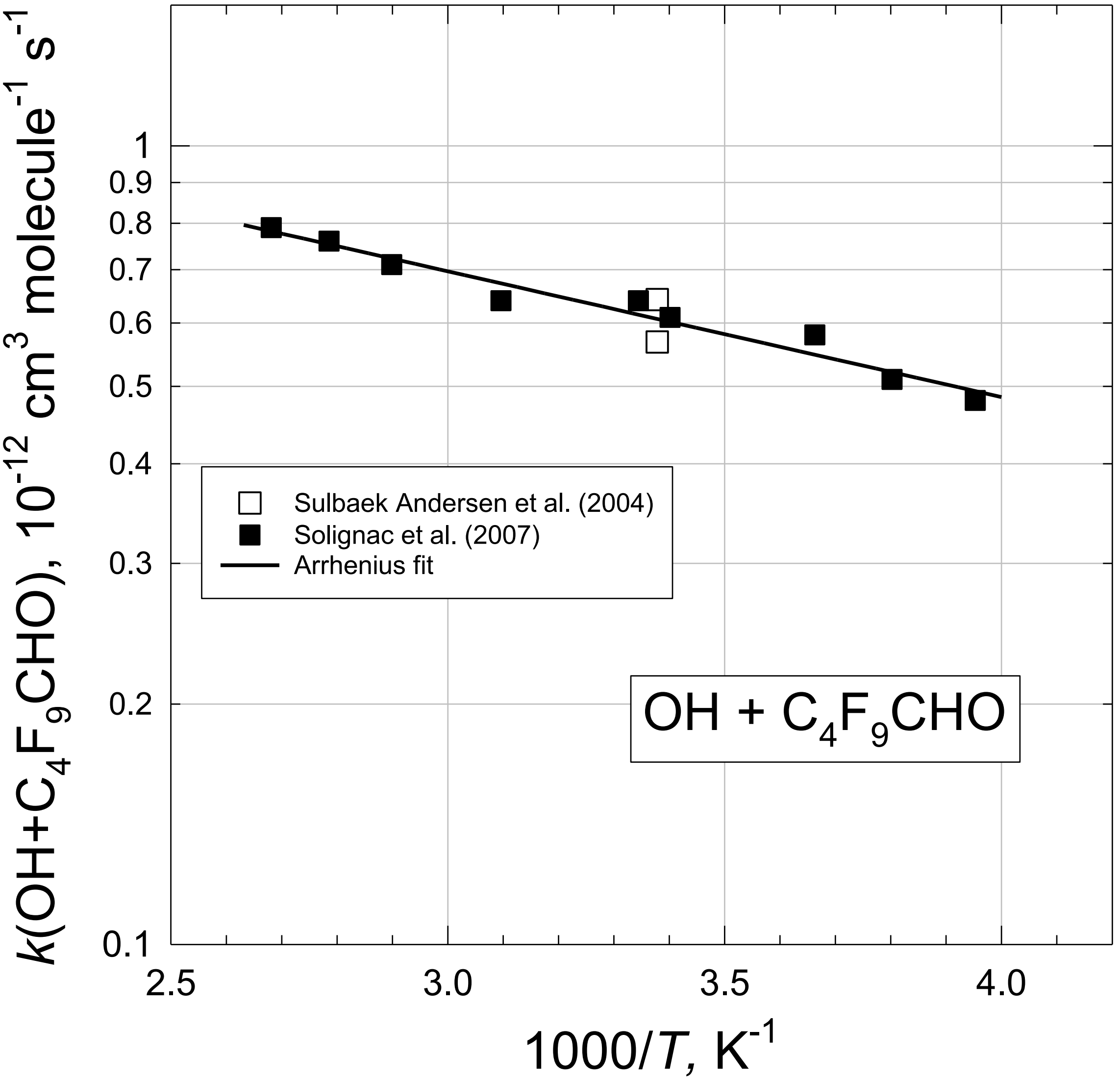
There is excellent agreement between the absolute rate data reported by Solignac et al. (2007) and the relative rate data reported by Sulbaek Andersen et al. (2004) at temperatures near 298 K. The Arrhenius expression $k(HO+C_4F_9CHO) = 2.0 \times 10^{-12} \exp(-365/T)$ from Solignac et al. (2007) is preferred and gives 6.1×10^{-13} cm^3 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 $C_4F_9C(O)$ radicals.

References

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

Solignac, G., Mellouki, A., Le Bras, G., Mu, Y., and Sidebottom, H.: Phys. Chem. Chem. Phys., 9, 4200, 2007.

Sulbaek Andersen, M. P., Nielsen, O. J., Hurley, M. D., Ball, J. C., Wallington, T. J., Stevens, J. E., Martin, J. W., Ellis, D. A., and Mabury, S. A.: J. Phys. Chem. A, 108, 5189, 2004.



oFOx101: HO + CF_3CH_2CHO

Last evaluated: June 2025; Last change in preferred values: June 2014.

$$HO + CF_3CH_2CHO \rightarrow CF_3CH_2CO + H_2O \quad (1)$$
$$\rightarrow CF_3CHCHO + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.96 \pm 0.04) \times 10^{-12}$	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		
Relative Rate Coefficients			
$(3.87 \pm 0.16) \times 10^{-12}$	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)
$(2.65 \pm 0.36) \times 10^{-12}$			

Comments

(a) HO radicals were generated by the 248 nm photolysis of H_2O_2 in 100 Torr (133 mbar) of helium diluent at 298 K.

(b) HO radicals were generated by the 248 nm photolysis of H_2O_2 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 O_3 at $\lambda \approx 310$ nm in the presence of H_2O vapor. The loss of CF_3CH_2CHO was monitored relative to C_2H_5OH and $HC(O)OC_2H_5$ in separate experiments using FTIR spectroscopy and rate coefficient ratios of $k(HO+CF_3CH_2CHO)/k(HO+C_2H_5OH) = 1.21 \pm 0.05$ and $k(HO+CF_3CH_2CHO)/k(HO+HC(O)OC_2H_5) = 3.51 \pm 0.09$ were reported. Scaling these ratios using $k(HO+C_2H_5OH) = 3.2 \times 10^{-12}$ (Atkinson et al., 2006) and $k(HO+HC(O)OC_2H_5) = 8.74 \times 10^{-13}$ (Calvert et al., 2011) gives $k(HO+CF_3CH_2CHO) = (3.87 \pm 0.16) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $(3.07 \pm 0.08) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(d) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr (933 mbar) of air in the presence of NO. C_2H_2 and C_2H_4 were used as reference compounds in separate experiments. The loss of CF_3CH_2CHO and the reference compounds were monitored using FTIR spectroscopy. Rate coefficient ratios of $k(HO+CF_3CH_2CHO)/k(HO+C_2H_2) = 3.18 \pm 0.35$ and $k(HO+CF_3CH_2CHO)/k(HO+C_2H_4) = 0.336 \pm 0.045$. Scaling these ratios using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO+CF_3CH_2CHO) = (2.48 \pm 0.27) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $(2.65 \pm 0.36) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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 $CF_3CH_2C(O)$ radicals.

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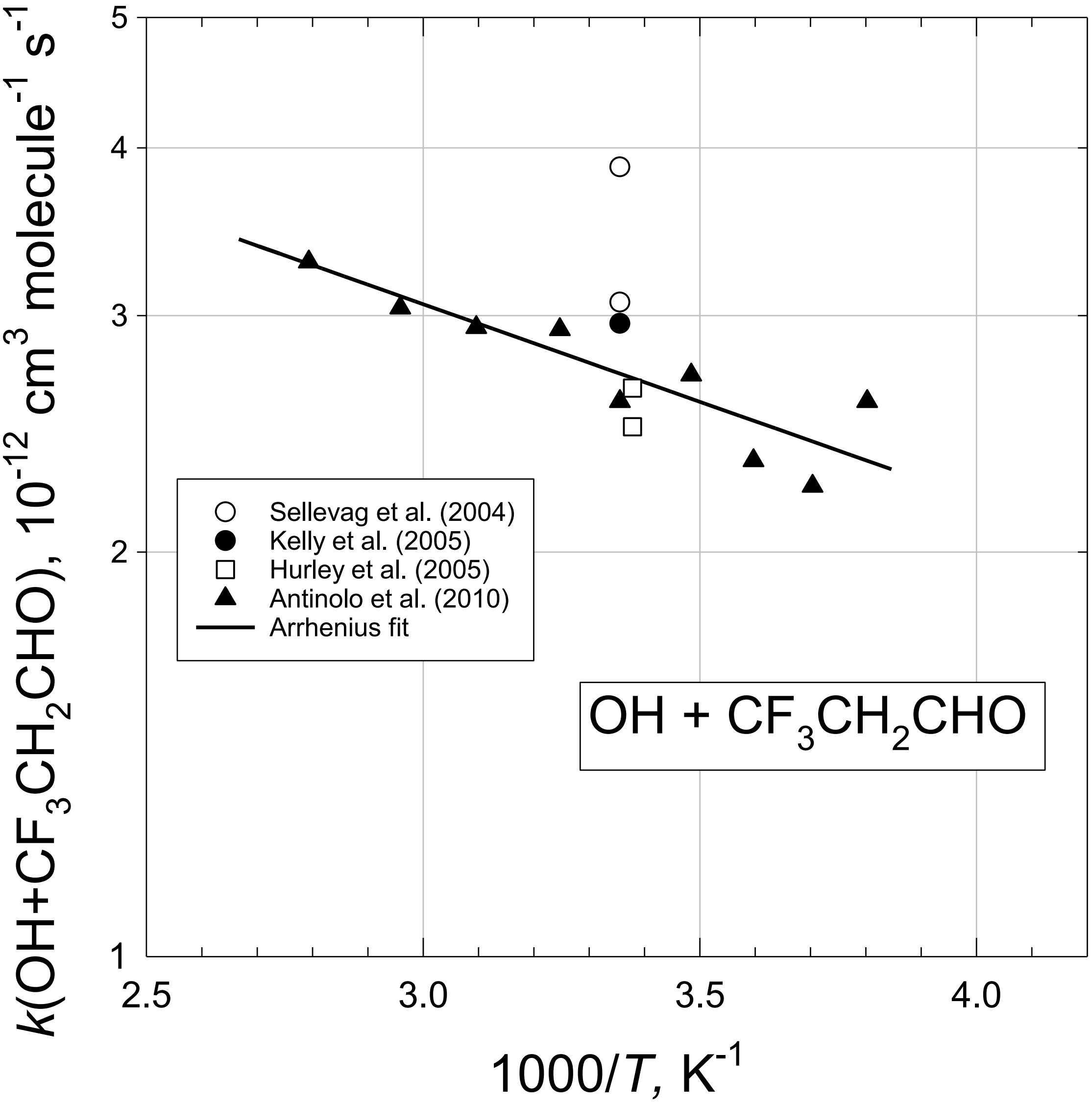

k(OH+CF$_3$CH$_2$CHO), 10^{-12} cm^3 molecule^{-1} s^{-1}
5
4
3
2
1
2.5
3.0
3.5
4.0
1000/T, K^{-1}
○ Sellevag et al. (2004)
● Kelly et al. (2005)
□ Hurley et al. (2005)
▲ Antinolo et al. (2010)
Arrhenius fit
OH + CF$_3$CH$_2$CHO

oFOx102: HO + n-$C_6F_{13}CH_2CHO$

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

$$HO + n\text{-}C_6F_{13}CH_2CHO \rightarrow n\text{-}C_6F_{13}CH_2CO + H_2O \qquad (1)$$

$$\rightarrow n\text{-}C_6F_{13}CHCHO + H_2O \qquad (2)$$

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

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in n-$C_6F_{13}CH_2CHO/C_2H_4/CH_3ONO$ mixtures in 700 Torr (933 mbar) of air diluent. The loss of $C_6F_{13}CH_2CHO$ and C_2H_4 were monitored using FTIR spectroscopy and a rate coefficient ratio of $k(HO+C_6F_{13}CH_2CHO)/k(HO+C_2H_4) = 0.25 \pm 0.03$ was obtained. Using $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+C_6F_{13}CH_2CHO) = (1.98 \pm 0.24) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Chiappero et al. (2010). The reaction is expected to proceed predominantly via abstraction of the aldehydic hydrogen giving $C_6F_{13}CH_2C(O)$ radicals.

References

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

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

oFOx103: HO + n-$C_8F_{17}CH_2CHO$

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

$$HO + n\text{-}C_8F_{17}CH_2CHO \rightarrow n\text{-}C_8F_{17}CH_2CO + H_2O \quad (1)$$
$$\rightarrow n\text{-}C_8F_{17}CHCHO + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in n-$C_8F_{17}CH_2CHO/C_2H_4/CH_3ONO$ mixtures in 700 Torr (933 mbar) of air diluent. The loss of $C_8F_{17}CH_2CHO$ and C_2H_4 were monitored using FTIR spectroscopy and a rate coefficient ratio of $k(HO+C_8F_{17}CH_2CHO)/k(HO+C_2H_4) = 0.23 \pm 0.04$ was obtained. Using $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+C_8F_{17}CH_2CHO) = (1.82 \pm 0.32) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Chiappero et al. (2008). The reaction is expected to proceed predominantly via abstraction of the aldehydic hydrogen giving $C_8F_{17}CH_2C(O)$ radicals.

References

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

Chiappero, M. S., Argüello, G. A., Hurley, M. D., and Wallington, T. J.: Chem. Phys. Lett., 461, 198, 2008.

oFOx104: HO + $C_2F_5C(O)CF(CF_3)_2$

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

HO + $C_2F_5C(O)CF(CF_3)_2$ → products **(1)**

Rate coefficient data ($k = k_1$)

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

Comments

(a) HO radicals were generated by photolysis of ozone at 254 nm in the presence of water vapor in 200 Torr (266 mbar) of helium diluent. The loss of $C_2F_5C(O)CF(CF_3)_2$ was measured relative to CH_4 and CH_3Cl. Following the generation of OH radicals in the system, CH_4 and CH_3Cl were observed to decay, but there was no discernible loss (<2%) of $C_2F_5C(O)CF(CF_3)_2$ (over and above that ascribed to photolysis). Using $k(HO+CH_4) = 6.4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) an upper limit of $k(HO+C_2F_5C(O)CF(CF_3)_2) < 5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} was derived.

Preferred Values

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

Comments on Preferred Values

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

References

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

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

oClOx92: OH + $CH_2ClC(O)CH_3$

Last evaluated: June 2025; Last change in preferred values: June 2010

$$OH + CH_2ClC(O)CH_3 \rightarrow CHClC(O)CH_3 + H_2O \quad (1)$$
$$\rightarrow CH_2ClC(O)CH_2 + H_2O \quad (2)$$

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

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

Comments

(a) OH radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2O vapour in 1 bar of O_2 diluent. CH_2ClCH_2Cl was used as the reference compound. Chemical analysis was achieved using FTIR spectroscopy and GC techniques and a rate coefficient ratio of $k(HO+CH_2ClC(O)CH_3)/k(HO+CH_2ClCH_2Cl) = 1.81 \pm 0.12$ was obtained. Using $k(HO+CH_2ClCH_2Cl) = 2.42 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2008) gives $k(HO+CH_2ClC(O)CH_3) = (4.38 \pm 0.29) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the study by Carr et al. (2003). The chlorine atom initiated oxidation of $CH_2ClC(O)CH_3$ was studied by Carr et al. (2003) in one atmosphere of O_2 and the formation of CO, CO_2, and HC(O)Cl 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 $CH_2ClC(O)CH_3$ 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, CO_2, and HC(O)Cl is probably the major atmospheric fate of $CH_2ClC(O)CH_3$.

References

Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington T. J.: Mechanisms of Atmospheric Oxidation of the Alkanes, Oxford University Press, New York, NY, 2008.

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Carr, S., Shallcross, D.E., Canosa-Mas, C.E., Wenger, J.C., Sidebottom, H.W., Treacy, J.J., and Wayne, R.P.: Phys. Chem. Chem. Phys., 5, 3874, 2003.

oClOx93: HO + $CHCl_2C(O)CH_3$

Last evaluated: June 2025; Last change in preferred values: June 2010.

$$HO + CHCl_2C(O)CH_3 \rightarrow CCl_2C(O)CH_3 + H_2O \quad (1)$$
$$\rightarrow CHCl_2C(O)CH_2 + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2O vapour in 1 bar of O_2 diluent. CH_2ClCH_2Cl was used as the reference compound. Chemical analysis was achieved using FTIR spectroscopy and GC techniques and a rate coefficient ratio of $k(HO+CHCl_2C(O)CH_3)/k(HO+CH_2ClCH_2Cl) = 1.66 \pm 0.11$ was obtained. Using $k(HO+CH_2ClCH_2Cl) = 2.42 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2008) gives $k(HO+CHCl_2C(O)CH_3) = (4.02 \pm 0.27) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the study by Carr et al. (2003). The chlorine-atom initiated oxidation of $CHCl_2C(O)CH_3$ was studied by Carr et al. (2003) in one atmosphere of O_2 and the formation of CO, CO_2, and $COCl_2$ 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 $CHCl_2C(O)CH_3$ 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, CO_2, and $COCl_2$ is probably the major atmospheric fate of $CHCl_2C(O)CH_3$.

References

Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S., and Wallington T. J.: Mechanisms of Atmospheric Oxidation of the Alkanes, Oxford University Press, New York, NY, 2008.

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oClOx94: OH + $CCl_3C(O)CH_3$

Last evaluated: June 2025; Last change in preferred values: June 2010.

$$OH + CCl_3C(O)CH_3 \rightarrow CCl_3C(O)CH_2 + H_2O \qquad (1)$$

Rate coefficient data ($k = k_1$)

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

Comments

(a) OH radicals were generated by the photolysis of O_3 at 254 nm in the presence of H_2O vapour in 1 bar of O_2 diluent. CH_3CN was used as the reference compound. Chemical analysis was achieved using FTIR spectroscopy and GC techniques and a rate coefficient ratio of $k(HO+CCl_3C(O)CH_3)/k(HO+CH_3CN) = 0.70 \pm 0.07$ was obtained. Using $k(HO+CH_3CN) = 2.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives $k(HO+CCl_3C(O)CH_3) = (1.54 \pm 0.15) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the study by Carr et al. (2003). The chlorine-atom initiated oxidation of $CCl_3C(O)CH_3$ was studied by Carr et al. (2003) in one atmosphere of O_2 and the formation of CO, CO_2, and $COCl_2$ 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 $CCl_3C(O)CH_3$ and the precise mechanism by which these products form is not clear. As discussed by Calvert et al. (2010), photolysis leading to the formation of CO, CO_2, and $COCl_2$ is probably the major atmospheric fate of $CCl_3C(O)CH_3$.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

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, 2011.

Carr, S., Shallcross, D. E., Canosa-Mas, C. E., Wenger, J. C., Sidebottom, H.W., Treacy, J. J., and Wayne, R. P.: Phys. Chem. Chem. Phys., 5, 3874, 2003.

oFOx105: HO + $C_2F_5C(O)OH$

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

$$HO + C_2F_5C(O)OH \rightarrow C_2F_5C(O)O + H_2O$$

Rate coefficient data

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in $C_2F_5C(O)OH/CH_3ONO/NO/(C_2H_2$ or $C_2H_4)$ mixtures in 700 Torr (933 mbar) of air. The loss of the reference compounds (C_2H_2 or C_2H_4) was monitored by FTIR spectroscopy. The loss of $C_2F_5C(O)OH$ was small and difficult to observe directly. The loss of $C_2F_5C(O)OH$ was calculated from the formation of COF_2 observed by FTIR spectroscopy with a molar yield assumed to be 193% (CF_3ONO_2 and $C_2F_5ONO_2$ are formed in small amounts). Experiments performed using $C_2F_5C(O)OH$, $C_3F_7C(O)OH$, and $C_4F_9C(O)OH$ gave indistinguishable values of the rate coefficient ratio $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+\text{reference})$. Analysis of the composite data set gave $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+C_2H_2) = 0.197 \pm 0.022$ and $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+C_2H_4) = 0.0198 \pm 0.0014$. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives the values of $k(HO+C_xF_{2x+1}CHO)$ listed in the table above.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the study by Hurley et al. (2004). The $C_2F_5C(O)O$ radical decomposes rapidly to give CO_2 and a C_2F_5 radical. As discussed by Ellis et al. (2004), in the atmosphere the C_2F_5 radical will be converted mainly into COF_2 with $CF_3C(O)OH$ formed as a minor product following reaction of $C_2F_5O_2$ radicals with CH_3O_2 radicals. As might be expected from their similar molecular structure, the reactivity of $C_2F_5C(O)OH$, $C_3F_7C(O)OH$, and $C_4F_9C(O)OH$ towards HO radicals are indistinguishable.

References

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

Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., and Wallington, T. J.: Environ. Sci. Tech., 38, 3316, 2004.

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

oFOx106: HO + *n*-$C_3F_7C(O)OH$

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

$$\mathbf{HO + \textit{n}\text{-}C_3F_7C(O)OH \rightarrow \textit{n}\text{-}C_3F_7C(O)O + H_2O}$$

Rate coefficient data

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in $C_3F_7C(O)OH/CH_3ONO/NO/(C_2H_2$ or $C_2H_4)$ mixtures in 700 Torr (933 mbar) of air. The loss of the reference compounds C_2H_2 or C_2H_4 was monitored by FTIR spectroscopy. The loss of $C_3F_7C(O)OH$ was small and difficult to observe directly. The loss of $C_3F_7C(O)OH$ was calculated from the formation of COF_2 observed by FTIR spectroscopy with a molar yield assumed to be 290% (CF_3ONO_2, $C_2F_5ONO_2$, and $C_3F_7ONO_2$ are formed in small amounts). Experiments performed using $C_2F_5C(O)OH$, $C_3F_7C(O)OH$, and $C_4F_9C(O)OH$ gave indistinguishable values of the rate coefficient ratio $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+reference)$. Analysis of the composite data set gave $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+C_2H_2) = 0.197 \pm 0.022$ and $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+C_2H_4) = 0.0198 \pm 0.0014$. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives the values of $k(HO+ C_xF_{2x+1}CHO)$ listed in the table above.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the study by Hurley et al. (2004). The $C_3F_7C(O)O$ radical decomposes rapidly to give CO_2 and a C_3F_7 radical. As discussed by Ellis et al. (2004), the C_3F_7 radical will be converted mainly into COF_2 with $CF_3C(O)OH$ and $C_2F_5C(O)OH$ formed as minor products following reactions of $C_2F_5O_2$ and $C_3F_7O_2$ radicals with CH_3O_2 radicals. As might be expected from their similar molecular structure, the reactivity of $C_2F_5C(O)OH$, $C_3F_7C(O)OH$, and $C_4F_9C(O)OH$ towards HO radicals are indistinguishable.

References

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

Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., and Wallington, T. J.: Environ. Sci. Tech., 38, 3316, 2004.

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

oFOx107: HO + *n*-$C_4F_9C(O)OH$

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

$$HO + n\text{-}C_4F_9C(O)OH \rightarrow n\text{-}C_4F_9C(O)O + H_2O$$

Rate coefficient data

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

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in $C_4F_9C(O)OH/CH_3ONO/NO/(C_2H_2$ or $C_2H_4)$ mixtures in 700 Torr (933 mbar) of air. The loss of the reference compounds C_2H_2 or C_2H_4 was monitored by FTIR spectroscopy. The loss of $C_4F_9C(O)OH$ was small and difficult to observe directly. The loss of $C_4F_9C(O)OH$ was calculated from the formation of COF_2 observed by FTIR spectroscopy. with a molar yield assumed to be 384% (nitrates are formed in small amounts). Experiments performed using $C_2F_5C(O)OH$, $C_3F_7C(O)OH$, and $C_4F_9C(O)OH$ gave indistinguishable values of the rate coefficient ratio $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+\text{reference})$. Analysis of the composite data set gave $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+C_2H_2) = 0.197 \pm 0.022$ and $k(HO+C_xF_{2x+1}C(O)OH)/k(HO+C_2H_4) = 0.0198 \pm 0.0014$. Using $k(HO+C_2H_2) = 7.8 \times 10^{-13}$ and $k(HO+C_2H_4) = 7.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006) gives the values of $k(HO+C_xF_{2x+1}CHO)$ listed in the table above.

Preferred Values

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

Comments on Preferred Values

The preferred value is based on the study by Hurley et al. (2004). The $C_4F_9C(O)O$ radical decomposes rapidly to give CO_2 and a C_4F_9 radical. As discussed by Ellis et al. (2005), the C_4F_9 radical will be converted mainly into COF_2 with $CF_3C(O)OH$, $C_2F_5C(O)OH$, and $C_3F_7C(O)OH$ formed as minor products from reactions involving CH_3O_2 radicals. As might be expected from their similar molecular structure, $C_4F_9C(O)OH$ has a reactivity towards HO radicals which is indistinguishable from those of $C_2F_5C(O)OH$ and $C_3F_7C(O)OH$.

References

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

Ellis, D. A., Martin, J. W., De Silva, A. O., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., and Wallington, T. J.: Environ. Sci. Tech., 38, 3316, 2004.

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

oFOx137: HO + CH_3OCHF_2

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

$$\mathbf{HO + CH_3OCHF_2 \rightarrow CH_2OCHF_2 + H_2O \qquad (1)}$$
$$\mathbf{\rightarrow CH_3OCF_2 + H_2O \qquad (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.16 \pm 0.42) \times 10^{-11} \exp[(-1728\pm133)/T]$	298-460	Orkin et al. (2014)	DF-EPR (a)
$(3.54 \pm 0.65) \times 10^{-14}$	298		

Comments

(a) HO radicals were generated by the reaction of H atoms with NO_2 in 2.5 Torr of helium diluent.

Preferred Values

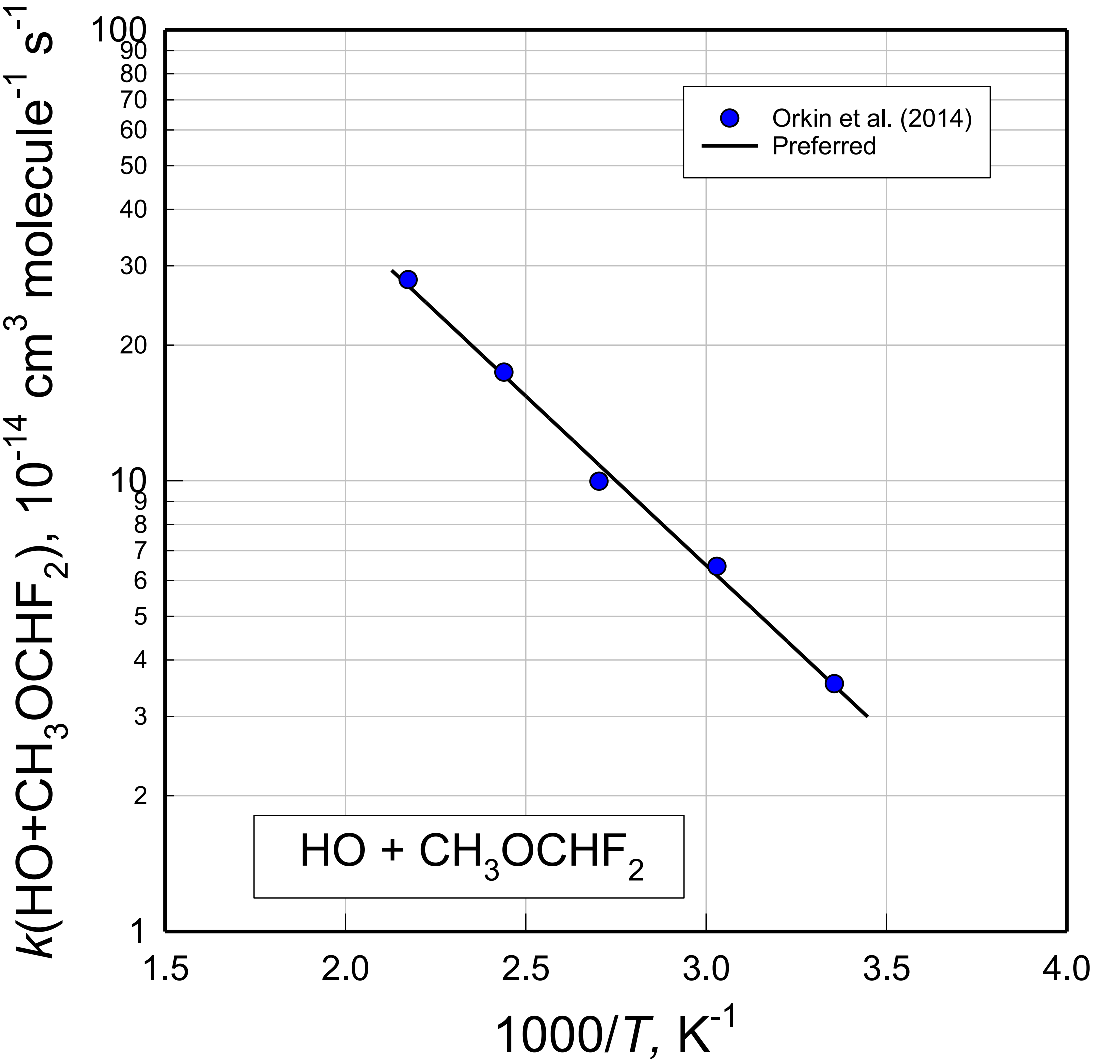
Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	3.52×10^{-14}	298
	$1.16 \times 10^{-11} \exp(-1728/T)$	290-470
Reliability		
$\Delta \log k$	0.15	298
$\Delta E/R$	±100	290-470

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.


Orkin et al. (2014)
Preferred
HO + CH_3OCHF_2
$k(HO+CH_3OCHF_2)$, 10^{-14} cm^3 $molecule^{-1}$ s^{-1}
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
1.5
2.0
2.5
3.0
3.5
4.0
1000/T, K^{-1}

oFOx138: HO + CH_3OCF_3

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

$$\mathbf{HO + CH_3OCF_3 \rightarrow CH_2OCF_3 + H_2O}$$

Rate coefficient data

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

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 reaction of H atoms with NO_2 in 2.5 Torr of helium diluent.

(c) HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. Experiments were conducted in which the loss of CF_3OCH_3 was measured relative to either CH_3CHF_2 or CHF_2Cl. The concentrations of CF_3OCH_3, CH_3CHF_2, and CH_2F_2 were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(HO + CF_3OCH_3)/k(HO + CH_3CHF_2) = (0.65 \pm 0.08) \exp[(190 \pm 43)/T]$ and $k(HO + CF_3OCH_3)/k(HO + CH_2F_2) = (1.55 \pm 0.10) \exp[(136 \pm 43)/T]$ are placed on an absolute basis using $k(HO + CH_3CHF_2) = 1.25 \times 10^{-12} \exp(-1070/T)$ and $k(HO + CH_2F_2) = 2.3 \times 10^{-12} \exp(-1590/T)$ (Atkinson et al., 2008) to give $k(HO + CF_3OCH_3) = (8.1 \pm 1.0) \times 10^{-13} \exp[(-880 \pm 43)/T]$ and $(3.6 \pm 1.0) \times 10^{-12} \exp[-(1454 \pm 43)/T]$ cm^3 molecule^{-1} s^{-1}. A fit to the combined data set (scaled using reference rate coefficients from Atkinson et al. 2008) gives $k(HO + CF_3OCH_3) = 1.18 \times 10^{-12} \exp(-1381/T)$ cm^3 molecule^{-1} s^{-1}.

(d) HO radicals were generated by the photolysis of ozone in the presence of water vapor in 100 Torr of helium diluent. Separate experiments were performed in which the loss CF_3OCH_3 was measured relative to either CH_4 or CH_3CCl_3. Placing the reported rate coefficient ratios on an absolute basis using $k(HO+CH_4) = 1.85 \times 10^{-12} \exp(-1690/T)$ and $k(HO + CH_3CCl_3) = 1.2 \times 10^{-12} \exp(-1440/T)$ (Atkinson et al., 2008) and fitting an Arrhenius expression to the results gives $k(HO+CH_3OCF_3) = (3.6 \pm 1.0) \times 10^{-12} \exp[(1454 \pm 43)/T]$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

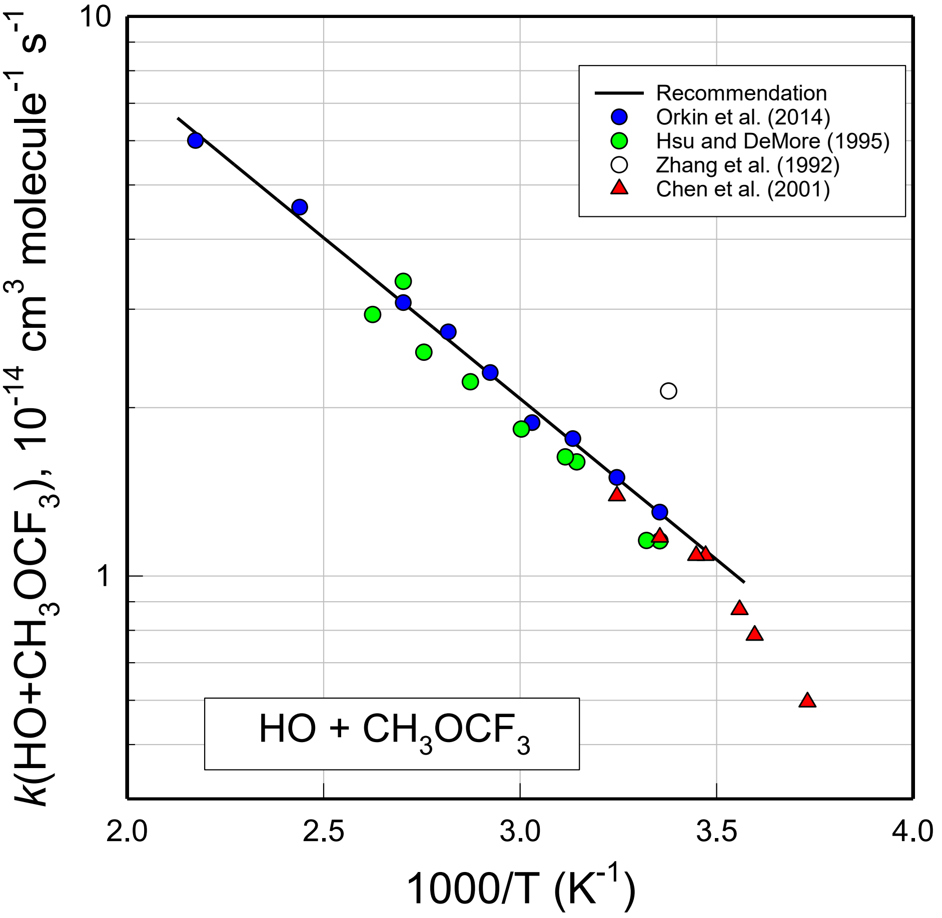
Δ E/R	±100	290-470

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

Chen, L., Kutsuna, S., Nohara, K., Takeuchi, K., and Ibusuki, T.: J. Phys. Chem. A: 105, 10854, 2001.
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.



oFOx139: HO + CHF_2OCHF_2

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

$$HO + CHF_2OCHF_2 \rightarrow CHF_2OCF_2 + H_2O$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.53 \pm 0.24) \times 10^{-14}$	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		
Relative Rate Coefficients			
$1.26 \times 10^{-12} \exp[(-1896)/T]$	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		

Comments

(a) HO radicals were generated by the photolysis of water vapor in 35 Torr (47 mbar) of argon and monitored by resonance fluorescence. Two sets of experiments were performed using different threshold voltages (3.3 kV or 4.6 kV) for the Xe flash lamp giving the values in the table.

(b) HO radicals were generated by the 248 nm photolysis of HNO_3 water vapor in 20 Torr (27 mbar) of argon or helium diluent and monitored by LIF.

(c) HO radicals were generated by the photolysis of water vapor in 100 Torr (133 mbar) of argon diluent.

(d) HO radicals were generated by the UV photolysis of O_3 in the presence of water vapor. FTIR spectroscopy was used to follow the loss of CHF_2OCHF_2 measured relative to CH_3CCl_3. The measured rate coefficient ratio of $k(HO + CHF_2OCHF_2)/k(HO + CH_3CCl_3) = (1.05 \pm 0.20) \exp[(-456 \pm 62)/T]$ is placed on an absolute basis using $k(HO + CH_3CCl_3) = 1.2 \times 10^{-12} \exp(-1440/T)$ (Atkinson et al., 2008) to give $k(HO + CHF_2OCHF_2) = 1.26 \times 10^{-12} \exp[(-1896)/T]$ cm^3 molecule^{-1} s^{-1}.

(e) HO radicals were generated by the photolysis of water vapor in helium diluent and the loss of CHF_2OCHF_2 was measured relative to that of CF_3CF_2H by GC-MS. Placing the reported rate coefficient ratios on an absolute basis using $k(HO + CF_3CF_2H) = 4.40 \times 10^{-13} \exp(-1630/T)$ (Atkinson et al., 2008) and fitting an Arrhenius expression to the results gives $k(HO + CHF_2OCHF_2) = (3.6 \pm 1.0) \times 10^{-12} \exp[(1454 \pm 43)/T]$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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

References

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Hsu, K.-J., and DeMore, W. B.: J. Phys. Chem., 99, 11141, 1995.
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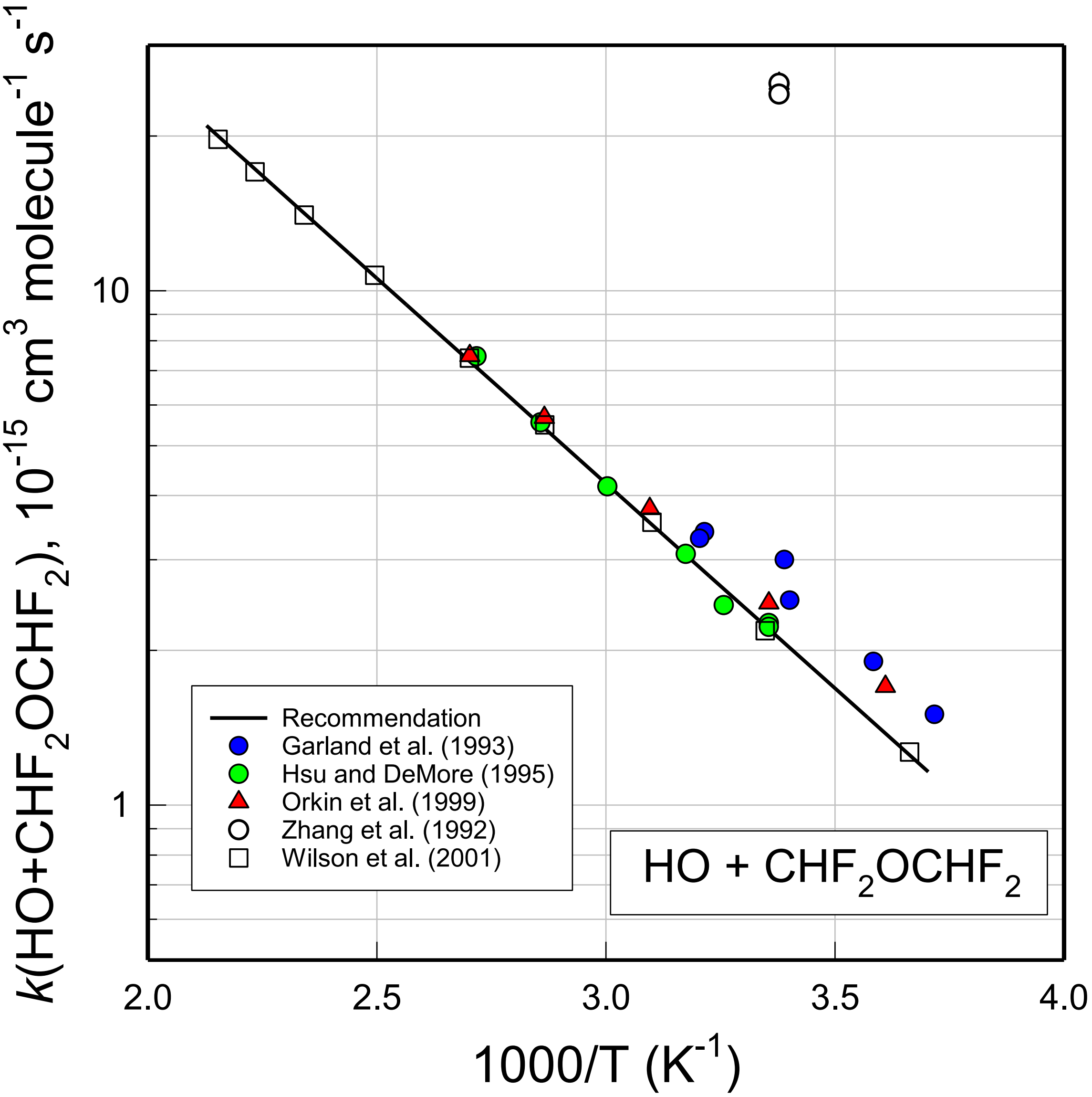
Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E.: J. Phys. Chem.: 96, 9301, 1992.


HO + CHF$_2$OCHF$_2$
Recommendation
Garland et al. (1993)
Hsu and DeMore (1995)
Orkin et al. (1999)
Zhang et al. (1992)
Wilson et al. (2001)
k(HO+CHF$_2$OCHF$_2$), 10^{-15} cm^3 molecule^{-1} s^{-1}
1000/T (K^{-1})
10
1
2.0
2.5
3.0
3.5
4.0

oFOx140: HO + CHF_2OCF_3

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

$$HO + CHF_2OCF_3 \rightarrow CF_2OCF_3 + H_2O$$

Rate coefficient data

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

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 UV photolysis of O_3 in the presence of water vapor. FTIR spectroscopy was used to follow the loss of CHF_2OCF_3 and the reference compounds CF_3H, CH_4, and CHF_2CF_3. Placing the measured rate coefficient ratios on an absolute basis using $k(HO + CF_3H) = 6.90 \times 10^{-13} \exp(-2340/T)$, $k(HO + CH_4) = 1.85 \times 10^{-12} \exp(-1690/T)$, and $k(HO + CHF_2CF_3H) = 4.40 \times 10^{-13} \exp(-1630/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006, 2008) and fitting an Arrhenius expression to the results gives $k(HO + CHF_2OCF_3) = 3.09 \times 10^{-13} \exp[(-1942)/T]$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	4.57×10^{-16}	298
	$3.09 \times 10^{-13} \exp(-1942/T)$	290-400
Reliability		
$\Delta \log k$	0.10	298
Δ E/R	±100	290-400

Comments on Preferred Values

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

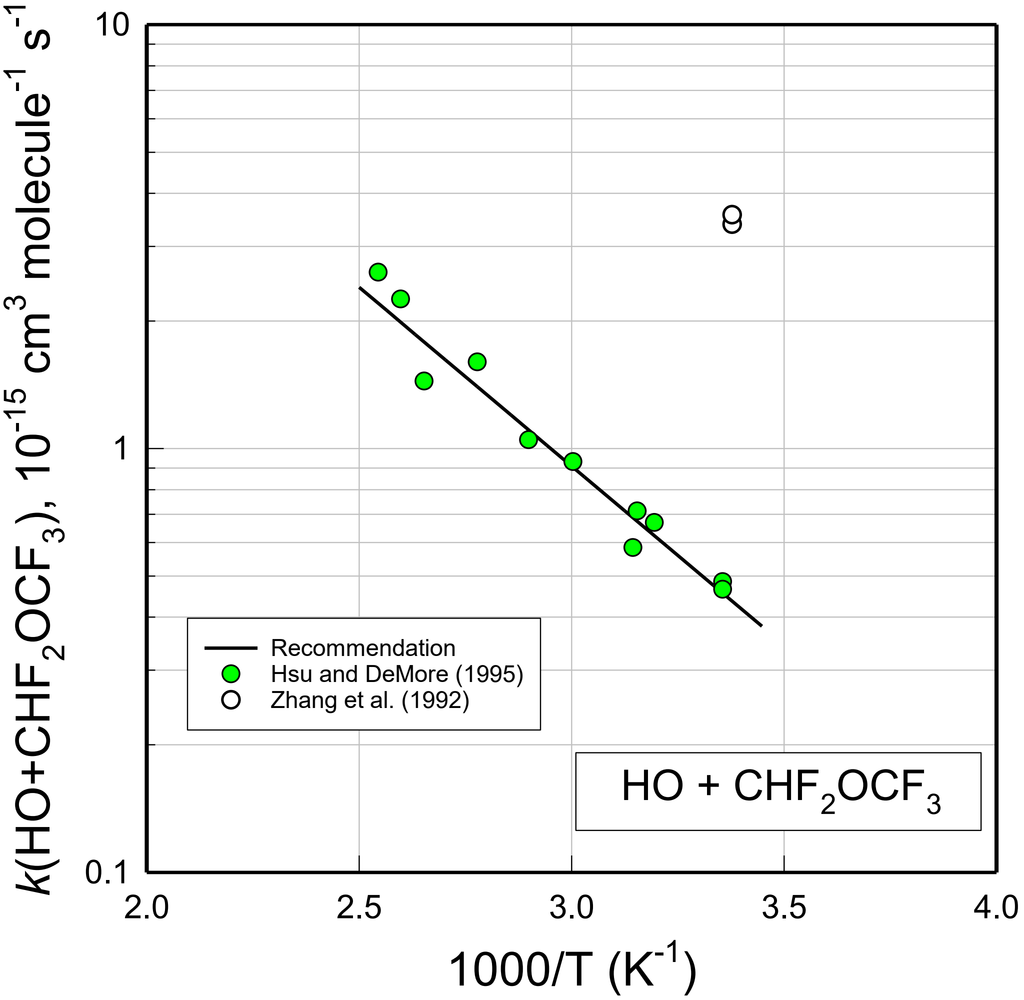
References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

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; IUPAC Subcommittee for Gas Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Hsu, K.-J. and DeMore, W. B.: J. Phys. Chem., 99, 11141, 1995.

Zhang, Z., Saini, R. D., Kurylo, M. J., and Huie, R. E.: J. Phys. Chem., 96, 9301, 1992.



oFOx141: $HO + CH_3OCHFCF_3$

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

$$HO + CH_3OCHFCF_3 \rightarrow CH_2OCHFCF_3 + H_2O \quad (1)$$
$$\rightarrow CH_3OCFCF_3 + H_2O \quad (2)$$

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

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

Comments

(a) HO radicals were generated by the photolysis of ozone in the presence of water vapor in 200 Torr of helium diluent. Separate experiments were performed in which the loss $CH_3OCHFCF_3$ was measured relative to either C_2H_6 or CH_3CHF_2. Placing the reported rate coefficient ratios on an absolute basis using $k(HO + C_2H_6) = 6.9 \times 10^{-12} \exp(-1000/T)$ and $k(HO + CH_3CHF_2) = 1.25 \times 10^{-12} \exp(-1070/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al. 2006, 2008) and fitting an Arrhenius expression to the results gives $k(HO + CH_3OCHFCF_3) = 1.74 \times 10^{-12} \exp[(-716)/T]$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

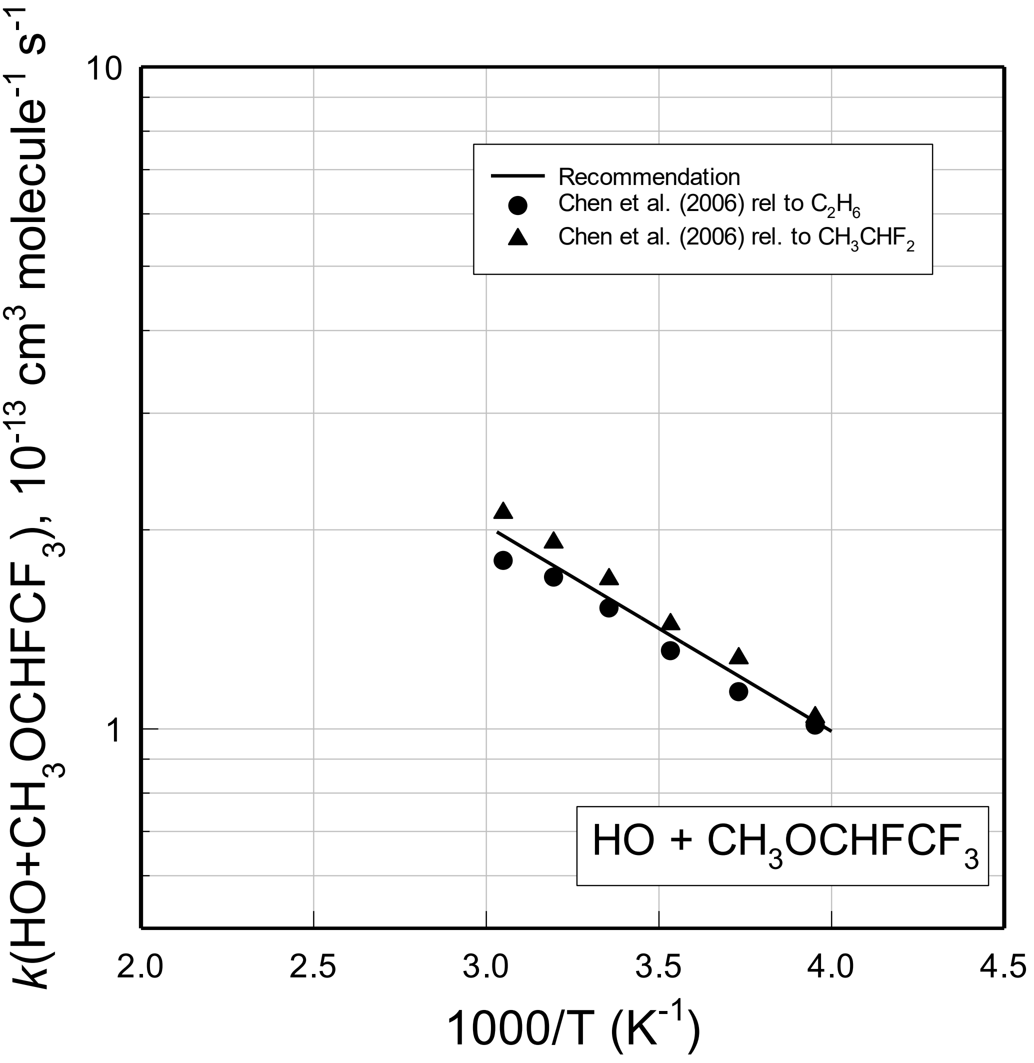
The preferred value is based on a fit to the results from the relative rate study of Chen et al. (2006).

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

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; IUPAC Subcommittee for Gas Kinetic Data Evaluation, https://iupac.aeris-data.fr/.

Chen, L., Kutsuna, S., Tokuhashi, K., and Sekiya, A.: J. Phys. Chem., 110, 12845, 2006.


10
1
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K^{-1})
k(HO+CH$_3$OCHFCF$_3$), 10^{-13} cm^3 molecule^{-1} s^{-1}
Recommendation
Chen et al. (2006) rel to C$_2$H$_6$
Chen et al. (2006) rel. to CH$_3$CHF$_2$
HO + CH$_3$OCHFCF$_3$

4894
4895

oFOx142: HO + $CH_3OCF_2CHF_2$

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

$$HO + CH_3OCF_2CHF_2 \rightarrow CH_2OCF_2CHF_2 + H_2O \quad (1)$$
$$\rightarrow CH_3OCF_2CF_2 + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.63 \pm 0.32) \times 10^{-13}$	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		

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 N_2O to produce $O(^1D)$ atoms in the presence of H_2O 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, $\lambda < 180$ nm) of H_2O 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 NO_2 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 /cm^3 molecule^{-1} s^{-1}	2.24×10^{-14}	298
	$2.50 \times 10^{-12} \exp(-1405/T)$	240-440
Reliability		
$\Delta \log k$	0.10	298
Δ E/R	±100	240-440

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.

References

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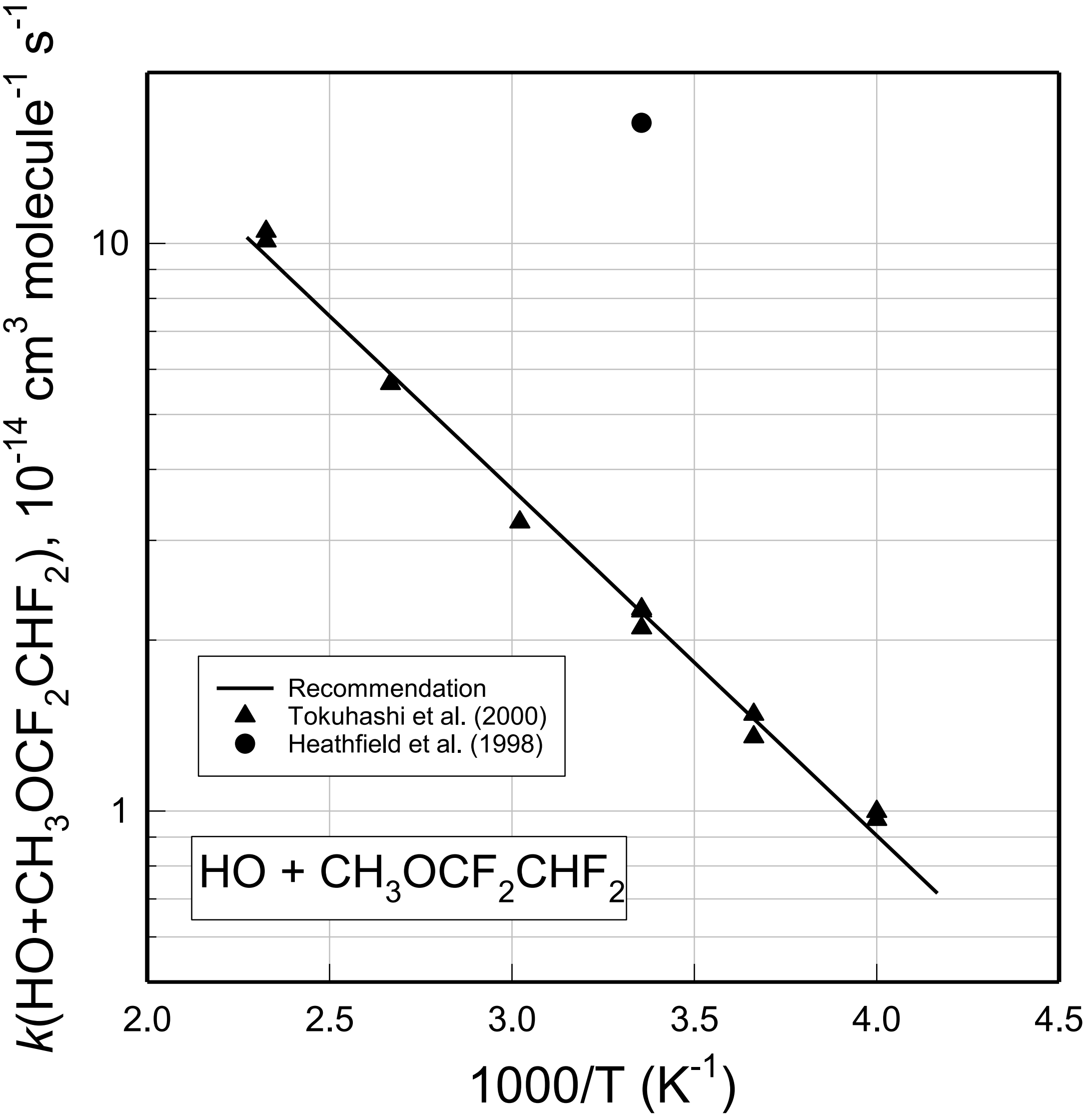

oFOx143: HO + $CH_3OCH_2CF_3$

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

$$HO + CH_3OCH_2CF_3 \rightarrow CH_2OCH_2CF_3 + H_2O \ (1)$$
$$\rightarrow CH_3OCHCF_3 + H_2O \ (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.24 \pm 0.67) \times 10^{-13}$	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)
$(6.88\pm0.21) \times 10^{-13}$	298		
Relative Rate Coefficients			
$(6.4\pm0.5) \times 10^{-13}$	298	Nolan et al. (1999)	RR (c)
$(6.24\pm0.33) \times 10^{-13}$	298	Oyaro et al. (2005)	RR (d)
$(5.17\pm0.54) \times 10^{-13}$			
$(4.71\pm0.37) \times 10^{-13}$	296	Østerstrøm et al. (2011)	RR (e)
$(4.16\pm0.39) \times 10^{-13}$			

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 H_2O_2 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 O_3 at 254 nm in the presence of H_2 in 1013 mbar of air diluent. The loss of $CH_3OCH_2CF_3$ was monitored relative to those of $CHCl_3$ and $CH_3C(O)OCH_3$ by GC/MS. Rate coefficient ratios of $k(HO + CH_3OCH_2CF_3)/k(HO + CHCl_3) = 5.94 \pm 0.31$ and $k(HO + CH_3OCH_2CF_3)/k(HO + CH_3C(O)OCH_3) = 2.87 \pm 0.305$ were reported. Using $k(HO + CHCl_3) = 1.05 \times 10^{-13}$ and $k(HO + CH_3C(O)OCH_3) == 1.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson et al., 2006, 2008) gives $k(HO + CH_3OCH_2CF_3) = (6.24\pm0.33) \times 10^{-13}$ and $(5.17\pm0.54) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(e) HO radicals were generated by the photolysis of CH_3ONO in 700 Torr of air diluent in the presence of NO. The loss of $CH_3OCH_2CF_3$ was monitored indirectly by the formation of its oxidation product COF_2 and was measured relative to that of C_2H_2 and C_2H_4. Rate coefficient ratios of $k(HO + CH_3OCH_2CF_3)/k(HO + C_2H_2) = 0.63 \pm 0.05$ and $k(HO + CH_3OCH_2CF_3)/k(HO + C_2H_4) = 0.053 \pm 0.005$ were reported. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in 700 Torr of air at 296 K (Atkinson et al., 2006) gives $k(HO + CH_3OCH_2CF_3) = (4.71\pm0.37) \times 10^{-13}$ and $(4.16\pm0.39) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	6.56×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	3.61×10^{-12} exp(-508/T)	260-360
Reliability		
Δ log k	0.10	298
Δ E/R	300	260-360

Comments on Preferred Values

The absolute rate measurements by Zhang et al. (1992) and Blázquez et al. (2022) at 298 K are in excellent agreement. Taking an average of the results from these studies gives the recommended rate coefficient at 298 K. The temperature dependence is taken from Blázquez et al. (2022) and the preexponential factor is scaled to reproduce the recommended k(298K) value. The results from the relative rate studies by Nolan et al. (1999) and Oyaro et al. (2005) are in good agreement while those from Østerstøm et al. (2012) are approximately 30% lower. Østerstøm et al. (2012) measured the loss of $CH_3OCH_2CF_3$ indirectly by the formation of its oxidation product COF_2 and assuming a molar yield of 45% which was determined in separate experiments. Given the good agreement of the results from the relative rate studies of Nolan et al. (1999) and Oyaro et al. (2005) with the absolute rate studies by Zhang et al. (1992) and Blázquez et al. (2022), it appears there were problems associated with the indirect method of monitoring loss of $CH_3OCH_2CF_3$ used by Østerstøm et al. (2012).

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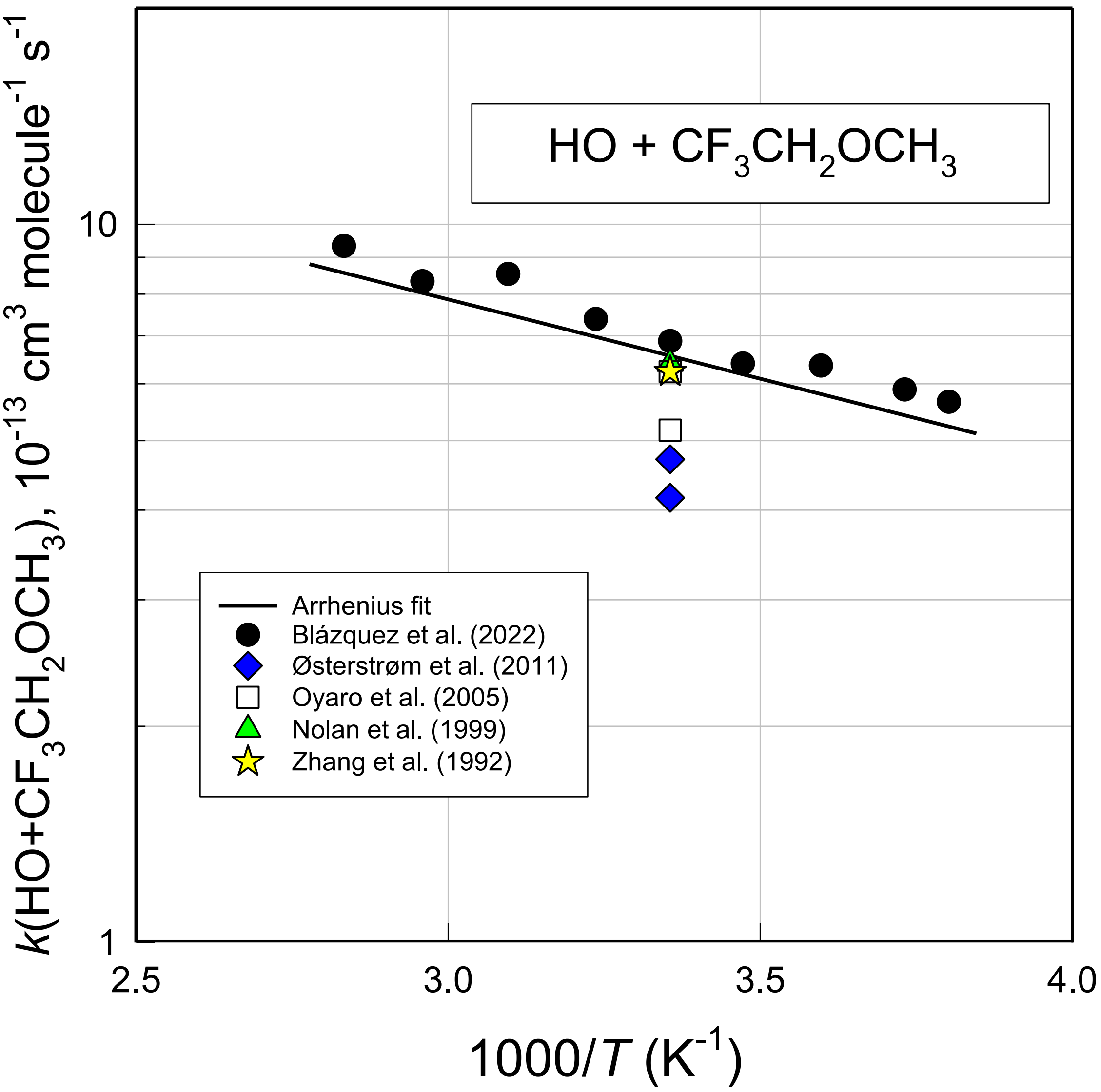
HO + $CF_3CH_2OCH_3$
$k(HO+CF_3CH_2OCH_3)$, 10^{-13} cm^3 $molecule^{-1}$ s^{-1}
10
1
2.5
3.0
3.5
4.0
1000/T (K^{-1})
Arrhenius fit
Blázquez et al. (2022)
Østerstrøm et al. (2011)
Oyaro et al. (2005)
Nolan et al. (1999)
Zhang et al. (1992)

oFOx144: HO + $CH_3OCF_2CF_3$

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

$HO + CH_3OCF_2CF_3 \rightarrow CH_2OCF_2CF_3 + H_2O$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.90^{+0.90}_{-0.61} \times 10^{-12}) \exp[(-1510\pm120)/T]$	250-430	Tokuhashi et al. (1999)	LP/FP/DF-LIF (a)
1.12×10^{-14}	298		
Relative Rate Coefficients			
$(1.12\pm0.15) \times 10^{-14}$	296	Østerstrøm et al. (2016)	RR (b)

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 photolysis (ArF laser) of N_2O to produce $O(^1D)$ atoms in the presence of H_2O 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, $\lambda < 180$ nm) of H_2O in 10-40 Torr (13-53 mbar) argon diluent. HO radicals in the DF-LIF experiments were generated by the reaction of H atoms with NO_2 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.

(b) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of $CH_3OC_2F_5$ was measured indirectly by measuring the formation of the product C_2F_5OCHO. C_2H_2 was used as the reference and a rate coefficient ratio $k(CH_3OC_2F_5)/k(C_2H_2) = 0.015\pm0.002$ was reported. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ (Atkinson et al., 2006) gives $k(HO + CH_3OC_2F_5) = (1.12\pm0.15) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.20×10^{-14}	298
	$1.84 \times 10^{-12} \exp(-1499/T)$	240-440
Reliability		
$\Delta \log k$	0.10	298
$\Delta E/R$	±100	240-440

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 reported in the relative rate study by Østerstrøm are consistent with the preferred values.

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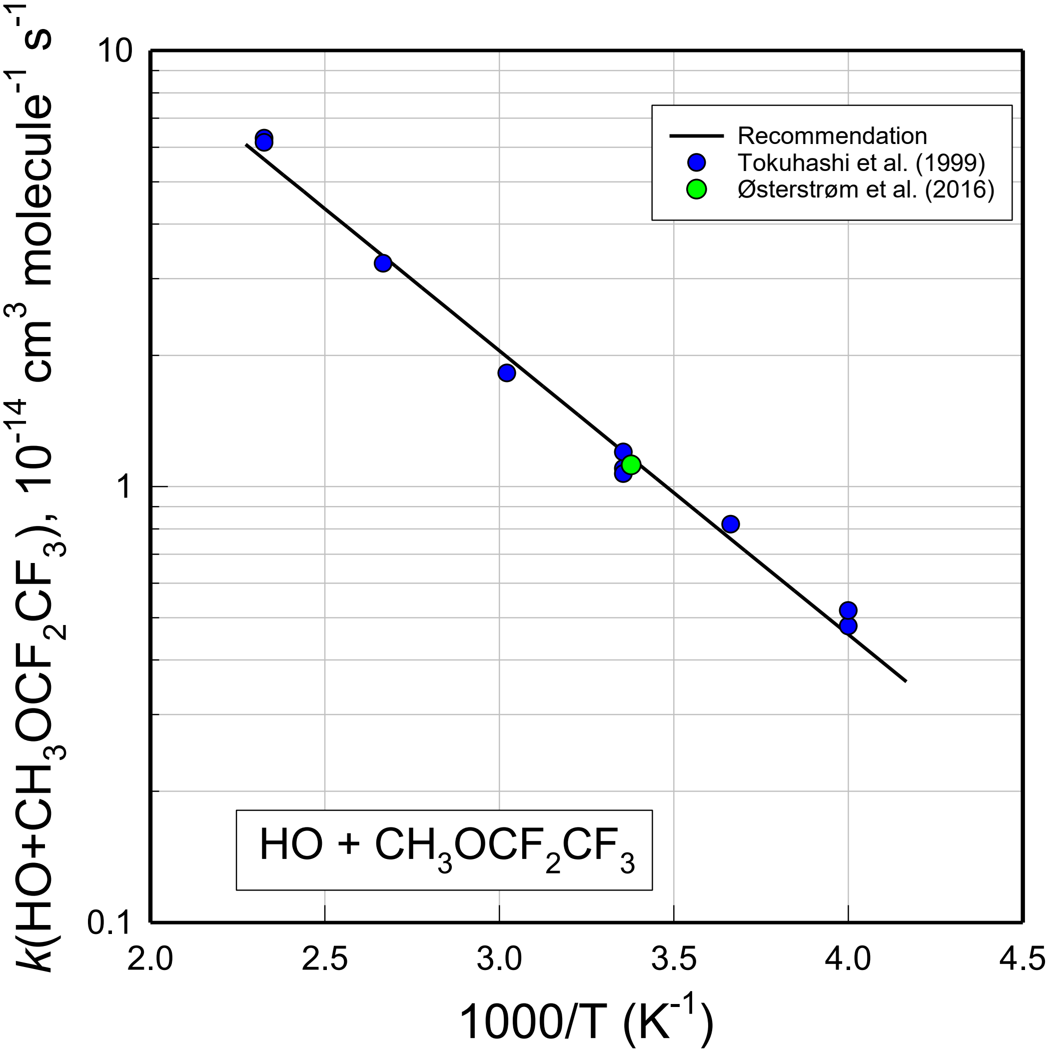

oFOx145: HO + $CH_3OCF_2CF_2CF_3$

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

$$HO + CH_3OCF_2CF_2CF_3 \rightarrow CH_2OCF_2CF_2CF_3 + H_2O$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.06^{+0.58}_{-0.45} \times 10^{-12})\exp[(-1540\pm80)/T]$	250-430	Tokuhashi et al. (1999)	LP/FP/DF-LIF (a)
1.13×10^{-14}	298		
$(2.0^{+1.2}_{-0.7}) \times 10^{-11} \exp[(-2130\pm290/T)]$	288-368	Bravo et al. (2010)	DF-MS (b)
$(1.54\pm0.05) \times 10^{-14}$	298		
Relative Rate Coefficients			
1.11×10^{-14}	295	Ninomiya et al. (2000)	RR (c)

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 photolysis (ArF laser) of N_2O to produce $O(^1D)$ atoms in the presence of H_2O 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, $\lambda < 180$ nm) of H_2O 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 NO_2 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.

(b) F atoms produced in a microwave discharge of F_2/He mixtures were reacted with H_2O to generate HO radicals. Experiments were conducted in a flow tube at a pressure of 1 Torr of helium diluent. HO radicals were monitored by mass spectroscopy by adding I_2 and detecting the HOI product.

(c) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of water vapor. Experiments were performed in approximately 200 Torr of helium diluent in the presence of 3-5 Torr of ozone and 2-3 Torr of water vapor. The loss of $CH_3OC_3F_7$ was measured relative to those of CH_4 and CH_3Cl and rate coefficient ratios of $k(HO + CH_3OC_3F_7)/k(HO + CH_4) = 1.68 \pm 0.20$ and $k(HO + CH_3OC_3F_7)/k(HO + CH_3Cl) = 0.35 \pm 0.03$ were reported. Using $k(HO + CH_4) = 6.01 \times 10^{-15}$ and $k(HO + CH_3Cl) = 3.47 \times 10^{-14}$ at 295 K (Atkinson et al., 2006) gives $k(HO + CH_3OC_3F_7) = (1.01\pm0.12) \times 10^{-14}$ and $(1.21\pm0.10) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	1.18×10^{-14}	298
	$1.98 \times 10^{-12} \exp(-1526/T)$	240-440
Reliability		
$\Delta \log k$	0.10	298
$\Delta E/R$	±100	240-440

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 $CH_3OCF_2CF_2CF_3$ 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.

References

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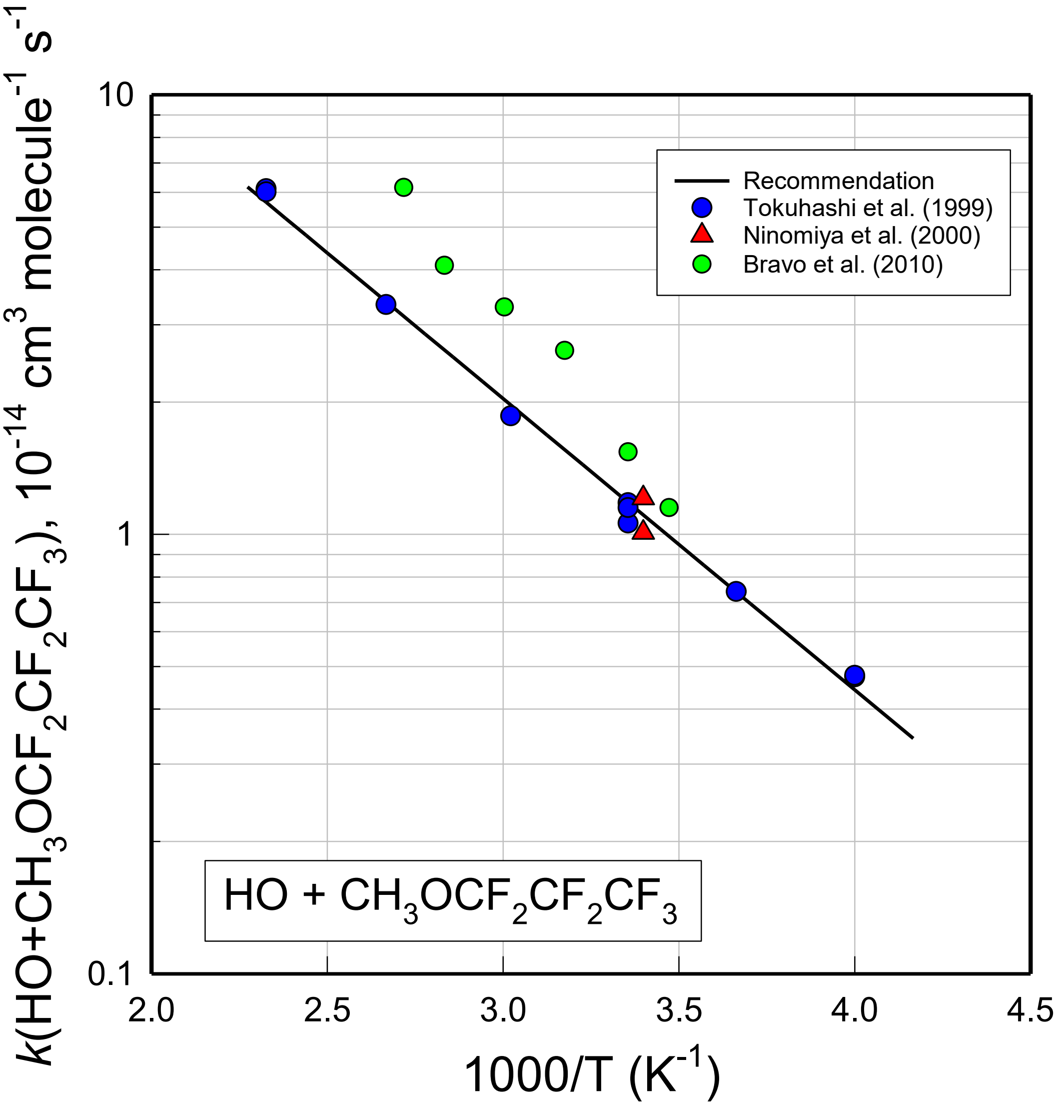

k(HO+CH3OCF2CF2CF3), 10-14 cm3 molecule-1 s-1
10
1
0.1
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K-1)
Recommendation
Tokuhashi et al. (1999)
Ninomiya et al. (2000)
Bravo et al. (2010)
HO + CH3OCF2CF2CF3

oFOx146: HO + $CH_3OCF(CF_3)_2$

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

$$HO + CH_3OCF(CF_3)_2 \rightarrow CH_2OCF(CF_3)_2 + H_2O$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.94^{+0.48}_{-0.38} \times 10^{-12})\exp[(-1450\pm70)/T]$	250-430	Tokuhashi et al. (1999)	LP/FP/DF-LIF (a)
1.48×10^{-14}	298		
Relative Rate Coefficients			
$(1.37 \pm 0.13) \times 10^{-14}$	296	Andersen et al. (2014)	RR (b)

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 photolysis (ArF laser) of N_2O to produce O(^{1}D) atoms in the presence of H_2O 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, $\lambda < 180$ nm) of H_2O 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 NO_2 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 by the photolysis of CH_3ONO in 700 Torr of air diluent. The loss of $CH_3OCF(CF_3)_2$ was monitored indirectly by the formation of its oxidation product $(CF_3)_2CFOCHO$ and was measured relative to that of C_2H_2. A rate coefficient ratio of $k(HO + CH_3OCF(CF_3)_2)/k(HO + C_2H_2) = 0.0183 \pm 0.0017$ was reported. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ in 700 Torr of air diluent at 296 K (Atkinson et al., 2006) gives $k(HO + CH_3OC_3F_7) = (1.37\pm0.13) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.52×10^{-14}	298
	$1.86 \times 10^{-12} \exp(-1432/T)$	240-440
Reliability		
$\Delta \log k$	0.10	298
$\Delta E/R$	±100	240-440

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 Andersen et al. (2014) are in excellent agreement with the results from the absolute study by Tokuhashi et al. (1999).

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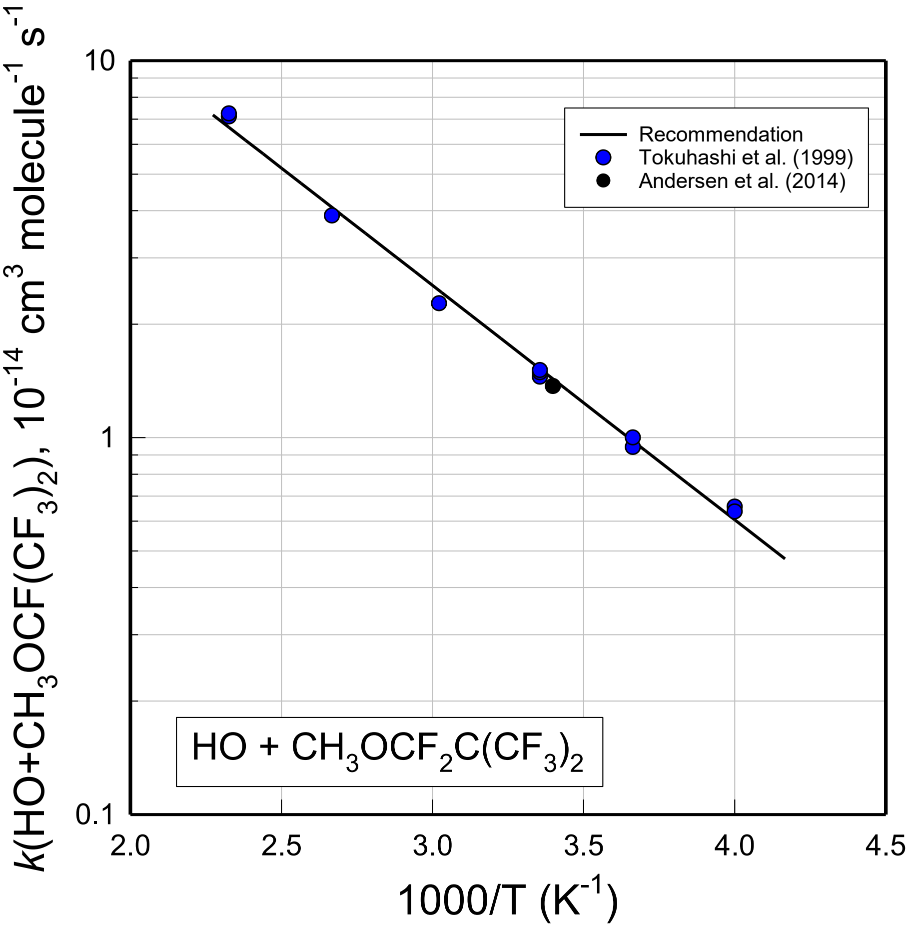

oFOx147: HO + $CH_3OC_4F_9$ (HFE-7100)

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

HO + $CH_3OC_4F_9$ (HFE-7100) → $CH_2OC_4F_9$ + H_2O

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./ K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.8^{+3.2}_{-1.5}) \times 10^{-11} \exp(-2200\pm490/T)$	288-368	Bravo et al. (2010)	DF-MS (a)
$(1.49 \pm 0.13) \times 10^{-14}$	298		
Relative Rate Coefficients			
$\sim1.2 \times 10^{-14}$	295	Wallington et al. (1997)	RR (b)
$(6.9 \pm 1.5) \times 10^{-15}$	295	Cavalli et al. (1998)	RR (c)
$(1.30\pm0.09) \times 10^{-14}$	298	Nolan et al. (1999)	RR (d)
$(1.53\pm0.10) \times 10^{-14}$	298	Oyaro and Nielsen (2003)	RR (e)
$1.10 \times 10^{-12} \exp(-1347/T)$	253-328	Chen et al. (2011) ***n*-$C_4F_9OCH_3$**	RR (f)
$(1.19\pm0.12) \times 10^{-14}$	298		
$1.21 \times 10^{-12} \exp(-1377/T)$	253-328	Chen et al. (2011) ***i*-$C_4F_9OCH_3$**	RR (f)
$(1.19\pm0.12) \times 10^{-14}$	298		

Comments

(a) F atoms produced in a microwave discharge of F_2/He mixtures were reacted with H_2O to generate HO radicals. Experiments were conducted in a flow tube at a pressure of 1 Torr of helium diluent. HO radicals were monitored by mass spectroscopy by adding I_2 and detecting the HOI product.

(b) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of water vapor. Experiments were performed in approximately 200 Torr of helium diluent in the presence of ~1 Torr of ozone. The sample of $CH_3OC_4F_9$ was a mixture of 95% *n*-$C_4F_9OCH_3$ ($CF_3CF_2CF_2CF_2OCH_3$) and 5% *i*-$C_4F_9OCH_3$ ($(CF_3)_2CFCF_2OCH_3$). The loss of $CH_3OC_4F_9$ was measured relative to those of CH_4 and CH_3Cl. Two experiments with CH_3Cl gave rate coefficient ratios of k(HO + $CH_3OC_4F_9$)/k(HO + CH_3Cl) = 0.35 and 0.32. Using k(HO + CH_3Cl) = 3.47×10^{-14} at 295 K (Atkinson et al., 2006) gives k(HO + $CH_3OC_4F_9$) = 1.2×10^{-14} and 1.1×10^{-14} cm^3 molecule^{-1} s^{-1}. Results from experiments using CH_4 were more scattered, but consistent with, those using CH_3Cl as reference.

(c) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of water vapor in 740 Torr (986 mbar) of air diluent. The sample of $CH_3OC_4F_9$ was a mixture of 25% *n*-$C_4F_9OCH_3$ ($CF_3CF_2CF_2CF_2OCH_3$) and 75% *i*-$C_4F_9OCH_3$ ($(CF_3)_2CFCF_2OCH_3$). The loss of $CH_3OC_4F_9$ was measured relative to that of CH_4. Rescaling the result using k(HO + CH_4) = 6.01×10^{-15} at 295 K (Atkinson et al., 2006) gives k(HO + $CH_3OC_4F_9$) = $(6.9 \pm 1.5) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

(d) HO radicals were generated by the 254 nm photolysis of ozone in the presence of water vapor in 1 atmosphere of air diluent. Neither the isomeric composition of $CH_3OC_4F_9$, nor the reference compound used, was specified.

(e) HO radicals were generated by the photolysis of ozone in the presence of hydrogen in 1 atmosphere of air diluent. The loss of $CH_3OC_4F_9$ was measured relative to CH_3CN and $CHCl_3$ using GC-MS and rate coefficient ratios of 0.663 ± 0.009 and 0.151 ± 0.004 were reported, respectively. Using k(HO+CH_3CN) = 2.2×10^{-14} and k(HO+$CHCl_3$) = 1.05×10^{-13} (IUPAC 2024) gives k(HO+ $CH_3OC_4F_9$) = $(1.46 \pm 0.02) \times 10^{-14}$ and $(1.59 \pm 0.04) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The average with uncertainties that encompass the extremes of the ranges is $k(\mathrm{HO+CH_3OC_4F_9}) = (1.53 \pm 0.10) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The commercial sample of $CH_3OC_4F_9$ used was an approximately 50:50 mixture of the *n*- and *i*- isomers. The isomers could not be resolved, and the measured rate coefficient is for the mixture.

(f) HO radicals were produced by the 254 nm photolysis of ozone in the presence of water vapor. The commercial sample of $C_4F_9OCH_3$ obtained for the experiments was a mixture of 36% *n*- $C_4F_9OCH_3$ and 64% *i*-$C_4F_9OCH_3$. GC-FID was used to monitor the decay of $C_4F_9OCH_3$ and the reference compounds (CF_3OCH_3 and $C_2F_5OCH_3$). The two isomers were resolved and rate coefficient ratios for both isomers were reported. Scaling the reported ratios using the IUPAC preferred values of $k(\mathrm{HO+CF_3OCH_3}) = 1.15 \times 10^{-12} \exp(-1324/T)$ and $k(\mathrm{HO+C_2F_5OCH_3}) = 1.84 \times 10^{-12} \exp(-1499/T)$ (IUPAC, 2023) and fitting the Arrhenius expression to the results gives $k(\mathrm{HO+}n\mathrm{-C_4F_9OCH_3}) = 1.10 \times 10^{-12} \exp(-1347/T)$ and $k(\mathrm{HO+}i\mathrm{-C_4F_9OCH_3}) = 1.21 \times 10^{-12} \exp(-1377/T)$ cm^3 molecule^{-1} s^{-1}. As shown in the figure below, there is no observable difference in the reactivity of the different isomers. A fit to the combined data set gives $k(\mathrm{HO+\ C_4F_9OCH_3}) = 1.15 \times 10^{-12} \exp(-1362/T)$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

Commercial samples of $C_4F_9OCH_3$ are supplied as mixtures of the *n*- and *i*- isomers. All studies except that of Chen et al. (2011) did not resolve the reactivity of the individual isomers and hence report results for the mixture of isomers. Chen et al. (2011) were able to distinguish the two isomers in their relative rate study and reported separate kinetic data for each isomer; $k(\mathrm{HO+}n\mathrm{-C_4F_9OCH_3}) = 1.10 \times 10^{-12} \exp(-1347/T)$ and $k(\mathrm{HO+}i\mathrm{-C_4F_9OCH_3}) = 1.21 \times 10^{-12} \exp(-1377/T)$ cm^3 molecule^{-1} s^{-1}. At 298 K the isomers have the same rate coefficient; 1.19×10^{-14} cm^3 molecule^{-1} s^{-1}. A fit to the combined data set gives $k(\mathrm{HO+C_4F_9OCH_3}) = 1.15 \times 10^{-12} \exp(-1362/T)$ cm^3 molecule^{-1} s^{-1} and is the preferred value. The 298 K rate coefficients reported by Wallington et al. (1997), Nolan et al. (1999), Oyaro and Nielsen (2003), and Bravo et al. (2010) for the mixtures of *n*- and *i*-isomers used in the different studies agree, within the likely combined experimental uncertainties, with that measured by Chen et al. (2011). For reasons which are unclear, the rate coefficient reported by Cavalli et al. (1997) is approximately 40% lower.

Bravo et al. (2010) used an absolute rate technique to study the reaction over the temperature range 288-368 K. The rate coefficients results reported by Bravo et al. (2010) are 25-100% larger than those from Chen et al. (2011). Tokuhashi et al. (1999) showed that the presence of reactive impurities can be problematic in studies of HO reactions with fluorinated ethers. 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.

The reaction of HO with $CH_3OC_4F_9$ proceeds via H-abstraction from the CH_3- which then leads to the formation of the formate:

$$HO + CH_3OC_4F_9 \rightarrow CH_2OC_4F_9 + H_2O$$
$$CH_2OC_4F_9 + O_2 + M \rightarrow C_4F_9OCH_2O_2 + M$$
$$C_4F_9OCH_2O_2 + NO \rightarrow C_4F_9OCH_2O + NO_2$$
$$C_4F_9OCH_2O + O_2 \rightarrow C_4F_9OC(O)H + HO_2$$

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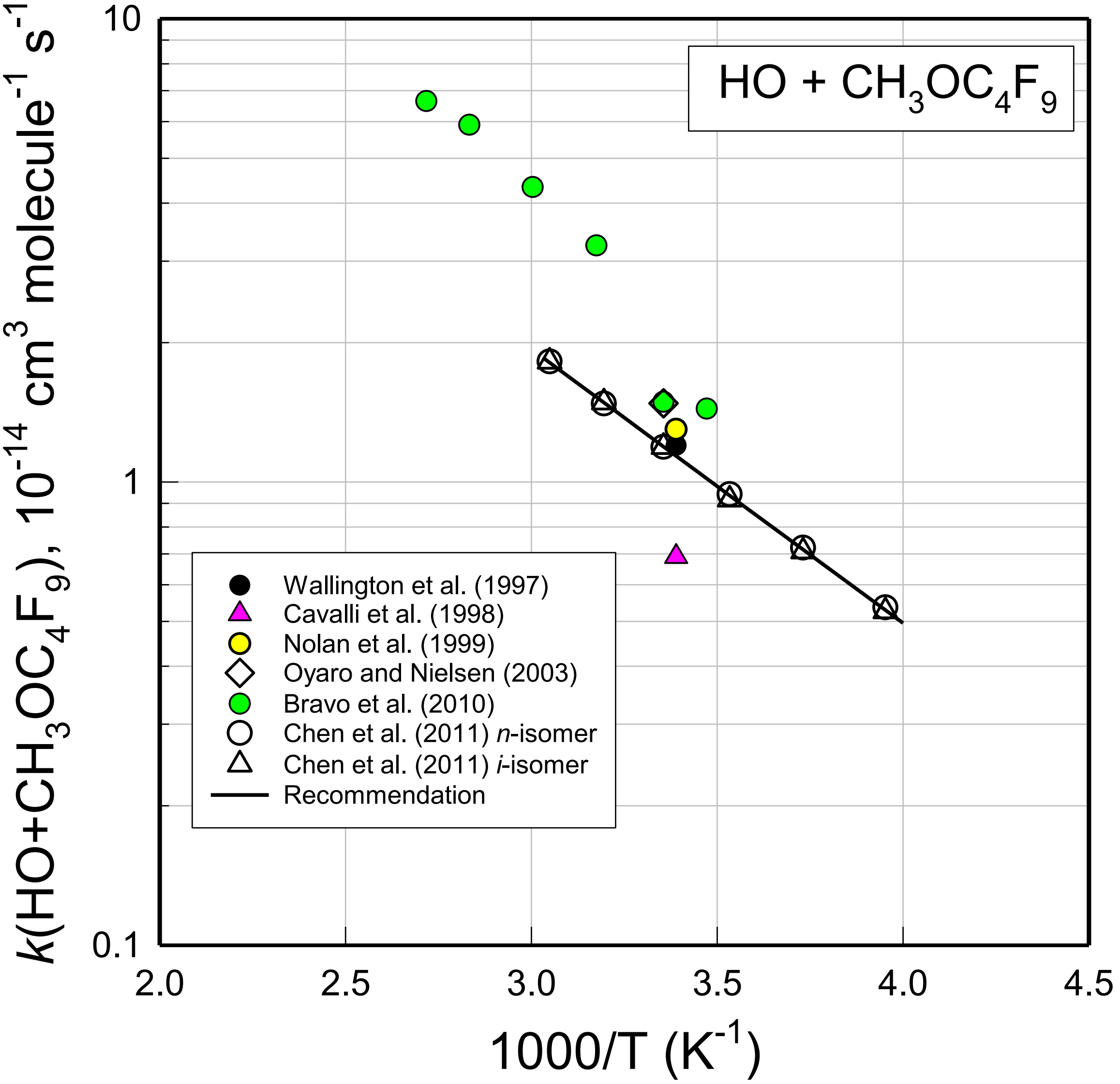
HO + CH3OC4F9
k(HO+CH3OC4F9), 10-14 cm3 molecule-1 s-1
10
1
0.1
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K-1)
Wallington et al. (1997)
Cavalli et al. (1998)
Nolan et al. (1999)
Oyaro and Nielsen (2003)
Bravo et al. (2010)
Chen et al. (2011) n-isomer
Chen et al. (2011) i-isomer
Recommendation

oFOx148: HO + $CH_3OCH(CF_3)_2$

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

$$\begin{aligned} \mathbf{HO + CH_3OCH(CF_3)_2} &\rightarrow \mathbf{CH_2OCH(CF_3)_2 + H_2O\ (1)} \\ &\ \mathbf{CH_3OC(CF_3)_2 + H_2O\ (2)} \end{aligned}$$

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

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

Comments

(a) HO radicals were generated by the flash photolysis of H_2O in 4 and 13.3 kPa (30 and 100 Torr) of argon diluent and monitored by resonance fluorescence at 308 nm. The sample of $CH_3OCH(CF_3)_2$ was purified using a preparative scale gas chromatograph before use.

(b) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of water vapor in 200 Torr (267 mbar) of O_2 diluent. The loss of $CH_3OCH(CF_3)_2$ was measured relative to those of C_2H_6 and CH_2Cl_2. The results obtained using the two different reference compounds were in excellent agreement. Using $k(HO + C_2H_6) = 6.90 \times 10^{-12} \exp(-1000/T)$ and $k(HO + CH_2Cl_2) = 1.80 \times 10^{-12} \exp(-860/T)$ cm^3 molecule^{-1} 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 $k(HO + CH_3OCH(CF_3)_2) = 1.22 \times 10^{-12} \exp(-508/T)$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

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

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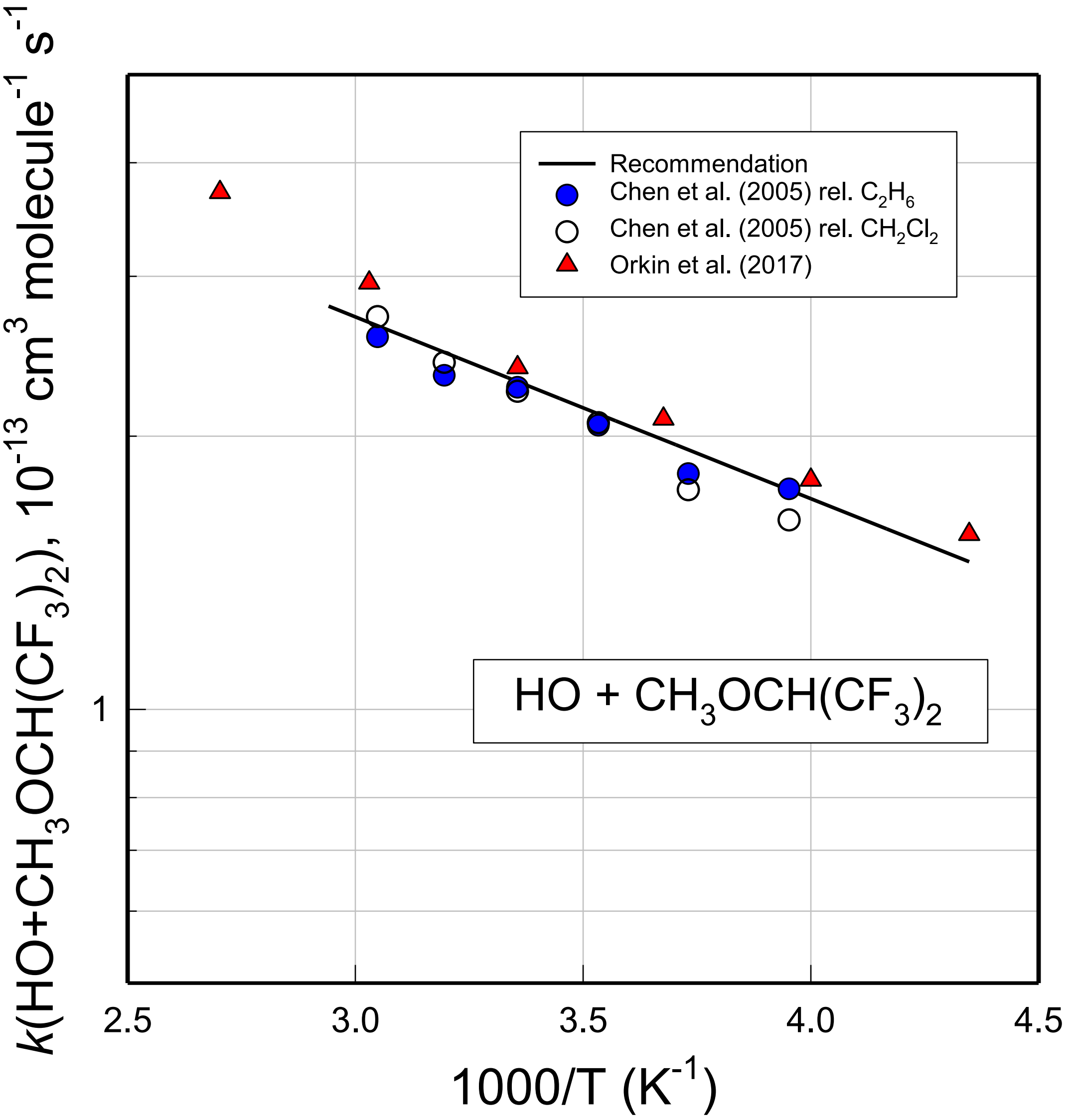

oFOx149: HO + $CH_2FOCH(CF_3)_2$ (Sevoflurane)

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

$$HO + CH_2FOCH(CF_3)_2 \text{ (Sevoflurane)} \rightarrow CHFOCH(CF_3)_2 + H_2O \quad (1)$$
$$\rightarrow CH_2FOC(CF_3)_2 + H_2O \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.53 \times 10^{-12} \exp(-900/T)$	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		
Relative Rate Coefficients			
$(2.98 \pm 0.18) \times 10^{-14}$	296	Sulbaek Andersen et al. (2012)	RR (e)
$(3.31 \pm 0.22) \times 10^{-14}$	296		

Comments

(a) HO radicals were generated by the reaction of H atoms with NO_2 in 1-8 – 6.3 Torr of helium diluent.

(b) HO radicals were produced by 248 nm photolysis of HNO_3 and monitored by laser long-path absorption at 308.42 nm. Experiments were performed in N_2 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 O_3 to give O(^{1}D) atoms which react with CH_4. 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 H_2O_2 or HNO_3 in 70-80 Torr of helium diluent and monitored by laser induced fluorescence.

(e) HO radicals were generated by the photolysis of CH_3ONO in the presence of NO in 700 Torr of air diluent. The loss of $CH_2FOCH(CF_3)_2$ was inferred from the formation of its oxidation product $FC(O)OCH(CF_3)_2$ measured using FTIR spectroscopy. C_2H_2 and C_2H_4 were used as reference compounds and rate coefficient ratios $k(HO + CH_2FOCH(CF_3)_2)/k(HO + C_2H_2) = (0.0399 \pm 0.0024)$ and $k(HO + CH_2FOCH(CF_3)_2)/k(HO + C_2H_4) = (4.22 \pm 0.28) \times 10^{-3}$ were reported. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + CH_2FOCH(CF_3)_2) = (2.98 \pm 0.18) \times 10^{-14}$ and $(3.31 \pm 0.22) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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

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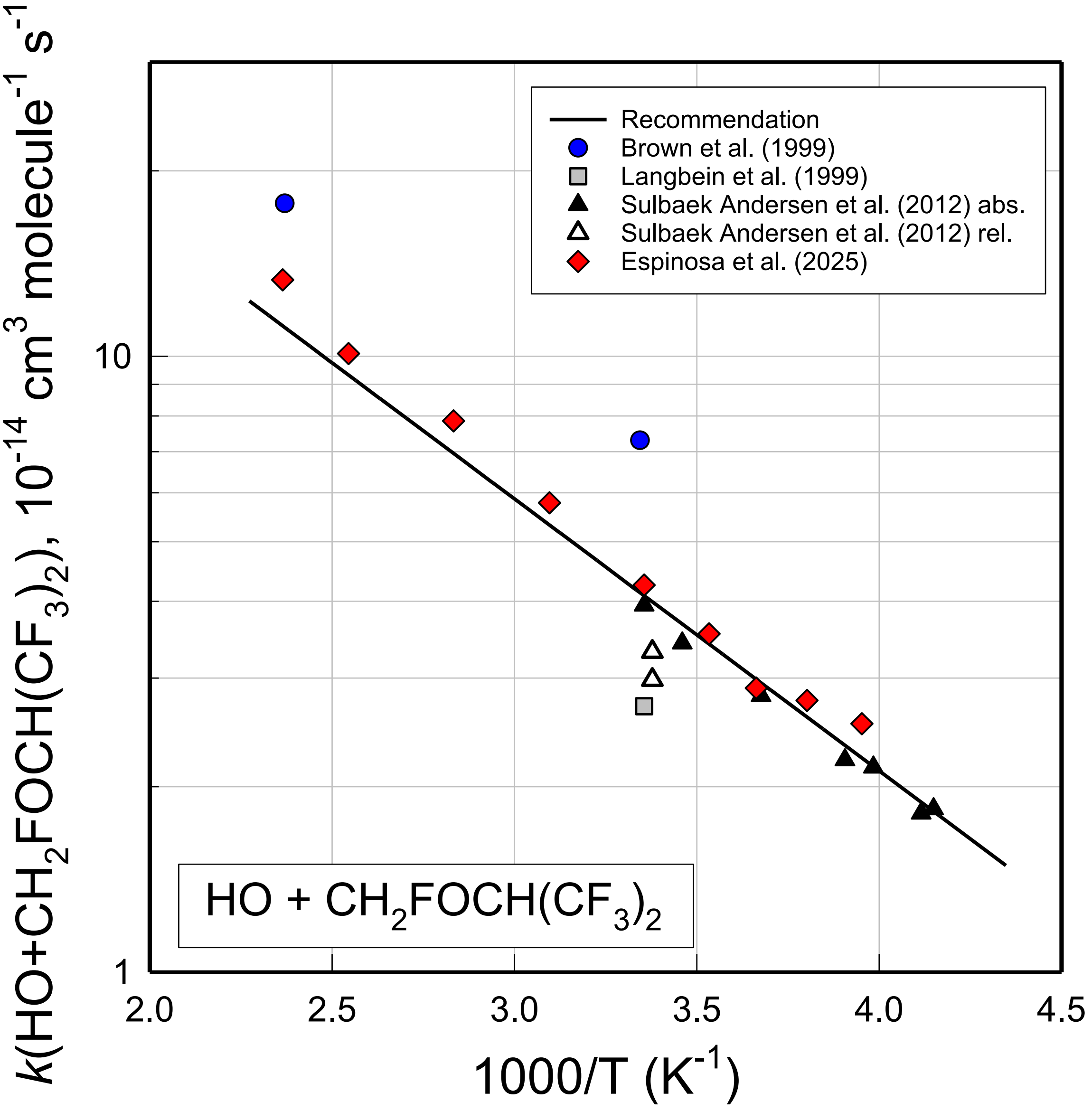
Recommendation
Brown et al. (1999)
Langbein et al. (1999)
Sulbaek Andersen et al. (2012) abs.
Sulbaek Andersen et al. (2012) rel.
Espinosa et al. (2025)
HO + $CH_2FOCH(CF_3)_2$
$k(HO+CH_2FOCH(CF_3)_2)$, 10^{-14} cm^3 $molecule^{-1}$ s^{-1}
10
1
2.0
2.5
3.0
3.5
4.0
4.5
1000/T (K^{-1})

oFOx150: HO + $CHF_2OCHFCF_3$ (Desflurane)

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

$$\mathrm{HO + CHF_2OCHFCF_3\ (Desflurane) \rightarrow CF_2OCHFCF_3 + H_2O\ (1)}$$
$$\mathrm{\rightarrow CHF_2OCFCF_3 + H_2O\ (2)}$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4.4 \pm 0.8) \times 10^{-15}$	298	Langbein et al. (1999)	PLP-UVA (a)
$(7.05\pm1.80) \times 10^{-13} \exp[(-1551\pm72)/T)]$	239-296	Sulbaek Andersen et al. (2012)	PLP-LIF (b)
$(3.73 \pm 0.08) \times 10^{-15}$	296		
Relative Rate Coefficients			
$(6.37\pm0.23) \times 10^{-15}$	298	Orayo et al. (2005)	RR (c)
$(5.40\pm0.17) \times 10^{-15}$	298		

Comments

(a) HO radicals were produced by 248 nm photolysis of HNO_3 and monitored by laser long-path absorption at 308.42 nm. Experiments were performed in N_2 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 O_3 to give $O(^1D)$ atoms which react with CH_4. 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 O_3 at 254 nm in the presence of H_2 in 1013 mbar of air diluent. The loss of $CHF_2OCHFCF_3$ was monitored relative to those of CH_3CCl_3 and CHF_2CH_2F by GC/MS. Rate coefficient ratios of $k(HO + CHF_2OCHFCF_3)/k(HO + CH_3CCl_3) = 0.67 \pm 0.024$ and $k(HO + CHF_2OCHFCF_3)/k(HO + CHF_2CH_2F) = 0.36 \pm 0.04$ were reported. Using $k(HO + CH_3CCl_3) = 9.5 \times 10^{-15}$ and $k(HO + CHF_2CH_2F) = 1.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson et al., 2006, 2008) gives $k(HO + CHF_2OCHFCF_3) = (6.37\pm0.23) \times 10^{-15}$ and $(5.40\pm0.17) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

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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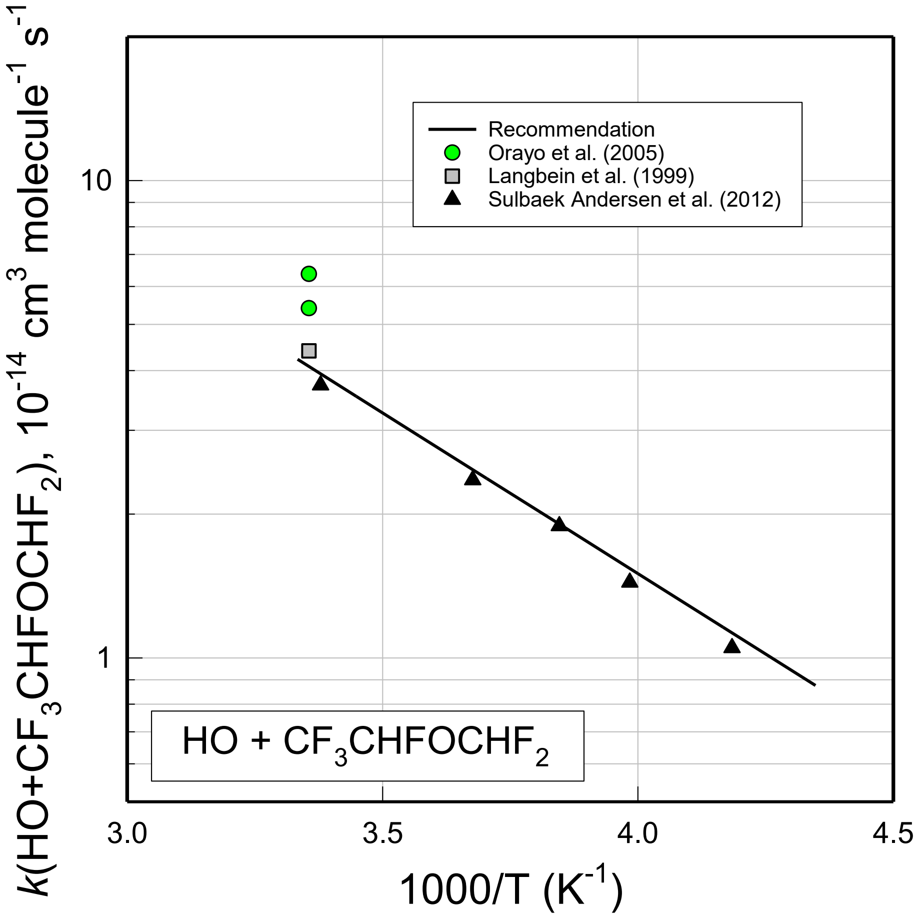


oFOx133: HO + $CF_3OCF=CF_2$

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

HO + $CF_3OCF=CF_2 \rightarrow$ products

Rate coefficient data

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

Comments

(a) HO radicals were produced by the reaction of F atoms with H_2O or by the reaction of H atoms with NO_2 in 1 Torr of He diluent at 298 K.

(b) HO radicals were produced by the pulsed xenon flash lamp photolysis of H_2O, or pulsed ArF eximer laser photolysis of N_2O to produce $O(^1D)$ atoms which were then reacted with either H_2O or CH_4 to give HO radicals, or pulsed laser photolysis of H_2O_2. Experiments were conducted in 5-200 Torr of helium, or argon, diluent. There was no discernible effect of pressure or diluent gas over the range studied. Reults from experiments using four different sources of HO radicals were indistinguishable.

(c) Photolysis of CH_3ONO in 700 Torr (933 mbar) of air diluent was used to generate HO radicals. The loss of $CF_3OCF=CF_2$ was measured relative to those of C_2H_2 and C_2H_4 and used to measure the rate coefficient ratios $k(CF_3OCF=CF_2)/k(C_2H_2) = 2.89\pm0.25$ and $k(CF_3OCF=CF_2)/\mathrm{k}(C_2H_4) = 0.29\pm0.02$. Using $k(HO + C_2H_2) = 7.47 \times 10^{-13}$ and $k(HO + C_2H_4) = 7.85 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + CF_3OCF=CF_2) = (2.16\pm0.19) \times 10^{-12}$ and $(2.28\pm0.16) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	2.96×10^{-12}	298
	$1.01 \times 10^{-12} \exp(320/T)$	250-430
Reliability		
$\Delta \log k$	0.10	298
$\Delta E/R$	±100	250-430

Comments on Preferred Values

While the rate coefficients measured at 298 K in the absolute rate studies by Li et al. (2000) and Tokuhashi et al. (2000) differ by only approximately 20%, the temperature dependencies measured in the two studies are strikingly different. It is well established that the mechanism of the reaction of HO radicals with alkenes is addition to the >C=C< bond and the temperature dependence reported by Li et al. (2000) is not physically plausible. The results from the relative rate study by Mashino et al. (2000) at 296 K are approximately 25% lower than the rate coefficient reported by Tokuhashi et al. (2000) at 298 K. Such a difference lies at the extreme end of the likely combined experimental uncertainties from the two studies. The preferred expression is taken from Tokuhashi et al. (2000) and gives $k(HO + CF_3OCF{=}CF_2) = 2.96 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

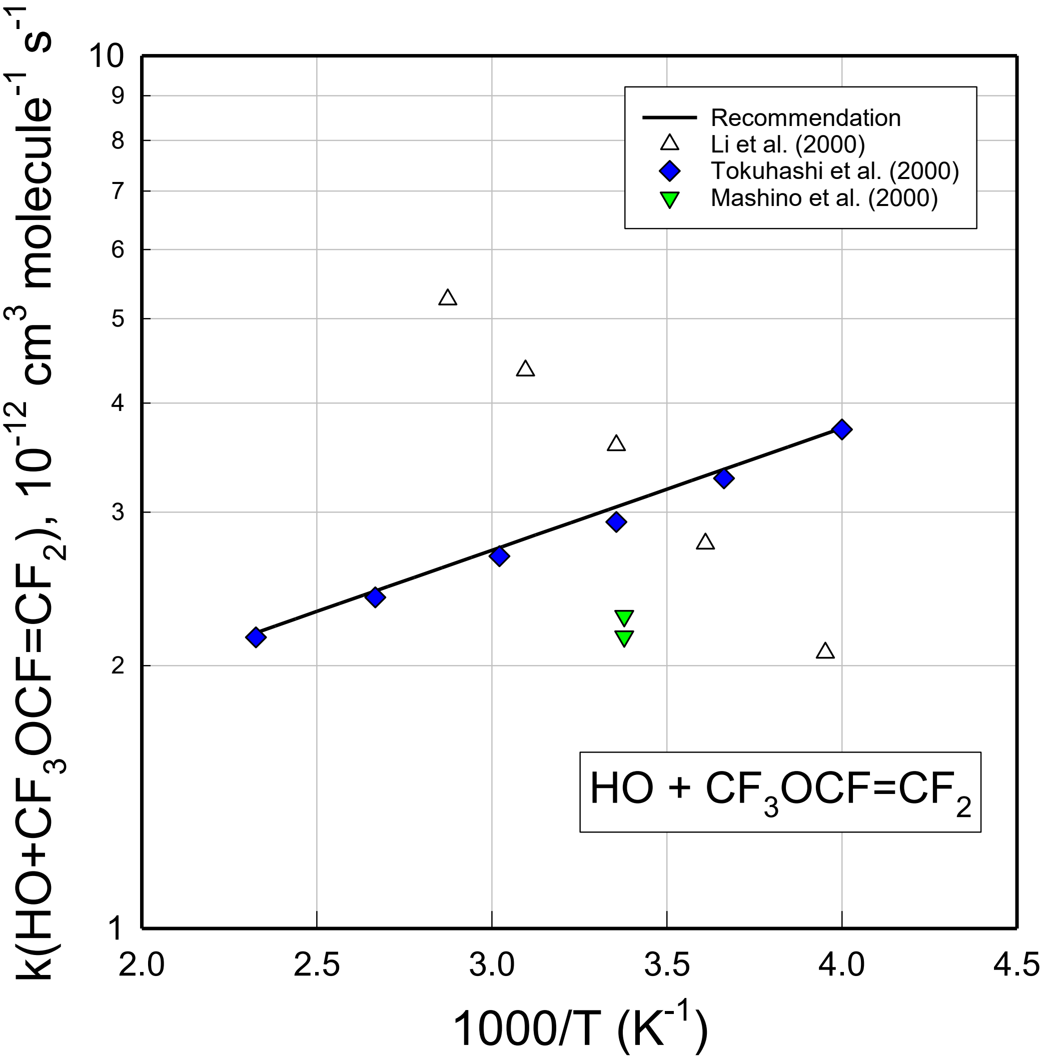
References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

Li, Z., Tao, Z., Naik, V., Good, D. A., Hansen, J. C., Jeong, G.-R., Francisco, J. S., Jain, A. K., and Wuebbles, D. J., J. Geophys. Res., 105, 4019, 2000.

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

Tokuhashi, K., Takahashi, A., Kaise, M., Kondo, S., Sekiya, A., and Fujimoto, E.: Chem. Phys. Lett., 325, 189, 2000.



oFOx134: HO + $C_2F_5OCF=CF_2$

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

HO + $C_2F_5OCF=CF_2 \rightarrow$ products

Rate coefficient data

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

Comments

(a) HO radicals were produced by the photolysis of H_2O_2 or HNO_3 at 248 nm in 50 or 100 Torr of N_2 diluent. The pseudo first order loss of HO radicals was measured in the presence of an excess of $C_2F_5OCF=CF_2$.

(b) HO radicals were produced by the photolysis of O_3 in the presence of H_2 in 1 atmosphere of air diluent. The loss of $C_2F_5OCF=CF_2$ was measured relative to that of C_3H_8 and a rate coefficient ratio of $k(C_2F_5OCF=CF_2)/k(C_3H_8) = 2.802 \pm 0.061$ was reported. Using $k(HO + C_3H_8) = 1.1 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(C_2F_5OCF=CF_2) = (3.08 \pm 0.07) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

(c) Photolysis of $CH_3ON0.6O$ in 1 bar of air diluent was used to generate HO radicals. The loss of $C_2F_5OCF=CF_2$ was measured relative to that of C_2H_4 and used to measure the rate coefficient ratio $k(C_2F_5OCF=CF_2)/k(C_2H_4) = 0.361 \pm 0.006$. Using $k(HO + C_2H_4) = 7.8 \times 10^{-12}$ (Atkinson et al., 2006) gives $k(HO + C_2F_5OCF=CF_2) = (2.82 \pm 0.05) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

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

Comments on Preferred Values

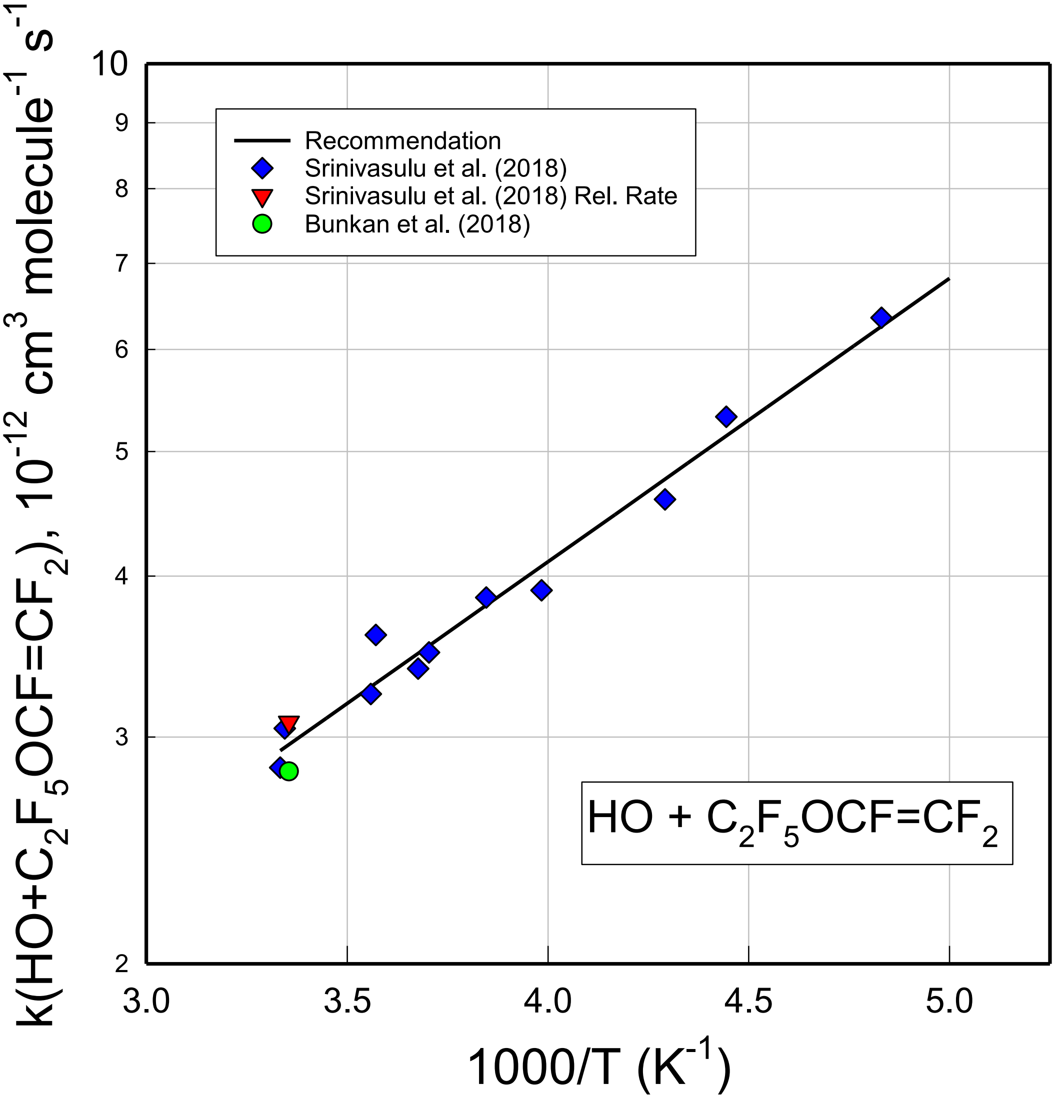
There is excellent agreement in the results from the absolute and relative rate studies by Srinivasula et al. (2018) and Bunkan et al. (2018) at 298-300 K. The preferred Arrhenius expression is taken from Srinivasula et al. (2018) which gives $k(HO + C_2F_5OCF=CF_2) = 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, https://iupac.aeris-data.fr/

Bunkan, A. J. C., Srinivasulu, G., Amedro, D., Wallington, T. J., and Crowley, J. N.: Phys. Chem. Chem. Phys., 20, 11306, 2018.

Srinivasulu, G., Bunkan, A. J. C., Amedro, D., and Crowley, J. N. : Phys. Chem. Chem. Phys., 20, 3761, 2018.



oFOx160: $CF_3C(O)O_2 + HO_2$

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

$$
\begin{aligned}
CF_3C(O)O_2 + HO_2 &\rightarrow CF_3C(O)OOH + O_2 &\quad (1)\\
&\rightarrow CF_3C(O)OH + O_3 &\quad (2)\\
&\rightarrow CF_3CO_2 + O_2 + HO &\quad (3)
\end{aligned}
$$

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

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

Comments

(a) Experiments were carried out in a 140 L static reactor with reactants and products analysed by FTIR. $CF_3C(O)O_2$ and HO_2 radicals were generated by the broad-band photolysis of Cl_2 in the presence of CF_3CHO and H_2 in air or O_2. The initial relative production rate of HO_2 to $CF_3C(O)O_2$ was varied from 0 to ~13; at the high end of the scale all $CF_3C(O)O_2$ radicals are expected to react with HO_2. The loss of CF_3CHO and the formation of $CF_3C(O)OOH$, $CF_3C(O)OH$ and COF_2 were used to derive branching ratios for k_1, k_2 and k_3 respectively. O_3, (co-produced with $CF_3C(O)OH$) was also observed and its yield was indistinguishable from that of $CF_3C(O)OH$.

Preferred Values

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

Comments on Preferred Values

There is very little experimental data on the reaction between $CF_3C(O)O_2$ and HO_2 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 ($CF_3C(O)OH$) with a branching ratio of 0.38 ± 0.04 is preffered over the peroxide (or peroxyacid $CF_3C(O)OOH$) with a branching ratio 0.09 ± 0.04. The most important pathway at room temperature is however formation of $CF_3CO_2 + O_2 + HO$ with a branching ratio of 0.56 ± 0.05. The initially formed CF_3CO_2 product decomposes to $CF_3 + CO_2$. By comparison with the larger experimental dataset on the analogous reaction of the non-fluorinated peroxy radical

$CH_3C(O)O_2$ (see IUPAC Data-Sheet HOx_VOC54) we may expect that the acid forming pathway (k_2) will gain in relative importance at the cost of k_1 and k_3 as the temperature decreases, but this requires experimental / theoretical confirmation.

In the absence of a direct measurement of k, we list the value for the non-fluorinated analogue $CH_3C(O)O_2$. This value and its temperature dependence need to be determined experimentally.

References

Sulbaek Andersen, M. P., Stenby, C., Nielsen, O. J., Hurley, M. D., Ball, J. C., Wallington, T. J., Martin, J. W., Ellis, D. A., and Mabury, S. A.: J. Phys. Chem. A, 108, 63252004.

oFOx161: $CF_3C(O)O_2$ + NO

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

$$CF_3C(O)O_2 + NO \rightarrow CF_3C(O)O + NO_2 \qquad (1)$$

Rate coefficient data

k / cm^3 molecule^{-1} 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		

Comments

(a) $CF_3C(O)O_2$ radicals were generated in the pulsed radiolysis of $SF_6/CF_3CHO/O_2$ mixtures. The conditions were chosen so that the fate of the initially formed CF_3CO radicals was reaction with O_2 to form $CF_3C(O)O_2$. By adding NO to the mixture (0-1 mbar), the rate coefficient for $CF_3C(O)O_2$ + NO was derived by monitoring the rate of formation of the NO_2 product via absorption spectroscopy at 400 nm.

(b) $CF_3C(O)O_2$ radicals were generated in the 351 nm flash photolysis of either Cl_2 or F_2 in the presence of $CF_3CHO/N_2/O_2$/NO mixtures. The rate coefficient for $CF_3C(O)O_2$ + NO was derived by monitoring the rate of loss of NO and formation of NO_2 via infra-red absorption spectroscopy.

Preferred Values

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

Comments on Preferred Values

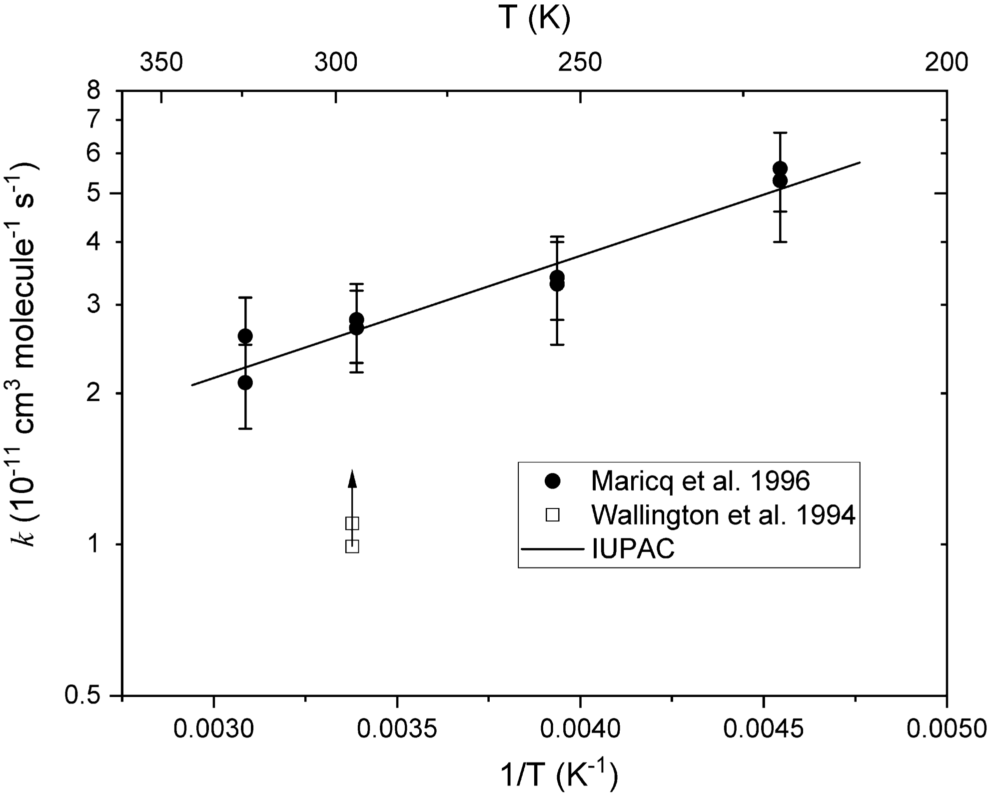
There are two kinetic studies on the reaction between $CF_3C(O)O_2$ and NO which (at the common temperature) are not in good agreement dispite the use of similar methods. The rate coefficient was derived by analysis of NO_2 formation (Wallington et al, 1994; Maricq et al., 1996) or NO loss (Maricq et al., 1996). In both cases, the analyses were complicated by reactions of NO_X with other radicals in the system.

Wallington et al. (1994) derived a room-temperaure rate coefficient of 1.1×10^{-11} cm^3 molecule^{-1} s^{-1} from a plot of the NO_2 formation rate-constant versus NO. However a large positive intercept and a NO_2 yield of 173 % indicated that other peroxy radicals (e.g. CF_3O_2) also converted NO to NO_2 and the authors preferred to report a lower limit of $k > 9.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Maricq et al. (1996) found that the time profiles of both NO and NO_X were impacted by reactions of NO with CF_3O_2 (to form NO_2) and with CF_3CO_2 and CF_3O (to remove NO) thus complicating the kinetic analysis. They found a much larger (factor 2.5) rate coefficient at room temperature than Wallington et al.

As the result of Maricq et al. (1996) is consistent with the lower limit of Wallngton et al. and is similar to the large rate coefficient for reaction of the non-fluorinated analogue ($CH_3C(O)O_2$) with NO, we adopt this as our preferred value, albeit with expanded uncertainty. Maricq et al (1996) observed a negative temperature dependence, which is consistent with the kinetic data on $CH_3C(O)O_2$ with NO and we adopt their measurement of the temperature dependence of *k*.

References

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



Rate coefficients for CF_3CO_3 + 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).

oFOx162: $CF_3C(O)O_2 + NO_2 + M$

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

$$CF_3C(O)O_2 + NO_2 + M \rightarrow CF_3C(O)O_2NO_2 + M \qquad (1)$$

Rate coefficient data

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

Comments

(a) $CF_3C(O)O_2$ radicals were generated in the pulsed radiolysis of $SF_6/CF_3CHO/O_2$ mixtures. The conditions were chosen so that the initially formed CF_3CO radicals were converted to $CF_3C(O)O_2$ in < 2 μs. The rate coefficient for $CF_3C(O)O_2 + NO_2$ was derived by monitoring the rate of loss of NO_2 via absorption spectroscopy at 400 nm.

Preferred Values

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

Comments on Preferred Values

The pulsed radiolysis experiments of Wallington et al. (1994) represent the only kinetic study of the reaction between $CF_3C(O)O_2$ and NO_2 which was limited to room temperature and a total pressure of 1bar SF_6. Although pseudo first-order kinetics appeared to be followed, the NO_2 concentration was significantly depleted during the reaction and corrections (≤ 12 %) were applied to take this into account. In addition, ≈ 15% of the initially formed $CF_3C(O)$ radicals decomposed to CF_3 (+ CO) with subsequent formation of CF_3O_2 which may also react with NO_2 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 $CF_3C(O)O_2$.

In line with other termolecular reactions between organic peroxy radicals NO_2, the reaction is likely to be in the high-pressure limit in the experiments of Wallington et al. (1994) at one bar SF_6.

References

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

oFOx163: $CF_3C(O)O_2NO_2$ + M

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

$$CF_3C(O)O_2NO_2 + M \rightarrow CF_3C(O)O_2 + NO_2 + M \qquad (1)$$

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		

[a] Expression derived by fitting to data listed at 933 mbar, [b] Expression derived by fitting to data listed at 8 mbar, [c] Expression derived by fitting to data listed at 30 mbar, [d] Value reported at 1000 mbar.

Comments

(a) $CF_3C(O)O_2$ radicals were generated in the broad-band (300-400 nm) photolysis of Cl_2 in the presence of CF_3CHO, O_2 and N_2 at a total pressure of 100 or 700 Torr (133 or 933 mbar) and converted to $CF_3C(O)O_2NO_2$ via addition of NO_2. When the NO_2 was completely depleted, NO was added and the first-oder rate of loss of $CF_3C(O)O_2NO_2$ monitored via IR-absorption features. Corrections (9-21%) were applied to the rate constants to take into account reformation of $CF_3C(O)O_2NO_2$ through recombination of the $CF_3C(O)O_2$ and NO_2 products.

(b) $CF_3C(O)O_2$ radicals were generated in the broad-band ($\lambda > 300$ nm) photolysis of Cl_2 in the presence of CF_3CHO, O_2 and N_2 at a total pressure of 100 or 700 Torr (133 or 933 mbar) and converted to $CF_3C(O)O_2NO_2$ via addition of NO_2. When the NO_2 was completely depleted, NO was added and the first-oder rate of loss of $CF_3C(O)O_2NO_2$ monitored via IR-absorption features. Corrections (10-25 %) were applied to the rate constants to take into account reformation of $CF_3C(O)O_2NO_2$ through recombination of the $CF_3C(O)O_2$ and NO_2 products.

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
Reliability		
$\Delta \log k$	± 0.3	296

Comments on Preferred Values

The two studies of the thermal decomposition of $CF_3C(O)O_2NO_2$ cover a limited ranges of pressures and temperatures. While the experiments of Zabel et al. (1994) show a clear pressure dependence (8-1000 mbar) at temperatures between ~ 314 and 320 K, the experiments of Wallington et al. (1994) at 303 K are independent of pressure between 100 and 933 mbar. Both studies indicate a strong dependence on temperature at all pressures (see Figure 1). In order to parameterise this termolecular reaction, rate coefficients at temperatures of exactly 303 K, 314 K and 320 K were calculated for each pressure studied using temperature dependent expressions (see parameters in the table above) derived by fitting to the individual datasets at single pressures. The results are shown in Figure 2. The solid lines are Troe-type fits to the data in which the temperature dependence of k_0 and k_∞ were taken from Zabel et al. (1994) as was the broadening factor, Fc, which they calculated using vibrational frequencies of $CF_3C(O)O_2NO_2$. The pre-exponential factor for k_0 was adjusted to best fit all datasets.

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

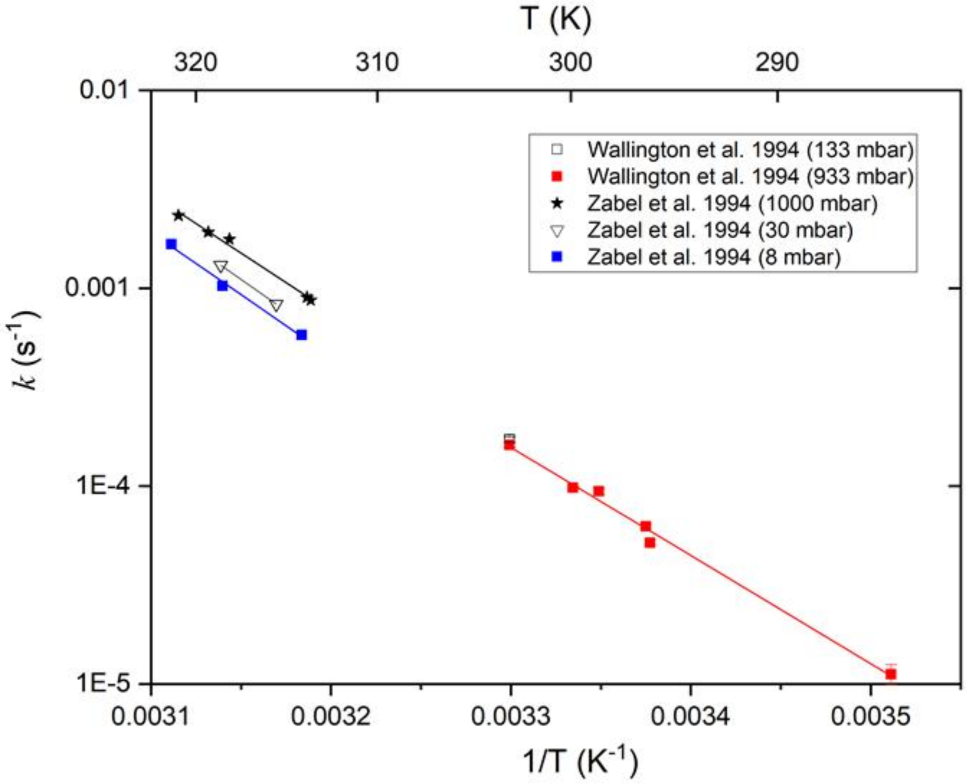
The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k:

=((5e-2*exp(-12350/*T*))*M*(1.1e17*exp(-14440/*T*)))/((5e-2*exp(-12350/*T*))*M+(1.1e17*exp(-14440/*T*)))*10^(log10(0.2)/(1+(log10((5e-2*exp(-12350/*T*))*M/(1.1e17*exp(-14440/*T*)))/(0.75-1.27*log10(0.2)))^2))

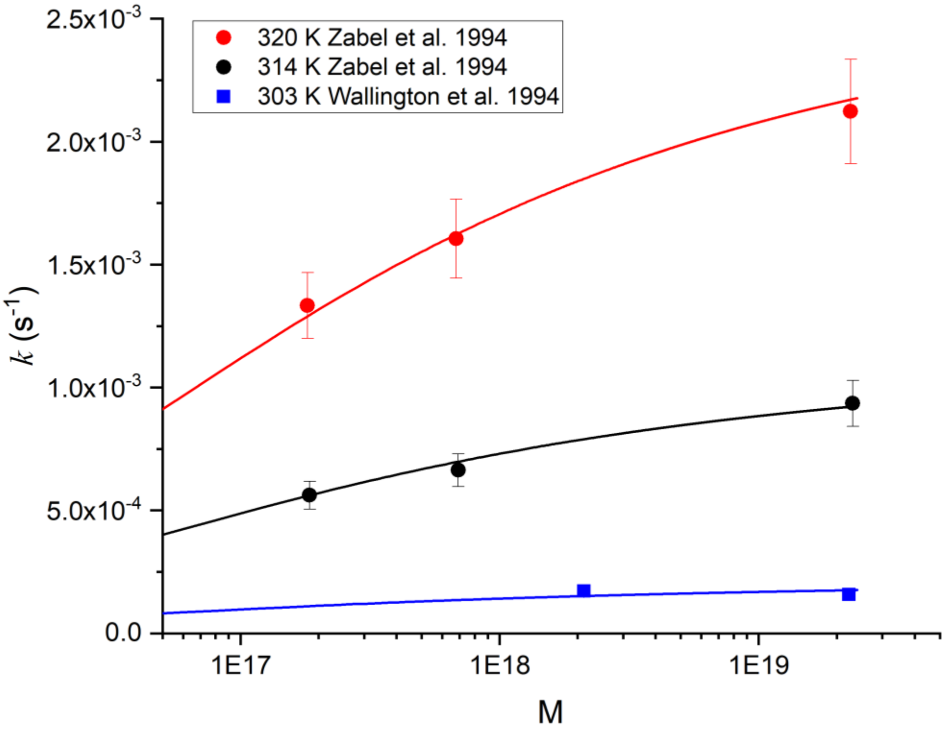
The molecular density, M = 7.243×10^{21}P(bar)/T(K)

References

Wallington, T. J., Hurley, M. D., Nielsen, O. J., and Sehested, J.: J. Phys. Chem., 98, 5686, 1994.
Zabel, F., Kirchner, F., and Becker, K. H.: Int. J. Chem. Kinet., 26, 827, 1994.



Measurements of the rate coefficient (k) for the thermal dissociation of $CF_3C(O)O_2NO_2$ at various temperatures and pressures. The solid lines are fits to the raw data at each pressure.



Pressure dependnce of k(T). Data points at single temperatures were calculated from fits to the raw data as shown in The solid lines are the IUPAC preferred values based on a fall off parameterisation.

PF5: $CHF_2CHO + h\nu$

Last evaluated: June 2025; last change in preferred values: June 2010.

$CHF_2CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		
$CHF_2CHO + h\nu$	$\rightarrow CHF_2 + HCO$	(1)
	$\rightarrow CHF_2CO + H$	(2)
	$\rightarrow CH_2F_2 + CO$	(3)

Absorption cross-section data

Wavelength range/nm	References	Comments
190-400	Sellevåg et al. (2005)	(a)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi = 0.30\pm0.05$	295-400	Sellevåg et al., 2005	(b)

Comments

(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 CHF_2CHO in pure dry air in the presence of an inert tracer (SF_6) added to monitor leakage from the chamber and an OH radical tracer (di-*n*-butyl ether) in the ~200 m^3 EUPHORE chamber facility under natural sunlight conditions. The measured loss rate of CHF_2CHO during a ~5 hr period around solar noon was corrected for loss via leakage from the chamber and reaction with OH radicals to yield $J_{obs} = (2.91 \pm 0.09) \times 10^{-5}$ s^{-1}. This was compared to the maximum photolysis rate of 9.8×10^{-5} 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 $J_{obs}/J_{calc} = 2.9 \times 10^{-5}/9.8 \times 10^{-5}$ gives the effective photolysis quantum yield from wavelengths relevant to the troposphere of 0.30 ± 0.05.

Preferred Values

Absorption cross-sections of CHF_2CHO at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/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		

Quantum Yields of CHF_2CHO

$\Phi_1 = 0.30$ at 295- 360 nm

Reliability

$\Delta\Phi_1 = \pm 0.10$

Comments on Preferred Values

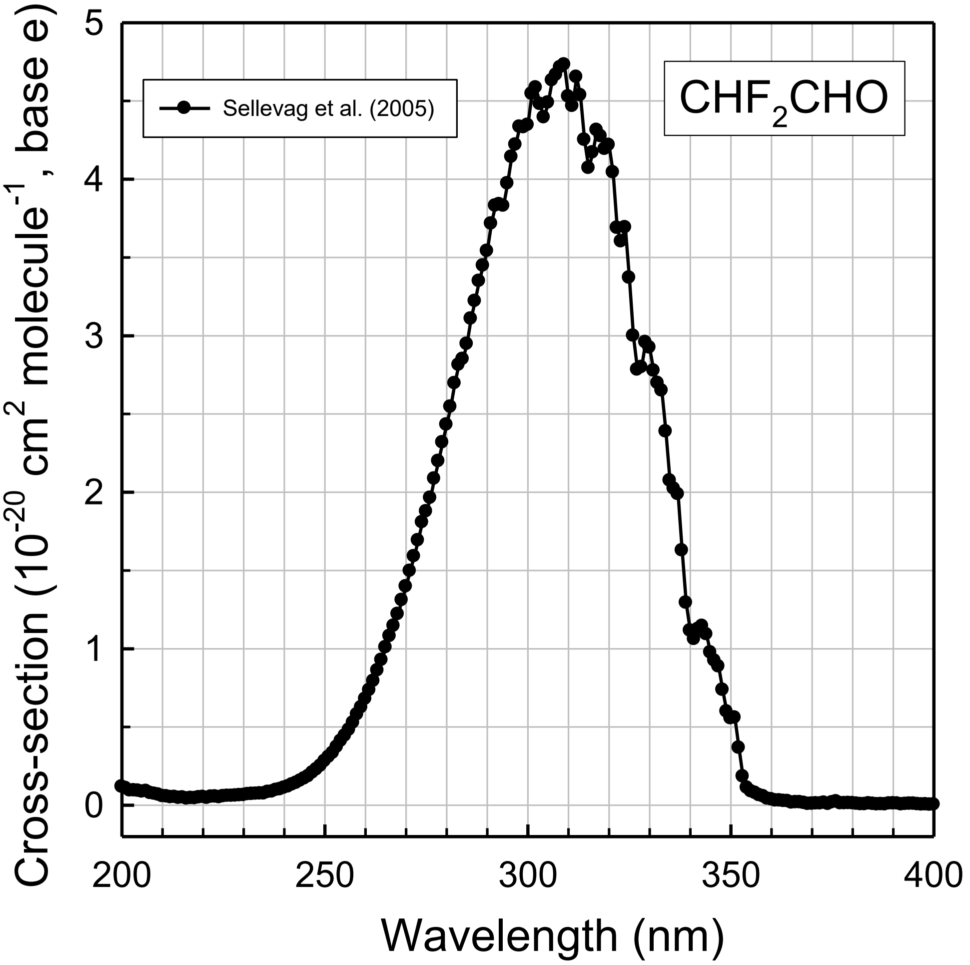
The preferred values for the cross-sections and quantum yield are taken from the study by Sellevåg et al. (2005). The photolysis of CHF_2CHO, presumably in air diluent (although this was not specified), at 310 nm was investigated by Sellevåg et al. (2005) and the formation of COF_2 and CO products was reported. There was no observable formation of CH_2F_2 consistent with the photolysis occurring via channel (1) to give CHF_2 and HCO radicals.

Calvert et al. (2010) assumed a wavelength independent quantum yield of 0.30 and estimated a photolysis lifetime for CHF_2CHO of 6 hours for overhead sun at 40°N latitude at 500 m altitude with an ozone column of 350 DU.

References

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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5809
5810

PF6: $C_2F_5CHO + h\nu$

Last evaluated: June 2025; last change in preferred values: June 2014.

$C_2F_5CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		
$C_2F_5CHO + h\nu$	$\rightarrow C_2F_5 + HCO$	(1)
	$\rightarrow C_2F_5CO + H$	(2)
	$\rightarrow C_2F_5H + CO$	(3)

Absorption cross-section data

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)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi_1 = 0.38\pm0.08$	254	Chiappero et al. (2006)	(f)
$\Phi_3 = 0.43\pm0.08$	254	Chiappero et al. (2006)	(f)
$\Phi_1 = 0.30\pm0.02$	308	Antiñolo et al. (2014)	(g)

Comments

(a) Absolute absorption cross-sections at 334, 313, 280.4, and 265.2 nm were measured using a UV spectrometer with the sample at 305 K.

(b) An absolute absorption cross-section at 319 nm was measured using a UV spectrometer

(c) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of C_2F_5CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(d) Absolute absorption cross-sections were measured using a diode array spectrometer at 269-297 K. The UV spectrum of C_2F_5CHO 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 over the range 248-297 K on the UV spectrum, however for reasons which are unclear the UV spectra at 308 K and 323 K reported in the supporting information are approximately 10% more intense than that at 298 K.

(e) Absolute absorption cross-sections were measured using a 0.5-m spectrograph with a coupled-charge device (CCD) detector with 0.5–9.8 Torr of C_2F_5CHO. The temperature range specified in the text of the paper is 269 – 298 K, but data in the supporting information cover the range 269 – 323 K. The spectrum had a peak at 308.13 ± 0.76 nm. Values of σ were given at 1 nm intervals.

(f) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of C_2F_5CHO 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 C_2F_5CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of C_2F_5NO and C_2F_5H were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).

(g) Photolysis quantum yield measured using acetaldehyde as a chemical actinometer with pulsed laser photolysis of C_2F_5CHO at 308 nm in 75 – 760 Torr (100 – 1013 mbar) of air at 298 K. The quantum yield at λ=308 nm was pressure dependent, ranging from (0.94 ± 0.28) at 75 Torr to (0.30 ± 0.02) at 760 Torr. The pressure dependence is characterized by the Stern−Volmer expression with a Stern-Volmer constant of $(1.22 \pm 0.52) \times 10^{-19}$ cm^3 $molecule^{-1}$. FTIR spectroscopy was used to identify the products following photolysis of C_2F_5CHO in air. From the observed product distribution, it was concluded that photolysis at 308 nm occurs predominantly, if not exclusively, via channel (1) to give C_2F_5 + HCO radicals.

Preferred Values

Absorption cross-sections of C_2F_5CHO at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/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

Quantum Yields of C_2F_5CHO

$$\Phi_1 = 0.38 \text{ at } 254 \text{ nm}$$
$$\Phi_3 = 0.43 \text{ at } 254 \text{ nm}$$
$$\Phi_1 = 0.30 \text{ at } 308 \text{ nm}$$

Reliability

$\Delta\Phi_1 = \pm\, 0.10$

$\Delta\Phi_3 = \pm\, 0.10$

Comments on Preferred Values

There is good agreement in the absorption cross sections measured at 298 K by Borkowski and Ausloss, (1962), Pritchard et al. (1962), Hashikawa et al. (2004), Chiappero et al. (2006), and Antiñolo et al. (2014). Taking an average of the results from Hashikawa et al. (2004), Chiappero et al. (2006), and Antiñolo et al. (2014) gives the recommended values. The quantum yield measurements at 254 nm reported by Chiappero et al. (2006) and at 308 nm by Antiñolo et al. (2014) are recommended.

Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.14 for C_2F_5CHO (based upon a linear interpolation of the measured quantum yields for CF_3CHO and C_4F_9CHO) 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 0.9 days at 11 km altitude and 2.5 days at 0 km. Antiñolo et al. (2014) assumed an exponential decrease of photolysis quantum yield with increasing wavelength from 0.81 at 254 nm (Chiappero et al., 2006) to 0.30 at 308 nm (Antiñolo et al., 2014) and lower for wavelengths longer than 308 nm. Antiñolo et al. (2014) estimated a photolysis lifetime of 3.5 hours at an altitude of 3.5 km and solar zenith angle of 16° (local noon in Ciudad Real, Spain, in summer). Photolysis is the dominant atmospheric fate of C_2F_5CHO.

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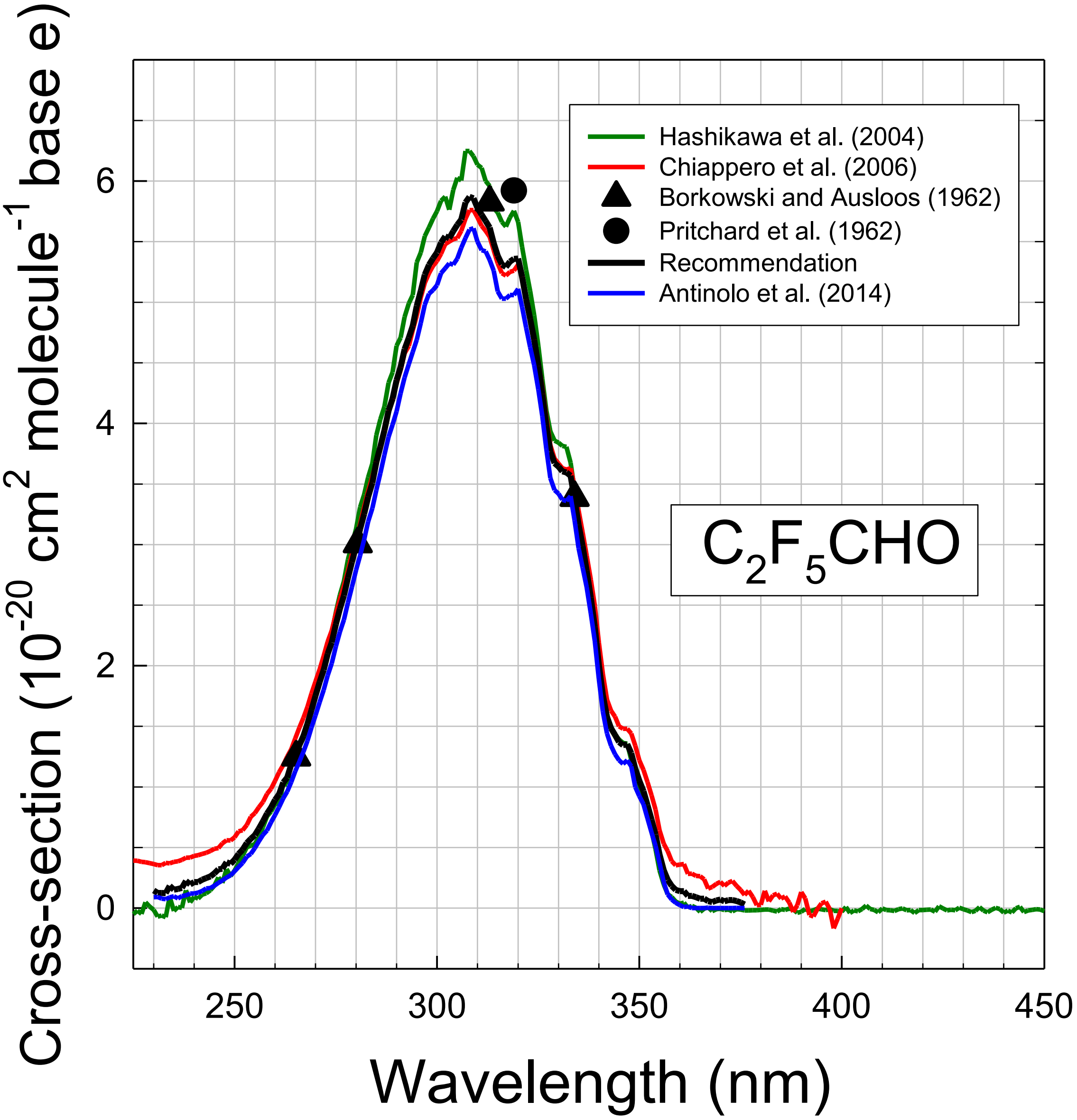

5903
5904
5905
5906

PF7: *n*-C_3F_7CHO + hν

Last evaluated: June 2025; last change in preferred values: June 2010.

n-$C_3F_7CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		
$C_2F_5CHO + h\nu$	$\rightarrow C_2F_5 + HCO$	(1)
	$\rightarrow C_2F_5CO + H$	(2)
	$\rightarrow C_2F_5H + CO$	(3)

Absorption cross-section data

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)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi_1 = 0.31\pm0.07$	254	Chiappero et al. (2006)	(e)
$\Phi_3 = 0.32\pm0.07$	254	Chiappero et al. (2006)	(e)
$\Phi_{Total} = 0.023\pm0.012$	290-400	Solignac et al. (2007)	(f)

Comments

(a) The absolute absorption cross-section at 319 nm was measured using a UV spectrometer.

(b) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of *n*-C_3F_7CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(c) Absolute absorption cross-sections were measured using a diode array spectrometer at 248-297 K. The UV spectrum of *n*-C_3F_7CHO 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.

(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*-C_3F_7CHO at 298 K. The UV spectrum of *n*-C_3F_7CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(e) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of *n*-C_3F_7CHO 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*-C_3F_7CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of *n*-C_3F_7NO and *n*-C_3F_7H were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).

(f) Photolysis of *n*-C_3F_7CHO in one atmosphere of pure dry air in the presence of an OH radical tracer (di-*n*-butyl ether) in the ~200 m^3 EUPHORE chamber facility under natural sunlight conditions. The measured rate of photolysis of n-C_3F_7CHO was (1.3 ± 0.6) x 10^{-5} s^{-1}. When compared to the maximum photolysis rate calculated using unit quantum yield for photodissociation across the atmospheric range of absorption of n-C_3F_7CHO a quantum yield of 0.023 ± 0.012 was derived.

Preferred Values

Absorption cross-sections of n-C_3F_7CHO at 298 K

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		

Quantum Yields of n-C_3F_7CHO

$\Phi_1 = 0.31$ at 254 nm
$\Phi_3 = 0.32$ at 254 nm

Reliability
$\Delta\Phi_1 = \pm 0.10$
$\Delta\Phi_3 = \pm 0.10$

Comments on Preferred Values

There is good agreement between the absorption cross sections measured by Borkowski and Ausloss, (1962), Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007). Taking an average of the results from Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007) gives the recommended values. The quantum yield measurements at 254 nm reported by Chiappero et al. (2006) and at 290-400 nm are recommended.

Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.11 for n-C_3F_7CHO (based upon a linear interpolation of the measured quantum yields for CF_3CHO and C_4F_9CHO) 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 0.75 days at 11 km altitude and 2 days at 0 km. Use of the recommended quantum yield of 0.023 in place of the value of 0.11 used by Chiappero et al. (2006) will increase the photolytic lifetimes by approximately a factor of 5. In either case, photolysis is the dominant atmospheric fate of n-C_3F_7CHO.

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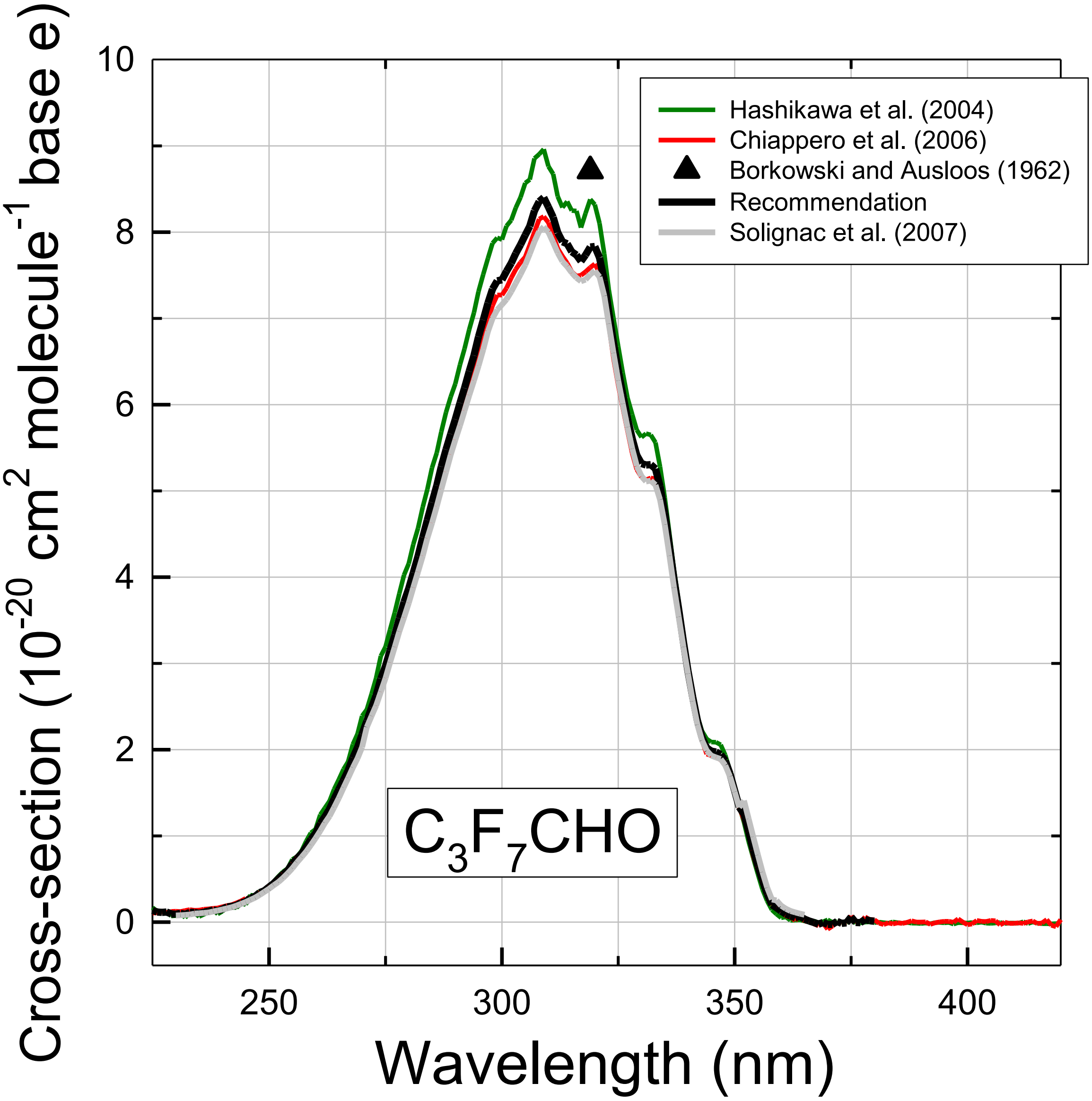
Solignac, G., Mellouki, A., Le Bras, G., Yujing, M., and Sidebottom, H.: Phys. Chem. Chem. Phys., 9, 4200, 2007.



PF8: n-C_4F_9CHO + hν

Last evaluated: June 2025; last change in preferred values: June 2010.

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n-C_4F_9CHO + hν → products

Primary photochemical transitions

Reaction		
n-C_4F_9CHO + hν	→ n-C_4F_9 + HCO	(1)
	→ n-C_4F_9CO + H	(2)
	→ n-C_4F_9H + CO	(3)

Absorption cross-section data

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)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi_1 = 0.31\pm0.08$	254	Chiappero et al. (2006)	(d)
$\Phi_3 = 0.29\pm0.07$	254	Chiappero et al. (2006)	(d)
$\Phi_{Total} = 0.08\pm0.02$	308	Chiappero et al. (2006)	(e)
$\Phi_{Total} = 0.029\pm0.015$	290-390	Solignac et al. (2007)	(f)

Comments

(a) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of n-C_4F_9CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(b) Absolute absorption cross-sections were measured using a diode array spectrometer at 248-297 K. The UV spectrum of n-C_4F_9CHO 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 discernable effect of temperature over the range studied on the UV spectrum.

(c) Absolute absorption cross-sections were measured with a resolution of 0.1 nm using a diode array spectrometer for 1.5–11.0 Torr (2.0-14.7 mbar) samples of n-C_4F_9CHO at 298 K. The UV spectrum of n-C_4F_9CHO shows a broad band, centered at 310 nm and extending out to approximately 360 nm. Values of σ were given at 1 nm intervals.

(d) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of n-C_4F_9CHO 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-C_4F_9CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of n-C_4F_9NO and n-C_4F_9H were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).

(e) Photolysis quantum yield measured using CH_3CHO as a chemical actinometer. Mixtures of n-C_4F_9CHO and NO (added as radical scavenger) in 700 Torr of N_2 diluent were irradiated using the 308 nm output of an excimer laser. The rate of loss of n-C_4F_9CHO was compared to that of CH_3CHO in back-to-back experiments. There was no evidence for the formation of n-C_4F_9H (<5% yield) following the irradiation of n-C_4F_9CHO–NO–N_2 mixtures showing that process (3) is not significant.

(f) Photolysis of n-C_4F_9CHO in one atmosphere of pure dry air in the presence of an OH radical tracer (di-n-butyl ether) in the ~200 m^3 EUPHORE chamber facility under natural sunlight conditions. The measured rate of photolysis of n-C_4F_9CHO was (1.9 ± 0.8) x 10^{-5} s^{-1}. When compared to the maximum photolysis rate calculated using unit quantum yield for photodissociation across the atmospheric range of absorption of n-C_4F_9CHO a quantum yield of 0.029 ± 0.015 was derived.

Preferred Values

Absorption cross-sections of n-C_4F_9CHO at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/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		

Quantum Yields of n-C_4F_9CHO

Φ_1 = 0.31 at 254 nm
Φ_3 = 0.29 at 254 nm
Φ_{Total} = 0.08 at 308 nm
Φ_{Total} = 0.03 at 290-390 nm

Reliability

$\Delta\Phi_1$ = ± 0.10 at 254 nm
$\Delta\Phi_3$ = ± 0.10 at 254 nm
$\Delta\Phi_{Total}$ = ± 0.04 at 308 nm
$\Delta\Phi_{Total}$ = 0.02 at 290-390 nm

Comments on Preferred Values

There is agreement between the absorption cross sections measured by Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007). Taking an average of the results from Hashikawa et al. (2004), Chiappero et al. (2006), and Solignac et al. (2007) gives the recommended values. The quantum yield measurements at 254 and 308 nm reported by Chiappero et al. (2006) are recommended.

Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.08 for n-C_4F_9CHO (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 0.75 days at 11 km altitude and 2 days at 0 km. Use of the recommended quantum yield of 0.03 in place of the value of 0.11 used by Chiappero et al. (2006) will increase the photolytic lifetimes by approximately a factor of 4. In either case, photolysis is the dominant atmospheric fate of *n*-C_4F_9CHO.

References

Chiappero M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C., Wallington, T. J., Waterland, R. L., and Buck, R. C.: J. Phys. Chem. A, 110, 11944, 2006.

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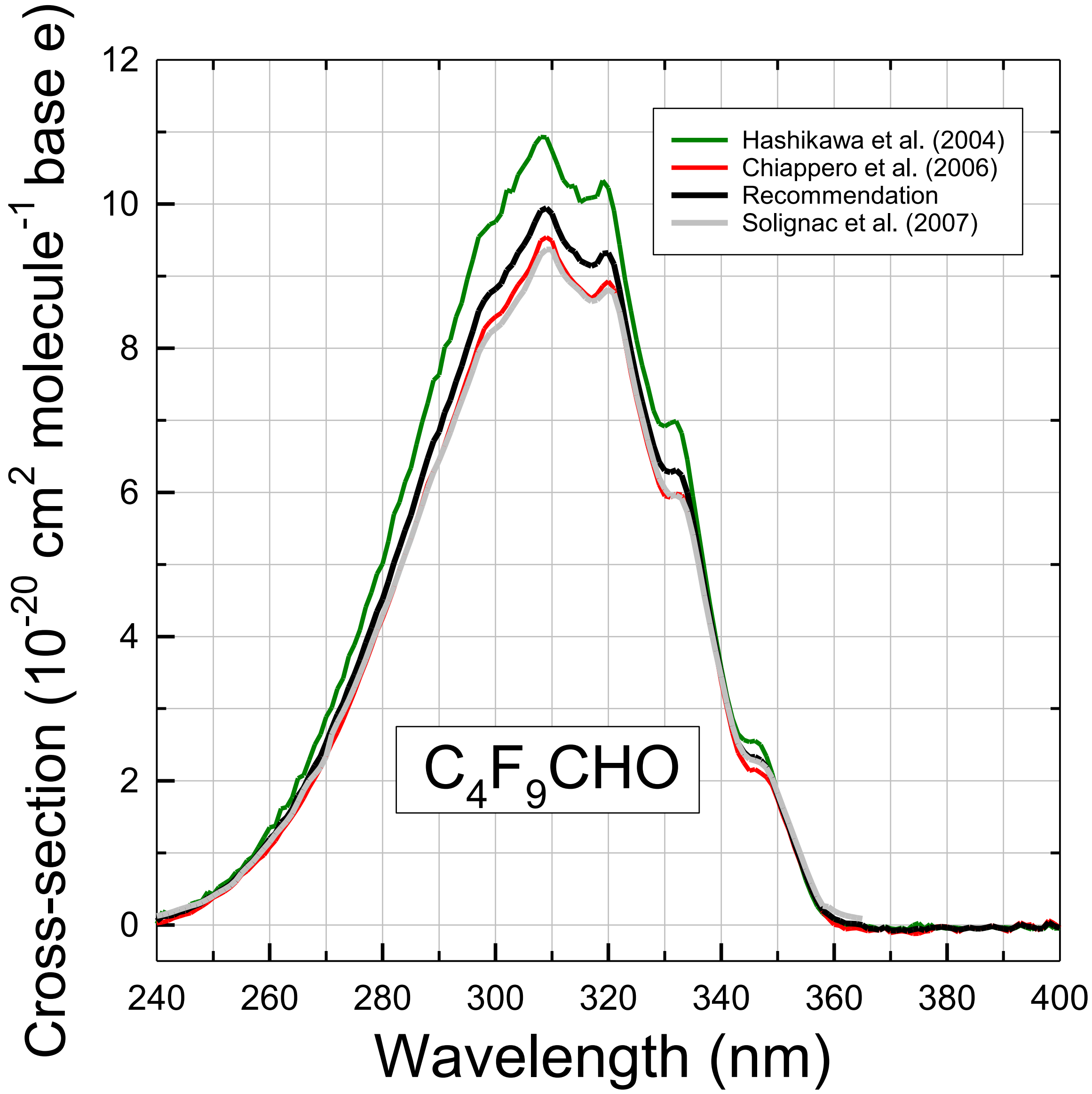


PF9: $CF_3CH_2CHO + h\nu$

Last evaluated: June 2025; last change in preferred values: June 2014.

$CF_3CH_2CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	
$CF_3CH_2CHO + h\nu \rightarrow CF_3CH_2 + HCO$	(1)
$\rightarrow CF_3CH_2CO + H$	(2)
$\rightarrow CF_3CH_3 + CO$	(3)

Absorption cross-section data

Wavelength range/nm	References	Comments
185-500	Sellevåg et al. (2004)	(a)
230-400	Chiappero et al. (2006)	(b)
230-350	Antiñolo et al. (2011)	(c)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi < 0.04$	290-400	Sellevåg et al. (2004)	(d)
$\Phi_1 = 0.38\pm0.09$	254	Chiappero et al. (2006)	(e)
$\Phi_3 = 0.36\pm0.07$	254	Chiappero et al. (2006)	(e)
$\Phi_{Total} = 0.04\pm0.01$	308	Chiappero et al. (2006)	(f)
$\Phi_{Total} = 0.023\pm0.012$	308	Antiñolo et al. (2011)	(g)

Comments

(a) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. The UV spectrum of CF_3CH_2CHO shows a broad band, centered at 295 nm and extending out to approximately 350 nm. Values of σ were given at 1 nm intervals.

(b) Absolute absorption cross-sections were measured using a diode array spectrometer at 248-297 K. The UV spectrum of CF_3CH_2CHO shows a broad band, centered at 295 nm and extending out to approximately 350 nm. Values of σ were given at 1 nm intervals. There was no discernable effect of temperature over the range studied on the UV spectrum.

(c) Absolute absorption cross-sections were measured using a 0.5-m spectrograph with a coupled-charge device (CCD) detector with 1.0−7.4 Torr of CF_3CH_2CHO at 269 – 323 K. The spectrum had a peak at 290.82 ± 0.22 nm. Values of σ were given at 1 nm intervals.

(d) Photolysis of CF_3CH_2CHO in pure dry air in the presence of an OH radical tracer (di-*n*-butyl ether) in the ~200 m^3 EUPHORE chamber facility under natural sunlight conditions. The measured first-order loss rate of CF_3CH_2CHO during a ~3 hr period around solar noon was 7.74 x 10^{-6} s^{-1}, essentially identical to the leak rate obtained from monitoring the decay of SF_6. After correction for the leak rate and reaction with OH radicals, the observed first-order loss rate of CF_3CH_2CHO ascribed to photolysis during this ~3 hr period was J_{obs} <1.5 x 10^{-6} s^{-1}. This was compared to the maximum photolysis rate of 3.4 x 10^{-5} 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_{obs}/J_{calc} = 1.5 x 10^{-6}/3.4 x 10^{-5} gives an upper limit for the photolysis quantum yield of <0.04. Solignac et al. (2007) reported quantum yields J_{obs}/J_{calc} = (0.023 ± 0.012), (0.029 ± 0.015), and (0.046 ± 0.028) for the photodissociation of C_3F_7CHO, C_4F_9CHO and $CF_3(CF_2)_5CHO$ in the EUPHORE chamber across the atmospheric range of absorption of the aldehydes. Solignac et al. (2007) suggested that the photolytic loss of CF_3CH_2CHO may have been underestimated by Sellevåg et al. (2004).

(e) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of 0.5-5.5 mbar of CF_3CH_2CHO and 20-70 mbar of NO (added as radical scavenger) were irradiated using a low pressure Hg lamp and the rate of loss of CF_3CH_2CHO was compared to that of perfluoroacetic anhydride in similar experiments. The formation of CF_3CH_2NO and CF_3CH_3 were measured by IR spectroscopy and used to derive quantum yields for processes (1) and (3).

(f) Photolysis quantum yield measured using CH_3CHO as a chemical actinometer. Mixtures of *n*-CF_3CH_2CHO and NO (added as radical scavenger) in 700 Torr of N_2 diluent were irradiated using the 308 nm output of an eximer laser. The rate of loss of CF_3CH_2CHO was compared to that of CH_3CHO in back-to-back experiments. There was no evidence for the formation of CF_3CH_3 (<5% yield) following the irradiation of CF_3CH_2CHO –NO–N_2 mixtures showing that process (3) is not significant.

(g) Photolysis quantum yield measured using NO_2 and acetaldehyde as chemical actinometers with pulsed laser photolysis of CF_3CH_2CHO at 308 nm in 25.4 – 760 Torr (34 – 1013 mbar) of air at 298 K. The quantum yield at λ=308 nm was pressure dependent, ranging from (0.142 ± 0.098) at 75 Torr to (0.023 ± 0.006) at 760 Torr. The pressure dependence is characterized by the Stern−Volmer expression with a Stern-Volmer constant of (3.25 ± 0.48) × 10^{-19} cm^3 $molecule^{-1}$. FTIR spectroscopy was used to identify the products following photolysis of CF_3CH_2CHO in air. From the observed product distribution it was concluded that photolysis at 308 nm occurs predominantly via channel (1) to give CF_3CH_2 + HCO radicals.

Preferred Values

Absorption cross-sections of CF_3CH_2CHO 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	

Quantum Yields of CF_3CH_2CHO

$\Phi_1 = 0.38$ at 254 nm
$\Phi_3 = 0.36$ at 254 nm
$\Phi_{Total} = 0.03$ at 308 nm

Reliability
$\Delta\Phi_1 = \pm 0.10$ at 254 nm
$\Delta\Phi_3 = \pm 0.10$ at 254 nm
$\Delta\Phi_{Total} = \pm 0.01$ 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 CF_3CH_2CHO (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 CF_3CH_2CHO and reported photolysis rates of 2.83×10^{-6} s^{-1} and 1.0×10^{-5} 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 CF_3CH_2CHO.

References

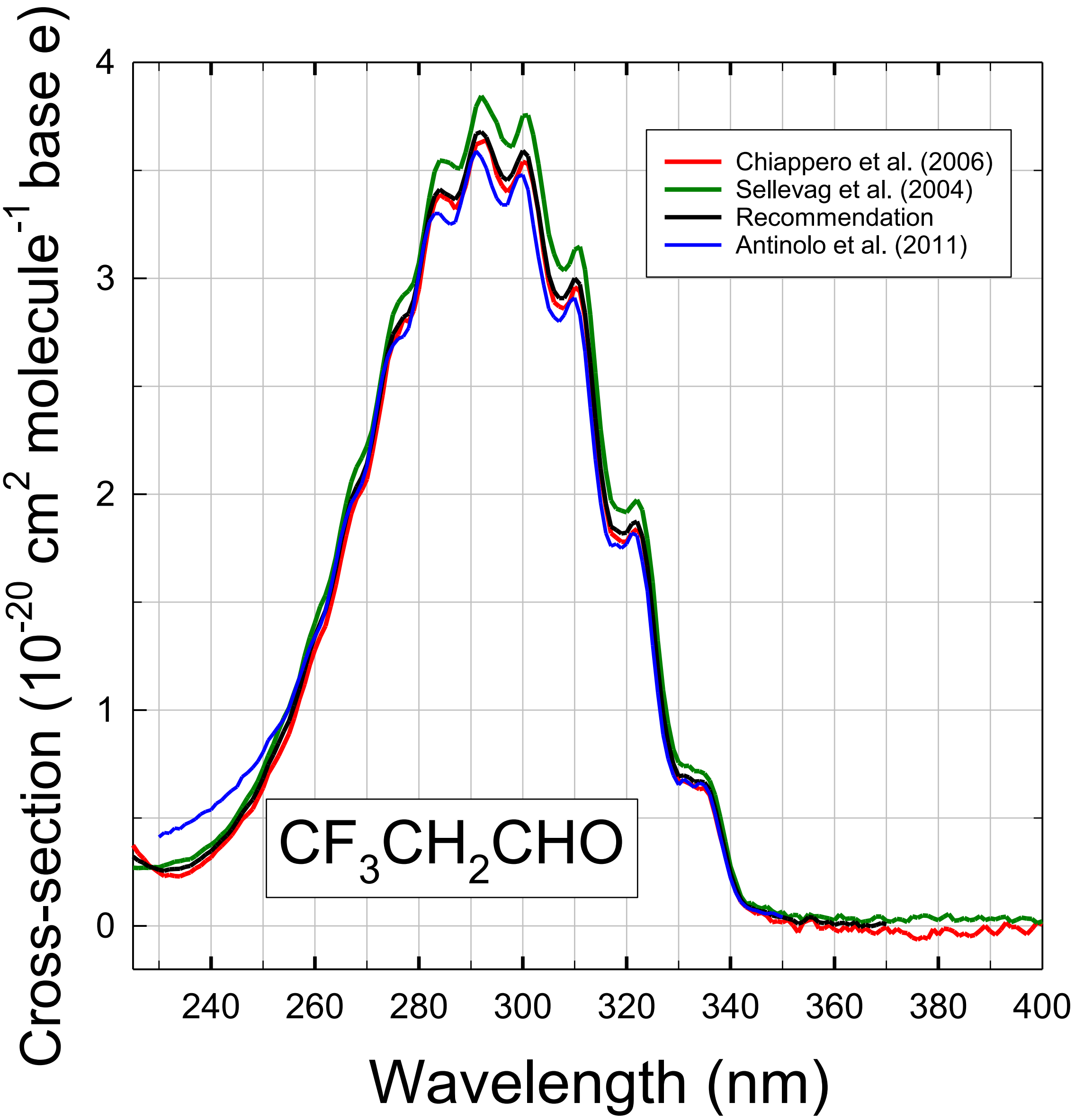
Antiñolo, M., Jiménez, E., and Albaladejo, J.: Phys. Chem. Chem. Phys. 13, 15936, 2011.

Chiappero M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C., Wallington, T. J., Waterland, R. L., and Buck, R. C.: J. Phys. Chem. A, 110, 11944, 2006.

Hashikawa, Y., Kawasaki, M., Waterland, R. L., Sulbaek Andersen, M. P., Nielsen, O. J., Hurley, M. D.; Ball, J. C.; and Wallington, T. J.: J. Fluorine Chem., 125, 1925, 2004.

Sellevåg, S. R., Kelly, T., Sidebottom, H., and Nielsen, C. J.: Phys. Chem. Chem. Phys., 6, 1243, 2004.

Solignac, G., Mellouki, A., Le Bras, G., Yujing, M., Sidebottom, H.: Phys. Chem. Chem. Phys. 9, 4200, 2007.


Cross-section (10^{-20} cm^2 molecule^{-1} base e)
Wavelength (nm)
0
1
2
3
4
240
260
280
300
320
340
360
380
400
Chiappero et al. (2006)
Sellevag et al. (2004)
Recommendation
Antinolo et al. (2011)
CF_3CH_2CHO

PF10: *n*-$C_6F_{13}CH_2CHO$ + hν

Last evaluated: June 2025; last change in preferred values: June 2010.

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n-$C_6F_{13}CH_2CHO + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		
n-$C_6F_{13}CH_2CHO$ + hν	→ *n*-$C_6F_{13}CH_2$ + HCO	(1)
	→ *n*-$C_6F_{13}CH_2CO$ + H	(2)
	→ *n*-$C_6F_{13}CH_3$ + CO	(3)

Absorption cross-section data

Wavelength range/nm	References	Comments
230-400	Chiappero et al. (2006)	(a)
230-350	Solignac et al. (2007)	(b)

Quantum yield data

Measurement	Wavelength/nm	References	Comments
$\Phi_{Total} = 0.55\pm0.09$	254	Chiappero et al. (2006)	(c)

Comments

(a) The UV absorption spectrum was recorded using a single sample of 1.5 mbar of *n*-$C_6F_{13}CH_2CHO$ in a 10 cm quartz cell using a diode array spectrometer at 297 K. The reported UV spectrum of *n*-$C_6F_{13}CH_2CHO$ shows a broad band centered at 295 nm and extending out to approximately 350 nm. Values of σ were given at 1 nm intervals.

(b) Absolute absorption cross-sections were measured with a resolution of 0.1 nm using a diode array spectrometer for 0.6–2.0 Torr (0.8-2.7 mbar) samples of *n*-$C_6F_{13}CH_2CHO$ in a 100 cm cell at 298 K. The UV spectrum of *n*-$C_6F_{13}CH_2CHO$ shows a broad band centered at 285 nm and extending out to approximately 350 nm. Values of σ were given at 1 nm intervals.

(c) Photolysis quantum yield measured using perfluoroacetic anhydride as a chemical actinometer. Mixtures of *n*-$C_6F_{13}CH_2CHO$ and NO (added as radical scavenger) were irradiated using a low pressure Hg lamp and the rate of loss of *n*-$C_6F_{13}CH_2CHO$ was compared to that of perfluoroacetic anhydride in similar experiments.

Preferred Values

Absorption cross-sections of n-$C_6F_{13}CH_2CHO$ at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/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

Quantum Yields of n-$C_6F_{13}CH_2CHO$

Φ_{Total} = 0.55 at 254 nm

Reliability

$\Delta\Phi_{Total} = \pm$ 0.10 at 254 nm

Comments on Preferred Values

The absorption spectrum reported by Chiappero et al. (2006) is based upon the measured absorption by one sample using a 10 cm pathlength and is considered less reliable than that measured by Solignac et al. (2007) using a range of sample partial pressures in a 100 cm absorption cell. The absorption spectrum from Solignac et al. (2007) is recommended.

Chiappero et al. (2006) assumed a wavelength independent photolysis quantum yield of 0.01 for n-$C_6F_{13}CH_2CHO$ (based on an assumption that the quantum yield depends inversely on the molecula size of the fluorinated aldehyde and that the quantum yield for photolysis of n-$C_6F_{13}CH_2CHO$ is approximately one quarter less than that for CF_3CH_2CHO 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 8 days at 11 km altitude and 20 days at 0 km. Measurements of the photolysis quantum yield at atmospherically relevant wavelengths are needed to better understand the role of photolysis in the atmospheric chemistry of this molecule.

References

Chiappero M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C., Wallington, T. J., Waterland, R. L., and Buck, R. C.: J. Phys. Chem. A, 110, 11944, 2006.

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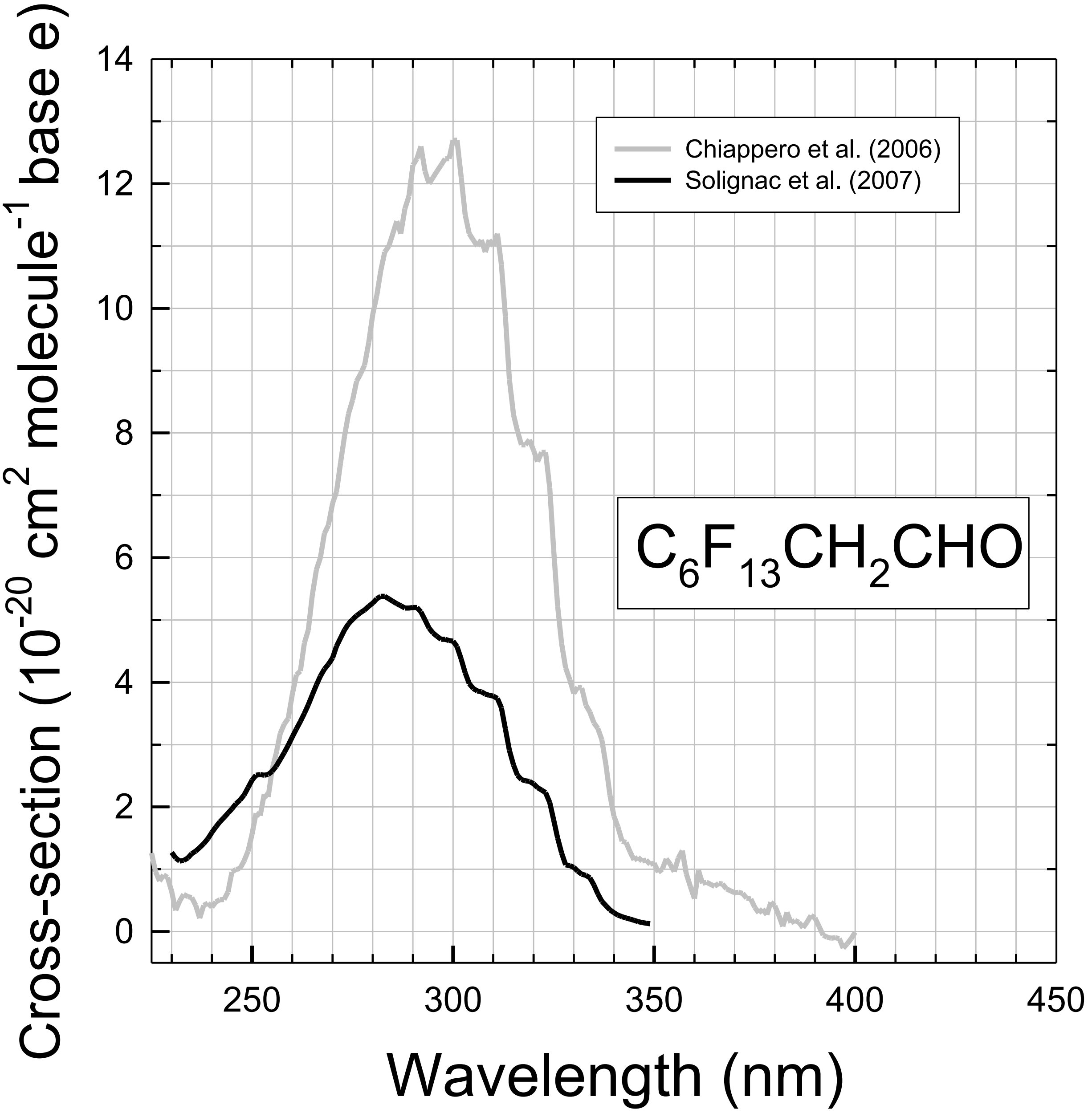

Cross-section (10^{-20} cm^2 molecule^{-1} base e)
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Chiappero et al. (2006)
Solignac et al. (2007)
$C_6F_{13}CH_2CHO$