

Supplement A to “Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VII - Criegee intermediates”:

Detailed data sheets for the reactions of O₃ with alkenes, prepared by the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation. The data sheets are also available at <http://iupac.pole-ether.fr/> (access date: September 2020), where a guide to data sheet format and evaluation methods is also provided.

Contents

A1. Data sheets for reactions of O₃ with small alkenes	1
Ox_VOC5: ethene	1
Ox_VOC6: propene	6
Ox_VOC16: but-1-ene	10
Ox_VOC17: <i>cis</i> -but-2-ene	14
Ox_VOC18: <i>trans</i> -but-2-ene	18
Ox_VOC15: 2-methylpropene	23
Ox_VOC41: 2,3-dimethylbut-2-ene	28
Ox_VOC7: isoprene	32
A2. Data sheets for reactions of O₃ with monoterpenes	38
Ox_VOC8: α-pinene	38
Ox_VOC19: β-pinene	43
Ox_VOC20: limonene	48
Ox_VOC21: camphene	53
Ox_VOC22: 2-carene	56
Ox_VOC23: 3-carene	58
Ox_VOC24: β-myrcene	61
Ox_VOC25: β-ocimene	65
Ox_VOC26: α-phellandrene	69
Ox_VOC27: β-phellandrene	71
Ox_VOC28: sabinene	73
Ox_VOC29: α-terpinene	76
Ox_VOC30: γ-terpinene	78
Ox_VOC31: terpinolene	80

A3. Data sheets for reactions of O₃ with sesquiterpenes	83
Ox_VOC32: β-caryophyllene	83
Ox_VOC33: α-cedrene	87
Ox_VOC34: α-copaene	90
Ox_VOC35: α-farnesene	92
Ox_VOC36: β-farnesene	94
Ox_VOC37: α-humulene	97
Ox_VOC38: isolongifolene	100
Ox_VOC39: longifolene	102
Ox_VOC40: valencene	103
A4. Abbreviations used in data sheets	104

A1. Data sheets for reactions of O₃ with small alkenes

Ox_VOC5: ethene

Last evaluated: August 2020; Last change in preferred values: June 2018

O₃ + C₂H₄ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$3.3 \times 10^{-15} \exp[-(2365 \pm 101)/T]$	178-233	DeMore, 1969	S-UVA (a)
1.18×10^{-18}	298*		
$(1.55 \pm 0.15) \times 10^{-18}$	299	Stedman et al., 1973	S-CL/GC-FID (a)
$9.0 \times 10^{-15} \exp[-(2557 \pm 167)/T]$	235-362	Herron and Huie, 1974	MS/MS (a)
1.69×10^{-18}	298*		
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar et al., 1974, 1976	S-CL/GC-FID (a)
$(1.69 \pm 0.13) \times 10^{-18}$	303	Toby et al., 1976	S-UVA (a)
4.4×10^{-19}	260	Adeniji et al., 1981	S-CL/GC-FID (a)
1.6×10^{-18}	294		
$(1.43 \pm 0.19) \times 10^{-18}$	296	Atkinson et al., 1982	S-CL/GC-FID (a)
$7.72 \times 10^{-15} \exp[-(2557 \pm 30)/T]$	232-298	Bahta et al., 1984	S-UVA (a)
$(1.45 \pm 0.10) \times 10^{-18}$	298		
$5.1 \times 10^{-15} \exp[-(2446 \pm 91)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(1.37 \pm 0.08) \times 10^{-18}$	298		
1.44×10^{-18}	298	Qi et al., 2006	S-FTIR (a)
$(1.46 \pm 0.13) \times 10^{-18}$	296	Søndergaard et al., 2007	S-FTIR (b)
$(1.35 \pm 0.11) \times 10^{-18}$	298	Wang et al., 2007	S-UVA (a)
$(1.72 \pm 0.35) \times 10^{-18}$	298	Wegener et al., 2007	S-UVA/GC-FID (c),(d)
$(1.45 \pm 0.25) \times 10^{-18}$	298	Alam et al., 2011	S-UVA/FTIR (c),(e)

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of ethene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- (b) k determined from the observed first-order rate of ethene decay in the presence of known excess concentrations of ozone, with both reagents measured by FTIR. Cyclohexane added to scavenge HO radicals.
- (c) Experiments carried out with comparable concentrations of each reagent, in the presence of an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with k optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and ethene (measured by the second technique shown).
- (d) CO added to scavenge HO radicals.
- (e) Either CO or cyclohexane added to scavenge HO radicals.

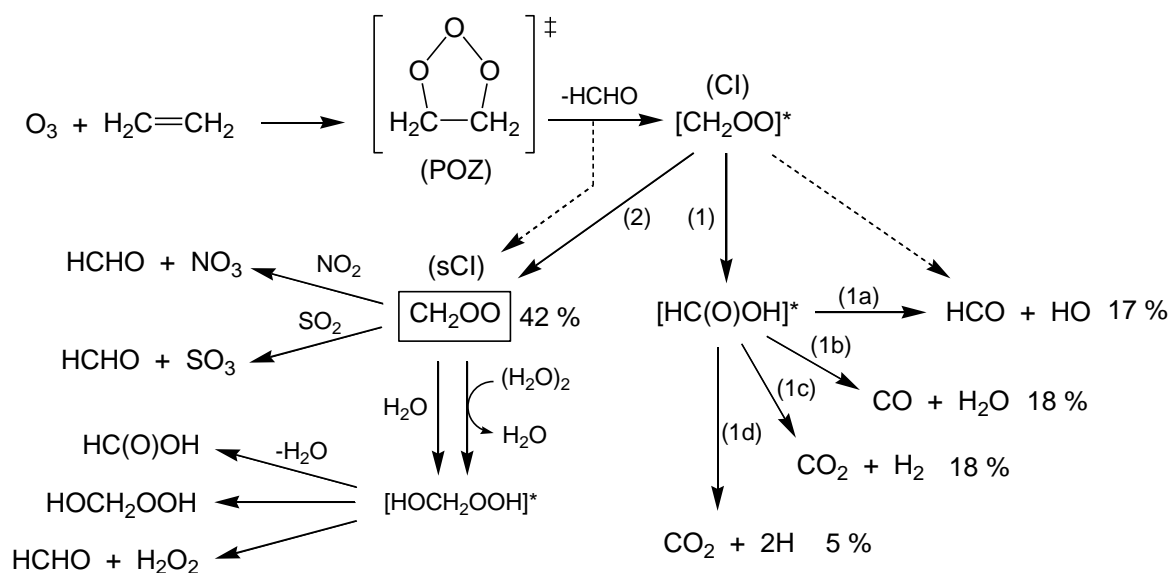
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.55×10^{-18}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$6.82 \times 10^{-15} \exp(-2500/T)$	180-360
<i>Reliability</i>		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 100	180-360

Comments on Preferred Values

The absolute kinetics determinations are in generally good agreement, with consistent values of the temperature coefficient (E/R) reported in a number of studies covering a wide combined temperature range. The preferred value of E/R is a rounded average of those reported by DeMore (1969), Herron and Huie (1974), Bahta et al. (1984) and Treacy et al. (1992). The preferred 298 K rate coefficient is an average of the room temperature determinations reported in all the studies tabulated above, corrected to 298 K, where necessary, using the preferred value of E/R . Note that the 298 K value tabulated here for DeMore et al. (1969) was obtained by extrapolation from the studied temperature range, and was not included in the average.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich “primary ozonide (POZ)” which rapidly decomposes to form an (excited) Criegee intermediate, $[\text{CH}_2\text{OO}]^*$ (CI), and formaldehyde, HCHO (e.g. Johnson and Marston, 2008), as represented in the schematic shown below:



The schematic also shows some established features of the further chemistry of $[\text{CH}_2\text{OO}]^*$, with suggested contributions of a number of product pathways at 298 K and atmospheric pressure, based on a consensus of the literature. Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Atkinson et al., 1992; Paulson et al., 1999; Rickard et al., 1999; Mihelcic et al., 1999; Fenske et al., 2000; Kroll et al., 2001; Alam et al., 2011), with yields in the range 12–22 % (preferred value, 17 ± 5 %). HO is believed to be formed mainly via an excited dioxirane

intermediate, which isomerises to form “hot” formic acid, $[\text{HC(O)OH}]^*$, before fragmenting to HO and HCO (or HO, H and CO) via reaction (1a) (Kroll et al., 2002; Johnson and Marston, 2008); although a minor contribution from direct decomposition of $[\text{CH}_2\text{OO}]^*$ (via a four-membered transition state) cannot be ruled out (Calvert et al., 2000). Formation of HO_2 radicals has also been reported (Mihelcic et al., 1999; Qi et al., 2006; Wegener et al., 2007; Alam et al., 2011), with yields in the range 10–50 % (preferred value, ~ 27 %). It can be formed from the reactions of O_2 with H and HCO, which are produced in reactions (1a) and (1d). The associated chemistry in reactions (1a)–(1d) also produces CO and CO_2 , and the relative contributions assigned to these product pathways are consistent with reported CO and CO_2 yields (e.g. Su et al., 1981; Atkinson, 1990; Thomas et al., 1993; Neeb et al., 1998).

There have been numerous determinations of the yield of the stabilized Criegee intermediate, CH_2OO (sCI), mainly based on addition of scavengers (H_2O , CO, HCHO, HCOOH , $\text{CF}_3\text{C(O)CF}_3$ and SO_2) to the system and quantification of the associated reaction products (Su et al., 1980; Kan et al., 1981; Hatakeyama et al., 1984; 1986; Horie and Moortgat, 1991; Neeb et al., 1996; 1998; Horie et al., 1999; Hasson et al., 2001; Alam et al., 2011; Newland et al., 2015; 2020). CH_2OO yields in the range 35–54 % have been obtained at room temperature and atmospheric pressure (preferred value, 42 ± 10 %). The yield appears to display a dependence on total pressure, with a significant fraction of stabilised CH_2OO reported to be formed at low pressures (Hatakeyama et al., 1986). By extrapolation of measurements made down to 13 mbar, they found the yield to be reduced by about a factor of two at zero pressure, suggesting significant (~ 20 %) direct formation of stabilised CH_2OO (and HCHO) from the decomposition of POZ.

Based on reported kinetic data (summarised and evaluated in datasheets CGI_1 to CGI_12), the major fate of CH_2OO under tropospheric conditions is expected to be removal via bimolecular reactions, particularly with $(\text{H}_2\text{O})_2$, as illustrated in the schematic above.

References

- Adeniji, A. A., Kerr, J. A. and Williams, M. R.: *Int. J. Chem. Kinet.*, 13, 209, 1981.
- Alam, M. S., Camredon, M., Rickard, A. R., Carr, T., Wyche, K. P., Hornsby, K. E., Monks, P. S. and Bloss, W. J.: *Phys. Chem. Chem. Phys.*, 13, 11002, 2011.
- Atkinson, R.: *Atmos. Environ.*, 24A, 1, 1990.
- Atkinson, R.: *J. Phys. Chem. Ref. Data*, 26, 215, 1997.
- Atkinson, R., Aschmann, S. M., Fitz, D. R., Winer, A. M. and Pitts Jr., J. N.: *Int. J. Chem. Kinet.*, 14, 13, 1982.
- Atkinson, R., Aschmann, S. M., Arey, J. and Shorees, B.: *J. Geophys. Res.*, 97, 6065, 1992.
- Bahta, A., Simonaitis, R. and Hecklen, J.: *Int. J. Chem. Kinet.*, 16, 1227, 1984.
- Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J. and Yarwood, G.: *The mechanisms of atmospheric oxidation of the alkenes*, Oxford University Press, Oxford. ISBN 0-19-513177-0, 2000.
- DeMore, W. B.: *Int. J. Chem. Kinet.*, 1, 209, 1969.
- Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: *J. Phys. Chem. A*, 104, 7821, 2000.
- Grosjean, E. and Grosjean, D.: *Environ. Sci. Technol.*, 30, 2036, 1996.
- Grosjean, E., de Andrade, J. B. and Grosjean, D.: *Environ. Sci. Technol.*, 30, 975, 1996.
- Hasson, A. S., Orzechowska, G. and Paulson, S. E.: *J. Geophys. Res.*, 106, 34131, 2001.
- Hatakeyama, S., Kobayashi, H. and Akimoto, H.: *J. Phys. Chem.*, 88, 4736, 1984.
- Hatakeyama, S., Kobayashi, H., Lin, Z.-Y., Takagi, H. and Akimoto, H.: *J. Phys. Chem.*, 90, 4131, 1986.
- Herron, J. T. and Huie, R. E.: *J. Phys. Chem.*, 78, 2085, 1974.
- Herron, J. T. and Huie, R. E.: *J. Am. Chem. Soc.*, 99, 5430, 1977.
- Horie, O. and Moortgat, G. K.: *Atmos. Environ.*, 25A, 1881, 1991.

Horie, O., Schafer, C. and Moortgat, G. K.: *Int. J. Chem. Kinet.*, 31, 261, 1999.

Japar, S. M., Wu, C. H. and Niki, H.: *J. Phys. Chem.*, 78, 2318, 1974.

Japar, S. M., Wu, C. H. and Niki, H.: *J. Phys. Chem.*, 80, 2057, 1976.

Johnson, D. and Marston, G.: *Chem. Soc. Rev.*, 37, 699, 2008.

Kan, C. S., Su, F., Calvert, J. G. and Shaw, J. H.: *J. Phys. Chem.*, 85, 2359, 1981.

Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: *J. Phys. Chem. A*, 105, 4446, 2001.

Kroll, J. H., Donahue, N. M., Cee, V. J., Demerjian, K. L. and Anderson, J. G.: *J. Am. Chem. Soc.*, 124, 8518, 2002.

Mihelcic, D., Heitlinger, M., Kley, D., Musgen P. and Volz-Thomas, A.: *Chem. Phys. Lett.*, 301, 559, 1999.

Neeb, P., Horie, O. and Moortgat, G. K.: *Int. J. Chem. Kinet.*, 28, 721, 1996.

Neeb, P., Horie, O. and Moortgat, G. K.: *J. Phys. Chem. A*, 102, 6778, 1998.

Newland, M. J., Rickard, A. R., Alam, M. S., Vereecken, L., Muñoz, A., Ródenas, M. and Bloss, W. J.: *Phys. Chem. Chem. Phys.*, 17, 4076-4088, 2015.

Newland, M. J., Nelson, B. S., Muñoz, A., Ródenas, M., Vera, T., Tárrega, J., and Rickard, A. R.: *Phys. Chem. Chem. Phys.*, 22, 13698, 2020.

Niki, H., Maker, P. D., Savage, C. M. and Breitenbach, L. P.: *J. Phys. Chem.*, 85, 1024, 1981.

Paulson, S. E., Fenske, J. D., Sen, A. D. and Callahan, T. W.: *J. Phys. Chem. A*, 103, 2050, 1999.

Qi, B., Sato, K., Imamura, T., Takami, A., Hatakeyama, S. and Ma, Y.: *Chem. Phys. Lett.*, 427, 461, 2006.

Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: *J. Phys. Chem. A*, 103, 7656, 1999.

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

Stedman, D. H., Wu, C. H. and Niki, H.: *J. Phys. Chem.*, 77, 2511, 1973.

Su, F., Calvert, J. G. and Shaw, J. H.: *J. Phys. Chem.*, 84, 239, 1980.

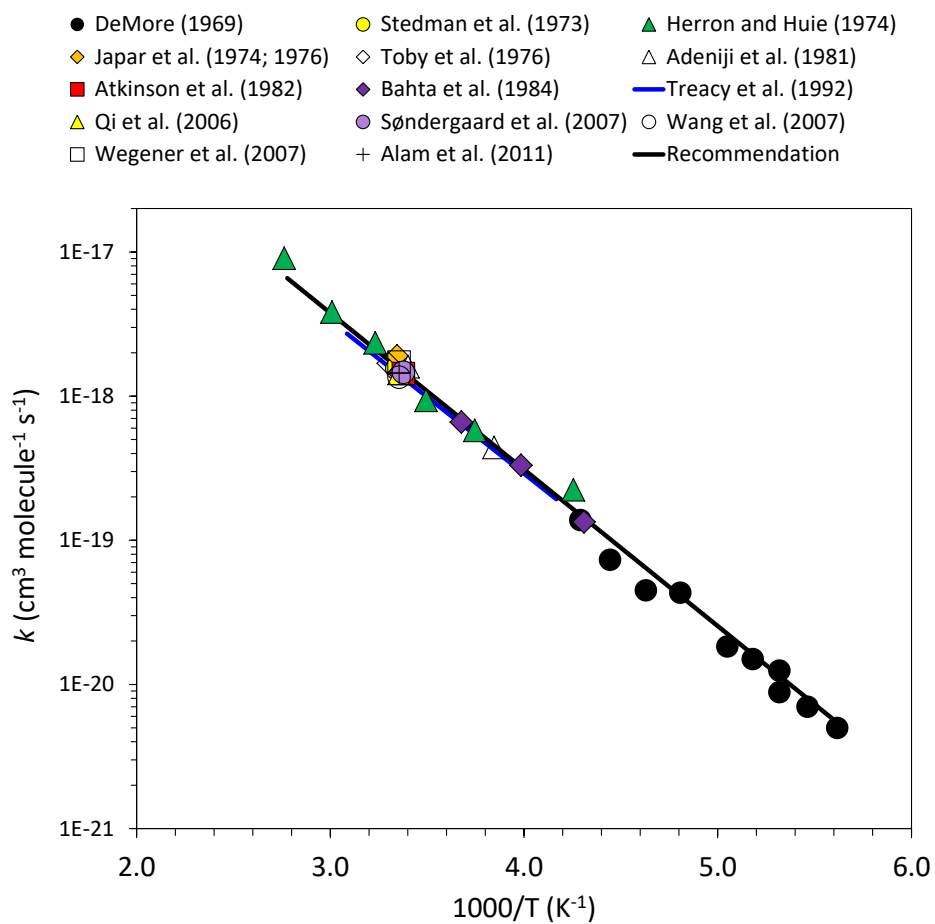
Thomas, W., Zabel, F., Becker, K. H. and Fink, E. H.: *Proceedings of the 1st European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants*, Varese, Italy, 207, 1993.

Toby, F. S., Toby, S. and O'Neal, H. E.: *Int. J. Chem. Kinet.*, 8, 25, 1976.

Treacy, J., El Hag, M., O'Farrell, D. and Sidebottom, H.: *Ber. Bunsenges. Phys. Chem.*, 96, 422, 1992.

Wang, H. T., Zhang, Y. J. and Mu, Y. J.: *J. Environ. Sci. Chi.*, 19, 641, 2007.

Wegener, R., Brauers, T., Koppmann, R., Bares, S. R., Rohrer, F., Tillmann, R., Wahner, A., Hansel, A. and Wisthaler, A.: *J. Geophys. Res. Atmos.*, 112, 2007, doi: 10.1029/2006JD007531.



Ox_VOC6: propene

Last evaluated: August 2020; Last change in preferred values: July 2018

O₃ + C₃H₆ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.26×10^{-17}	295	Cox and Penkett, 1972	S-CL/GC-FID (a)
$(1.25 \pm 0.10) \times 10^{-17}$	299	Stedman et al., 1973	S-CL/GC-FID (a)
$6.14 \times 10^{-15} \exp[-(1897 \pm 109)/T]$	235-362	Herron and Huie, 1974	MS/MS (a),(b)
1.06×10^{-17}	298*		
$(1.3 \pm 0.1) \times 10^{-17}$	299	Japar et al., 1974, 1976	S-CL/GC-FID (a)
5.1×10^{-18}	260	Adeniji et al., 1981	S-CL/GC-FID (a)
1.26×10^{-17}	294		
$(1.04 \pm 0.14) \times 10^{-17}$	296	Atkinson et al., 1982	S-CL/GC-FID (a)
$4.9 \times 10^{-15} \exp[-(1858 \pm 70)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(9.4 \pm 0.4) \times 10^{-18}$	298		
1.15×10^{-17}	296 ± 2	Neeb and Moortgat, 1999	S-FTIR (c)
$5.8 \times 10^{-15} \exp[-(1907 \pm 53)/T]$	282-314	Jia et al., 2006	S-UVA/GC-FID (a)
1.01×10^{-17}	300		
$(1.06 \pm 0.12) \times 10^{-17}$	298	Wegener et al., 2007	S-UVA/GC-FID (d)

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of propene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- (b) Due to a typographical error, the lowest temperature studied was 235.0 K and not 250.0 K as stated in Table 2 of Herron and Huie (1974).
- (c) k determined from the observed first-order rate of propene decay in the presence of known excess concentrations of ozone, with both reagents measured by FTIR. Cyclohexane added to scavenge HO radicals.
- (d) Experiments carried out with comparable concentrations of each reagent, in the presence of excess CO as an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with k optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and propene (measured by the second technique shown).

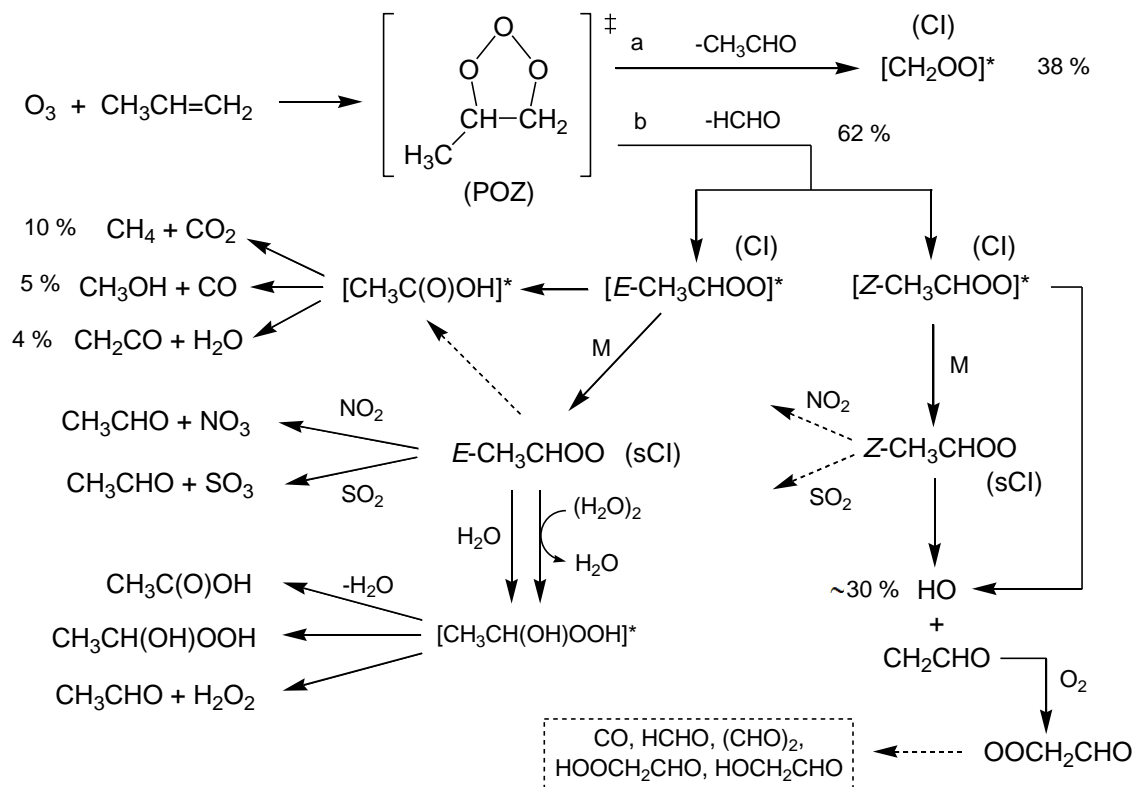
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.05×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$5.77 \times 10^{-15} \exp(-1880/T)$	230-370
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298
$\Delta E/R$	± 100	230-370

Comments on Preferred Values

The absolute kinetics determinations are in generally good agreement, with consistent values of the temperature coefficient (E/R) reported in a number of studies. The preferred value of E/R is a rounded average of those reported by Herron and Huie (1974) and Treacy et al. (1992), which is also consistent with those reported by Adeniji et al. (1981) and Jia et al. (2006) over narrow temperature ranges. The preferred value of k at 298 K is an average of the room temperature determinations reported by Herron and Huie (1974), Atkinson et al. (1982), Treacy et al. (1992), Neeb and Moortgat (1999), Jia et al. (2006) and Wegener et al. (2007), corrected to 298 K, where necessary, using the preferred value of E/R . The other tabulated determinations are consistent with this recommendation, being about 20-30 % higher than the preferred value.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich “primary ozonide (POZ)” which rapidly decomposes to form two sets of “primary” carbonyl product plus (excited) Criegee intermediate, as shown in the schematic below. Reported primary yields of acetaldehyde (CH_3CHO) and formaldehyde (HCHO) suggest important contributions from both decomposition channels, (a) and (b), with $k_b/(k_a+k_b)$ lying in the range 0.60-0.65 (Horie and Moortgat 1991; Grosjean et al., 1996; Tuazon et al., 1997; Rickard et al., 1999; Newland et al., 2020), consistent with the values given in the schematic.



The further chemistry of $[\text{CH}_2\text{OO}]^*$, formed from channel (a), is expected to follow the pathways described in the data sheet for the $\text{O}_3 + \text{C}_2\text{H}_4$ reaction (Ox_VOC5), although their relative importance is not necessarily the same. Channel (b) forms either $[E\text{-CH}_3\text{CHOO}]^*$ or $[Z\text{-CH}_3\text{CHOO}]^*$, in conjunction with HCHO. The schematic above shows some established features of the further chemistry of these excited Criegee intermediates, with suggested contributions of a number of product pathways at 298 K and atmospheric pressure, based on a consensus of the literature. They may either decompose via a number of possible pathways, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI), i.e. $E\text{-CH}_3\text{CHOO}$ and $Z\text{-CH}_3\text{CHOO}$ (Fenske et al., 2000a).

Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Atkinson and Aschmann, 1993; Neeb and Moortgat, 1999; Paulson et al., 1999; Rickard et al., 1999; Aschmann et al., 2003; Wegener et al., 2007; Qi et al., 2009; Alam et al., 2013), with yields in the range 30–40 % (preferred value, 36 ± 4 %). HO is expected to be formed mainly from either $[Z\text{-CH}_3\text{CHOO}]^*$ or $Z\text{-CH}_3\text{CHOO}$, by an accepted decomposition mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000b; Kroll et al., 2001), also forming the vinoxy radical (CH_2CHO) as a co-product. A minor contribution to HO formation may also result from decomposition of $[\text{CH}_2\text{OO}]^*$. Assuming that the relative importance of the reaction pathways for $[\text{CH}_2\text{OO}]^*$ formed from propene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene, this contribution is estimated to be about 6 %, suggesting that decomposition of $[Z\text{-CH}_3\text{CHOO}]^*$ and $Z\text{-CH}_3\text{CHOO}$ contributes about 30 %. The vinoxy radical (CH_2CHO) reacts with O_2 under atmospheric conditions. At 1 bar, this is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO, HO_2 and other peroxy radicals) to form a number of products as shown, including secondary HCHO and glyoxal, $(\text{CHO})_2$, which has been reported to be formed with a yield of about 3 % (Tuazon et al., 1997). At pressures below about 270 mbar, the (chemically-activated) peroxy radical adduct has also been reported to decompose (e.g. to form $\text{HO} + \text{HCHO} + \text{CO}$), thereby providing a small secondary source of HO radicals (Oguchi et al., 2004).

Evidence for the decomposition pathways for $[E\text{-CH}_3\text{CHOO}]^*$ shown in the schematic (proceeding via formation of “hot” acetic acid, $[\text{CH}_3\text{C}(\text{O})\text{OH}]^*$) has been reported by Tuazon et al. (1997), with the suggested contributions based on the yields of methane (CH_4), methanol (CH_3OH) and ketene (CH_2CO) reported in that study.

The total yield of stabilized Criegee intermediates (sCI) in the system ($\text{CH}_2\text{OO} + E\text{-CH}_3\text{CHOO} + Z\text{-CH}_3\text{CHOO}$) at atmospheric pressure has been determined by scavenging with added SO_2 and quantifying the associated products, H_2SO_4 (Hatekayama et al., 1984) or HCHO and CH_3CHO (Newland et al., 2020). The recommended total yield, based on these studies, is 30 ± 10 %. Newland et al. (2020) report that CH_2OO makes a major contribution, accounting for about two-thirds of the total.

Based on reported kinetic data (summarised and evaluated in datasheets CGI_15 to CGI_17), the major fate of $E\text{-CH}_3\text{CHOO}$ under tropospheric conditions is expected to be removal via bimolecular reactions, in particular with H_2O and $(\text{H}_2\text{O})_2$, as illustrated in the schematic above. The major fate of $Z\text{-CH}_3\text{CHOO}$ is expected to be thermal decomposition, as described above.

References

- Adeniji, A. A., Kerr, J. A. and Williams, M. R.: Int. J. Chem. Kinet., 13, 209, 1981.
 Alam, M. S., Rickard, A. R., Camredon, M., Wyche, K. P., Carr, T., Hornsby, K. E., Monks, P. S. and Bloss, W. J.: J. Phys. Chem., 117, 12468, 2013.
 Aschmann, S. M., Tuazon, E. C., Arey, J. and Atkinson, R.: J. Phys. Chem. A, 107, 2247, 2003.
 Atkinson, R. and Aschmann, S. M.: Environ. Sci. Technol., 27, 1357, 1993.
 Atkinson, R., Aschmann, S. M., Fitz, D. R., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 14, 13, 1982.
 Cox, R. A. and Penkett, S. A.: J. Chem. Soc., Faraday Trans. 1, 68, 1735, 1972.
 Fenske, J. D., Hasson, A. S., Ho, A. W. and Paulson, S. E.: J. Phys. Chem. A, 104, 9921, 2000a.

Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: J. Phys. Chem. A, 104, 7821, 2000b.

Grosjean, E., de Andrade, J. B. and Grosjean, D.: Environ. Sci. Technol., 30, 975, 1996.

Hatakeyama, S., Kobayashi, H. and Akimoto, H.: J. Phys. Chem., 88, 4736, 1984.

Herron, J. T. and Huie, R. E.: J. Phys. Chem., 78, 2085, 1974.

Horie, O. and Moortgat, G. K.: Atmos. Environ., 25A, 1881, 1991.

Japar, S. M., Wu, C. H. and Niki, H.: J. Phys. Chem., 78, 2318, 1974.

Japar, S. M., Wu, C. H. and Niki, H.: J. Phys. Chem., 80, 2057, 1976.

Jia, L., Xu, L., Ge, M., Du, L., Wang, G. and Zhuang, G.: Acta Phys. -Chim. Sin., 22(10), 1260, 2006.

Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: J. Phys. Chem. A, 105, 4446, 2001.

Neeb, P. and Moortgat, G. K.: J. Phys. Chem. A, 103, 9003, 1999.

Newland, M. J., Nelson, B. S., Muñoz, A., Ródenas, M., Vera, T., Tárrega, J., and Rickard, A. R.: Phys. Chem. Chem. Phys., 22, 13698, 2020.

Oguchi, T, Sato, Y., Matsui, H., 18th Symposium on Gas Kinetics, Bristol, UK, 2004. Poster B13.

Paulson, S. E., Fenske, J. D., Sen, A. D. and Callahan, T. W.: J. Phys. Chem. A, 103, 2050, 1999.

Qi, B., Yang, B., Wang, Z. Q., Yang, H. Y. and Liu, L.: Sci. China, Ser. B: Chem., 52, 356, 2009.

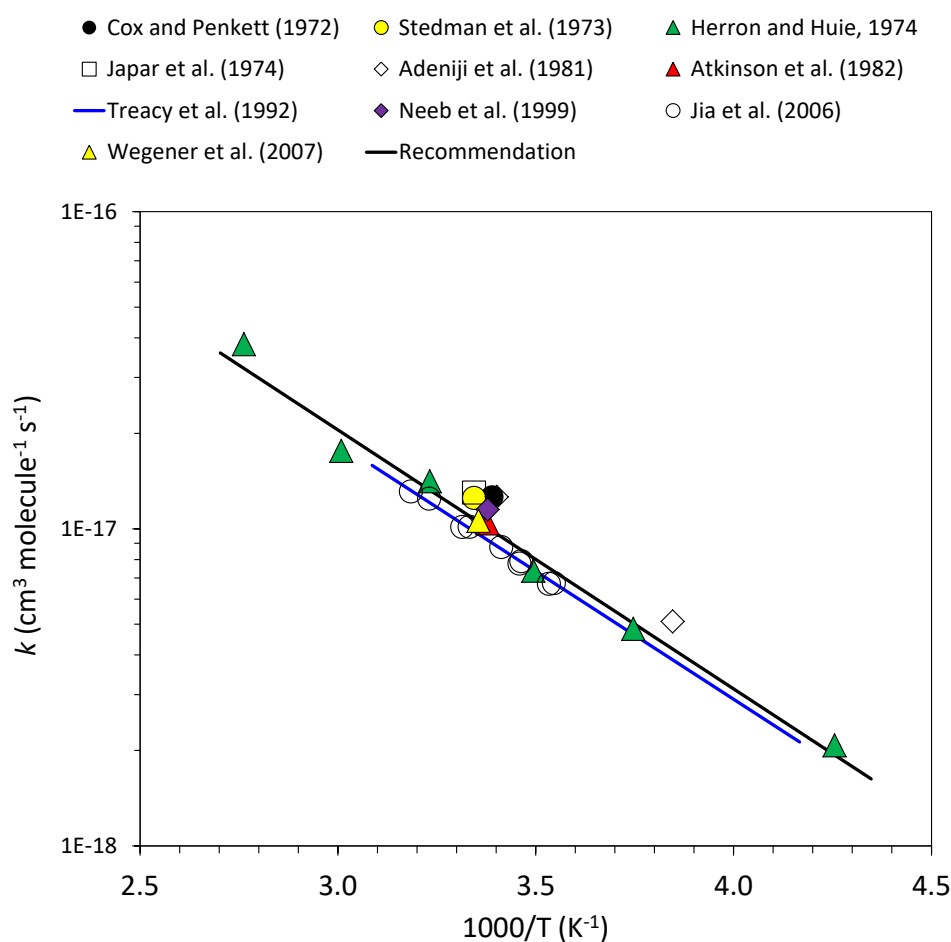
Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: J. Phys. Chem. A, 103, 7656, 1999.

Stedman, D. H., Wu, C. H. and Niki, H.: J. Phys. Chem., 77, 2511, 1973.

Treacy, J., El Hag, M., O'Farrell, D. and Sidebottom, H.: Ber. Bunsenges. Phys. Chem., 96, 422, 1992.

Tuazon, E. C., Aschmann, S. M., Arey, J. and Atkinson, R.: Environ. Sci. Technol., 31, 3004, 1997.

Wegener, R., Brauers, T., Koppmann, R., Bares, S. R., Rohrer, F., Tillmann, R., Wahner, A., Hansel, A. and Wisthaler, A.: J. Geophys. Res. Atmos., 112, 2007, doi: 10.1029/2006JD007531.



Ox_VOC16: but-1-ene

Last evaluated: July 2018; Last change in preferred values: July 2018

O₃ + but-1-ene → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.23 \pm 0.04) \times 10^{-17}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
$2.93 \times 10^{-15} \exp[-(1686 \pm 20)/T]$	225-363	Huie and Herron, 1975	MS/MS (a)
1.03×10^{-17}	298*		
5.3×10^{-18}	260 ± 2	Adeniji et al., 1981	S-CL/GC-FID (a)
1.24×10^{-17}	294 ± 2		
$3.7 \times 10^{-15} \exp[-(1801 \pm 155)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(8.8 \pm 0.6) \times 10^{-18}$	298		
$(9.64 \pm 0.87) \times 10^{-18}$	298	Wegener et al., 2007	S-UVA/GC-FID (b)
$3.5 \times 10^{-15} \exp[-(1756 \pm 84)/T]$	294.9-350.2	Shi et al., 2011	S-UVA (a)
9.66×10^{-18}	298*		
<i>Relative Rate Coefficients</i>			
$(9.85 \pm 0.03) \times 10^{-18}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (c)
$4.0 \times 10^{-15} \exp[-(1754 \pm 46)/T]$	278-353	Avzianova and Ariya, 2002	RR/GC-FID (d)
$(1.14 \pm 0.09) \times 10^{-17}$	298		

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of but-1-ene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- (b) Experiments carried out with comparable concentrations of each reagent, in the presence of excess CO as an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with k optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and but-1-ene (measured by the second technique shown).
- (c) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of but-1-ene and propene (the reference compound) were measured by GC. The measured value of $k(\text{O}_3 + \text{but-1-ene})/k(\text{O}_3 + \text{propene}) = 0.975 \pm 0.030$ is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (d) Relative rate study, with 1,3,5-trimethylbenzene present to scavenge HO radicals. The concentrations of but-1-ene and propene (the reference compound) were measured by GC. The measured rate coefficient ratios were not tabulated. The expression $k(\text{O}_3 + \text{but-1-ene})/k(\text{O}_3 + \text{propene}) = 0.694 \exp[(126 \pm 46)/T]$, derived from the data, is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 5.77 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

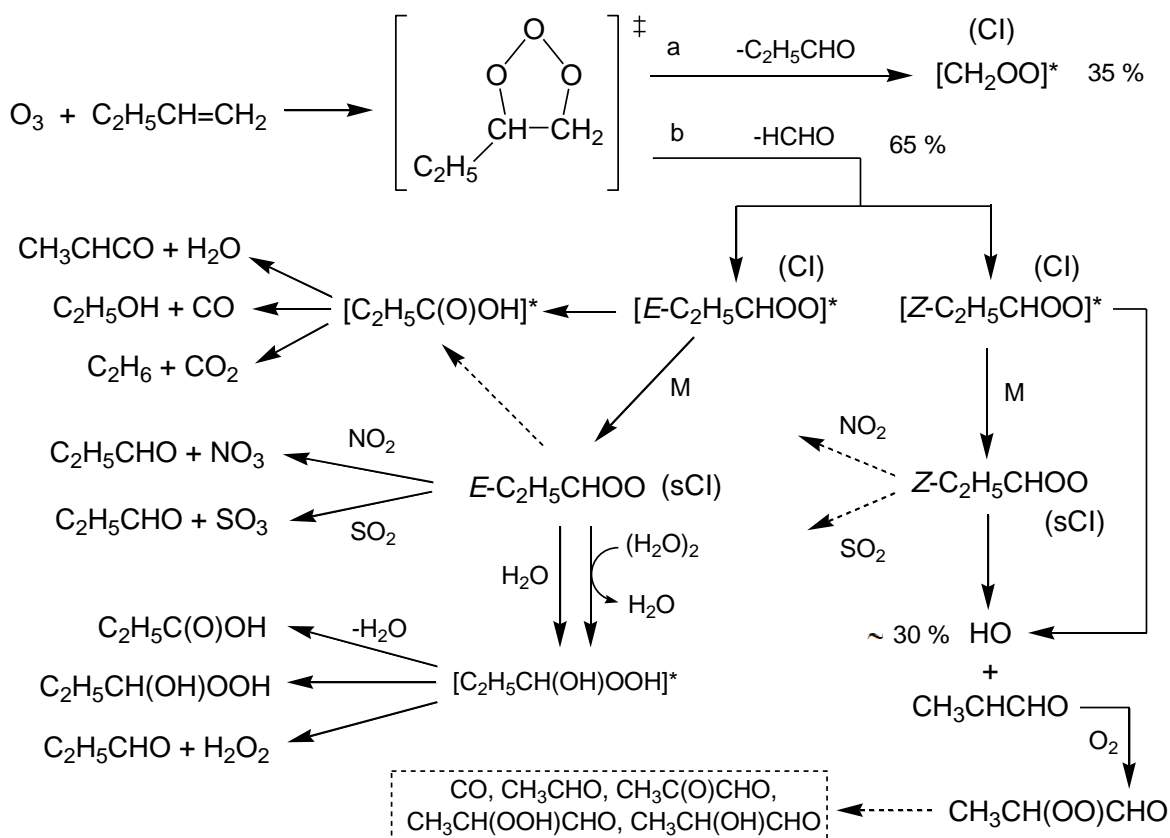
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.0×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.55 \times 10^{-15} \exp(-1750/T)$	220-370
<i>Reliability</i>		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 200	220-370

Comments on Preferred Values

The kinetics determinations are in generally good agreement, with consistent values of the temperature coefficient (E/R) reported in a number of studies. The preferred value of E/R is the average of those reported by Huie and Herron (1975), Treacy et al. (1992), Avzianova and Ariya (2002) and Shi et al. (2011), which is also consistent with the relative values reported at 260 K and 294 K by Adeniji et al. (1981). The preferred value of k at 298 K is an average of the room temperature determinations reported by Huie and Herron (1975), Treacy et al. (1992), Greene and Atkinson (1992), Avzianova and Ariya (2002), Wegener et al. (2007) and Shi et al. (2011), corrected to 298 K, where necessary, using the preferred value of E/R . The other tabulated determinations are consistent with this recommendation, being about 20-30 % higher than the preferred value.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich “primary ozonide” which rapidly decomposes to form two sets of primary carbonyl product plus (excited) Criegee intermediate, as shown in the schematic below. Reported primary yields of propanal ($\text{C}_2\text{H}_5\text{CHO}$) and formaldehyde (HCHO) suggest important contributions from both decomposition channels, (a) and (b), with $k_b/(k_a+k_b) \approx 0.65$ (Grosjean et al., 1996; Paulson et al., 1999; Hasson et al., 2001).



The further chemistry of $[\text{CH}_2\text{OO}]^*$ is expected to follow the pathways described in the data sheet for the $\text{O}_3 + \text{C}_2\text{H}_4$ reaction (Ox_VOC5), although their relative importance is not necessarily the same. Channel (b) forms either $[\text{E-C}_2\text{H}_5\text{CHOO}]^*$ or $[\text{Z-C}_2\text{H}_5\text{CHOO}]^*$, in conjunction with HCHO . The schematic above shows some probable features of the further chemistry of these excited Criegee intermediates, based partly by analogy with *E*- and *Z*- $[\text{CH}_3\text{CHOO}]^*$ conformers formed in the $\text{O}_3 + \text{C}_3\text{H}_6$ system (Ox_VOC6). Where shown, product yields are appropriate to 298 K and atmospheric pressure. $[\text{E-C}_2\text{H}_5\text{CHOO}]^*$ and $[\text{Z-C}_2\text{H}_5\text{CHOO}]^*$ may either decompose via a number of possible pathways, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI), i.e. *E*- $\text{C}_2\text{H}_5\text{CHOO}$ and *Z*- $\text{C}_2\text{H}_5\text{CHOO}$ (Fenske et al., 2000a).

Direct and indirect evidence for the formation of HO radicals has been reported in several studies (e.g. Atkinson and Aschmann, 1993; Paulson et al., 1999; Fenske et al., 2000b; Wegener et al., 2007; Alam et al., 2013), with yields in the range 26–56 % (preferred value, 38 ± 18 %). HO is expected to be formed mainly from either $[\text{Z-C}_2\text{H}_5\text{CHOO}]^*$ or *Z*- $\text{C}_2\text{H}_5\text{CHOO}$, by an accepted decomposition mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000b; Kroll et al., 2001), also forming the 2-methylvinoxy radical (CH_3CHCHO) as a co-product. A minor contribution to HO formation may also result from decomposition of $[\text{CH}_2\text{OO}]^*$. Assuming that the relative importance of the reaction pathways for $[\text{CH}_2\text{OO}]^*$ formed from but-1-ene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene, this contribution is estimated to be about 6 %, suggesting that decomposition of $[\text{Z-C}_2\text{H}_5\text{CHOO}]^*$ and *Z*- $\text{C}_2\text{H}_5\text{CHOO}$ contributes about 30 %. The 2-methylvinoxy radical (CH_3CHCHO) reacts with O_2 under atmospheric conditions (Oguchi et al., 2001). At 1 bar, this is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO, HO_2 and other peroxy radicals) to form a number of products as shown. No direct evidence has been reported for the other decomposition pathways shown for $[\text{E-C}_2\text{H}_5\text{CHOO}]^*$ (proceeding via formation of “hot” propanoic acid, $[\text{CH}_3\text{C}(\text{O})\text{OH}]^*$), but they are inferred from the corresponding products reported for the reaction of ozone with propene (see datasheet Ox_VOC6).

The total yield of stabilized Criegee intermediates (sCI) in the system ($\text{CH}_2\text{OO} + \text{E-C}_2\text{H}_5\text{CHOO} + \text{Z-C}_2\text{H}_5\text{CHOO}$) has been reported to be 27 % by Hasson et al. (2001), based on scavenging with added H_2O and quantification of the yields of associated products (HOCH_2OOH , $\text{C}_2\text{H}_5\text{CHO}$ and H_2O_2). Assuming that the relative importance of the reaction pathways for $[\text{CH}_2\text{OO}]^*$ formed from but-1-ene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene, CH_2OO makes a significant estimated contribution (~ 15 %) to the total sCI yield.

The major fate of *E*- CH_3CHOO under tropospheric conditions is expected to be removal via bimolecular reactions, particularly with H_2O and $(\text{H}_2\text{O})_2$, as illustrated in the schematic above. The major fate of *Z*- $\text{C}_2\text{H}_5\text{CHOO}$ is expected to be thermal decomposition, as described above.

References

- Adeniji, S. A., Kerr, J. A. and Williams, M. R.: Int. J. Chem. Kinet., 13, 209, 1981.
 Alam, M. S., Rickard, A. R., Camredon, M., Wyche, K. P., Carr, T., Hornsby, K. E., Monks, P. S. and Bloss, W. J.: J. Phys. Chem., 117, 12468, 2013.
 Atkinson, R. and Aschmann, S. M.: Environ. Sci. Technol., 27, 1357, 1993.
 Avzianova, E. V. and Ariya, P. A.: Int. J. Chem. Kinet., 34, 678, 2002.
 Fenske, J. D., Hasson, A. S., Ho, A. W. and Paulson, S. E.: J. Phys. Chem. A, 104, 9921, 2000a.
 Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: J. Phys. Chem. A, 104, 7821, 2000b.
 Greene, C. R. and Atkinson, R.: Int. J. Chem. Kinet., 24, 803, 1992.
 Grosjean, E., de Andrade, J. B. and Grosjean, D.: Environ. Sci. Technol., 30, 975, 1996.
 Hasson, A. A., Ho, A. W., Kuwata, K. T. and Paulson, S. E.: J. Geophys. Res., 106, 34143, 2001.
 Huie, R. E. and Herron, J. T.: Int. J. Chem. Kinet., Symp. 1, 165, 1975.
 Japar, S. M., Wu, C. H. and Niki, H.: J. Phys. Chem., 78, 2318, 1974.

Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: J. Phys. Chem. A, 105, 4446, 2001.

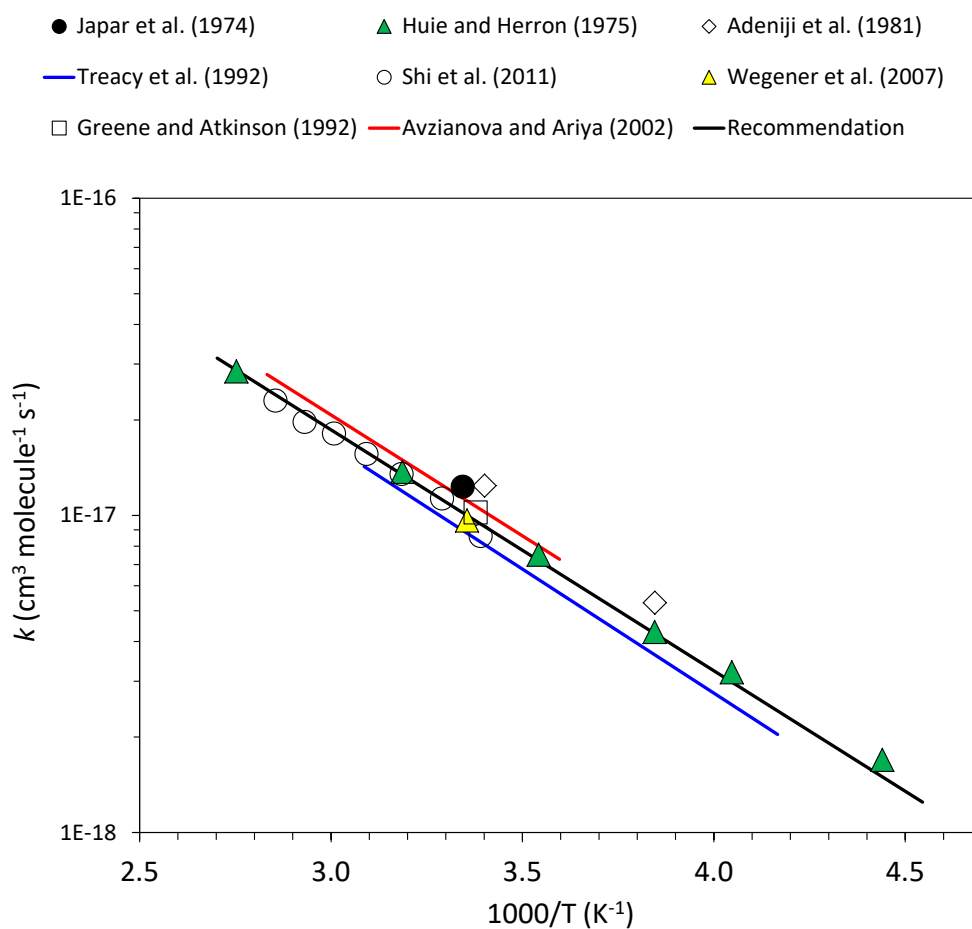
Oguchi, T., Miyoshi, A., Koshi, M., Matsui, H. and Washida, N.: J. Phys. Chem. A, 105, 378, 2001.

Paulson, S. E., Chung, M. Y., Hasson, A. S.: J. Phys. Chem. A, 103, 8125, 1999.

Shi, Y.Z., Xu, Y.F. and Jia, L.: Int. J. Chem. Kinet., 43, 238, 2011.

Treacy, J., El Haag, M., O'Farrell, D. and Sidebottom, H.: Ber. Bunsenges. Phys. Chem., 96, 422, 1992.

Wegener, R., Brauers, T., Koppmann, R., Bares, S. R., Rohrer, F., Tillmann, R., Wahner, A., Hansel, A. and Wisthaler, A.: J. Geophys. Res. Atmos., 112, 2007, doi: 10.1029/2006JD007531.



Ox_VOC17: *cis*-but-2-ene

Last evaluated: July 2018; Last change in preferred values: July 2018

O₃ + *cis*-but-2-ene → products**Rate coefficient data**

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.41×10^{-16}	296	Cox and Penkett, 1972	S-CL/GC-FID (a)
$(1.05 \pm 0.32) \times 10^{-16}$	298	Finlayson et al., 1974	S-UVA/GC-FID (a)
$(1.61 \pm 0.07) \times 10^{-16}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
$3.11 \times 10^{-15} \exp[-(956 \pm 54)/T]$	225-364	Huie and Herron, 1975	MS/MS (a)
1.26×10^{-16}	298*		
$(1.38 \pm 0.16) \times 10^{-16}$	297 ± 1	Atkinson et al., 1983	S-CL/GC-FID (a)
$3.4 \times 10^{-15} \exp[-(979 \pm 22)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(1.23 \pm 0.18) \times 10^{-16}$	298		
$(1.29 \pm 0.11) \times 10^{-16}$	298	Wegener et al., 2007	S-UVA/GC-FID (b)
<i>Relative Rate Coefficients</i>			
$(1.29 \pm 0.08) \times 10^{-16}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (c)

Comments

- (a) *k* determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of *cis*-but-2-ene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- (b) Experiments carried out with comparable concentrations of each reagent, in the presence of excess CO as an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with *k* optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and *cis*-but-2-ene (measured by the second technique shown).
- (c) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of *cis*-but-2-ene and propene (the reference compound) were measured by GC. The measured value of $k(\text{O}_3 + \text{cis-but-2-ene})/k(\text{O}_3 + \text{propene}) = 12.8 \pm 0.8$ is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

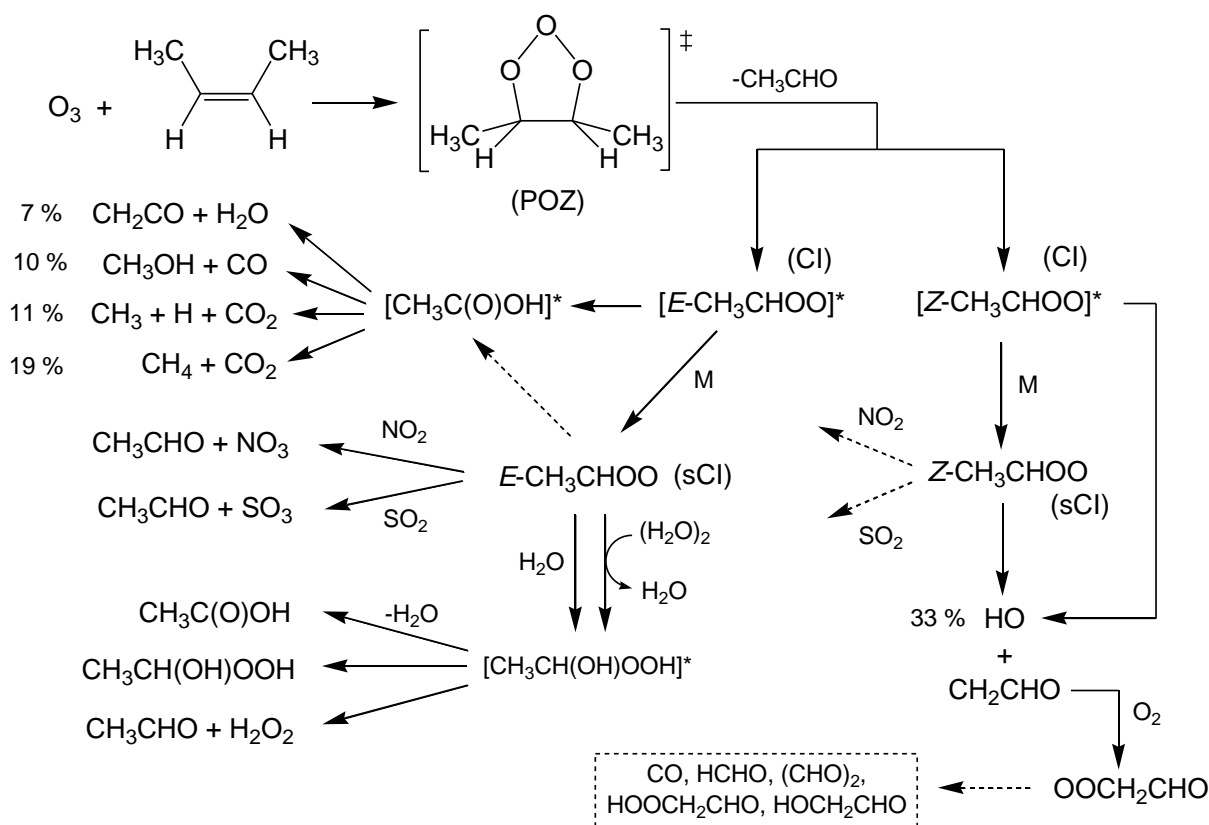
Preferred Values

Parameter	Value	T/K
<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	1.3×10^{-16}	298
<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	$3.37 \times 10^{-15} \exp(-970/T)$	220-370
<i>Reliability</i>		
Δ log <i>k</i>	± 0.05	298
Δ E/R	± 200	220-370

Comments on Preferred Values

The kinetics determinations are in generally good agreement. The preferred value of E/R is based on the average of those reported by Huie and Herron (1975) and Treacy et al. (1992), which are in good agreement. The preferred value of k at 298 K is an average of the room temperature determinations reported by Huie and Herron (1975), Atkinson et al. (1983), Treacy et al. (1992), Greene and Atkinson (1992) and Wegener et al. (2007), corrected to 298 K, where necessary, using the preferred value of E/R . These values agree to within $\pm 7\%$ of the preferred value. The earlier tabulated determinations of Cox and Penkett (1972), Finlayson et al. (1974) and Japar et al. (1974) are also consistent with this recommendation, deviating by less than 25 % from the preferred value.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich “primary ozonide (POZ)” which rapidly decomposes to form acetaldehyde, CH_3CHO , and one or other of the (excited) Criegee intermediate conformers, $[E-CH_3CHOO]^*$ and $[Z-CH_3CHOO]^*$, as represented in the schematic shown below. Some features of the further chemistry are also shown, with suggested approximate contributions of a number of product pathways at 298 K and atmospheric pressure inferred from reported end product studies.



It should be noted that the contributions of the pathways differ from those suggested for $[E-CH_3CHOO]^*$ and $[Z-CH_3CHOO]^*$ formed from the reactions of O_3 with both propene (datasheet Ox_VOC6) and *trans*-but-2-ene (datasheet Ox_VOC18), indicating that the fates of the Criegee intermediates are probably sensitive to their level of excitation, and that this can differ from one system to another. $[E-CH_3CHOO]^*$ and $[Z-CH_3CHOO]^*$ may either decompose via a number of possible pathways, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI), i.e. $E-CH_3CHOO$ and $Z-CH_3CHOO$ (Fenske et al., 2000a).

Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Atkinson and Aschmann, 1993; McGill et al., 1999; Orzechowska and Paulson, 2002; Wegener et al., 2007; Alam et al., 2013), with yields in the range 18–41 % (preferred value, $33 \pm 7\%$). HO is expected to be formed mainly from either $[Z-CH_3CHOO]^*$ or $Z-CH_3CHOO$, by an accepted

decomposition mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000b; Kroll et al., 2001), also forming the vinoxy radical (CH_2CHO) as a co-product. CH_2CHO reacts with O_2 under atmospheric conditions. At 1 bar, this is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO , HO_2 and other peroxy radicals) to form a number of products as shown. These include HCHO which has been reported to be formed with yields in the range 13-18 % in a number of studies (Horie et al., 1994; 1997; Grosjean et al., 1996; Tuazon et al., 1997) and glyoxal, $(\text{CHO})_2$, which has been reported to be formed with a yield of about 7 % (Tuazon et al., 1997). At pressures below about 270 mbar, the (chemically-activated) peroxy radical adduct has also been reported to decompose (e.g. to form $\text{HO} + \text{HCHO} + \text{CO}$), thereby providing a small secondary source of HO radicals (Oguchi et al., 2004).

Evidence for the decomposition pathways for $[\text{E-CH}_3\text{CHOO}]^*$ shown in the schematic (proceeding via formation of “hot” acetic acid, $[\text{CH}_3\text{C}(\text{O})\text{OH}]^*$) has been reported in a number of studies, with the suggested contributions approximately based on the yields of CO_2 , methane (CH_4), methanol (CH_3OH) and ketene (CH_2CO) reported by Tuazon et al. (1997) and Horie et al. (1997), and HO_2 (formed from reaction of H with O_2) reported by Alam et al. (2013).

The total yield of stabilized Criegee intermediates ($\text{E-CH}_3\text{CHOO}$ and $\text{Z-CH}_3\text{CHOO}$) in the system has been measured in a number of studies, with reported values in the range 18–43 %. The preferred value, 38 ± 10 %, is based on that measured by Newland et al. (2015), using scavenging with added SO_2 and quantification of SO_2 removed. Consistent with this, CH_3CHO yields slightly greater than unity (1.1-1.2) have been reported in a number of studies in the presence of H_2O (Grosjean et al., 1996; Tuazon et al., 1997; Wegener et al., 2007), suggesting a CH_3CHO yield of about 10-20 % from the reactions of sCI under these conditions. Based on the reported rate coefficients for their reactions with H_2O , and the relatively rapid decomposition of $\text{Z-CH}_3\text{CHOO}$, it is possible that only $\text{E-CH}_3\text{CHOO}$ is scavenged significantly by reaction with H_2O in these studies.

Based on reported kinetic data (summarised and evaluated in datasheets CGI_15 to CGI_17), the major fate of $\text{E-CH}_3\text{CHOO}$ under tropospheric conditions is expected to be removal via bimolecular reactions, in particular with H_2O and $(\text{H}_2\text{O})_2$, as illustrated in the schematic above. The major fate of $\text{Z-CH}_3\text{CHOO}$ is expected to be thermal decomposition, as described above.

References

- Alam, M. S., Rickard, A. R., Camredon, M., Wyche, K. P., Carr, T., Hornsby, K. E., Monks, P. S. and Bloss, W. J.: J. Phys. Chem., 117, 12468, 2013.
- Atkinson, R., Aschmann, S. M., Carter, W. P. L. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 15, 721, 1983.
- Atkinson, R. and Aschmann, S. M.: Environ. Sci. Technol., 27, 1357, 1993.
- Cox, R. A. and Penkett, S. A.: J. Chem. Soc., Faraday Trans. 1, 68, 1735, 1972.
- Fenske, J. D., Hasson, A. S., Ho, A. W. and Paulson, S. E.: J. Phys. Chem. A, 104, 9921, 2000a.
- Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: J. Phys. Chem. A, 104, 7821, 2000b.
- Finlayson, B. J., Pitts, J. N. and Atkinson R.: J. Am. Chem. Soc., 96, 5356, 1974.
- Greene, C. R. and Atkinson, R.: Int. J. Chem. Kinet., 24, 803, 1992.
- Grosjean, E., de Andrade, J. B. and Grosjean, D.: Environ. Sci. Technol., 30, 975, 1996.
- Horie, O., Neeb, P. and Moortgat, G. K.: Int. J. Chem. Kinet., 26, 1075, 1994.
- Horie, O., Neeb, P. and Moortgat, G. K.: Int. J. Chem. Kinet., 29, 461, 1997.
- Huie, R. E. and Herron, J. T.: Int. J. Chem. Kinet., Symp. 1, 165, 1975.
- Japar, S. M., Wu, C. H. and Niki, H.: J. Phys. Chem., 78, 2318, 1974.
- Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: J. Phys. Chem. A, 105, 4446, 2001.
- McGill, C. D., Rickard, A. R., Johnson, D. and Marston, G.: Chemosphere, 38, 1205, 1999.

Newland, M. J., Rickard, A. R., Alam, M. S., Vereecken, L., Muñoz, A., Ródenas, M. and Bloss, W. J.: Phys. Chem. Chem. Phys., 17, 4076, 2015.

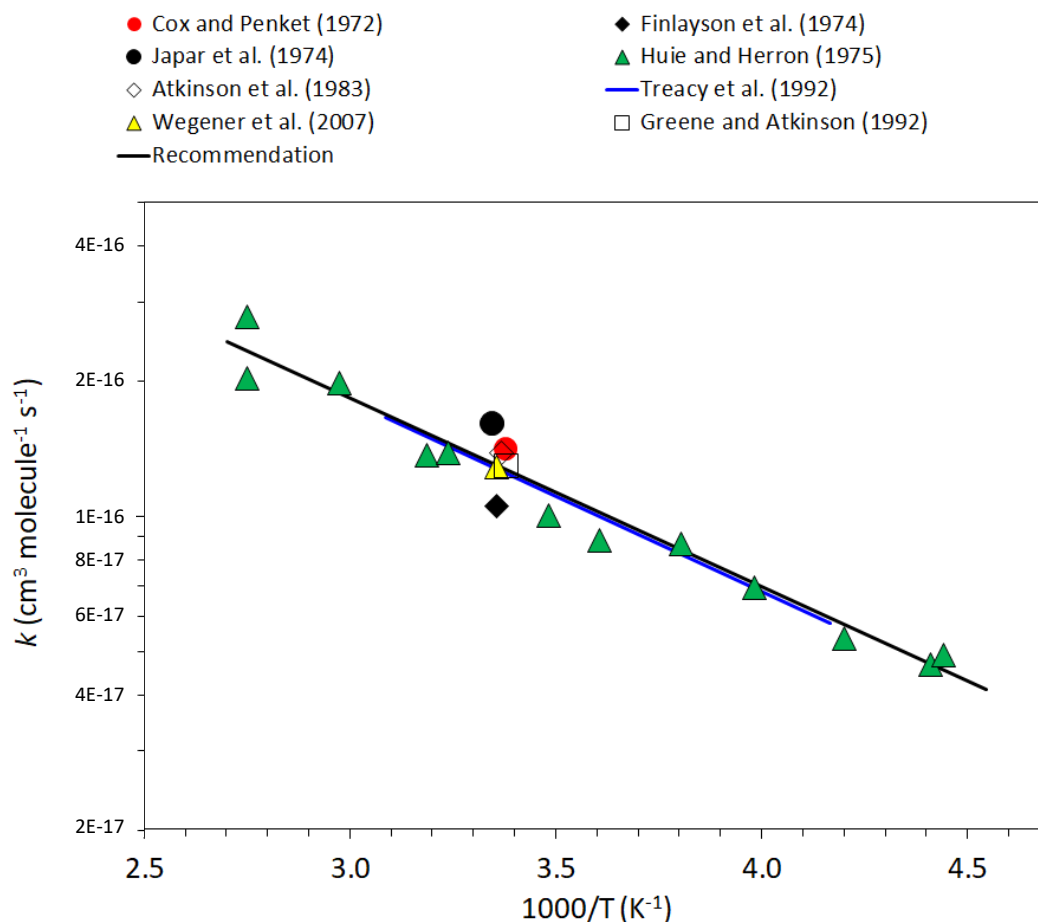
Oguchi, T, Sato, Y., Matsui, H., 18th Symposium on Gas Kinetics, Bristol, UK, 2004. Poster B13.

Orzechowska, G. and Paulson, S. E.: Atmos. Environ., 36, 571, 2002.

Treacy, J., El Hag, M., O'Farrell, D. and Sidebottom, H.: Ber. Bunsenges. Phys. Chem., 96, 422, 1992.

Tuazon, E. C., Aschmann, S. M., Arey, J. and Atkinson, R.: Environ. Sci. Technol., 31, 3004, 1997.

Wegener, R., Brauers, T., Koppmann, R., Bares, S. R., Rohrer, F., Tillmann, R., Wahner, A., Hansel, A. and Wisthaler, A.: J. Geophys. Res. Atmos., 112, 2007, doi: 10.1029/2006JD007531.



Ox_VOC18: *trans*-but-2-ene

Last evaluated: March 2020; Last change in preferred values: July 2018

O₃ + *trans*-but-2-ene → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
2.57×10^{-16}	296	Cox and Penkett, 1972	S-CL/GC-FID (a)
$(2.75 \pm 0.23) \times 10^{-16}$	299 ± 2	Stedman et al., 1973	S-CL (a)
$(2.60 \pm 0.09) \times 10^{-16}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
$5.96 \times 10^{-15} \exp[-(1051 \pm 43)/T]$	225-364	Huie and Herron, 1975	MS/MS (a)
1.76×10^{-16}	298*		
$(2.56 \pm 0.15) \times 10^{-16}$	299 ± 2	Japar et al., 1976	S-CL/GC-FID (a),(b)
2.88×10^{-16}	294 ± 2	Adeniji et al., 1981	S-CL (a)
$6.7 \times 10^{-15} \exp[-(1066 \pm 115)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(1.81 \pm 0.06) \times 10^{-16}$	298		
$(2.38 \pm 0.15) \times 10^{-16}$	298	Wegener et al., 2007	S-UVA/GC-FID (c)
<i>Relative Rate Coefficients</i>			
$(2.10 \pm 0.10) \times 10^{-16}$	297 ± 2	Nolting et al., 1988	RR/GC-FID (d)
$(2.17 \pm 0.15) \times 10^{-16}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (e)
$5.86 \times 10^{-15} \exp[-(1149 \pm 54)/T]$	278-353	Avzianova and Ariya, 2002	RR/GC-FID (f)
$(1.86 \pm 0.12) \times 10^{-16}$	298		

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of *trans*-but-2-ene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- (b) Experiments carried out in air and helium diluent gas. The rate coefficient in the table is that measured in air. A slightly higher rate coefficient of $(2.83 \pm 0.07) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was measured in helium diluent, consistent with data from a comprehensive study of the effects of O₂ on the measured rate coefficients for O₃ + propene, which showed that secondary reactions occurred in the absence of O₂.
- (c) Experiments carried out with comparable concentrations of each reagent, in the presence of excess CO as an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with k optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and *trans*-but-2-ene (measured by the second technique shown).
- (d) The concentrations of *trans*-but-2-ene and *cis*-but-2-ene (the reference compound) were measured in the presence of O₃ by GC. It appears from the publication that an HO radical scavenger was not present. The measured rate coefficient ratio $k(\text{O}_3 + \textit{trans}\text{-but-2-ene})/k(\text{O}_3 + \textit{cis}\text{-but-2-ene})$ is placed on an absolute basis using $k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 1.29 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation).
- (e) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of *trans*-but-2-ene and propene (the reference compound) were measured by GC. The measured value of

$k(\text{O}_3 + \text{trans-but-2-ene})/k(\text{O}_3 + \text{propene}) = 21.5 \pm 1.5$ is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

- (f) Relative rate method carried out at 760 Torr (1.013 bar) of air diluent in a 3 L volume Pyrex reactor, with 1,3,5-trimethylbenzene being present to scavenge the HO radicals formed. The concentrations of *trans*-but-2-ene and *cis*-but-2-ene (the reference compound) were monitored by GC. The measured rate coefficient ratios were placed on an absolute basis by Avzianova and Ariya (2002) using the Arrhenius expression of Treacy et al. (1992) for $\text{O}_3 + \text{cis-but-2-ene}$. The measured rate coefficient ratios were not tabulated, except at room temperature, assumed to be 298 K. The rate coefficient ratio $k(\text{O}_3 + \text{trans-but-2-ene})/k(\text{O}_3 + \text{cis-but-2-ene}) = 1.74 \exp[-(179 \pm 54)/T]$, derived from the data provided in Avzianova and Ariya (2002), is placed on an absolute basis using $k(\text{O}_3 + \text{cis-but-2-ene}) = 3.37 \times 10^{-15} \exp(-970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). The 298 K rate coefficient calculated from the Arrhenius expression ($1.24 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is a factor of 1.5 lower than the room temperature rate coefficient cited by Avzianova and Ariya (2002). The Arrhenius expression reported by Avzianova and Ariya (2002) therefore appears to be in error.

Preferred Values

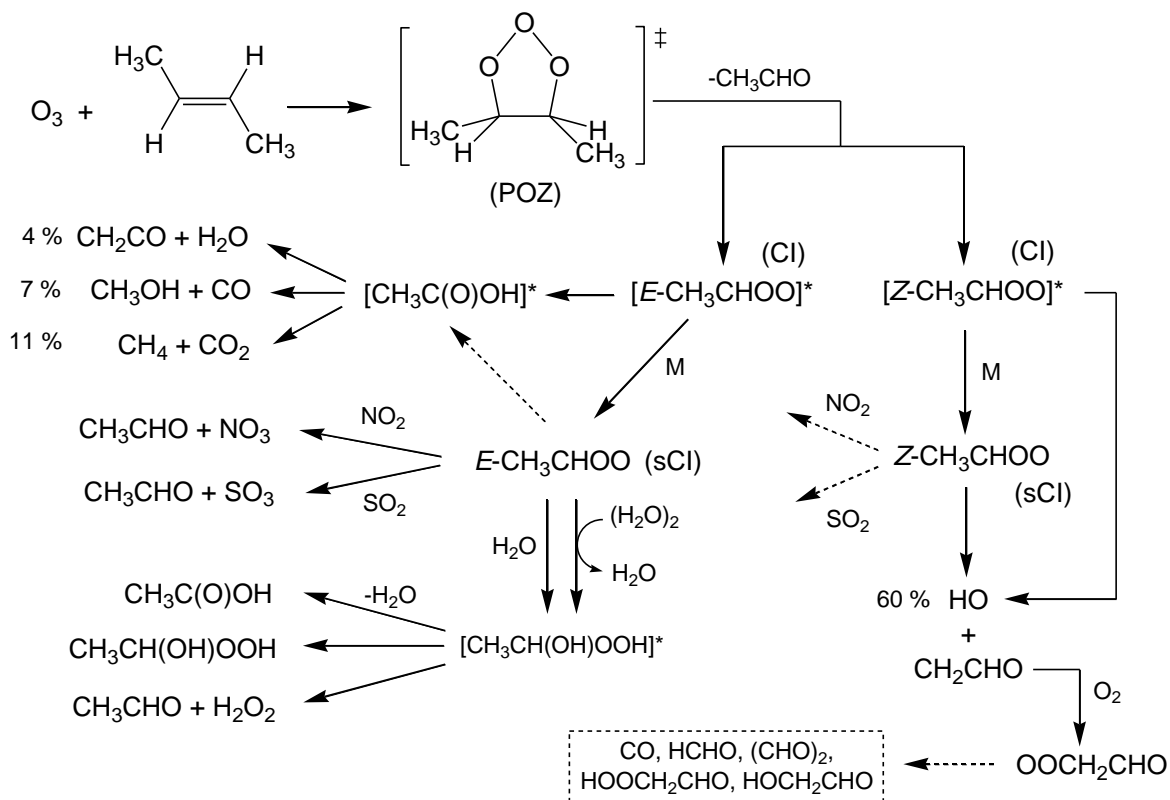
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.0×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.0 \times 10^{-15} \exp(-1060/T)$	220-370
<i>Reliability</i>		
$\Delta \log k$	± 0.1	298
$\Delta E/R$	± 200	220-370

Comments on Preferred Values

The preferred value of E/R is based on the average of those reported by Huie and Herron (1975) and Treacy et al. (1992), which are in good agreement. The Arrhenius parameters given by Avzianova and Ariya (2002) are inconsistent with the reported room temperature value of k (see comment (f)), although their value of E/R lies within the uncertainty bounds assigned to the preferred value.

There is some disagreement in the reported room temperature values of k . The preferred value of k at 298 K is based on the average of the direct determinations of Huie and Herron (1975), Treacy et al. (1992) and Wegener et al. (2007) and the relative rate determinations of Greene and Atkinson (1992) and Avzianova and Ariya (2002), corrected to 298 K, where necessary, using the preferred value of E/R . These values are in reasonable agreement, lying within $\pm 20\%$ of the preferred value. The relative rate experiments of Nolting et al. (1988) were apparently carried out without an ozone scavenger, although their reported value of k is consistent with the recommendation. The remaining absolute determinations report values of k lying about 30-50 % higher than the preferred value.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich “primary ozonide (POZ)” which rapidly decomposes to form acetaldehyde, CH_3CHO , and one or other of the (excited) Criegee intermediate conformers, $[E\text{-CH}_3\text{CHOO}]^*$ and $[Z\text{-CH}_3\text{CHOO}]^*$, as represented in the schematic shown below. Some features of the further chemistry are also shown, with suggested approximate contributions of a number of product pathways at 298 K and atmospheric pressure inferred from reported end product studies.



It should be noted that the contributions of the pathways differ from those suggested for $[E-\text{CH}_3\text{CHOO}]^*$ and $[Z-\text{CH}_3\text{CHOO}]^*$ formed from the reactions of O_3 with both propene (datasheet Ox_VOC6) and *cis*-but-2-ene (datasheet Ox_VOC17), indicating that the fates of the Criegee intermediates are probably sensitive to their level of excitation, and that this can differ from one system to another. $[E-\text{CH}_3\text{CHOO}]^*$ and $[Z-\text{CH}_3\text{CHOO}]^*$ may either decompose via a number of possible pathways, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI), i.e. $E-\text{CH}_3\text{CHOO}$ and $Z-\text{CH}_3\text{CHOO}$ (Fenske et al., 2000a).

Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Atkinson and Aschmann, 1993; McGill et al., 1999; Orzechowska and Paulson, 2002; Hasson et al., 2003; Wegener et al., 2007; Alam et al., 2013), with yields in the range 54–64 % (preferred value, 60 ± 6 %) reported at atmospheric pressure. Similar yields have also been reported at low pressures by Donahue et al. (1998), (68 ± 9 %), and Kroll et al. (2001), ~ 60 %. HO is expected to be formed mainly from either $[Z-\text{CH}_3\text{CHOO}]^*$ or $Z-\text{CH}_3\text{CHOO}$, by an accepted decomposition mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000b; Kroll et al., 2001), also forming the vinyloxy radical (CH_2CHO) as a co-product. CH_2CHO reacts with O_2 under atmospheric conditions. At 1 bar, this is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO, HO_2 and other peroxy radicals) to form a number of products as shown. These include HCHO which has been reported to be formed with yields in the range 13–29 % in a number of studies (Horie et al., 1994; 1997; Grosjean et al., 1996; Tuazon et al., 1997) and glyoxal, $(\text{CHO})_2$, which has been reported to be formed with a yield of about 10 % (Tuazon et al., 1997). At pressures below about 270 mbar, the (chemically-activated) peroxy radical adduct has also been reported to decompose (e.g. to form $\text{HO} + \text{HCHO} + \text{CO}$), thereby providing a small secondary source of HO radicals (Oguchi et al., 2004).

Evidence for the decomposition pathways for $[E-\text{CH}_3\text{CHOO}]^*$ shown in the schematic (proceeding via formation of “hot” acetic acid, $[CH_3C(O)OH]^*$) has been reported in a number of studies, with the suggested contributions approximately based on the yields of methane (CH_4), methanol (CH_3OH) and

ketene (CH_2CO) reported by Tuazon et al. (1997) and Horie et al. (1997). However, the reported yields of CO_2 in the same studies (about 23–29%) are not fully accounted for by these contributions.

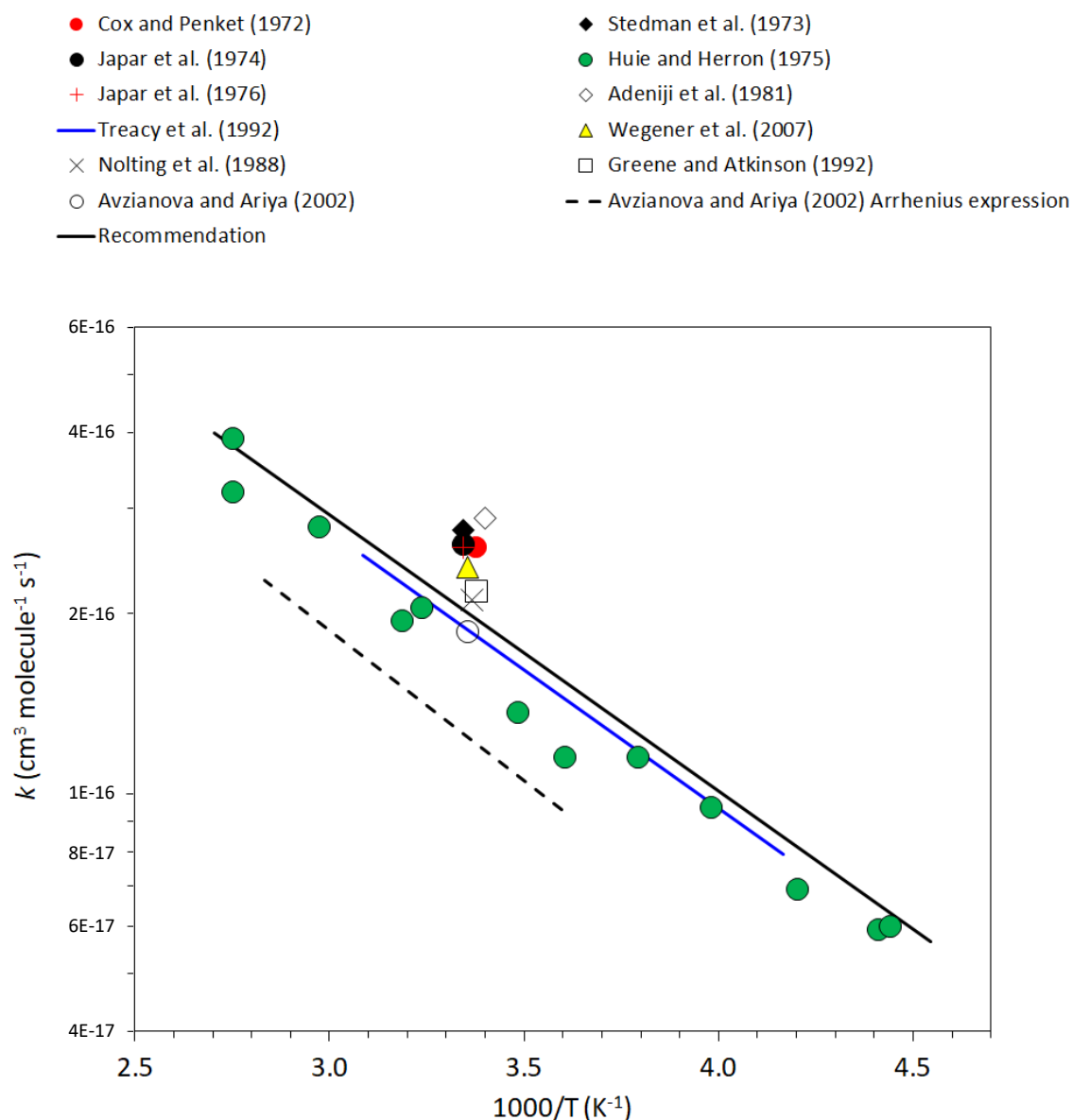
There have been a number of determinations of the yield of the stabilized Criegee intermediates (*E*- CH_3CHOO and *Z*- CH_3CHOO), mainly based on addition of scavengers (H_2O , SO_2 and $\text{CF}_3\text{C}(\text{O})\text{CF}_3$) to the system and quantification of the associated reaction products (Cox and Penkett, 1972; Hatakeyama and Akimoto, 1994; Rickard et al., 1999; Horie et al., 1999; Hasson et al., 2001; Berndt et al., 2014; Newland et al., 2015; Hakala and Donahue, 2018). The reported yields show some disagreement, lying in the range 13–53 % (preferred value 43 ± 10 %). Consistent with this, CH_3CHO yields slightly greater than unity (1.1–1.2) have been reported in a number of studies in the presence of H_2O (Grosjean et al., 1996; Tuazon et al., 1997; Hasson et al., 2001), suggesting a CH_3CHO yield of about 10–20 % from the reactions of sCI under these conditions. Based on the reported rate coefficients for their reactions with H_2O , and the relatively rapid decomposition of *Z*- CH_3CHOO , it is possible that only *E*- CH_3CHOO is scavenged significantly by reaction with H_2O in these studies.

Based on reported kinetic data (summarised and evaluated in datasheets CGI_15 to CGI_17), the major fate of *E*- CH_3CHOO under tropospheric conditions is expected to be removal via bimolecular reactions, in particular with H_2O and $(\text{H}_2\text{O})_2$, as illustrated in the schematic above. The major fate of *Z*- CH_3CHOO is expected to be thermal decomposition, as described above.

References

- Adeniji, A. A., Kerr, J. A. and Williams, M. R.: *Int. J. Chem. Kinet.*, 13, 209, 1981.
- Alam, M. S., Rickard, A. R., Camredon, M., Wyche, K. P., Carr, T., Hornsby, K. E., Monks, P. S. and Bloss, W. J.: *J. Phys. Chem.*, 117, 12468, 2013.
- Atkinson, R. and Aschmann, S. M.: *Environ. Sci. Technol.*, 27, 1357, 1993.
- Avzianova, E. V. and Ariya, P. A.: *Int. J. Chem. Kinet.*, 34, 678, 2002.
- Berndt, T., Jokinen, T., Sipilä, M., Mauldin, R. L., Herrmann, H., Stratmann, F., Junninen, H. and Kulmala, M.: *Atmos. Environ.*, 89, 603, 2014.
- Cox, R. A. and Penkett, S. A.: *J. Chem. Soc., Faraday Trans. 1*, 68, 1735, 1972.
- Donahue, N. M., Kroll, J. H., Anderson, J. G. and Demerjian, K. L.: *Geophys. Res. Lett.*, 25, 59, 1998.
- Fenske, J. D., Hasson, A. S., Ho, A. W. and Paulson, S. E.: *J. Phys. Chem. A*, 104, 9921, 2000a.
- Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: *J. Phys. Chem. A*, 104, 7821, 2000b.
- Greene, C. R. and Atkinson, R.: *Int. J. Chem. Kinet.*, 24, 803, 1992.
- Grosjean, E., de Andrade, J. B. and Grosjean, D.: *Environ. Sci. Technol.*, 30, 975, 1996.
- Hakala, J. P. and Donahue, N. M.: *J. Phys. Chem. A*, 122, 9426, 2018.
- Hatakeyama, S. and Akimoto, H.: *Res. Chem. Intermed.*, 20, 503, 1994.
- Hasson, A. S., Orzechowska, G. and Paulson, S. E.: *J. Geophys. Res.*, 106, 34131, 2001.
- Hasson, A. S., Chung, M. Y., Kuwata, K. T., Converse, A. D., Krohn, D. and Paulson, S. E.: *J. Phys. Chem. A*, 107, 6176, 2003.
- Horie, O., Neeb, P. and Moortgat, G. K.: *Int. J. Chem. Kinet.*, 26, 1075, 1994.
- Horie, O., Neeb, P. and Moortgat, G. K.: *Int. J. Chem. Kinet.*, 29, 461, 1997.
- Horie, O., Schafer, C. and Moortgat, G. K.: *Int. J. Chem. Kinet.*, 31, 261, 1999.
- Huie, R. E. and Herron, J. T.: *Int. J. Chem. Kinet., Symp. 1*, 165, 1975.
- Japar, S. M., Wu, C. H. and Niki, H.: *J. Phys. Chem.*, 78, 2318, 1974.
- Japar, S. M., Wu, C. H. and Niki, H.: *J. Phys. Chem.*, 80, 2057, 1976.
- Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: *J. Phys. Chem. A*, 105, 4446, 2001.
- McGill, C. D., Rickard, A. R., Johnson, D. and Marston, G.: *Chemosphere*, 38, 1205, 1999.
- Newland, M. J., Rickard, A. R., Alam, M. S., Vereecken, L., Muñoz, A., Ródenas, M. and Bloss, W. J.: *Phys. Chem. Chem. Phys.*, 17, 4076, 2015.

Oguchi, T, Sato, Y., Matsui, H., 18th Symposium on Gas Kinetics, Bristol, UK, 2004. Poster B13.
 Orzechowska, G. and Paulson, S. E.: Atmos. Environ., 36, 571, 2002.
 Nolting, F., Behnke, W. and Zetzsch, C.: J. Atmos. Chem., 6, 47, 1988.
 Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: J. Phys. Chem. A, 103, 7656, 1999.
 Stedman, D. H., Wu, C. H. and Niki, H.: J. Phys. Chem., 77, 2511, 1973.
 Treacy, J., El Hag, M., O'Farrell, D. and Sidebottom, H.: Ber. Bunsenges. Phys. Chem., 96, 422, 1992.
 Tuazon, E. C., Aschmann, S. M., Arey, J. and Atkinson, R.: Environ. Sci. Technol., 31, 3004, 1997.
 Wegener, R., Brauers, T., Koppmann, R., Bares, S. R., Rohrer, F., Tillmann, R., Wahner, A., Hansel, A. and Wisthaler, A.: J. Geophys. Res. Atmos., 112, 2007, doi: 10.1029/2006JD007531.



Ox_VOC15: 2-methylpropene

Last evaluated: August 2020; Last change in preferred values: July 2018

O₃ + 2-methylpropene → products**Rate coefficient data**

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.8×10^{-17}	283 ± 2	Becker et al., 1974	S-UVA (a)
$(1.36 \pm 0.02) \times 10^{-17}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
$3.17 \times 10^{-15} \exp[-(1671 \pm 23)/T]$	225-363	Huie and Herron, 1975	MS/MS (a)
1.16×10^{-17}	298*		
1.45×10^{-17}	295 ± 1	Grimsrud et al., 1975	F-CL (a)
1.2×10^{-17}	294 ± 2	Adeniji et al., 1981	S-CL (a)
$2.5 \times 10^{-15} \exp[-(1592 \pm 115)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(1.09 \pm 0.18) \times 10^{-17}$	298		
1.24×10^{-17}	296 ± 2	Neeb and Moortgat, 1999	S-FTIR (b)
$(1.11 \pm 0.12) \times 10^{-17}$	298	Wegener et al., 2007	S-UVA/GC-FID (c)
$3.39 \times 10^{-15} \exp[-(1697 \pm 52)/T]$	295.6-349.8	Shi et al., 2011	S-UVA (a)
$(1.09 \pm 0.02) \times 10^{-17}$	295.6		
<i>Relative Rate Coefficients</i>			
$(1.15 \pm 0.04) \times 10^{-17}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (d)
$1.89 \times 10^{-15} \exp[-(2122 \pm 102)/T]$	278-353	Avzianova and Ariya, 2002	RR/GC-FID (e)
$(1.10 \pm 0.07) \times 10^{-17}$	298		

Comments

- (a) *k* determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of 2-methylpropene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- (b) *k* determined from the observed first-order rate of propene decay in the presence of known excess concentrations of ozone, with both reagents measured by FTIR. Cyclohexane added to scavenge HO radicals.
- (c) Experiments carried out with comparable concentrations of each reagent, in the presence of excess CO as an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with *k* optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and 2-methylpropene (measured by the second technique shown).
- (d) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of 2-methylpropene and propene (the reference compound) were measured by GC. The measured value of $k(\text{O}_3 + 2\text{-methylpropene})/k(\text{O}_3 + \text{propene}) = 1.14 \pm 0.04$ is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (e) Relative rate method carried out at 760 Torr (1.013 bar) of air diluent in a 3 L volume Pyrex reactor, with 1,3,5-trimethylbenzene being present to scavenge the HO radicals formed. The concentrations of 2-methylpropene and propene (the reference compound) were monitored by GC. The measured rate coefficient ratios were placed on an absolute basis by Avzianova and Ariya

(2002) using the Arrhenius expression of Treacy et al. (1992) for $\text{O}_3 + \text{propene}$. The measured rate coefficient ratios were not tabulated, except at room temperature, assumed to be 298 K. The rate coefficient ratio $k(\text{O}_3 + 2\text{-methylpropene})/k(\text{O}_3 + \text{propene}) = 0.327 \exp[-(242 \pm 102)/T]$, derived from the data provided in Avzianova and Ariya (2002), is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 5.5 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). The 298 K rate coefficient calculated from the Arrhenius expression ($1.52 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is a factor of 7 lower than the room temperature rate coefficient cited by Avzianova and Ariya (2002), and their Arrhenius plots indicate that the temperature dependence for $\text{O}_3 + 2\text{-methylpropene}$ is similar to that for $\text{O}_3 + \text{but-1-ene}$ ($E/R = 1750 \text{ K}$). The Arrhenius expression cited by Avzianova and Ariya (2002) is clearly in error.

Preferred Values

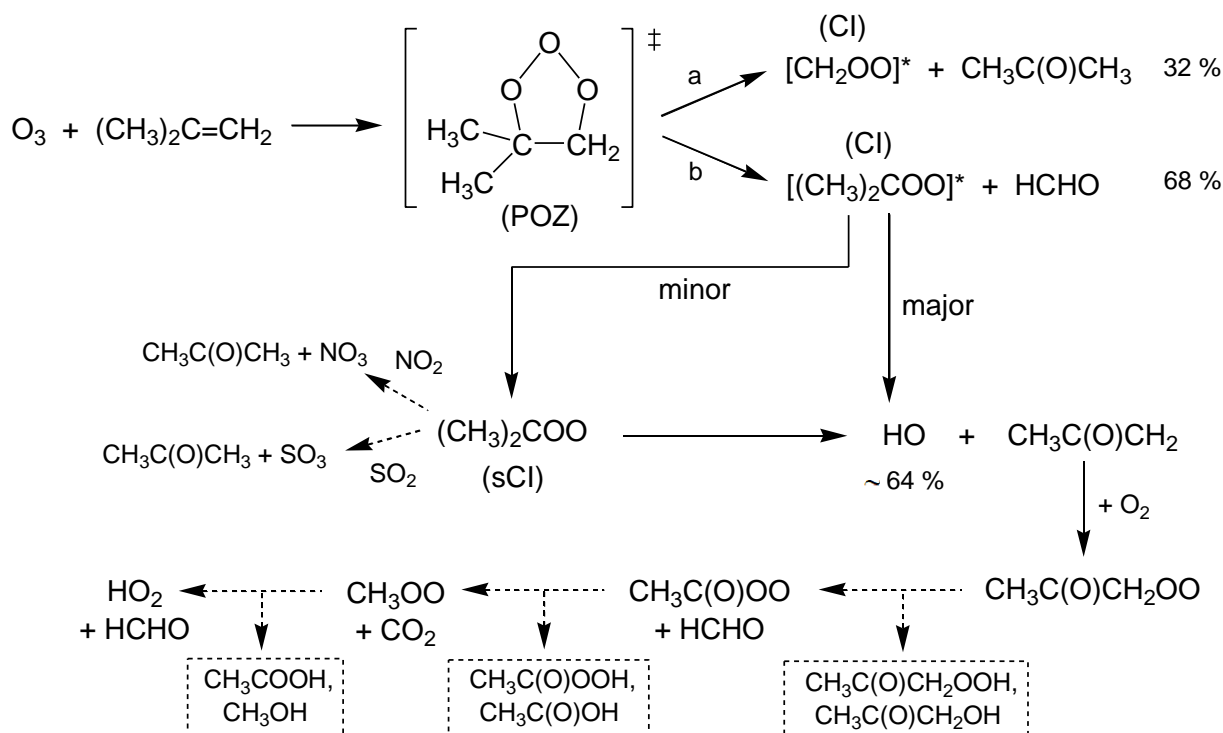
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.15×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.92 \times 10^{-15} \exp(-1650/T)$	220-370
<i>Reliability</i>		
$\Delta \log k$	± 0.05	298
$\Delta E/R$	± 200	220-370

Comments on Preferred Values

The preferred value of E/R is based on the average of those reported by Huie and Herron (1975), Treacy et al. (1992) and Shi et al. (2011), which are in good agreement. The Arrhenius parameters given by Avzianova and Ariya (2002) are inconsistent with the reported room temperature value of k (see comment (e)), and their value of E/R is significantly greater than the preferred value.

The preferred value of k at 298 K is based on the average of the direct determinations of Huie and Herron (1975), Treacy et al. (1992), Wegener et al. (2007) and Shi et al. (2011) and the relative rate determinations of Greene and Atkinson (1992) and Avzianova and Ariya (2002), corrected to 298 K, where necessary, using the preferred value of E/R . These values are in very good agreement, lying within $\pm 5 \%$ of the preferred value. The absolute determinations of Japar et al. (1974), Adeniji et al. (1981) and Neeb and Moorgat (1999) are also consistent with the preferred value, lying 12-16 % higher. Grimsrud et al. (1975) and Becker et al. (1983) report values of k lying about 30 % and a factor of two higher, respectively.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich “primary ozonide” which rapidly decomposes to form two sets of primary carbonyl product plus (excited) Criegee intermediate, as shown in the schematic below. Reported yields of acetone ($\text{CH}_3\text{C}(\text{O})\text{CH}_3$) and formaldehyde (HCHO) suggest important contributions from both decomposition channels, (a) and (b), with HCHO also expected to have secondary sources (see below). Values of $k_a/(k_a+k_b)$ lying in the range 0.28-0.35 can be inferred from the reported molar yields of acetone (Grosjean et al., 1996; Tuazon et al., 1997; Neeb and Moortgat, 1999; Newland et al., 2020), consistent with the value given in the schematic.



The further chemistry of $[\text{CH}_2\text{OO}]^*$ is expected to follow the pathways described in the data sheet for the $\text{O}_3 + \text{C}_2\text{H}_4$ reaction (Ox_VOC5), although their relative importance is not necessarily the same. The schematic above shows some established features of the further chemistry of $[(\text{CH}_3)_2\text{COO}]^*$, with suggested approximate contributions of the product pathways at 298 K and atmospheric pressure inferred from reported end product studies.

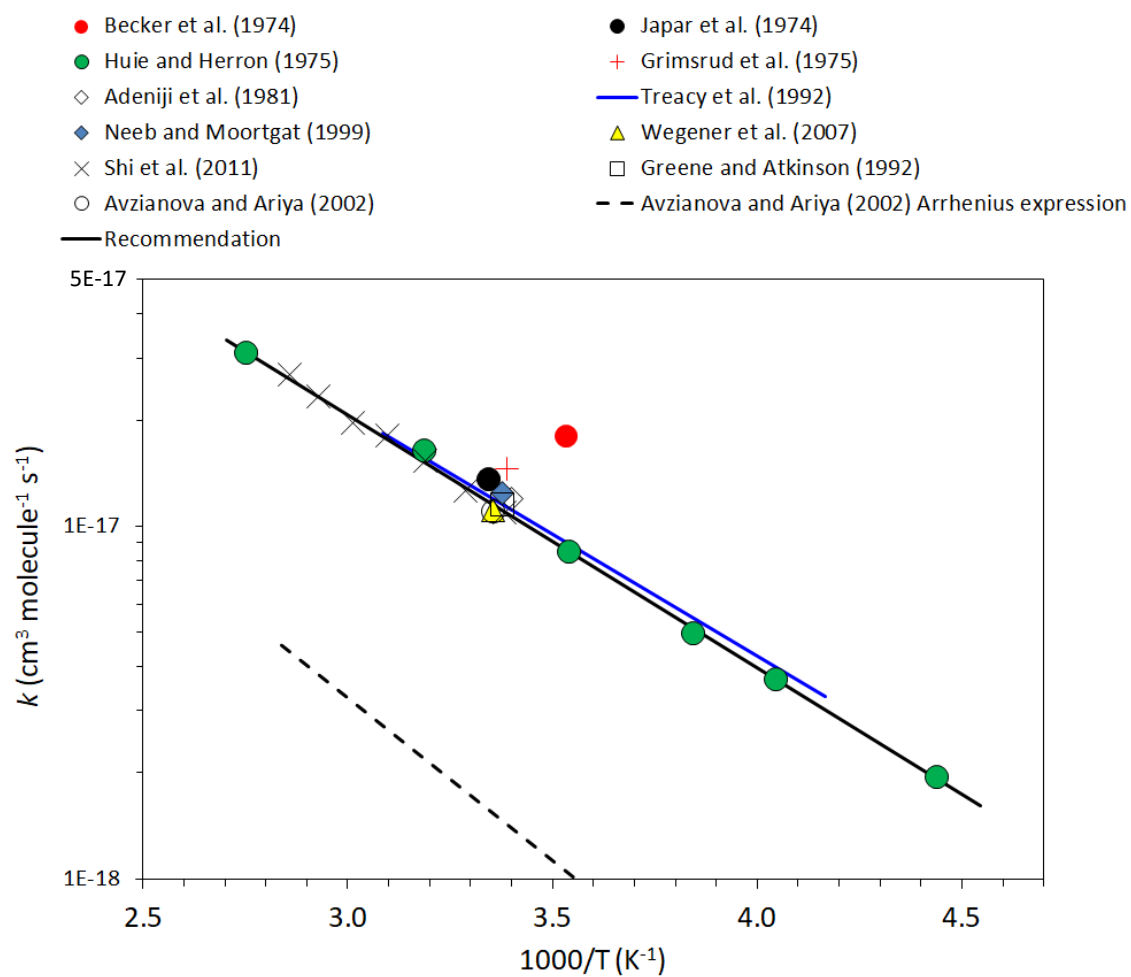
$[(\text{CH}_3)_2\text{COO}]^*$ may either decompose, or be collisionally deactivated to form the stabilized Criegee intermediate $(\text{CH}_3)_2\text{COO}$ (sCI). The total yield of stabilized Criegee intermediates (i.e. CH_2OO and $(\text{CH}_3)_2\text{COO}$) has been determined by scavenging with added SO_2 and quantifying the associated products, H_2SO_4 (Hatekayama et al., 1986) or HCHO and $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ (Newland et al., 2020). The recommended total yield, based on these studies, is $21 \pm 5 \%$. Newland et al. (2020) report that CH_2OO and $(\text{CH}_3)_2\text{COO}$ account for about 70 % and 30 % of the total sCI yield, respectively. Consistent with this, Neeb et al. (1997) inferred a yield of 13 % specifically for CH_2OO , based on scavenging with added H_2O and quantification of the product HOCH_2OOH . This suggests that the major fate of $[(\text{CH}_3)_2\text{COO}]^*$ formed from 2-methylpropene ozonolysis is decomposition, with only a minor fraction stabilized to form $(\text{CH}_3)_2\text{COO}$.

The dominant decomposition route for both $[(\text{CH}_3)_2\text{COO}]^*$ and $(\text{CH}_3)_2\text{COO}$ is expected to form HO radicals by an accepted decomposition mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000; Kroll et al., 2001), also forming the 1-methylvinoxy or acetylonyl radical $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ as a co-product. Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Atkinson and Aschmann, 1993; Neeb and Moortgat, 1999; Paulson et al., 1999; Rickard et al., 1999; Wegener et al., 2007; Alam et al., 2013), with yields in the range 60–84 % (preferred value, 69 %). A minor contribution to HO formation may also result from decomposition of $[\text{CH}_2\text{OO}]^*$. Assuming that the relative importance of the reaction pathways for $[\text{CH}_2\text{OO}]^*$ formed from 2-methylpropene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene, this contribution is estimated to be about 5 %, suggesting that decomposition of $[(\text{CH}_3)_2\text{COO}]^*$ and $(\text{CH}_3)_2\text{COO}$ contributes about 64 %. Based on reported kinetic data (summarised and evaluated in datasheets CGI_14 and CGI_18 to CGI_20), decomposition is also expected to be the major fate of $(\text{CH}_3)_2\text{COO}$ under tropospheric conditions.

The acetyl radical ($\text{CH}_3\text{C}(\text{O})\text{CH}_2$) reacts with O_2 under atmospheric conditions. This is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO , HO_2 and other peroxy radicals) initiating reaction sequences forming a large number of potential products, with examples shown in the schematic. These include methyl glyoxal ($\text{CH}_3\text{C}(\text{O})\text{CHO}$), hydroxyacetone ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$), methanol (CH_3OH) and CO_2 , which have been reported to be formed with respective yields of about 15 %, 7 %, 5 % and 28 % (Neeb and Moortgat, 1999; Tuazon et al., 1997). CO_2 may also be formed from the decomposition of $[\text{CH}_2\text{OO}]^*$, with an estimated yield of about 7 % (assuming the relative importance of the pathways is similar to those in the ethene system). The chemistry also results in significant secondary formation of HCHO . Total molar yields in the range 95–119 % have been reported by Grosjean et al. (1996), Tuazon et al. (1997), Neeb and Moortgat (1999) and Newland et al. (2020), which is consistent with major primary and secondary sources in the system.

References

- Adeniji, A. A., Kerr, J. A. and Williams, M. R.: *Int. J. Chem. Kinet.*, 13, 209, 1981.
- Alam, M. S., Rickard, A. R., Camredon, M., Wyche, K. P., Carr, T., Hornsby, K. E., Monks, P. S. and Bloss, W. J.: *J. Phys. Chem.*, 117, 12468, 2013.
- Becker, K. H., Schurath, U. and Seitz, H.: *Int. J. Chem. Kinet.*, 6, 725, 1974.
- Atkinson, R. and Aschmann, S. M.: *Environ. Sci. Technol.*, 27, 1357, 1993.
- Avzianova, E. V. and Ariya, P. A.: *Int. J. Chem. Kinet.*, 34, 678, 2002.
- Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: *J. Phys. Chem. A*, 104, 7821, 2000.
- Greene, C. R. and Atkinson, R.: *Int. J. Chem. Kinet.*, 24, 803, 1992.
- Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: *Int. J. Chem. Kinet., Symp. 1*, 183, 1975.
- Grosjean, E., de Andrade, J. B. and Grosjean, D.: *Environ. Sci. Technol.*, 30, 975, 1996.
- Huie, R. E. and Herron, J. T.: *Int. J. Chem. Kinet., Symp. 1*, 165, 1975.
- Japar, S. M., Wu, C. H. and Niki, H.: *J. Phys. Chem.*, 78, 2318, 1974.
- Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: *J. Phys. Chem. A*, 105, 4446, 2001.
- Shi, Y. Z., Xu, Y. F. and Jia, L.: *Int. J. Chem. Kinet.*, 43, 238, 2011.
- Neeb, P. and Moortgat, G. K.: *J. Phys. Chem. A*, 103, 9003, 1999.
- Neeb, P., Sauer, F., Horie, O. and Moortgat, G. K.: *Atmos. Environ.*, 31, 1417, 1997.
- Newland, M. J., Nelson, B. S., Muñoz, A., Ródenas, M., Vera, T., Tárrega, J., and Rickard, A. R.: *Phys. Chem. Chem. Phys.*, 22, 13698, 2020.
- Paulson, S. E., Chung, M. Y., Hasson, A. S.: *J. Phys. Chem. A*, 103, 8125, 1999.
- Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: *J. Phys. Chem. A*, 103, 7656, 1999.
- Treacy, J., El Hag, M., O'Farrell, D. and Sidebottom, H.: *Ber. Bunsenges. Phys. Chem.*, 96, 422, 1992.
- Tuazon, E. C., Aschmann, S. M., Arey, J. and Atkinson, R.: *Environ. Sci. Technol.*, 31, 3004, 1997.
- Wegener, R., Brauers, T., Koppmann, R., Bares, S. R., Rohrer, F., Tillmann, R., Wahner, A., Hansel, A. and Wisthaler, A.: *J. Geophys. Res. Atmos.*, 112, 2007, doi: 10.1029/2006JD007531.



Ox_VOC41: 2,3-dimethylbut-2-ene

Last evaluated: August 2020; Last change in preferred values: July 2018

O₃ + 2,3-dimethylbut-2-ene → products**Rate coefficient data**

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
(1.51 ± 0.08) × 10 ⁻¹⁵	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
2.82 × 10 ⁻¹⁵ exp[-(294 ± 196)/T]	227-363	Huie and Herron, 1975	MS/MS (a)
1.05 × 10 ⁻¹⁵	298*		
(1.0 ± 0.2) × 10 ⁻¹⁵	295 ± 0.5	Witter et al., 2002	S-UVA/FTIR (b)
<i>Relative Rate Coefficients</i>			
(1.24 ± 0.11) × 10 ⁻¹⁶	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (c)

Comments

- (a) *k* determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of 2,3-dimethylbut-2-ene (measured by the second technique shown) in air.
- (b) Experiments carried out with comparable concentrations of each reagent, in the absence of an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with *k* optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and 2,3-dimethylbut-2-ene (measured by the second technique shown).
- (c) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of 2,3-dimethylbut-2-ene and propene (the reference compound) were measured by GC. The measured value of $k(\text{O}_3 + 2,3\text{-dimethylbut-2-ene})/k(\text{O}_3 + \text{propene}) = 123 \pm 11$ is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

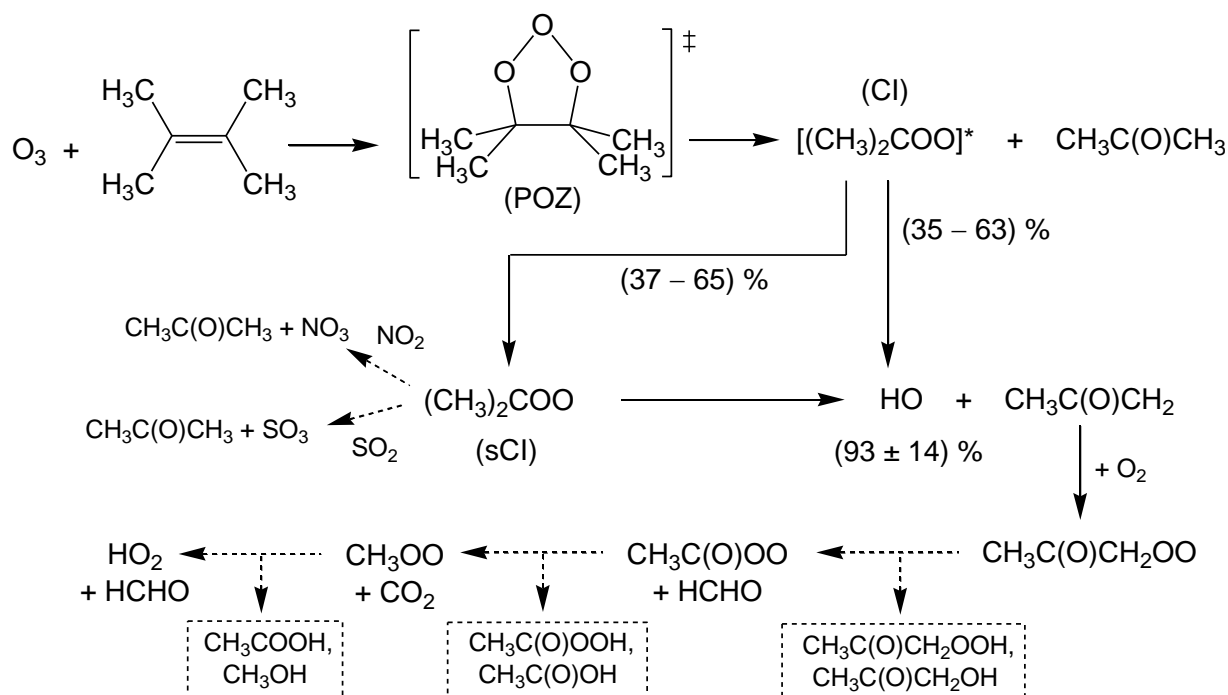
Preferred Values

Parameter	Value	T/K
<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	1.1 × 10 ⁻¹⁵	298
<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	3.0 × 10 ⁻¹⁵ exp(-300/T)	220-370
<i>Reliability</i>		
Δ log <i>k</i>	± 0.08	298
Δ E/R	± 200	220-370

Comments on Preferred Values

The preferred value of E/R is based on the approximate, sole determination of Huie and Herron (1975). The preferred value of k at 298 K is based on the average of the direct determinations of Huie and Herron (1975) and Witter et al. (2002), and the relative rate determination of Greene and Atkinson (1992), corrected to 298 K, where necessary, using the preferred value of E/R . These values are in good agreement, lying within $\pm 15\%$ of the preferred value. Japar et al. (1974) report a comparable value of k , lying about 35 % higher than the preferred value.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich “primary ozonide (POZ)” which rapidly decomposes to form an (excited) Criegee intermediate (CI), $[(CH_3)_2COO]^*$, and acetone, $CH_3C(O)CH_3$, as represented in the schematic shown below. The schematic also shows some established features of the further chemistry of $[(CH_3)_2COO]^*$, with suggested approximate contributions of the product pathways at 298 K and atmospheric pressure inferred from reported end product studies.



$[(CH_3)_2COO]^*$ may either decompose, or be collisionally deactivated to form the stabilized Criegee intermediate $(CH_3)_2COO$ (sCI). The yield of sCI has been determined in a number of studies, based on scavenging with added SO_2 , and quantification of the product H_2SO_4 . The yield has been shown to be dependent on pressure (Drodz et al., 2011; Hakala and Donahue, 2016; Campos-Pineda and Zhang, 2017), suggesting a small nascent yield of sCI, 12–15 %, at zero pressure. There is some disagreement in the yields measured at higher pressures, although more recent studies (Berndt et al., 2014; Newland et al., 2015, 2020; Hakala and Donahue, 2016) report relatively consistent values in the range 31–45 % at atmospheric pressure (preferred value $38 \pm 10\%$).

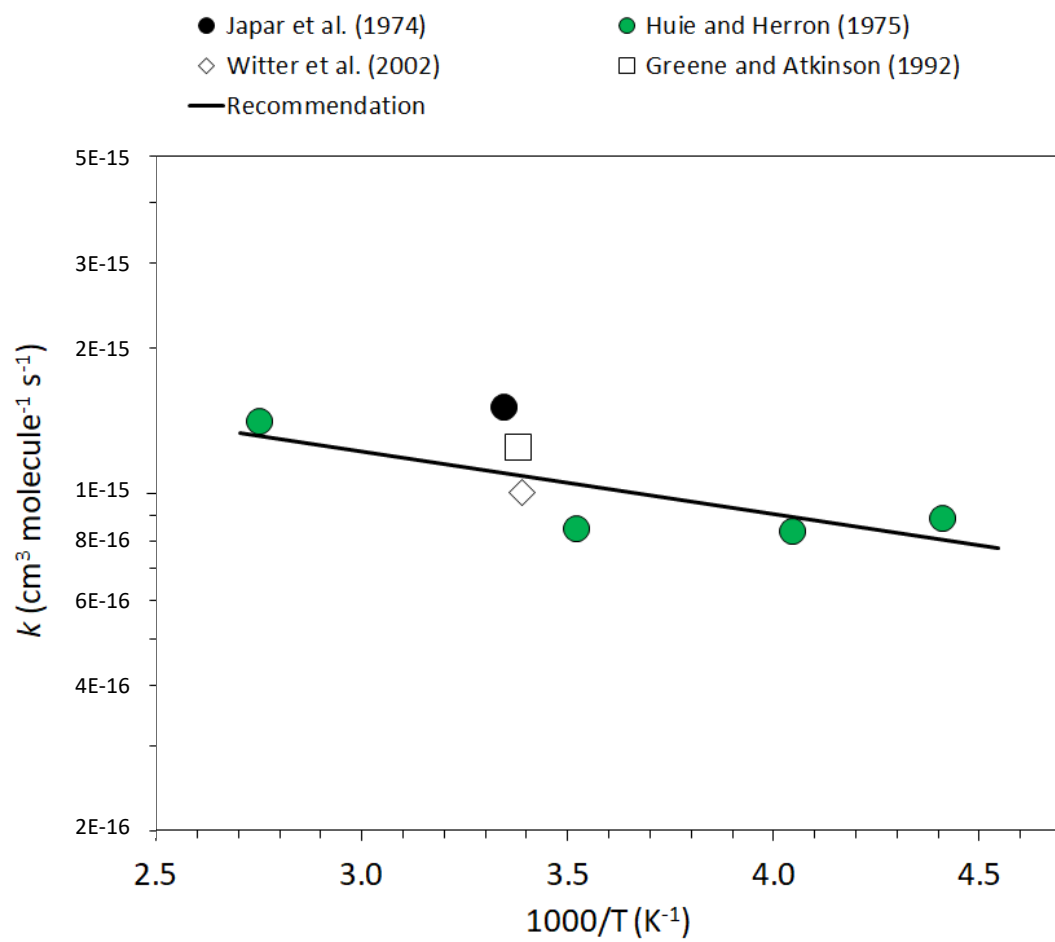
The dominant decomposition route for both the excited and stabilized Criegee intermediates is expected to form HO radicals by an accepted decomposition mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000; Kroll et al., 2001), also forming the methylvinoyl or acetyl radical ($CH_3C(O)CH_2$) as a co-product. Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Chew and Atkinson, 1996; Rickard et al., 1999; Fenske et al., 2000; Siese et al., 2001; Orzechowska and Paulson, 2002; Aschmann et al., 2003; Berndt and Böge, 2006; Alam et al., 2013), with yields in the range 80–107 % at close to atmospheric pressure (preferred value, $93 \pm 14\%$). This suggests that decomposition is almost the

exclusive fate for $(\text{CH}_3)_2\text{COO}$ under typical experimental conditions, with only a minor fraction removed by bimolecular reaction. Consistent with this, reported yields of acetone ($\text{CH}_3\text{C}(\text{O})\text{CH}_3$) in experiments employing an HO radical scavenger are close to unity (e.g. Grosjean and Grosjean, 1996; Tuazon et al., 1997; Wedian and Atkinson, 2010; Newland et al., 2020) indicating that its secondary formation from bimolecular reactions of $(\text{CH}_3)_2\text{COO}$ is limited. Based on reported kinetic data (summarised and evaluated in datasheets CGI_14 and CGI_18 to CGI_20), decomposition is also the major fate of $(\text{CH}_3)_2\text{COO}$ under tropospheric conditions.

The acetonyl radical ($\text{CH}_3\text{C}(\text{O})\text{CH}_2$) reacts with O_2 under atmospheric conditions. This is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO, HO_2 and other peroxy radicals) initiating reaction sequences forming a large number of potential products, with examples shown in the schematic. These include formaldehyde (HCHO), methyl glyoxal ($\text{CH}_3\text{C}(\text{O})\text{CHO}$), hydroxyacetone ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$), methanol (CH_3OH) and CO_2 , which have been reported to be formed in experimental studies employing HO scavengers (e.g. Grosjean and Grosjean, 1996; Tuazon et al., 1997; Wedian and Atkinson, 2010). The approximate reported yields are 29-43 % for HCHO , 30 % for methyl glyoxal and hydroxyacetone collectively, 6 % for CH_3OH and 28 % for CO_2 .

References

- Alam, M. S., Rickard, A. R., Camredon, M., Wyche, K. P., Carr, T., Hornsby, K. E., Monks, P. S. and Bloss, W. J.: *J. Phys. Chem.*, 117, 12468, 2013.
- Aschmann, S. M., Tuazon, E. C., Arey, J. and Atkinson, R.: *J. Phys. Chem. A*, 107, 2247, 2003.
- Berndt, T. and Böge, O.: *Phys. Chem. Chem. Phys.*, 8, 1205, 2006.
- Berndt, T., Jokinen, T., Sipilä, M., Mauldin, R. L., Herrmann, H., Stratmann, F., Junninen, H. and Kulmala, M.: *Atmos. Environ.*, 89, 603, 2014.
- Campos-Pineda, M. and Zhang, J.: *Chem. Phys. Lett.*, 683, 647, 2017.
- Chew, A. A. and Atkinson, R.: *J. Geophys. Res.*, 101, 28649, 1996.
- Drozd, G. T., Kroll, J. and Donahue, N. M.: *J. Phys. Chem. A*, 115, 161, 2011.
- Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: *J. Phys. Chem. A*, 104, 7821, 2000.
- Greene, C. R. and Atkinson, R.: *Int. J. Chem. Kinet.*, 24, 803, 1992.
- Grosjean, E. and Grosjean, D.: *Environ. Sci. Technol.* 30, 2036, 1996.
- Hakala, J. P. and Donahue, N. M.: *J. Phys. Chem. A*, 120, 2173, 2016.
- Huie, R. E. and Herron, J. T.: *Int. J. Chem. Kinet., Symp.* 1, 165, 1975.
- Japar, S. M., Wu, C. H. and Niki, H.: *J. Phys. Chem.*, 78, 2318, 1974.
- Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: *J. Phys. Chem. A*, 105, 4446, 2001.
- Newland, M. J., Rickard, A. R., Alam, M. S., Vereecken, L., Muñoz, A., Ródenas, M. and Bloss, W. J.: *Phys. Chem. Chem. Phys.*, 17, 4076, 2015.
- Newland, M. J., Nelson, B. S., Muñoz, A., Ródenas, M., Vera, T., Tárrega, J., and Rickard, A. R.: *Phys. Chem. Chem. Phys.*, 22, 13698, 2020.
- Orzechowska, G. and Paulson, S. E.: *Atmos. Environ.*, 36, 571, 2002.
- Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: *J. Phys. Chem. A*, 103, 7656, 1999.
- Siese, M., Becker, K. H., Brockmann, K. J., Geiger, H., Hofzumahaus, A., Holland, F., Mihelcic, D. and Wirtz, K.: *Environ. Sci. Technol.*, 35, 4660, 2001.
- Tuazon, E. C., Aschmann, S. M., Arey, J. and Atkinson, R.: *Environ. Sci. Technol.*, 31, 3004, 1997.
- Wedian, F. Z. and Atkinson, D. B.: *J. Atmos. Chem.*, 66, 65, 2010.
- Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: *Int. J. Chem. Kinet.*, 34, 394, 2002.



Ox_VOC7: isoprene

Last evaluated: March 2020; Last change in preferred values: July 2018

O₃ + CH₂=C(CH₃)CH=CH₂ (isoprene) → products**Rate coefficient data**

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.27 × 10 ⁻¹⁷	295 ± 1	Arnts and Gay, 1979	S-CL/GC (a)
7.0 × 10 ⁻¹⁸	260 ± 2	Adeniji et al., 1981	S-CL/GC-FID (a)
1.65 × 10 ⁻¹⁷	294 ± 2		
1.54 × 10 ⁻¹⁴ exp[-(2153 ± 430)/T]	278-323	Atkinson et al., 1982	S-CL/GC-FID (a)
(1.17 ± 0.19) × 10 ⁻¹⁷	296 ± 2		
7.8 × 10 ⁻¹⁵ exp[-(1913 ± 139)/T]	242-323	Treacy et al., 1992	S-CL (a)
(1.28 ± 0.12) × 10 ⁻¹⁷	298		
(8.95 ± 0.25) × 10 ⁻¹⁸	293 ± 2	Grosjean et al., 1993	S-UVA/FTIR (a)
(1.13 ± 0.32) × 10 ⁻¹⁷	291 ± 2	Grosjean and Grosjean, 1996	S-UVA/FTIR (a)
1.30 × 10 ⁻¹⁷	296 ± 2	Neeb et al., 1999	S-FTIR (b)
(1.19 ± 0.09) × 10 ⁻¹⁷	293 ± 2	Klawatsch-Carrasco et al., 2004	S-FTIR (c)
(9.6 ± 0.7) × 10 ⁻¹⁸	286	Karl et al., 2004	S-UVA/GC-FID (d)
(1.24 ± 0.03) × 10 ⁻¹⁷	298 ± 1	Sato et al., 2013	S-FTIR (e)
(1.13 ± 0.17) × 10 ⁻¹⁷	294 ± 2	Ren et al., 2017	S-UVA/FTIR (f)
(9.3 ± 0.7) × 10 ⁻¹⁸	285 ± 2		
(8.6 ± 0.5) × 10 ⁻¹⁸	285 ± 2	Ren et al., 2017	S-UVA/FTIR (a)
<i>Relative Rate Coefficients</i>			
(1.22 ± 0.02) × 10 ⁻¹⁷	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (g)
9.96 × 10 ⁻¹⁵ exp[-(1973 ± 42)/T]	257-324	Khamaganov and Hites, 2001	RR-MS (h,i)
(1.31 ± 0.08) × 10 ⁻¹⁷	298		
1.69 × 10 ⁻¹⁴ exp[-(2080 ± 120)/T]	242-324	Khamaganov and Hites, 2001	RR-MS (h,j)
(1.56 ± 0.13) × 10 ⁻¹⁷	298		
1.31 × 10 ⁻¹⁴ exp[-(2056 ± 87)/T]	242-324	Khamaganov and Hites, 2001	RR-MS (h,k)
(1.31 ± 0.07) × 10 ⁻¹⁷	298		
9.45 × 10 ⁻¹⁵ exp[-(1963 ± 72)/T]	258-324	Khamaganov and Hites, 2001	RR-MS (h,l)
(1.31 ± 0.08) × 10 ⁻¹⁷	298		
1.43 × 10 ⁻¹⁴ exp[-(2015 ± 149)/T]	278-353	Avzianova and Ariya, 2002	RR/GC-FID (m)
(1.23 ± 0.03) × 10 ⁻¹⁷	298		

Comments

- (a) *k* determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of isoprene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- (b) *k* determined from the observed first-order rate of isoprene decay in the presence of known excess concentrations of ozone, with both reagents measured by FTIR. Cyclohexane added to scavenge HO radicals.
- (c) Both reagents measured by FTIR. Experiments carried out with isoprene in slight excess, in the presence of excess CO as an HO radical scavenger. A value of *k* was retrieved for each time point during reagent decay in two experiments, based on the observed loss of ozone and the measured

concentration of isoprene. The quoted value of k was based on the average of 27 time point determinations.

- (d) k determined from the observed rate of isoprene decay (measured by GC-FID) in the presence of known excess, but changing, concentrations of ozone (measured by UVA), using numerical integration. CO added to scavenge HO radicals.
- (e) k determined from the observed rate of isoprene decay in the presence of known excess, but changing, concentrations of ozone, using numerical integration. Both reagents were measured by FTIR. Experiments were carried out using four HO scavengers (cyclohexane, CO, hexane and diethyl ether), leading to respective values of k (in units $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of 1.22 ± 0.07 , 1.24 ± 0.07 , 1.28 ± 0.03 and 1.23 ± 0.09 . The tabulated value is the average of these determinations. A higher value of $(1.47 \pm 0.04) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained in the absence of an HO scavenger.
- (f) k determined from the observed first-order rate of isoprene decay (measured by FTIR) in the presence of known excess concentrations of ozone (measured by UVA). Cyclohexane added to scavenge HO radicals. Rate coefficients approximately 15 % higher value were obtained in the absence of an HO scavenger.
- (g) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured value of $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{propene}) = 1.21 \pm 0.02$ is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (h) Relative rate method carried out at 760 Torr (1.013 bar) of helium diluent in a 192 cm^3 volume cylindrical quartz reactor, with ethanol or acetaldehyde being present to scavenge the HO radicals formed. The concentrations of isoprene and the reference compound were monitored by MS.
- (i) With 2-methylpropene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + 2\text{-methylpropene})$ are placed on an absolute basis using a rate coefficient of $k(\text{O}_3 + 2\text{-methylpropene}) = 2.92 \times 10^{-15} \exp(-1650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendation). Note that in Table 3 of Khamaganov and Hites (2001), the rate coefficient ratios stated to be relative to 2-methylpropene appear (Table 7 and Figure 4) to be relative to but-1-ene, and *vice versa*.
- (j) With *cis*-but-2-ene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{cis-but-2-ene})$ are placed on an absolute basis using $k(\text{O}_3 + \text{cis-2-butene}) = 3.37 \times 10^{-15} \exp(-970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendation).
- (k) With 1-butene as the reference compound. The measured rate coefficient ratios [see Comment (e)] $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{but-1-ene})$ are placed on an absolute basis using $k(\text{O}_3 + 1\text{-butene}) = 3.55 \times 10^{-15} \exp(-1750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendation).
- (l) With 2,3-dimethyl-1,3-butadiene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-1,3-diene})$ are placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-1,3-butadiene}) = 6.9 \times 10^{-15} \exp(-1668/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- (m) Relative rate study, with 1,3,5-trimethylbenzene present to scavenge HO radicals. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratios were not tabulated, except at room temperature, assumed to be 298 K. The expression $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{propene}) = 2.47 \exp[(135 \pm 149)/T]$, derived from the data, is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 5.77 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). Note that the 298 K rate coefficient calculated from the reported Arrhenius expression is about 30 % higher than the measured value (see table).

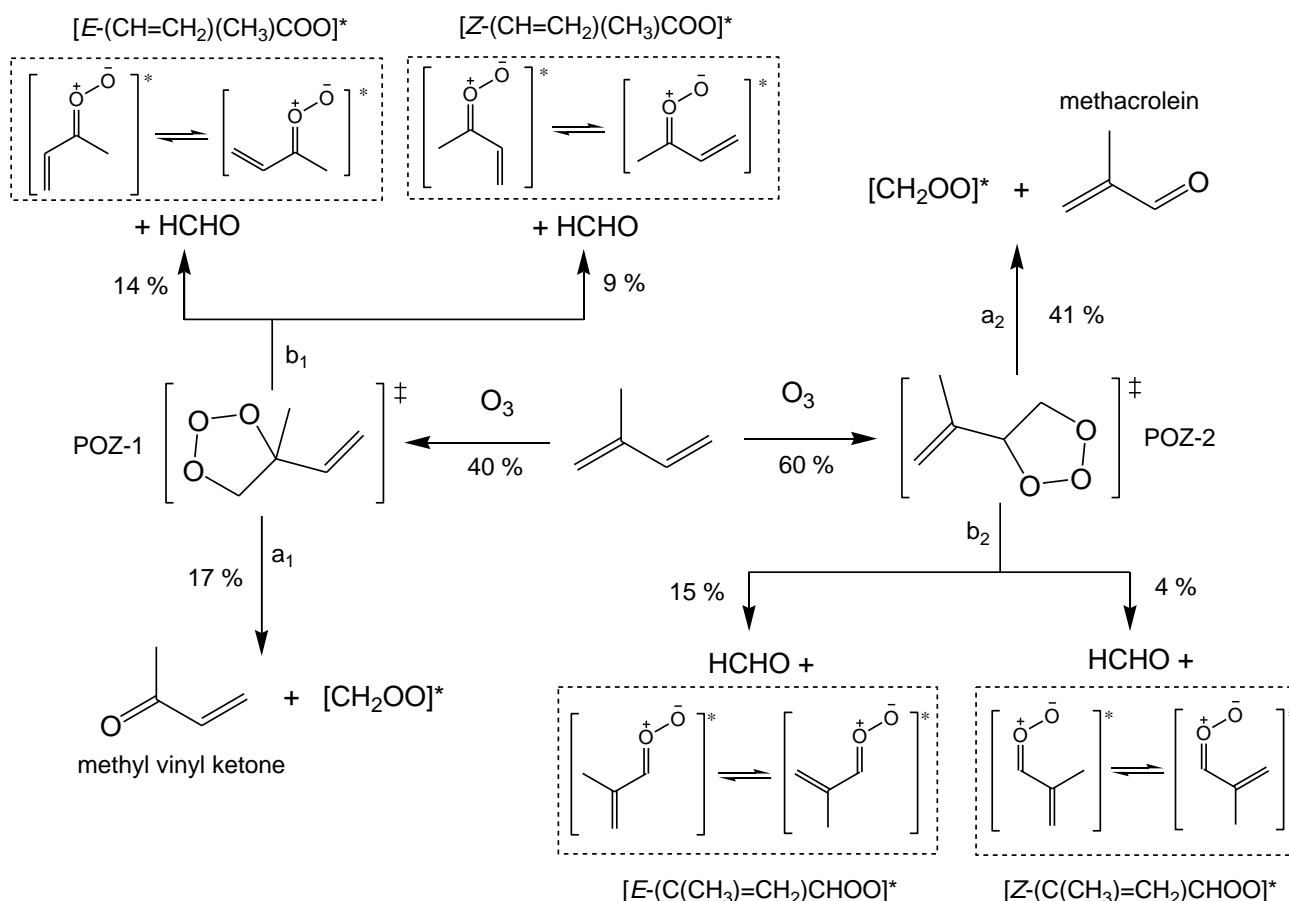
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.28×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.05 \times 10^{-14} \exp(-2000/T)$	240-360
<i>Reliability</i>		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 200	240-360

Comments on Preferred Values

The kinetics determinations are in generally good agreement, with consistent values of the temperature coefficient (E/R) reported in a number of studies. The preferred value of E/R is the average of those reported by Treacy et al. (1992), Khamaganov and Hites (2001) and Avzianova and Ariya (2002). The preferred value of k at 298 K is an average of the room temperature determinations reported by Atkinson et al. (1982), Treacy et al. (1992), Greene and Atkinson (1992), Grosjean and Grosjean (1996), Neeb and Moortgat (1999), Khamaganov and Hites (2001), Avzianova and Ariya (2002), Karl et al. (2004), Sato et al. (2013) and Ren et al. (2017), corrected to 298 K, where necessary, using the preferred value of E/R .

It is well established that the reaction proceeds by initial addition of O_3 to either of the $\text{C}=\text{C}$ bonds in the conjugated diene system, forming a pair of energy-rich primary ozonides (POZ-1 and POZ-2) as shown in the schematic below.



POZ-1 rapidly decomposes to form either methyl vinyl ketone and the (excited) Criegee intermediate, $[\text{CH}_2\text{OO}]^*$ (route a_1); or formaldehyde (HCHO) in conjunction with either $[E-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}]^*$ or $[Z-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}]^*$ (route b_1). Similarly, POZ-2 decomposes to form either methacrolein and $[\text{CH}_2\text{OO}]^*$ (route a_2); or HCHO in conjunction with either $[E-(\text{C}(\text{CH}_3)=\text{CH}_2)\text{CHOO}]^*$ or $[Z-(\text{C}(\text{CH}_3)=\text{CH}_2)\text{CHOO}]^*$ (route b_2). Reported molar yields of the C_4 carbonyls, methacrolein (0.32 – 0.44) and methyl vinyl ketone (0.13 – 0.18) are consistent with their formation mainly as primary products (e.g. Aschmann and Atkinson, 1994; Grosjean et al., 1993; Rickard et al., 1999; Nguyen et al., 2016). These yields suggest significant contributions from initial addition of O_3 to each $\text{C}=\text{C}$ bond in isoprene, and from decomposition routes a_1 for POZ-1 and a_2 for POZ-2. Reported molar yields of HCHO (0.79 – 0.90; Grosjean et al., 1993; Nguyen et al., 2016) are consistent with the operation of decomposition routes b_1 and b_2 , with HCHO formed directly and from the subsequent chemistry of both sets of C_4 Criegee intermediate and $[\text{CH}_2\text{OO}]^*$. The contributions assigned to the channels in the schematic are taken from Nguyen et al. (2016), and are a combination of their results and information from the literature.

The excited Criegee intermediates may either decompose/isomerize, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI). A number of relatively recent studies report total sCI yields that are in good agreement, based on scavenging with added SO_2 or H_2O and quantification of the associated products or reagent removal (Sipilä et al., 2014; Newland et al., 2015; Nguyen et al., 2016). We recommend a yield of 0.65 ± 0.10 , based on consideration of these results (see data sheet CGI_21). The information suggests that CH_2OO makes a major contribution to the total, as a result of near-quantitative stabilization of $[\text{CH}_2\text{OO}]^*$. The contribution of the C_4 sCI isomers is therefore believed to be comparatively limited (particularly under atmospheric conditions), partly because they are not stabilized to the same extent as CH_2OO , but also because very rapid unimolecular reactions are estimated to be available for stabilized $Z-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}$ and $Z-(\text{C}(\text{CH}_3)=\text{CH}_2)\text{CHOO}$ (Vereecken et al., 2017), with decomposition likely also the major fate for $E-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}$. Based on reported kinetic data (summarised and evaluated in datasheets CGI_1 to CGI_12), the major fate of CH_2OO under tropospheric conditions is expected to be removal via bimolecular reactions, e.g. with $(\text{H}_2\text{O})_2$, NO_2 and SO_2 .

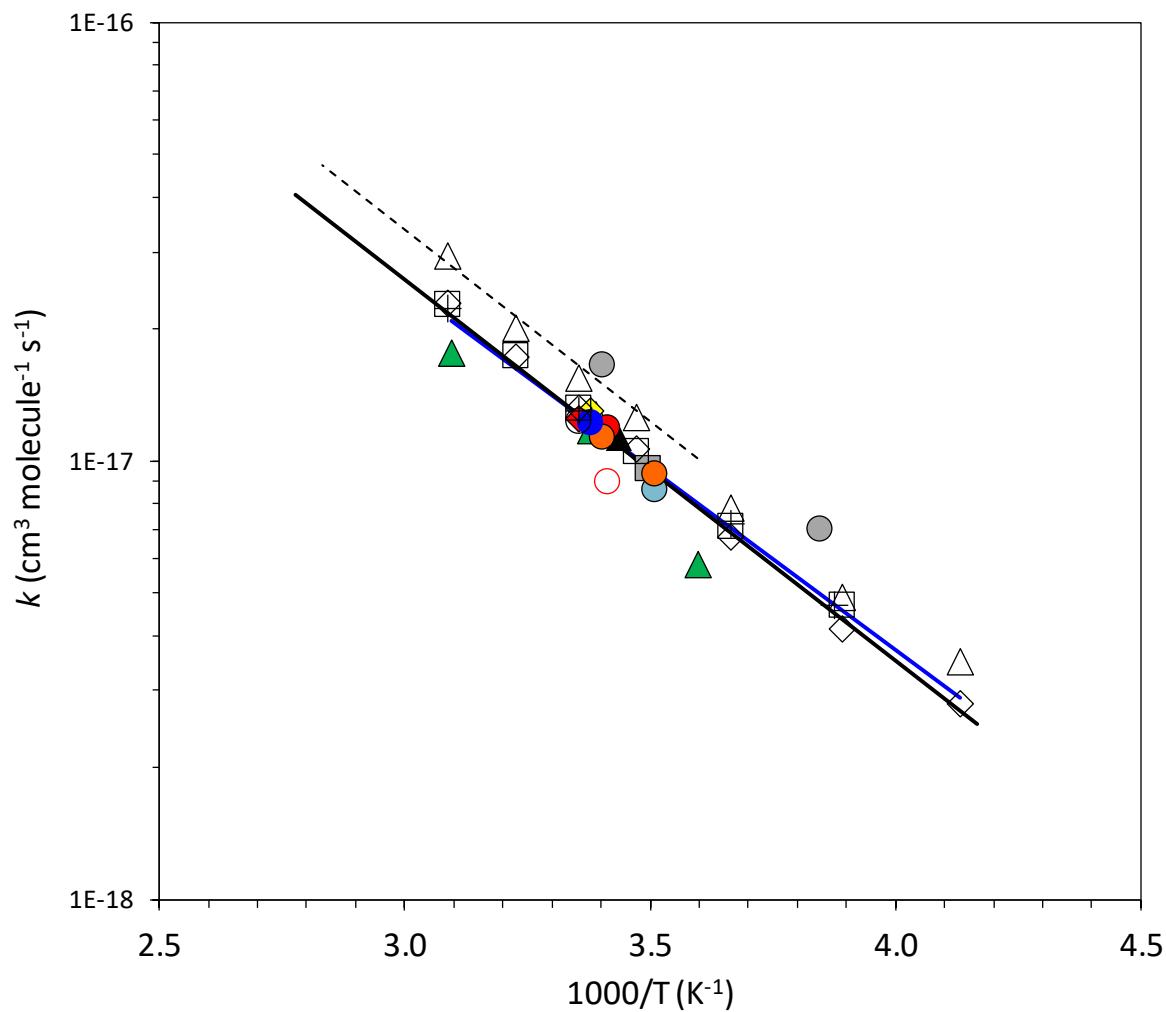
Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Aschmann et al., 1996; Paulson et al., 1998; Neeb and Moortgat, 1999; Malkin et al., 2010; Nguyen et al., 2016; Ren et al., 2017), with yields in the range 0.24-0.28 (preferred value, 0.26 ± 0.04). An important contribution to HO formation is expected to result from (excited or stabilized) $E-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}$, by an accepted decomposition mechanism involving migration of a β -hydrogen from the $-\text{CH}_3$ group via a vinyl hydroperoxide intermediate (Fenske et al., 2000; Kroll et al., 2001; Barber et al., 2018), also forming the $\text{CH}_2=\text{CHC}(=\text{O})\text{CH}_2$ radical as a co-product. However, additional indirect HO formation may result from the further chemistry of $\text{CH}_2=\text{CHC}(=\text{O})\text{CH}_2$, and following decomposition of the other C_4 Criegee intermediates, as described in the detailed mechanisms presented by Nguyen et al. (2016). These mechanisms also include significant secondary sources of HCHO, and can account for the reported formation of a number of C_1 - C_3 products (e.g. pyruvic acid and methyl glyoxal) in low yields (Grosjean et al., 1993).

References

- Adeniji, S. A., Kerr, J. A. and Williams, M. R.: Int. J. Chem. Kinet., 13, 209, 1981.
- Arnts, R. R. and Gay Jr., B. W.: Photochemistry of Some Naturally Emitted Hydrocarbons, U.S. Environmental Protection Agency Report No. EPA-600/3-79-081, Environmental Sciences Research Laboratory, Office of Research and Development, Research Triangle Park, NC, September 1979.
- Aschmann, S. M. and Atkinson, R.: Environ. Sci. Technol., 28, 1539, 1994.
- Aschmann, S. M., Arey, J., and Atkinson, R.: Atmos. Environ., 30, 2939-2943, 1996.

- Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: *Atmos. Environ.*, 16, 1017, 1982.
- Avzianova, E. V. and Ariya, P. A.: *Int. J. Chem. Kinet.*, 34, 678, 2002.
- Barber, V. P., Pandit, S., Green, A. M., Trongsiwat, N., Walsh, P. J., Klippenstein, S. R. and Lester, M. I.: *J. Am. Chem. Soc.*, 140, 10866, 2018.
- Fenske, J. D., Hasson, A. S., Paulson, S. E., Kuwata, K. T., Ho, A. and Houk, K. N.: *J. Phys. Chem. A*, 104, 7821, 2000b.
- Greene, C. R. and Atkinson, R.: *Int. J. Chem. Kinet.*, 24, 803, 1992.
- Grosjean, D., Williams II, E. L. and Grosjean, E.: *Environ. Sci. Technol.*, 27, 830, 1993.
- Grosjean, E. and Grosjean, D.: *Int. J. Chem. Kinet.*, 28, 911, 1996.
- Karl, M., Brauers, Th., Dorn, H.-P., Holland, F., Komenda, M., Poppe, D., Rohrer, F., Rupp, L., Schaub, A. and Wahner, A.: *Geophys. Res. Lett.*, 31, L05117, doi: 10.1029/2003GL019189, 2004.
- Khamaganov, V. G. and Hites, R. A.: *J. Phys. Chem. A*, 105, 815, 2001.
- Klawatsch-Carrasco, N., Doussin, J. F. and Carlier, P.: *Int. J. Chem. Kinet.*, 36, 152, 2004.
- Kroll, J. H., Sahay, S. R., Anderson, J. G., Demerjian, K. L. and Donahue, N. M.: *J. Phys. Chem. A*, 105, 4446, 2001.
- Malkin, T. L., Goddard, A., Heard, D. E. and Seakins, P. W.: *Atmos. Chem. Phys.*, 10, 1441-1459, 2010.
- Neeb, P. and Moortgat, G. K.: *J. Phys. Chem. A*, 103, 9003, 1999.
- Newland, M. J., Rickard, A. R., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.: *Atmos. Chem. Phys.*, 15, 9521-9536, <https://doi.org/10.5194/acp-15-9521-2015>, 2015.
- Nguyen, T. B., Tyndall, G. S., Crounse, J. D., Teng, A. P., Bates, K. H., Schwantes, R. H., Coggon, M. M., Zhang, L., Feiner, P., Müller, D. O., Skog, K. M., Rivera-Rios, J. C., Dorris, M., Olson, K. F., Koss, A., Wild, R. J., Brown, S. S., Goldstein, A. H., de Gouw, J. A., Brune, W. H., Keutsch, F. N., Seinfeld, J. H. and Wennberg, P. O.: *Phys. Chem. Chem. Phys.*, 18, 10241, 2016.
- Paulson, S. E., Chung, M., Sen, A. D. and Orzechowska, G.: *J. Geophys. Res.-Atmos.*, 103, 25533-25539, 1998.
- Ren, Y., Grosselin, B., Daële, V. and Mellouki, A.: *Faraday Discuss.*, 200, 289, 2017.
- Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: *J. Phys. Chem. A*, 103, 7656, 1999.
- Sato, K., Inomata, S., Xing, J.-H., Imamura, T., Uchida, R., Fukuda, S., Nakagawa, K., Hirokawa, J., Okumura, M. and Tohno, S.: *Atmos. Environ.*, 79, 147, 2013.
- Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin III, R. L., Kurtén, T., Paasonen, P., Sarnela, N., Ehn, M., Junninen, H., Rissanen, M. P., Thornton, J., Stratmann, F., Herrmann, H., Worsnop, D. R., Kulmala, M., Kerminen, V.-M., and Petäjä, T.: *Atmos. Chem. Phys.*, 14, 12143, <https://doi.org/10.5194/acp-14-12143-2014>, 2014.
- Treacy, J., El Haag, M., O'Farrell, D. and Sidebottom, H.: *Ber. Bunsenges. Phys. Chem.*, 96, 422, 1992.
- Vereecken, L., Novelli, A. and Taraborrelli, D.: *Phys. Chem. Chem. Phys.*, 19, 31599, 2017.

- △ Arnts and Gay (1979)
- ▲ Atkinson et al. (1982)
- Grosjean et al. (1993)
- ◇ Neeb and Moortgat (1999)
- Karl et al. (2004)
- Ren et al. (2017) isoprene excess
- Greene and Atkinson (1992)
- △ Khamanagov and Hites (2001) relative to cis-but-2-ene
- + Khamanagov and Hites (2001) relative to 2,3-dimethyl-buta-1,3-diene
- - - Avzianova and Ariya (2002) Arrhenius expression
- Adeniji et al. (1981)
- Treacy et al. (1992)
- ▲ Grosjean and Grosjean (1996)
- Klawatsch-Carrasco et al. (2004)
- ◇ Sato et al. (2013)
- Ren et al. (2017) ozone excess
- Khamanagov and Hites (2001) relative to 2-methylpropene
- ◇ Khamanagov and Hites (2001) relative to but-1-ene
- Avzianova and Ariya (2002)
- Recommendation



A2. Data sheets for reactions of O₃ with monoterpenes

Ox_VOC8: α -pinene

Last evaluated: August 2020; Last change in preferred values: August 2018



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.6×10^{-16}	294	Ripperton et al., 1972	S-CL
$(3.3 \pm 0.3) \times 10^{-16}$	298	Japar et al., 1974	S-CL
1.45×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
$9.4 \times 10^{-16} \exp[-(731 \pm 173)/T]$	276-324	Atkinson et al., 1982	S-CL/GC (a)
$(8.4 \pm 1.9) \times 10^{-17}$	296 ± 2		
$(9.71 \pm 1.06) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (b)
$1.4 \times 10^{-15} \exp[-(833 \pm 86)/T]$	243.1-303.2	Tillmann et al., 2009	S-UVA/MS (c)
$(9.0 \pm 0.6) \times 10^{-17}$	303.2		
$(1.1 \pm 0.1) \times 10^{-16}$	296 ± 1	Bernard et al., 2012	F-CL (d)
<i>Relative Rate Coefficients</i>			
$(8.54 \pm 1.29) \times 10^{-17}$	297 ± 2	Nolting et al., 1988	RR-GC (e)
$6.0 \times 10^{-16} \exp[-(560 \pm 87)/T]$	288-363	Khamaganov and Hites, 2001	RR-MS (f,g)
$(9.39 \pm 0.46) \times 10^{-17}$	298		
$3.8 \times 10^{-16} \exp[-(447 \pm 303)/T]$	288-343	Khamaganov and Hites, 2001	RR-MS (f,h)
$(8.26 \pm 0.34) \times 10^{-17}$	298		
$(1.06 \pm 0.09) \times 10^{-16}$	295 ± 0.5	Witter et al., 2002	RR-GC (i)
$(9.26 \pm 0.84) \times 10^{-17}$	302 ± 1	Bernard et al., 2012	RR-IR (j,k)
$(1.03 \pm 0.04) \times 10^{-16}$	302 ± 1		RR-IR (j,l)
$(1.13 \pm 0.14) \times 10^{-16}$	298 ± 2	Stewart et al., 2013	RR-GC (m)

α -pinene is 2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of α -pinene (measured by GC-FID). Experiments were carried out either in a 175 L Teflon bag or in the SAPRC 5800 L Teflon-coated environmental chamber.
- (b) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of α -pinene (measured by GC-FID). Experiments were carried out in a 160 L Teflon chamber. From measurements of the absolute rate coefficient for the reaction of O₃ with sabinene and the ratio $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \text{sabinene})$, a rate coefficient of $k(\text{O}_3 + \alpha\text{-pinene}) = (7.99 \pm 1.20) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was also derived.

- (c) k determined from the observed first-order rate of ozone decay (measured with a UV absorption monitor) in the presence of known excess concentrations of α -pinene (measured by PTR-MS) and cyclohexane to scavenge HO radicals. Experiments were carried out at atmospheric pressure in a thermostatically-controlled 84.3 m³ aluminium chamber.
- (d) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of α -pinene, in a flow reactor at a total pressure of ~ 1 bar.
- (e) The concentrations of a series of alkenes (including α -pinene and *cis*-but-2-ene, the reference compound) were monitored by GC in a 520 L Pyrex chamber at ~ 1 bar pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{cis}\text{-but-2-ene})$ is placed on an absolute basis using a rate coefficient at 297 K of $k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 1.29 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). Details concerning the reactant mixtures and the presence or absence of an HO radical scavenger were not reported.
- (f) The concentrations of α -pinene and but-1-ene or 2-methylpropene (the reference compounds) were monitored by MS in reacting O₃ - α -pinene - but-1-ene (or 2-methylpropene) - acetaldehyde (or ethanol) [HO radical scavengers] - He mixtures in a 192 cm³ volume quartz vessel at ~ 1 bar pressure. The measured rate coefficient ratios $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \text{but-1-ene}) = 0.17 \exp[(1190 \pm 87)/T]$ and $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + 2\text{-methylpropene}) = 0.13 \exp[(1203 \pm 303)/T]$ are placed on an absolute basis using $k(\text{O}_3 + \text{but-1-ene}) = 3.55 \times 10^{-15} \exp(-1750/T)$ and $k(\text{O}_3 + 2\text{-methylpropene}) = 2.92 \times 10^{-15} \exp(-1650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendations). Khamaganov and Hites (2001) also report the Arrhenius expression, $k(\text{O}_3 + \alpha\text{-pinene}) = 4.8 \times 10^{-16} \exp[-(530 \pm 150)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 288-363 K and $k(\text{O}_3 + \alpha\text{-pinene}) = (8.41 \pm 0.74) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, based on the combined data.
- (g) Relative to $k(\text{O}_3 + \text{but-1-ene})$.
- (h) Relative to $k(\text{O}_3 + 2\text{-methylpropene})$.
- (i) The concentrations of α -pinene and 2-methylbut-2-ene (the reference compound) were monitored by GC in reacting O₃ - α -pinene - 2-methylbut-2-ene - *m*-xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + 2\text{-methylbut-2-ene}) = 0.270 \pm 0.022$ is placed on an absolute basis using a rate coefficient at 295 K of $k(\text{O}_3 + 2\text{-methylbut-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).
- (j) The concentrations of α -pinene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O₃ - α -pinene - reference compound - cyclohexane (HO radical scavenger) - air mixtures in a 7300 L Teflon chamber at ~ 1 bar pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \text{cyclohexene}) = 1.09 \pm 0.10$ and $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{cis}\text{-cyclooctene}) = 0.27 \pm 0.01$, are placed on an absolute basis using $k(\text{O}_3 + \text{cyclohexene}) = 8.50 \times 10^{-17}$ and $k(\text{O}_3 + \textit{cis}\text{-cyclooctene}) = 3.80 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 302 K (Atkinson and Arey, 2003a).
- (k) Relative to $k(\text{O}_3 + \text{cyclohexene})$.
- (l) Relative to $k(\text{O}_3 + \textit{cis}\text{-cyclooctene})$.
- (m) The concentrations of α -pinene and cycloheptene (the reference compound) were monitored by GC-FID in flowing mixtures of O₃, α -pinene, cycloheptene, cyclohexane (the HO radical scavenger) and air at 760 Torr (1.013 bar) pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \text{cycloheptene}) = 0.453 \pm 0.036$ is placed on an absolute basis using a rate coefficient at 298 K of $k(\text{O}_3 + \text{cycloheptene}) = 2.50 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).

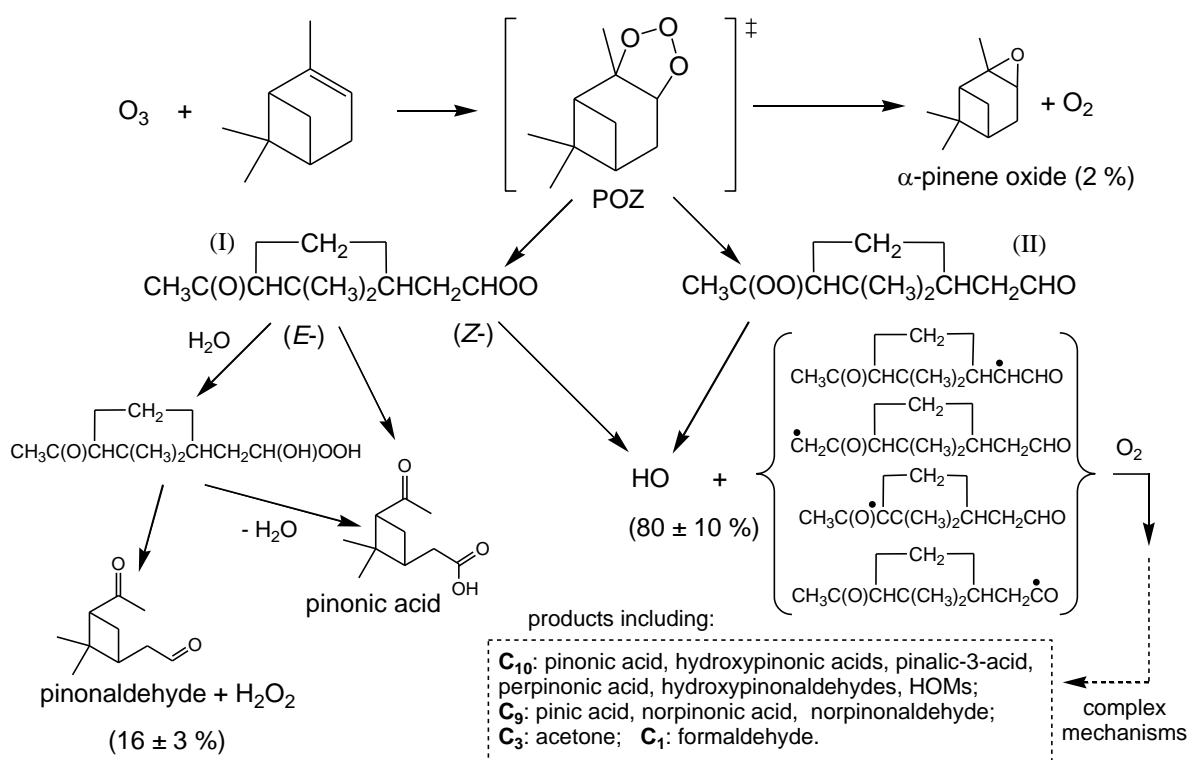
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	9.6×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$8.22 \times 10^{-16} \exp(-640/T)$	240-370
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298
$\Delta E/R$	± 300	240-370

Comments on Preferred Values

The room temperature rate coefficients reported by Ripperton et al. (1972), Japar et al. (1974) and Grimsrud et al. (1975) are significantly higher than the more recent measurements of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001), Witter et al. (2002), Tillmann et al. (2009), Bernard et al. (2012) and Stewart et al. (2013); although there is still a significant amount of scatter between the room temperature rate coefficients of these more recent measurements. The preferred temperature dependence is obtained from a simple average of the temperature dependences obtained by Atkinson et al. (1982), Khamaganov and Hites (2001) and Tillmann et al. (2009). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001), Witter et al. (2002), Tillmann et al. (2009), Bernard et al. (2012) and Stewart et al. (2013), corrected to 298 K where necessary using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value.

Product yields and mechanistic information have been reported in a number of studies, as summarized in the reviews of Atkinson and Arey (2003b) and Johnson and Marston (2008). The reaction proceeds by initial addition of O_3 to the $\text{C}=\text{C}$ bond in α -pinene to form a “primary ozonide (POZ)” which rapidly decomposes, mainly to form two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the following schematic:



The stabilization of the Criegee intermediates is reported to be limited, with a preferred stabilized Criegee intermediate (sCI) yield of 0.18 ± 0.05 recommended at atmospheric pressure, based on the determinations of Sipilä et al. (2014) (adjusted using the preferred value of k) and Newland et al. (2018), and also consistent with Drozd and Donahue (2011). Whether excited or stabilized, the *Z*- conformer of Criegee intermediate (I) and Criegee intermediate (II) mainly decompose to form HO radicals and a number of β -oxo alkyl radicals, as shown in the schematic. The further chemistry of the β -oxo alkyl radicals may form a number of reported multifunctional organic products containing hydroxy, hydroperoxy, carbonyl and acid functionalities (e.g. Johnson and Marston, 2008), including a small yield of highly oxidized multifunctional organic compounds, HOMs, with very high oxygen to carbon ratios (e.g. Ehn et al., 2012). Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (Atkinson et al., 1992; Chew and Atkinson, 1996; Paulson et al., 1998; Rickard et al., 1999; Siese et al., 2001; Aschmann et al., 2002; Berndt et al., 2003; Presto and Donahue, 2004; Forester and Wells, 2011), with yields in the range 0.68-0.91 (preferred value, 0.80 ± 0.10). Formation of HO via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) is not possible for the *E*- conformer of Criegee Intermediate (I) (e.g. see Johnson and Marston, 2008). If stabilized, this is expected to react predominantly with H₂O under atmospheric conditions, leading to the formation of pinonaldehyde and H₂O₂, or pinonic acid. Consensus yields are shown for α -pinene oxide and pinonaldehyde.

References

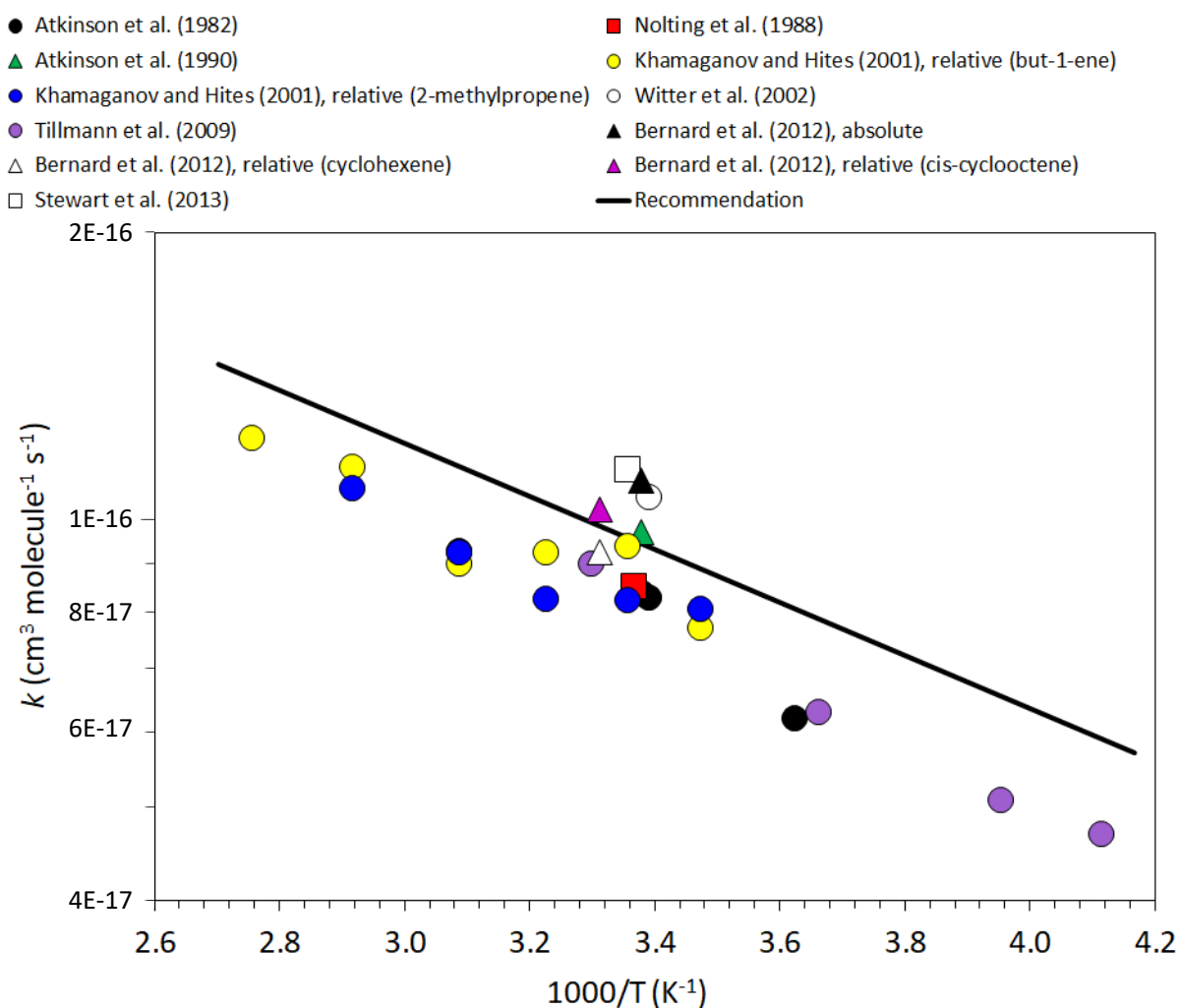
- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003a.
- Atkinson, R. and Arey, J.: Atmos. Environ., 37 Suppl. 2, S197, 2003b.
- Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: Atmos. Environ., 16, 1017, 1982.
- Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
- Atkinson, R., Aschmann, S. M., Arey, J. and Shorees, B.: J. Geophys. Res., 97, 6065, 1992.
- Bernard, F., Fedioun, I., Peyroux, F., Quilgars, A., Daële, V. and Mellouki, A.: J. Aerosol Sci., 43, 14, 2012.
- Berndt, T., Böge, O and Stratmann, F: Atmos. Environ., 37, 3933, 2003.
- Chew, A. A. and Atkinson, R.: J. Geophys. Res., 101, 28649, 1996.
- Drozd, G. T. and Donahue, N. M.: J. Phys. Chem. A, 115, 4381, 2011.
- Ehn, M., Kleist, E., Junninen, H., Petäjä, T., Lönn, G., Schobesberger, S., Dal Maso, M., Trimborn, A., Kulmala, M., Worsnop, D. R., Wahner, A., Wildt, J., and Mentel, Th. F.: Atmos. Chem. Phys., 12, 5113, 2012.
- Forester, C. D. and Wells, J. R.: Indoor Air, 21, 400, 2011.
- Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: Int. J. Chem. Kinet., Symp. 1, 183, 1975.
- Japar, S. M., Wu, C. H. and Niki, H.: Environ. Lett., 7, 245, 1974.
- Johnson, D. and Marston, G.: Chem. Soc. Rev., 37, 699, 2008.
- Khamaganov, V. G. and Hites, R. A.: J. Phys. Chem. A, 105, 815, 2001.
- Newland, M. J., Rickard, A. R., Sherwen, T., Evans, M. J., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.: Atmos. Chem. Phys., 18, 6095, 2018.
- Nolting, F., Behnke, W. and Zetzsch, C.: J. Atmos. Chem., 6, 47, 1988.
- Paulson, S. E., Chung, M., Sen, A. D. and Orzechowska, G.: J. Geophys. Res.-Atmos., 103, 25533, 1998.
- Presto, A. A. and Donahue, N. M.: J. Phys. Chem. A, 108, 9096, 2004.
- Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: J. Phys. Chem. A, 103, 7656, 1999.
- Ripperton, L. A., Jeffries, H. E. and White, O.: Adv. Chem. Ser., 113, 219, 1972.
- Siese, M., Becker, K. H., Brockmann, K. J., Geiger, H., Hofzumahaus, A., Holland, F., Mihelcic, D. and Wirtz, K.: Environ. Sci. Technol., 35, 4660, 2001.

Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin III, R. L., Kurtén, T., Paasonen, P., Sarnela, N., Ehn, M., Junninen, H., Rissanen, M. P., Thornton, J., Stratmann, F., Herrmann, H., Worsnop, D. R., Kulmala, M., Kerminen, V.-M., and Petäjä, T.: Atmos. Chem. Phys., 14, 12143, 2014.

Stewart, D. J., Almarok, S. H., Lockhart, J. P., Mohamed, O. M., Nutt, D. R., Pfrang, C., Marston, G.: Atmos. Environ., 70, 227, 2013.

Tillmann, R., Saathoff, H., Brauers, T., Kiendler-Scharra, A. and Mentel, T. F.: Phys. Chem. Chem. Phys., 11, 2323, 2009.

Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: Int. J. Chem. Kinet., 34, 394, 2002.



Ox_VOC19: β -pinene

Last evaluated: August 2020; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
6.5×10^{-17}	294	Ripperton et al., 1972	S-CL
3.6×10^{-17}	295 ± 1	Grimsrud et al., 1975	F-CL
$(2.1 \pm 0.5) \times 10^{-17}$	296 ± 2	Atkinson et al., 1982	S-CL/GC (a)
$(1.48 \pm 0.17) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (b)
$(1.22 \pm 0.13) \times 10^{-17}$	295 ± 1	Grosjean et al., 1993	S-UVA (c)
<i>Relative Rate Coefficients</i>			
$(1.39 \pm 0.20) \times 10^{-17}$	297 ± 2	Nolting et al., 1988	RR-GC (d)
$(1.82 \pm 0.22) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	RR-GC (e)
$(2.39 \pm 0.27) \times 10^{-17}$	298 ± 2	Johnson et al., 2000	RR-GC (f)
$1.72 \times 10^{-15} \exp[-(1278 \pm 84)/T]$	298-363	Khamaganov and Hites, 2001	RR-MS (g,h)
$(2.34 \pm 0.13) \times 10^{-17}$	298		
$(2.25 \pm 0.19) \times 10^{-17}$	298	Khamaganov and Hites, 2001	RR-MS (g,i)

 β -pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane**Comments**

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of β -pinene (measured by GC-FID). Experiments were carried out either in a 175 L Teflon bag or in the SAPRC 5800 L Teflon-coated environmental chamber.
- (b) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of β -pinene (measured by GC-FID). Experiments were carried out in a 160 L Teflon chamber.
- (c) k determined from the observed first-order rate of ozone decay (measured by UV photometry) in the presence of excess concentrations of β -pinene, with cyclohexane to scavenge HO radicals. Experiments were carried out in a 3.5 m³ Teflon chamber.
- (d) The concentrations of a series of alkenes (including β -pinene and *cis*-but-2-ene, the reference compound) were monitored by GC in a 520 L Pyrex chamber at ~1 bar pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + \textit{cis}\text{-but-2-ene})$ is placed on an absolute basis using a rate coefficient of $k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 1.29 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation). Details concerning the reactant mixtures and the presence or absence of an HO radical scavenger were not reported.
- (e) The concentrations of a series of alkenes (including β -pinene and α -pinene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 +$

- α -pinene) = $9.46 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (f) The concentrations of β -pinene and 2-methylpropene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 50 L collapsible Teflon chamber at 760 Torr (1013 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + 2\text{-methylpropene})$ is placed on an absolute basis using $k(\text{O}_3 + 2\text{-methylpropene}) = 1.15 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (g) The concentrations of β -pinene and *cis*-but-2-ene or but-1-ene (the reference compounds) were monitored by MS in reacting O_3 - β -pinene - *cis*-but-2-ene (or but-1-ene) - acetaldehyde (or ethanol) - He mixtures in a 192 cm^3 volume quartz vessel at ~ 1 bar pressure, with acetaldehyde or ethanol being present to scavenge HO radicals. The measured rate coefficient ratios $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + \textit{cis}$ -but-2-ene) = $0.51 \exp[(-308 \pm 84)/T]$ and $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + \text{but-1-ene}) = (2.25 \pm 0.19)$ at 298 K are placed on an absolute basis using $k(\text{O}_3 + \textit{cis}$ -but-2-ene) = $3.37 \times 10^{-15} \exp(-970/T)$ and $k(\text{O}_3 + \text{but-1-ene}) = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendations).
- (h) Relative to $k(\text{O}_3 + \textit{cis}$ -but-2-ene). Identical rate coefficients obtained at 298 K for two enantiomers of β -pinene, (+)- β -pinene and (-)- β -pinene, indicating no associated steric effects on the reaction. Measurements at other temperatures obtained using (+)- β -pinene.
- (i) Relative to $k(\text{O}_3 + \text{but-1-ene})$, using (+)- β -pinene.

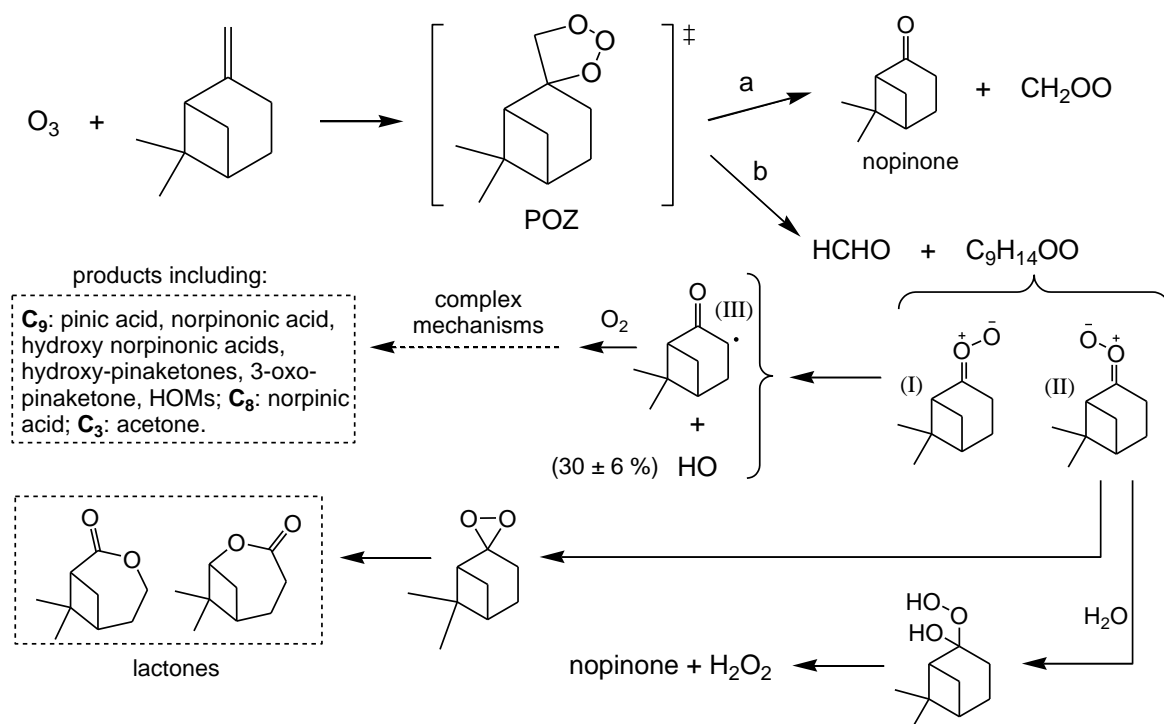
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.9×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.39 \times 10^{-15} \exp(-1280/T)$	290-370
<i>Reliability</i>		
$\Delta \log k$	± 0.25	298
$\Delta E/R$	± 300	290-370

Comments on Preferred Values

The room temperature rate coefficients reported by Ripperton et al. (1972) and Grimsrud et al. (1975) are significantly higher than the more recent measurements of Atkinson et al. (1982, 1990), Nolting et al. (1988), Grosjean et al. (1993), Johnson et al. (2000) and Khamaganov and Hites (2001); although there is still a significant amount of scatter between the room temperature rate coefficients of these more recent measurements. The preferred temperature dependence is based on that reported by Khamaganov and Hites (2001). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1982, 1990), Nolting et al. (1988), Grosjean et al. (1993), Johnson et al. (2000) and Khamaganov and Hites (2001), corrected to 298 K where necessary using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value.

The reaction proceeds by initial addition of O_3 to the C=C bond to form a “primary ozonide (POZ)” which rapidly decomposes to form two sets of “primary” carbonyl product plus Criegee intermediate, as shown in the following schematic:



Product yields have been reported in a number of studies, allowing some possible features of the subsequent mechanism to be characterized. The carbonyl compound, nopinone, has been reported to be formed with yields in the range 16 % to 23 % under dry conditions in the presence of an HO radical scavenger (Grosjean et al., 1993; Hakola et al., 1994; Yu et al., 1999; Winterhalter et al., 2000; Ma and Marston, 2008), suggesting a relative importance of the two decomposition channels, $k_b/k_a \approx 4$. The dominance of channel (b) is also supported by the results of theoretical studies (Zhang and Zhang, 2005; Nguyen et al., 2009). Reported yields of HCHO are also consistent with channel (b) being the major decomposition route for POZ (e.g. Atkinson and Arey, 2003), although it is likely partially sequestered in the form of a secondary ozonide following reaction with the C₉ Criegee intermediate, C₉H₁₄OO, under many reported experimental conditions (e.g. see Winterhalter et al., 2000; Carlsson et al., 2012).

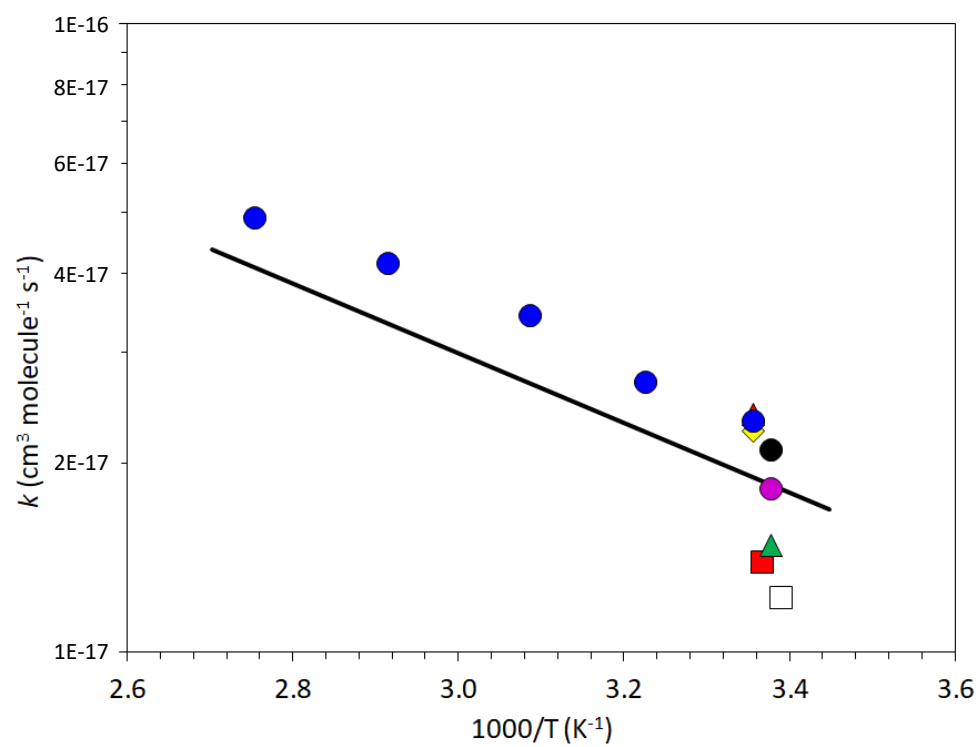
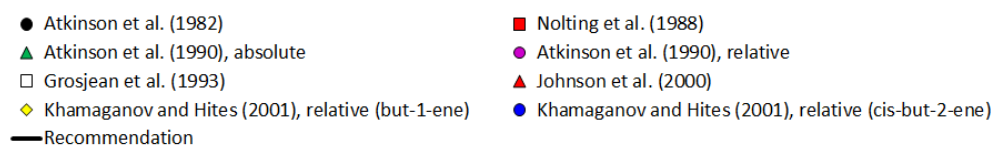
The Criegee intermediate, CH₂OO (formed from the minor channel (a)), is expected to be almost fully stabilised at atmospheric pressure (Nguyen et al., 2009). Based on reported kinetic data (summarised and evaluated in datasheets CGI_1 to CGI_12), the major fate of CH₂OO under tropospheric conditions is expected to be removal via bimolecular reactions, particularly with (H₂O)₂. Substantial stabilisation of the major C₉ Criegee intermediate, C₉H₁₄OO (formed from channel (b)), has also been reported (Winterhalter et al., 2000; Ahrens et al., 2014), based on scavenging with added H₂O or SO₂ and quantification of the additional nopinone formed. A corresponding yield of 0.35 ± 0.05 was reported by Winterhalter et al. (2000), with support from the subsequent theoretical study of Nguyen et al. (2009). Taking account of the additional contribution of CH₂OO, this is consistent with a total stabilised Criegee intermediate (sCI) yield of about 0.5, which agrees with that reported by Newland et al (2018), 0.60 ± 0.03 , based on scavenging of both CH₂OO and C₉H₁₄OO and with added SO₂ and quantifying its removal. Based on these observations, we recommend an sCI yield of 0.55 ± 0.10 .

Indirect evidence for the formation of HO radicals from β -pinene ozonolysis has been reported by Atkinson et al. (1992) and Rickard et al. (1999), with respective yields of $0.35^{+0.18}_{-0.12}$ and 0.26 ± 0.06 (preferred value, 0.30 ± 0.06). This is expected to result from reactions of the Criegee intermediate C₉H₁₄OO formed in channel (b), which has the two conformers, (I) and (II), shown in the schematic. In practice, formation of HO via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) may only be possible for conformer (I), owing to the relevant β -hydrogen in conformer (II) being at the bridgehead of a constrained bicyclic structure (e.g. see

Rickard et al., 1999; Nguyen et al., 2009); and this helps to explain the relatively low HO yield from β -pinene ozonolysis. The alternative decomposition route, via a dioxirane intermediate, is available for conformer (II), and formation of the lactone products has been reported (Griesbaum et al., 1998). However, if stabilized, conformer (II) is likely to react predominantly with H_2O under atmospheric conditions (Vereecken et al., 2017), forming additional nopinone and H_2O_2 , for which evidence was reported by Winterhalter et al. (2000) and Ma and Marston (2008). The generation of HO is accompanied by the formation of the β -oxo alkyl radical (III), the further chemistry of which may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (e.g. Winterhalter et al., 2000; Ma and Marston, 2008), including a small yield of highly oxidized multifunctional organic compounds, HOMs, with very high oxygen to carbon ratios (e.g. Ehn et al., 2012).

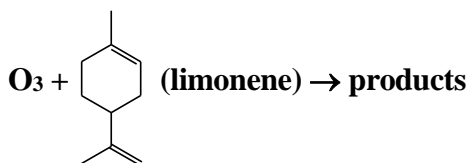
References

- Ahrens, J., Carlsson, P. T. M., Hertl, N., Olzmann, M., Pfeifle, M., Wolf, J. L. and Zeuch, T.: *Angew. Chem. Int. Ed.*, 53, 715, 2014.
- Atkinson, R. and Arey, J.: *Atmos. Environ.*, 37 Suppl. 2, S197, 2003.
- Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: *Atmos. Environ.*, 16, 1017, 1982.
- Atkinson, R., Hasegawa, D. and Aschmann, S. M.: *Int. J. Chem. Kinet.*, 22, 871, 1990.
- Atkinson, R., Aschmann, S. M., Arey, J. and Shorees, B.: *J. Geophys. Res.*, 97, 6065, 1992.
- Carlsson, P. T. M., Keunecke, C., Krüger, B. C., Maaß, M. C. and Zeuch, T.: *Phys. Chem. Chem. Phys.*, 14, 15637, 2012.
- Ehn, M., Kleist, E., Junninen, H., Petäjä, T., Lönn, G., Schobesberger, S., Dal Maso, M., Trimborn, A., Kulmala, M., Worsnop, D. R., Wahner, A., Wildt, J., and Mentel, Th. F.: *Atmos. Chem. Phys.*, 12, 5113, 2012.
- Griesbaum, K., Miclaus, V., and Jung, I. C.: *Environ. Sci. Technol.*, 32, 647, 1998.
- Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: *Int. J. Chem. Kinet., Symp.* 1, 183, 1975.
- Grosjean, D., Williams II, E. L., Grosjean, E., Andino, J. M. and Seinfeld, J. H.: *Environ. Sci. Technol.*, 27, 2754, 1993.
- Hakola, H., Arey, J., Aschmann, S. M., and Atkinson, R.: *J. Atmos. Chem.* 18, 75, 1994.
- Hatakeyama, S., Izumi, K., Fukuyama, T., and Akimoto, H.: *J. Geophys. Res.*, 94, 13013, 1989.
- Johnson, D., Rickard, A. R., McGill, C. D. and Marston, G.: *Phys. Chem. Chem. Phys.*, 2, 323, 2000.
- Khamaganov, V. G. and Hites, R. A.: *J. Phys. Chem. A*, 105, 815, 2001.
- Ma, Y. and Marston, G.: *Phys. Chem. Chem. Phys.*, 10, 6115, 2008.
- Newland, M. J., Rickard, A. R., Sherwen, T., Evans, M. J., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.: *Atmos. Chem. Phys.*, 18, 6095, 2018.
- Nguyen, T. L., Peeters, J. and Vereecken, L.: *Phys. Chem. Chem. Phys.*, 11, 5643, 2009.
- Nolting, F., Behnke, W. and Zetzsch, C.: *J. Atmos. Chem.*, 6, 47, 1988.
- Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: *J. Phys. Chem. A*, 103, 7656, 1999.
- Ripperton, L. A., Jeffries, H. E. and White, O.: *Adv. Chem. Ser.*, 113, 219, 1972.
- Vereecken, L., Novelli, A. and Taraborrelli, D.: *Phys. Chem. Chem. Phys.*, 19, 31599, 2017.
- Winterhalter, R., Neeb, P., Grossmann, D., Kolloff, A., Horie, O. and Moortgat, G.: *J. Atmos. Chem.*, 35, 165, 2000.
- Yu, J., Cocker III, D. R., Griffin, R. J., Flagan, R. C. and Seinfeld, J. H.: *J. Atmos. Chem.*, 34, 207, 1999.
- Zhang, D. and Zhang, R.: *J. Chem. Phys.*, 122, 114308, 2005.



Ox_VOC20: limonene

Last evaluated: August 2020; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
6.4×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
3.5×10^{-16}	297.3	Zhang et al., 1994	S-CL/GC (a)
$(3.8 \pm 0.3) \times 10^{-16}$	297 ± 1	Bernard et al., 2012	F-CL (b)
<i>Relative Rate Coefficients</i>			
$(2.27 \pm 0.23) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (c)
$(2.10 \pm 0.07) \times 10^{-16}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (d)
$2.97 \times 10^{-15} \exp[-(771 \pm 76)/T]$	298-363	Khamaganov and Hites, 2001	RR-MS (e,f)
$(2.24 \pm 0.16) \times 10^{-16}$	298		
$(2.20 \pm 0.19) \times 10^{-16}$	298	Khamaganov and Hites, 2001	RR-MS (e,g)
$(2.06 \pm 0.21) \times 10^{-16}$	298	Khamaganov and Hites, 2001	RR-MS (e,h)
$(2.44 \pm 0.30) \times 10^{-16}$	295 ± 0.5	Witter et al., 2002	RR-GC (i)
$(1.95 \pm 0.17) \times 10^{-16}$	302 ± 1	Bernard et al., 2012	RR-IR (j,k)
$(2.10 \pm 0.31) \times 10^{-16}$	303 ± 1		RR-IR (j,l)

limonene is 4-isopropenyl-1-methyl-cyclohexene

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in an experiment with a known excess concentration of limonene (measured by GC-FID), in a 4300 L Teflon chamber.
- (b) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of limonene, in a flow reactor at a total pressure of ~1 bar.
- (c) The concentrations of a series of alkenes (including limonene and α -pinene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-pinene}) = 9.46 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (d) The concentrations of limonene and *cis*-but-2-ene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{cis-but-2-ene})$ is placed on an absolute basis using $k(\text{O}_3 + \text{cis-but-2-ene}) = 1.27 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (e) The concentrations of limonene and *cis*-but-2-ene, but-1-ene or 2-methylpropene (the reference compounds) were monitored by MS in reacting O₃ - limonene - reference compound - acetaldehyde (or ethanol) - He mixtures in a 192 cm³ volume quartz vessel at ~1 bar pressure, with acetaldehyde or

ethanol being present to scavenge HO radicals. The measured rate coefficient ratios $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{cis-but-2-ene}) = 0.88 \exp[(-199 \pm 76)/T]$; and $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{but-1-ene}) = (22.04 \pm 1.92)$ and $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{2-methylpropene}) = (17.88 \pm 1.84)$ at 298 K are placed on an absolute basis using $k(\text{O}_3 + \text{cis-but-2-ene}) = 3.37 \times 10^{-15} \exp(-970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; and $k(\text{O}_3 + \text{but-1-ene}) = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + \text{2-methylpropene}) = 1.15 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendations).

- (f) Relative to $k(\text{O}_3 + \text{cis-but-2-ene})$.
- (g) Relative to $k(\text{O}_3 + \text{but-1-ene})$.
- (h) Relative to $k(\text{O}_3 + \text{2-methylpropene})$.
- (i) The concentrations of limonene and 2-methylbut-2-ene (the reference compound) were monitored by GC in reacting O_3 - limonene - 2-methylbut-2-ene - *m*-xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{2-methylbut-2-ene}) = 0.622 \pm 0.024$ is placed on an absolute basis using $k(\text{O}_3 + \text{2-methylbut-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson and Arey, 2003).
- (j) The concentrations of limonene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O_3 - limonene - reference compound - cyclohexane (HO radical scavenger) - air mixtures in a 7300 L Teflon chamber at ~1 bar pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{cyclohexene}) = 2.3 \pm 0.2$ and $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{cis-cyclooctene}) = 0.55 \pm 0.08$, are placed on an absolute basis using $k(\text{O}_3 + \text{cyclohexene}) = 8.50 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 302 K and $k(\text{O}_3 + \text{cis-cyclooctene}) = 3.81 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K (Atkinson and Arey, 2003).
- (k) Relative to $k(\text{O}_3 + \text{cyclohexene})$.
- (l) Relative to $k(\text{O}_3 + \text{cis-cyclooctene})$.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.2×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.91 \times 10^{-15} \exp(-770/T)$	290-370
<i>Reliability</i>		
$\Delta \log k$	± 0.10	298
$\Delta E/R$	± 300	290-370

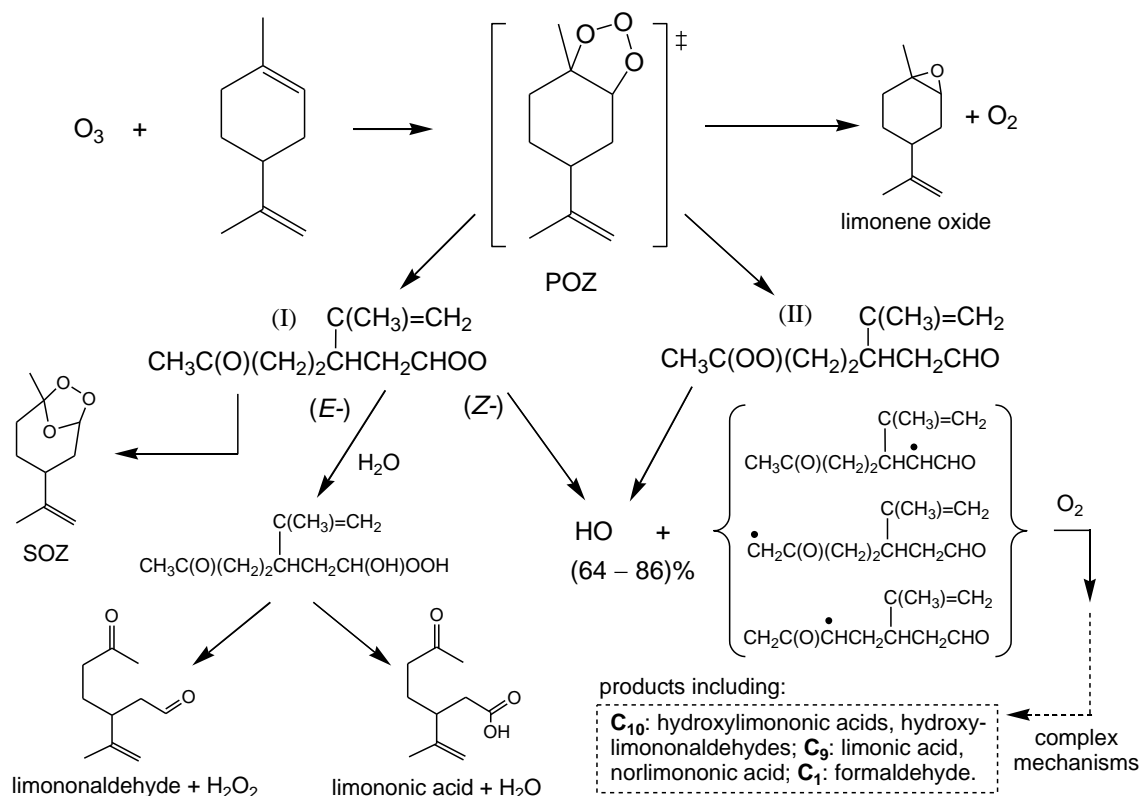
Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is an average of the relative rate coefficient determinations of Atkinson et al. (1990), Shu and Atkinson (1994), Khamaganov and Hites (2001), Witter et al. (2002) and Bernard et al. (2012), which are in very good agreement. The absolute rate coefficient determinations of Zhang et al. (1994) and Bernard et al. (2012) provide measurements of k that are approaching a factor of two higher than the relative rate determinations. The reason for this consistent discrepancy is currently unknown. The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for limonene, and also for several other terpenes, appear to be systematically high. The preferred temperature dependence is based on that reported by Khamaganov and Hites (2001), with the pre-exponential factor adjusted to return the 298 K preferred value.

The reaction may proceed by initial addition of O_3 to either of the endocyclic or exocyclic C=C bonds in limonene. Comparison of k for the reaction of ozone with limonene with that reported for the

reaction of ozone with the limonene oxidation product, limononaldehyde (3-isopropenyl-6-oxo-heptanal), which retains the “exocyclic” C=C bond (Calogirou et al., 1999), suggests that the reaction of O₃ with limonene occurs predominantly (≈ 95 %) at the endocyclic bond. Support for this comes from the low reported yield (≈ 2 %) of the product limona ketone (4-acetyl-1-methylcyclohexene), which is an expected significant product of the ozonolysis of the exocyclic bond (Grosjean et al., 1993; Forester and Wells, 2009).

The addition of O₃ to the endocyclic C=C bond in limonene forms a “primary ozonide (POZ)” which rapidly decomposes, mainly to form two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the following schematic:



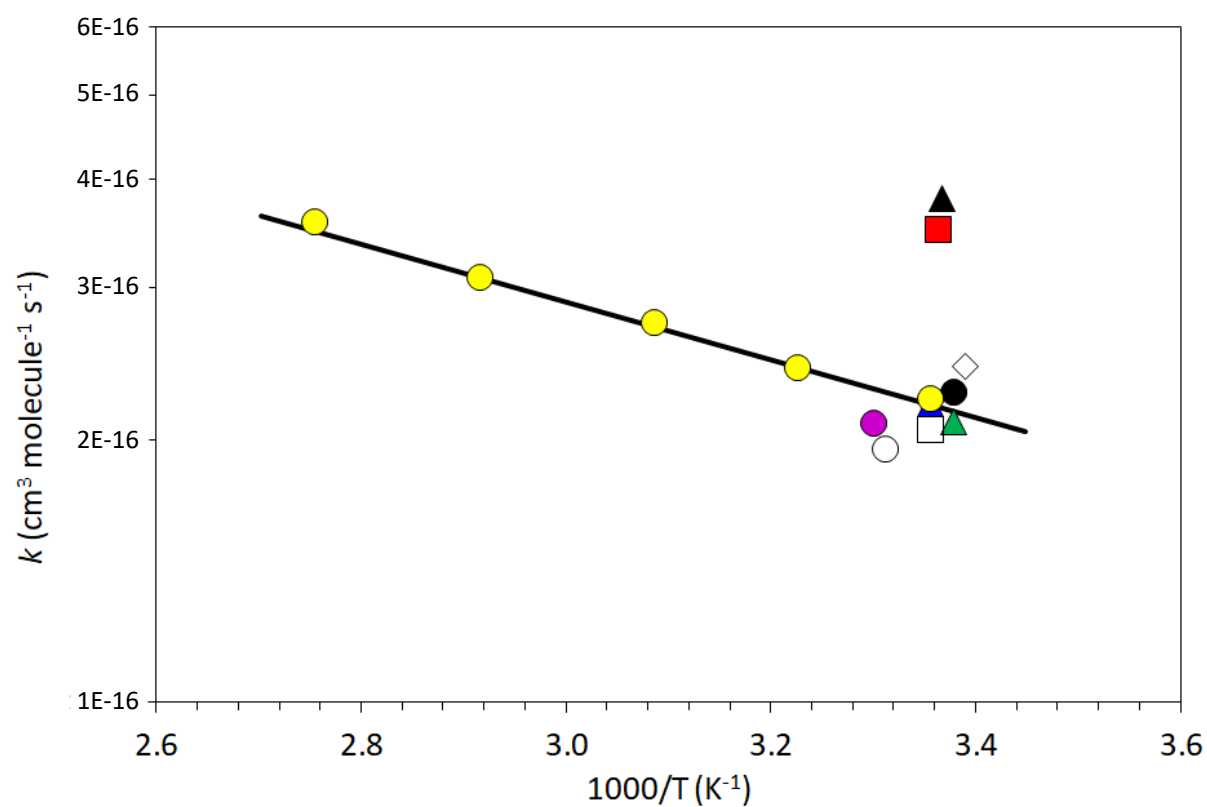
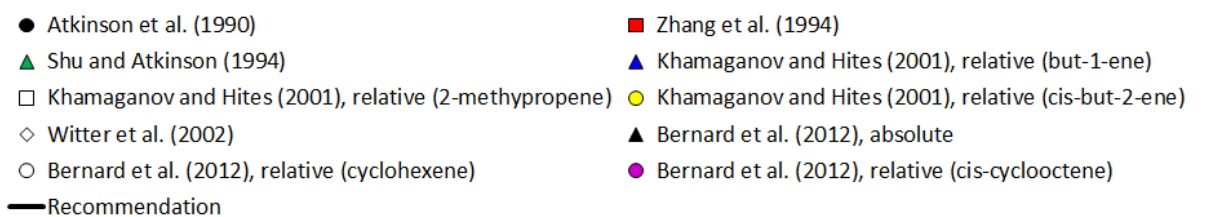
The Criegee intermediates are only partially stabilized under atmospheric conditions, with a preferred stabilized Criegee intermediate (sCI) yield of 0.27 ± 0.10 recommended at atmospheric pressure, based on the determinations Sipilä et al. (2014) (adjusted using the preferred value of k) and Newland et al. (2018). Whether excited or stabilized, the Z- conformer of Criegee intermediate (I) and Criegee intermediate (II) mainly decompose to form HO radicals, which are expected to be formed in conjunction with a number of β-oxo alkenyl radicals, as shown in the schematic. HO radical yields in the range 64 % – 86 % (preferred value 66 ± 4 %) have been reported (Atkinson et al., 1992; Aschmann et al., 2002; Herrmann et al., 2010; Forester and Wells, 2011). The further chemistry of the β-oxo alkenyl radicals may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (Glasius et al., 2000; Warscheid and Hoffmann, 2001; Leungsakul et al., 2005; Nørgaard et al., 2013; Hammes et al., 2019), and also formaldehyde, which has been reported to be formed with a yield of 10 % (Grosjean et al., 1993) and 19 % (Ruppert et al., 1999). A contribution (< 5 %) to the formaldehyde yield also probably results from the minor ozonolysis of the exocyclic C=C bond in limonene.

Products likely to be produced from alternative reactions of the Criegee intermediates have also been detected, for example the “secondary ozonide (SOZ)” (Nørgaard et al., 2013), which can potentially be formed from ring closure of either (I) or (II). Limononic acid (3-isopropenyl-6-oxo-heptanoic acid) has

been reported to be formed in very low yield from the ozonolysis of limonene under nominally dry conditions (Hammes et al., 2019). A systematic increase was observed in the presence of water vapour, consistent with its formation from the reaction of H₂O with the (stabilized) *E*- conformer of Criegee intermediate (I). Limononaldehyde (3-isopropenyl-6-oxo-heptanal) has also been reported to be formed in low yield (between 0.4 % and 4 %) (Glasius et al., 2000; Clausen et al., 2001; Forester et al., 2009) under nominally dry conditions. Although no systematic investigations of the effect of water vapour on the yield have apparently been reported, limononaldehyde is also predicted to be formed (with H₂O₂) from reaction of H₂O with the (stabilized) *E*- conformer of Criegee intermediate (I). Some support for this comes from the reported high yield (\approx 33 %) of H₂O₂ from limonene ozonolysis at close to 100 % relative humidity (Hewitt and Kok, 1991).

References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
- Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
- Atkinson, R., Aschmann, S. M., Arey, J. and Shorees, B.: J. Geophys. Res., 97, 6065, 1992.
- Bernard, F., Fedioun, I., Peyroux, F., Quilgars, A., Daële, V. and Mellouki, A.: J. Aerosol Sci., 43, 14, 2012.
- Calogirou, A., Jensen, N. R., Nielsen, C. J., Kotzias, D. and Hjorth, J.: Environ. Sci. Technol., 33, 453, 1999.
- Clausen, P. A., Wilkins, C. K., Wolkoff, P. and Nielsen, G. D: Environ. Int., 26, 511, 2001.
- Forester, C. D. and Wells, J. R.: Environ. Sci. Technol., 43, 3561, 2009.
- Forester, C. D. and Wells, J. R.: Indoor Air, 21, 400, 2011.
- Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R., Hjorth, J., Kotzias, D. and Larsen, B. R.: Environ. Sci. Technol., 34, 1001, 2000.
- Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: Int. J. Chem. Kinet., Symp. 1, 183, 1975.
- Grosjean, D., Williams II, E. L., Grosjean, E., Andino, J. M. and Seinfeld, J. H.: Environ. Sci. Technol., 27, 2754, 1993.
- Hammes, J., Lutz, A., Mentel, T., Faxon, C., and Hallquist, M.: Atmos. Chem. Phys., 19, 13037, 2019.
- Herrmann, F., Winterhalter, R., Moortgat, G. K. and Williams, J.: Atmos. Environ., 44, 3458, 2010.
- Hewitt, C. N. and Kok, G. L.: J. Atmos. Chem., 12, 181, 1991.
- Khamaganov, V. G. and Hites, R. A.: J. Phys. Chem. A, 105, 815, 2001.
- Leungsakul, S., Jaoui, M. and Kamens, R. M.: Environ. Sci. Technol., 39, 9583, 2005.
- Newland, M. J., Rickard, A. R., Sherwen, T., Evans, M. J., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.: Atmos. Chem. Phys., 18, 6095, 2018.
- Nørgaard, A. W., Vibenholt, A., Benassi, M., Clausen, P.A., Wolkoff, P.: J. Am. Soc. Mass Spectrom., 24, 1090, 2013.
- Ruppert, L., Becker, K. H., Nozière, B. and Spittler, M.: In: Borrell, P.M., Borrell, P. (Eds.), Transport and Chemical Transformation in the Troposphere. Proceedings of the EUROTRAC-2 Symposium '98. WIT press, Southampton, UK, pp. 63–68.
- Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.
- Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin III, R. L., Kurtén, T., Paasonen, P., Sarnela, N., Ehn, M., Junninen, H., Rissanen, M. P., Thornton, J., Stratmann, F., Herrmann, H., Worsnop, D. R., Kulmala, M., Kerminen, V.-M., and Petäjä, T.: Atmos. Chem. Phys., 14, 12143, 2014.
- Warscheid, B. and Hoffmann, T.: Rapid Commun. Mass Spectrom., 15, 2259, 2001.
- Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: Int. J. Chem. Kinet., 34, 394, 2002.
- Zhang, J., Wilson, W. E., and Liroy, P. J.: Environ. Sci. Technol., 28, 1975, 1994.



Ox_VOC21: camphene

Last evaluated: August 2018; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.0 \pm 1.7) \times 10^{-19}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (a)
<i>Relative Rate Coefficients</i>			
$(4.3 \pm 0.5) \times 10^{-19}$	298 ± 2	Johnson et al., 2000	RR-GC (b)
$(5.5 \pm 1.2) \times 10^{-19}$	298 ± 2	Gaona-Colmán et al., 2017	RR-FTIR (c)
$9.8 \times 10^{-18} \exp[(-859 \pm 53)/T]$	288-311		

camphene is 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of camphene (measured by GC-FID). Experiments were carried out at a total pressure of 980 mbar in a 160 L Teflon chamber. k was corrected to account for the presence of a ~10 % monoterpene impurity of comparable ozone reactivity in the camphene sample, which was tentatively identified as the structurally-similar monoterpene, α -fenchene.
- (b) The concentrations of camphene and ethene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 50 L collapsible Teflon chamber at 760 Torr (1013 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \text{camphene})/k(\text{O}_3 + \text{ethene})$ is placed on an absolute basis using $k(\text{O}_3 + \text{ethene}) = 1.55 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (c) The concentrations of camphene and ethene or o-cresol (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 50 L collapsible Teflon chamber at 760 Torr (1013 mbar) pressure of purified air in the presence of O_3 . Experiments performed at 298 K carried out using both ethene and o-cresol as reference compounds; with only ethene used at other temperatures. The measured rate coefficient ratios $k(\text{O}_3 + \text{camphene})/k(\text{O}_3 + \text{ethene})$ and $k(\text{O}_3 + \text{camphene})/k(\text{O}_3 + \text{o-cresol})$ are placed on an absolute basis using $k(\text{O}_3 + \text{ethene}) = 6.82 \times 10^{-15} \exp(-2500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + \text{o-cresol}) = 2.6 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendations).

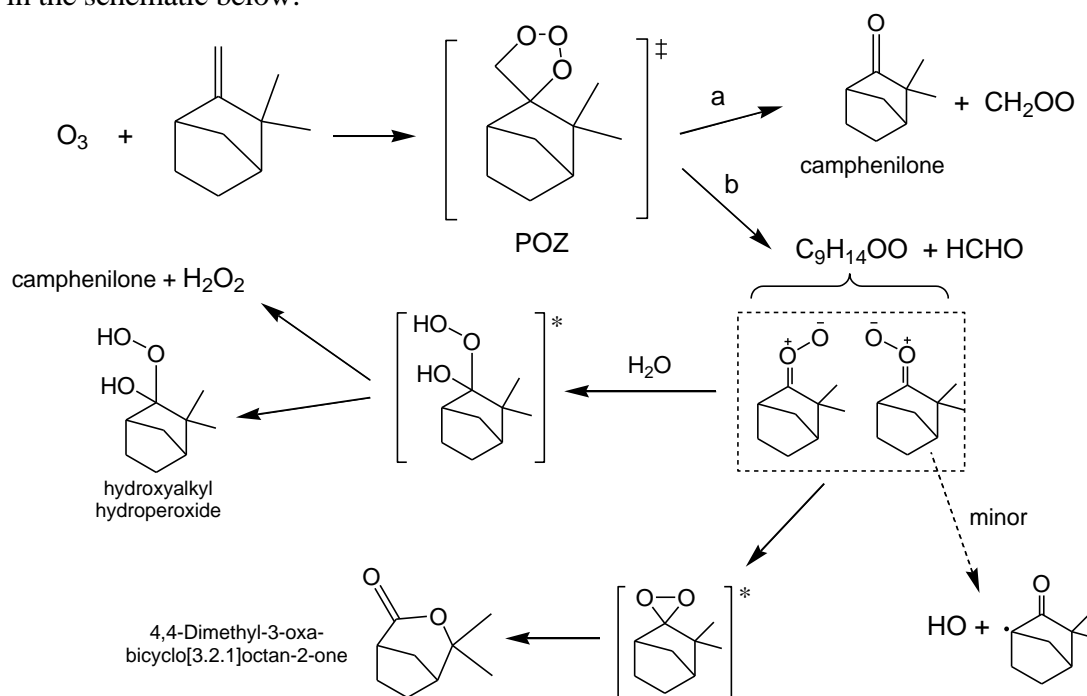
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.0×10^{-19}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$9.0 \times 10^{-18} \exp(-860/T)$	285-315
<i>Reliability</i>		
$\Delta \log k$	± 0.30	298
$\Delta E/R$	± 500	285-315

Comments on Preferred Values

The preferred value of E/R is based on the sole temperature dependence study of Gaona-Colmán et al. (2017), which covered only a narrow temperature range. Confirmatory studies of the temperature dependence are required. The preferred 298 K rate coefficient is a rounded average of the relative rate determinations of Johnson et al. (2000) and Gaona-Colmán et al. (2017), which are in good agreement. The absolute determination of Atkinson et al. (1990) required correction for the presence of an impurity, but the reported value of k lies within the assigned uncertainty range in the preferred value.

The reaction proceeds by initial addition of O_3 to the $\text{C}=\text{C}$ bond to form a “primary ozonide (POZ)” which rapidly decomposes to form two sets of “primary” carbonyl product plus Criegee intermediate, as shown in the schematic below:



Camphenilone (3,3-dimethyl-bicyclo[2.2.1]heptan-2-one) is expected to be formed in conjunction with the Criegee intermediate CH_2OO (channel (a)), and has been reported as a significant product, formed with a yield of $(36 \pm 6) \%$ (Hakola et al., 1994). Channel (b) is expected to form HCHO and the Criegee intermediate $\text{C}_9\text{H}_{14}\text{OO}$, although there have been no reported measurements of the yield of HCHO .

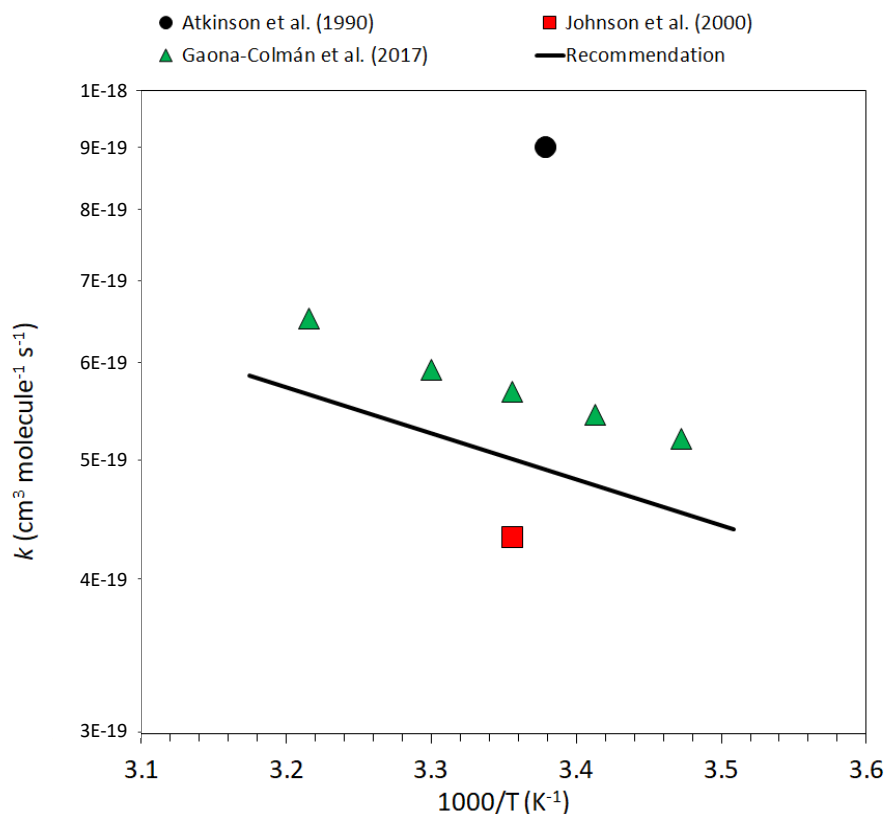
The Criegee intermediate, CH_2OO (formed from channel (a)), is expected to be almost fully stabilised at atmospheric pressure, by analogy with the β -pinene system (Nguyen et al., 2009). Based on reported kinetic data (summarised and evaluated in datasheets CGI_1 to CGI_12), the major fate of CH_2OO under tropospheric conditions is expected to be removal via bimolecular reactions, particularly

with (H₂O)₂. Partial stabilisation of the C₉ Criegee intermediate, C₉H₁₄OO (formed from channel (b)), has also been inferred by Hasson et al. (2001), based on scavenging with added H₂O and observation of the corresponding products.

Atkinson et al. (1992) have reported an upper limit HO yield of $\leq 18\%$ for the reaction of O₃ with camphene, indicating that HO formation from the decomposition of C₉H₁₄OO is also a minor route. The formation of HO via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) may be inhibited owing to the only β -hydrogen in C₉H₁₄OO being at the bridgehead of a constrained bicyclic structure, as discussed by Rickard et al. (1999) and Nguyen et al. (2009) for the structurally-similar isomeric Criegee intermediate formed from β -pinene ozonolysis. The alternative well-documented decomposition route, via a dioxirane intermediate (e.g. Johnson and Marston, 2008), leads to the formation of a lactone (4,4-dimethyl-3-oxa-bicyclo[3.2.1]octan-2-one), which has been reported to be a significant product (yield $\approx 20\%$) by Hakola et al. (1994). If stabilized, C₉H₁₄OO may also potentially react with H₂O under atmospheric conditions. Based on the results of Hasson et al. (2001), this leads mainly to formation of the hydroxyalkyl hydroperoxide shown in the schematic, with minor formation of camphenilone and H₂O₂.

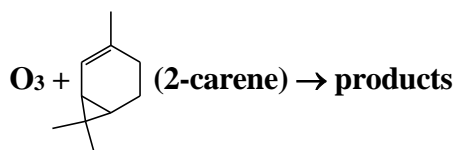
References

- Atkinson, R., Aschmann, S. M. and Arey, J.: Atmos. Environ., 24A, 2647, 1990.
 Atkinson, R., Aschmann, S. M., Arey, J. and Shorees, B.: J. Geophys. Res., 97, 6065, 1992.
 Gaona-Colmán, E., Blanco, M. B., Barnes, I., Wiesen, P. and Teruel, M. A.: RSC Adv., 7, 2733, 2017.
 Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
 Hasson, A. A., Ho, A. W., Kuwata, K. T. and Paulson, S. E.: J. Geophys. Res., 106, 34143, 2001.
 Johnson, D. and Marston, G.: Chem. Soc. Rev., 37, 699, 2008.
 Johnson, D., Rickard, A. R., McGill, C. D. and Marston, G.: Phys. Chem. Chem. Phys., 2, 323, 2000.
 Nguyen, T. L., Peeters, J. and Vereecken, L.: Phys. Chem. Chem. Phys., 11, 5643, 2009.
 Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: J. Phys. Chem. A, 103, 7656, 1999.



Ox_VOC22: 2-carene

Last evaluated: August 2018; Last change in preferred values: September 2013

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.32 \pm 0.30) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (a)
<i>Relative Rate Coefficients</i>			
$(2.56 \pm 0.27) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (b)

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of 2-carene (measured by GC-FID). Experiments were carried out in a 160 L Teflon chamber.
- (b) The concentrations of a series of alkenes (including 2-carene and α -pinene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \text{2-carene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-pinene}) = 9.46 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

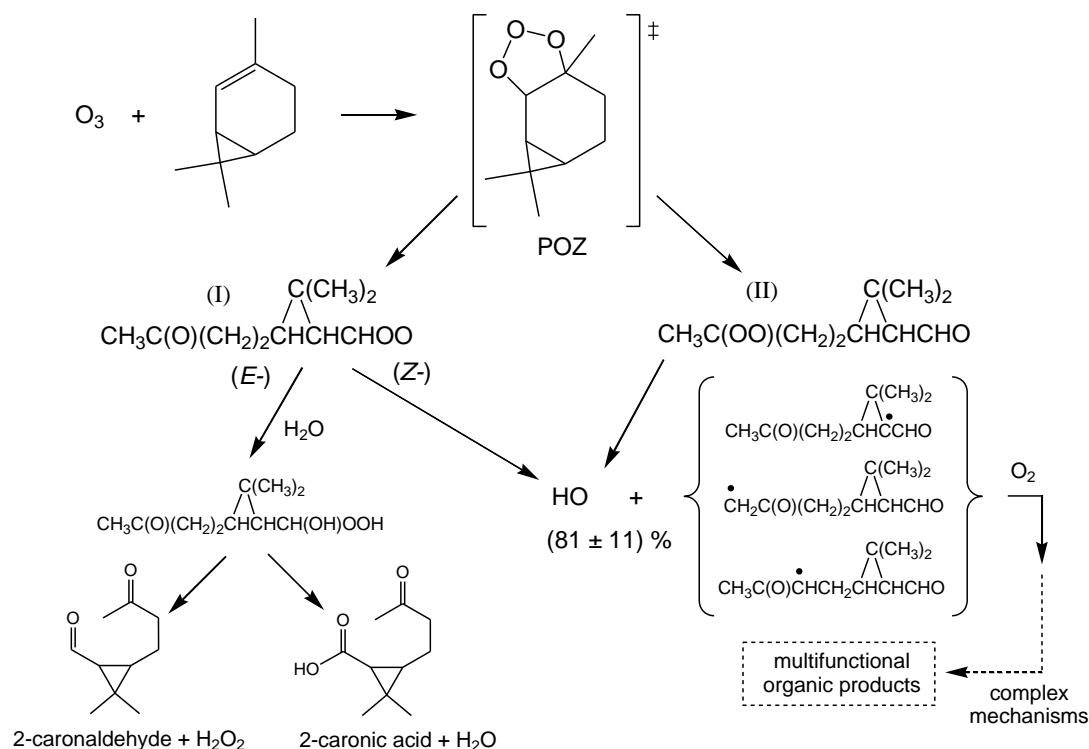
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.4×10^{-16}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.20	298

Comments on Preferred Values

The preferred value of the rate coefficient is the average of the absolute and relative rate coefficients reported by Atkinson et al. (1990), the only study of the kinetics of the reaction to date. Confirmatory studies are required.

There has been only limited product and mechanistic information reported in the literature. Based on general understanding of the reactions of ozone with alkenes and terpenes, the reaction is expected to proceed by initial addition of O_3 to the C=C bond in 2-carene to form a “primary ozonide (POZ)” which rapidly decomposes, mainly to form two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the following schematic:



Based on the high reported yield of HO radicals, (81 ± 11 %) (Aschmann et al., 2002), it is likely that the Criegee intermediates mainly decompose to form HO radicals and a number of β -oxo alkyl radicals, as shown above. The further chemistry of the β -oxo alkyl radicals is expected to form a number of multifunctional organic products containing hydroxy, hydroperoxy, carbonyl and acid functionalities, but there have been no reported studies identifying organic products.

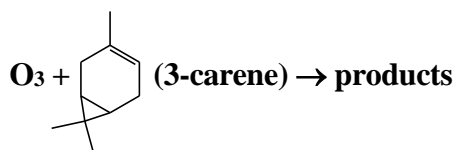
Formation of HO via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) is not possible for the *E*- conformer of Criegee Intermediate (I) (e.g. see Johnson and Marston, 2008). If stabilized, this is expected to react predominantly with H_2O under atmospheric conditions, leading to the formation of 2-caronaldehyde and H_2O_2 , or 2-caronic acid. Some support for this comes from the significant yield (≈ 18 %) of H_2O_2 from 2-carene ozonolysis at close to 100 % relative humidity (Hewitt and Kok, 1991).

References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
 Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
 Hewitt, C. N. and Kok, G. L.: J. Atmos. Chem., 12, 181, 1991.
 Johnson, D. and Marston, G.: Chem. Soc. Rev., 37, 699, 2008.

Ox_VOC23: 3-carene

Last evaluated: August 2018; Last change in preferred values: September 2013

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.2×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
$(5.20 \pm 0.56) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (a)
<i>Relative Rate Coefficients</i>			
$(4.12 \pm 0.44) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	RR-GC (b)
$(5.60 \pm 0.95) \times 10^{-17}$	295 ± 0.5	Witter et al., 2002	RR-GC (c)

3-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-3-ene

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of 3-carene (measured by GC-FID). Experiments were carried out in a 160 L Teflon chamber. The presence of impurities in the 3-carene sample (3 % of sabinene and/or β -pinene and 2.9 % of limonene) was reported, such that the measured value of k was believed to be overestimated by up to about 20 %.
- (b) The concentrations of a series of alkenes (including 3-carene and α -pinene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + 3\text{-carene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-pinene}) = 9.46 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (c) The concentrations of 3-carene and 2-methylbut-2-ene (the reference compound) were monitored by GC in reacting O_3 - 3-carene - 2-methylbut-2-ene - m -xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio of $k(\text{O}_3 + 3\text{-carene})/k(\text{O}_3 + 2\text{-methylbut-2-ene}) = 0.143 \pm 0.018$ is placed on an absolute basis using a rate coefficient at 295 K of $k(\text{O}_3 + 2\text{-methylbut-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

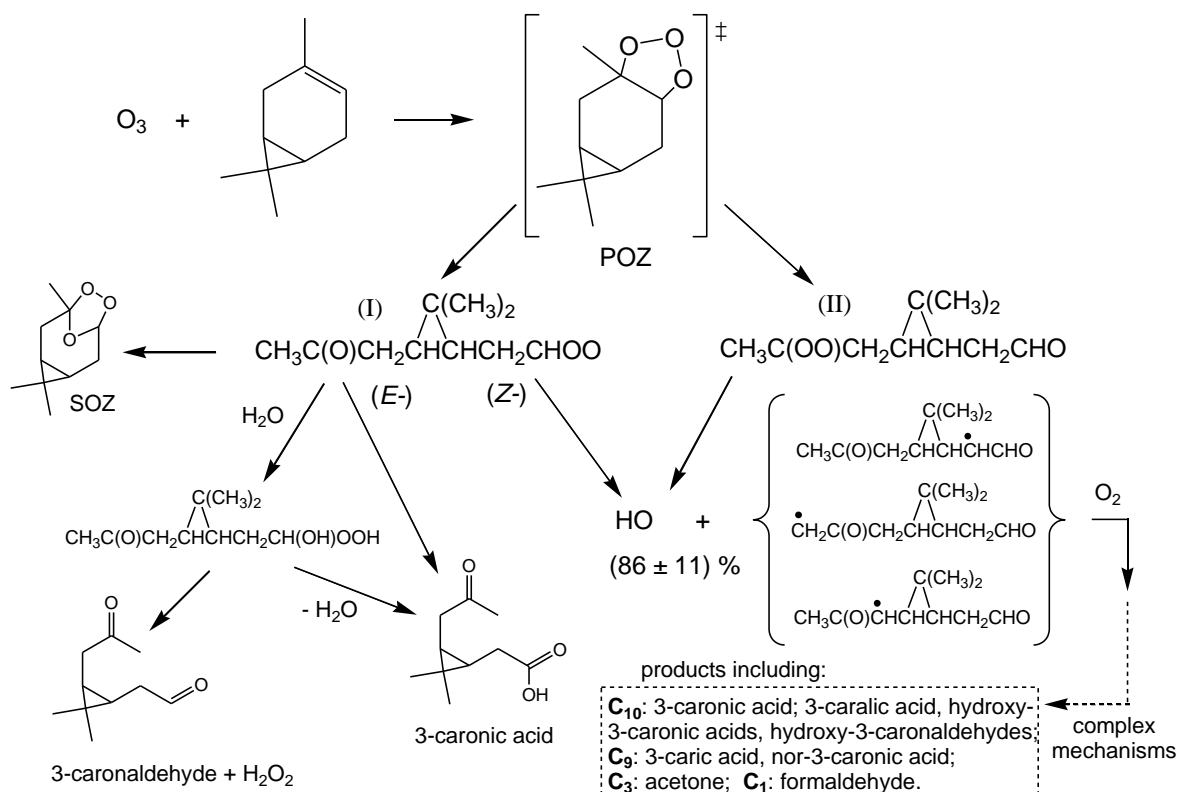
Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4.9×10^{-17}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.20	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is an average of the relative rate coefficient determinations of Atkinson et al. (1990) and Witter et al. (2002), which are in agreement to within their combined uncertainty limits. The absolute rate coefficient determination of Atkinson et al. (1990) was reported to be potentially influenced by the presence of reactive impurities in the 3-carene sample (see comment (b)), and is therefore not included in the average; although it is consistent with the preferred value of k . The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for 3-carene, and also for several other terpenes, appear to be systematically high.

The reaction proceeds by initial addition of O_3 to the C=C bond in 3-carene to form a “primary ozonide (POZ)” which rapidly decomposes, mainly to form two carbonyl-substituted Criegee intermediates (I) and (II), as represented in the following schematic:



The Criegee intermediates mainly decompose to form HO radicals, which are expected to be formed in conjunction with a number of β -oxo alkyl radicals. A yield of HO radical yields of (86 ± 11) % has been reported by Aschmann et al. (2002). The further chemistry of the β -oxo alkyl radicals may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (Yu et al., 1999; Glasius et al., 2000; Warscheid and Hoffmann, 2001; Ma et al., 2009); and also acetone and formaldehyde, which have been reported to be formed with respective yields of (14 $^{+8}_{-4}$) % (Reissel et al., 1999; Orlando et al., 2000; Lee et al., 2006) and (25 ± 2) % (Lee et al., 2006).

Products likely to be produced from alternative reactions of the Criegee intermediates have also been detected, for example the secondary ozonide (SOZ) (Vibenholt et al., 2009), which can potentially be formed from ring closure of either (I) or (II). 3-caronaldehyde has been reported to be formed with total yields in the range (8.5 – 25) % under nominally dry conditions (Yu et al., 1999; Ma et al., 2009), with Ma et al. (2009) reporting an increasing yield with increasing relative humidity. 3-caronaldehyde is therefore likely to be formed with H_2O_2 from the reaction of H_2O with the (stabilized) *E*- conformer of

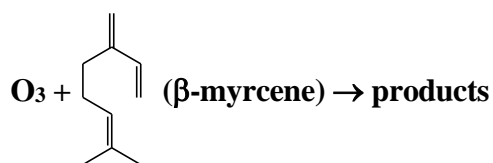
Criegee intermediate (I), which would also be predicted to be its dominant reaction under atmospheric conditions.

References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
- Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
- Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R., Hjorth, J., Kotzias, D. and Larsen, B. R.: Environ. Sci. Technol., 34, 1001, 2000.
- Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: Int. J. Chem. Kinet., Symp. 1, 183, 1975.
- Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: J. Geophys. Res., 111, D07302, doi:10.1029/2005JD006437, 2006.
- Ma, Y., Porter, R. A., Chappell, D., Russell, A. T. and Marston, G.: Phys. Chem. Chem. Phys., 11, 4184, 2009.
- Orlando, J. J., Nozière, B., Tyndall, G. S., Orzechowska, G. E., Paulson, S. E. and Rudich, Y.: J. Geophys. Res., 105, 11561, 2000.
- Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.
- Vibenholt, A., Nørsgaard, A. W., Clausen, P. A. and Wolkoff, P.: Chemosphere, 76, 572, 2009.
- Warscheid, B. and Hoffmann, T.: Rapid Commun. Mass Spectrom., 15, 2259, 2001.
- Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: Int. J. Chem. Kinet., 34, 394, 2002.
- Yu, J., Cocker III, D. R., Griffin, R. J., Flagan, R. C., Seinfeld, J. H.: J. Atmos. Chem., 34, 207, 1999.

Ox_VOC24: β -myrcene

Last evaluated: August 2020; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.25×10^{-15}	295 ± 1	Grimsrud et al., 1975	F-CL
$(5.7 \pm 1.6) \times 10^{-16}$	298 ± 1	Bernard et al., 2012	F-CL (a)
<i>Relative Rate Coefficients</i>			
$(5.01 \pm 0.81) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (b)
$(4.59 \pm 0.57) \times 10^{-16}$	296 ± 2	Witter et al., 2002	RR-GC (c)
$2.33 \times 10^{-15} \exp[-(521 \pm 109/T)]$	298-318	Kim et al., 2011	RR-MS (d)
$(4.05^{+0.31}_{-0.29}) \times 10^{-16}$	298		
$(4.90 \pm 0.69) \times 10^{-16}$	303 ± 1	Bernard et al., 2012	RR-IR (e,f)
$(3.82 \pm 0.38) \times 10^{-16}$	304 ± 1		RR-IR (e,g)

myrcene is 7-methyl-3-methylene-octa-1,6-diene

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of β -myrcene, in a flow reactor at a total pressure of ~ 1 bar.
- (b) The concentrations of a series of alkenes (including β -myrcene and limonene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + \text{limonene})$ is placed on an absolute basis using $k(\text{O}_3 + \text{limonene}) = 2.16 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (c) The concentrations of β -myrcene and 2-methyl-but-2-ene (the reference compound) were monitored by GC in reacting O_3 - β -myrcene - 2-methyl-but-2-ene - *m*-xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 1.17 \pm 0.06$ is placed on an absolute basis using $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson and Arey, 2003).
- (d) The concentrations of β -myrcene and *trans*-but-2-ene (the reference compound) were monitored by MS in reacting O_3 - β -myrcene - *trans*-but-2-ene - acetaldehyde - He mixtures in a 160 cm^3 volume quartz vessel at ~ 1 bar pressure, with acetaldehyde being present to scavenge HO radicals. The measured rate coefficient ratios $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + \text{trans-but-2-ene})$ are placed on an absolute basis using $k(\text{O}_3 + \text{trans-but-2-ene}) = 7.0 \times 10^{-15} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (e) The concentrations of β -myrcene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O_3 - myrcene - reference compound - cyclohexane (HO radical

scavenger) - air mixtures in a 7300 L Teflon chamber at ~1 bar pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + \text{cyclohexene}) = 5.7 \pm 0.8$ and $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + \text{cis-cyclooctene}) = 1.0 \pm 0.1$, are placed on an absolute basis using $k(\text{O}_3 + \text{cyclohexene}) = 8.60 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K and $k(\text{O}_3 + \text{cis-cyclooctene}) = 3.82 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 304 K (Atkinson and Arey, 2003).

(f) Relative to $k(\text{O}_3 + \text{cyclohexene})$.

(g) Relative to $k(\text{O}_3 + \text{cis-cyclooctene})$.

Preferred Values

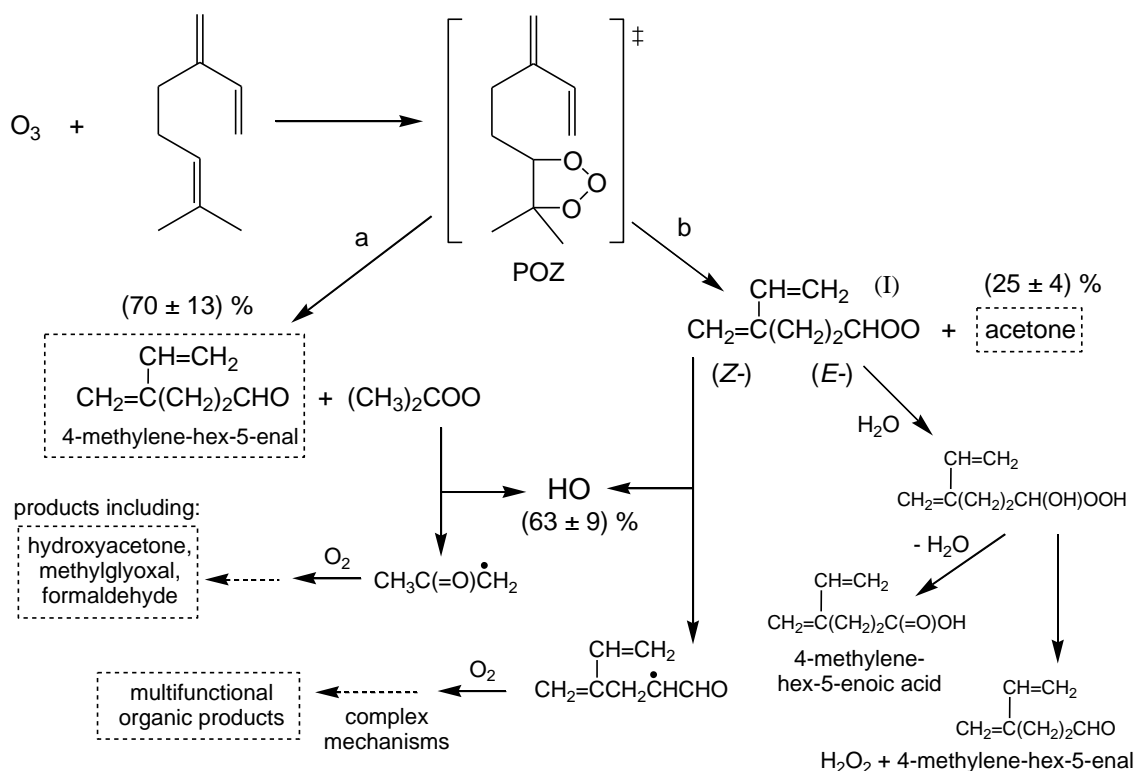
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4.7×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.69 \times 10^{-15} \exp(-520/T)$	290-320
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	± 300	290-320

Comments on Preferred Values

The preferred value of E/R is based on the sole temperature dependence study of Kim et al. (2011). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1990), Witter et al. (2002), Kim et al. (2011) and Bernard et al. (2012), corrected to 298 K where necessary using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value. The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for β -myrcene, and also for several other terpenes, appear to be systematically high.

The reaction may proceed by initial addition of O_3 to any of the three C=C bonds in β -myrcene. Comparison of k for the reaction of O_3 with β -myrcene with that reported for the reaction of O_3 with the β -myrcene oxidation product 4-methylene-hex-5-enal, which retains the two conjugated terminal C=C bonds (Baker et al., 2004), suggests that the reaction of O_3 with β -myrcene occurs predominantly ($\approx 97\%$) at the internal C=C bond; and this is largely supported by the observed product distribution and yields in reported product studies.

The addition of O_3 to the internal C=C bond in β -myrcene forms a “primary ozonide (POZ)” which rapidly decomposes to form two sets of “primary” carbonyl product plus Criegee intermediate, as shown in the schematic below. Acetone has been reported to be formed with a yield of $(25 \pm 4)\%$ (Reissell et al., 1999; 2002; Ruppert et al., 1999; Orlando et al., 2000; Newland et al., 2020), and 4-methylene-hex-5-enal with a yield of $(70 \pm 13)\%$ (Reissell et al., 2002). This suggests important contributions from both decomposition channels, (a) and (b), as shown in the schematic, but with the dominance of channel (a) being consistent with that typically observed for primary ozonides formed from alkenes of generic structure $\text{R}_1(\text{R}_2)\text{C}=\text{CHR}_3$ (Rickard et al., 1999).



The Criegee intermediates are only partially stabilized under atmospheric conditions, with a preferred stabilized Criegee intermediate (sCI) yield of 0.46 ± 0.15 recommended at atmospheric pressure, based on the determination Newland et al. (2020). The dimethyl-substituted Criegee intermediate (CH₃)₂COO (whether excited or stabilized) decomposes almost exclusively to form HO radicals and the acetyl radical (see discussion in data sheet Ox_VOC41), the further chemistry of which leads to the formation of a number of products, including hydroxyacetone and formaldehyde. These products have been reported to be formed with respective yields of 19 % (Ruppert et al., 1999) and (26 – 51) % (Ruppert et al., 1999; Lee et al., 2006) from the ozonolysis of β -myrcene. A contribution (< 3 %) to the formaldehyde yield also probably results from the minor ozonolysis of the terminal C=C bonds in β -myrcene. HO radicals have been reported to be formed with a yield of (63 ± 9) % (Aschmann et al., 2002).

The Z- conformer of Criegee intermediate (I), formed in channel (b), may also decompose to form HO radicals and the β -oxo-dienyl radical shown in the schematic. HO formation via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) is unavailable for the E- conformer. If stabilized, this is likely to react predominantly with H₂O under atmospheric conditions, potentially forming additional 4-methylene-hex-5-enal and H₂O₂, or 4-methylene-hex-5-enoic acid, as shown in the schematic.

References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
- Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
- Baker, J., Arey, J. and Atkinson, R.: J. Atmos. Chem., 48, 241, 2004.
- Bernard, F., Fedioun, I., Peyroux, F., Quilgars, A., Daële, V. and Mellouki, A.: J. Aerosol Sci., 43, 14, 2012.
- Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: Int. J. Chem. Kinet., Symp. 1, 183, 1975.
- Kim, D., Stevens, P. S. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.

Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: J. Geophys. Res., 111, D07302, doi:10.1029/2005JD006437, 2006.

Newland, M. J., Nelson, B. S., Muñoz, A., Ródenas, M., Vera, T., Tárrega, J., and Rickard, A. R.: Phys. Chem. Chem. Phys., 22, 13698, 2020.

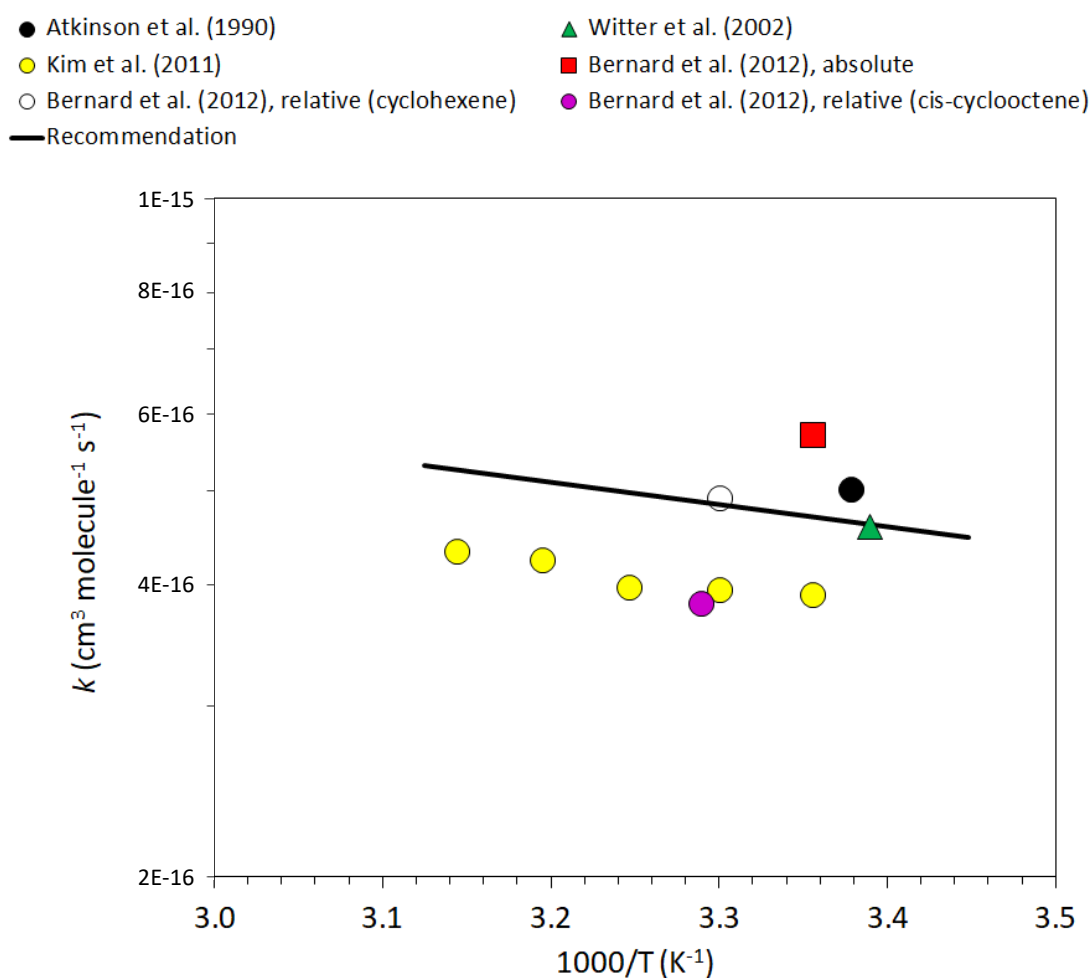
Orlando, J. J., Noziere, B., Tyndall, G. S., Orzechowska, G. E., Paulson, S. E. and Rudich, Y.: J. Geophys. Res., 105(D9), 11,561, 2000.

Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.

Reissell, A., Aschmann, S.M., Atkinson, R. and Arey, J.: J. Geophys. Res., 107 (D12), 4138, doi:10.1029/2001JD001234, 2002.

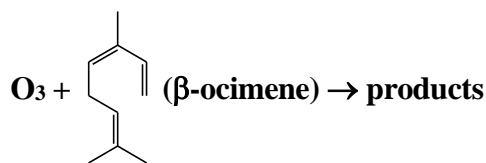
Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: J. Phys. Chem. A, 103, 7656, 1999.

Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: Int. J. Chem. Kinet., 34, 394, 2002.



Ox_VOC25: β -ocimene

Last evaluated: August 2018; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
2.0×10^{-15}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(5.75 \pm 0.88) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (a)
$(5.29 \pm 0.77) \times 10^{-16}$	296 ± 2	Witter et al., 2002	RR-GC (b)
$3.32 \times 10^{-15} \exp[-(627 \pm 110/T)]$	298-318	Kim et al., 2011	RR-MS (c)
$(4.05^{+0.32}_{-0.30}) \times 10^{-16}$	298		

ocimene is 3,7-dimethyl-octa-1,3,6-triene

Comments

- (a) The concentrations of a series of alkenes (including *trans*- β -ocimene and limonene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-ocimene})/k(\text{O}_3 + \textit{limonene})$ is placed on an absolute basis using $k(\text{O}_3 + \textit{limonene}) = 2.16 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (b) The concentrations of *trans*- β -ocimene and 2-methyl-but-2-ene (the reference compound) were monitored by GC in reacting O_3 - *trans*- β -ocimene - 2-methyl-but-2-ene - *m*-xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-ocimene})/k(\text{O}_3 + \textit{2-methyl-but-2-ene}) = 1.35 \pm 0.08$ is placed on an absolute basis using $k(\text{O}_3 + \textit{2-methyl-but-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson and Arey, 2003).
- (c) The concentrations of β -ocimene and *trans*-but-2-ene (the reference compound) were monitored by MS in reacting O_3 - β -ocimene - *trans*-but-2-ene - acetaldehyde - He mixtures in a 160 cm^3 volume quartz vessel at ~ 1 bar pressure, with acetaldehyde being present to scavenge HO radicals. The measured rate coefficient ratios $k(\text{O}_3 + \beta\text{-ocimene})/k(\text{O}_3 + \textit{trans}\text{-but-2-ene})$ are placed on an absolute basis using $k(\text{O}_3 + \textit{trans}\text{-but-2-ene}) = 7.0 \times 10^{-15} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

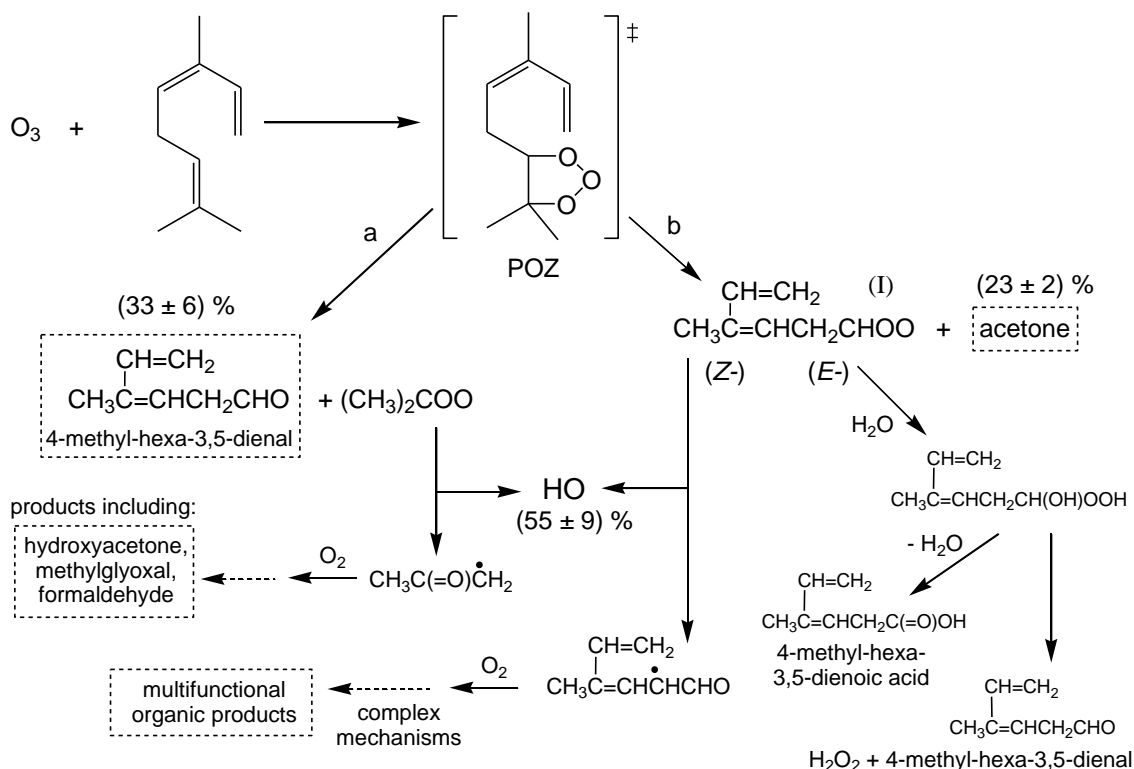
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.1×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$4.15 \times 10^{-15} \exp(-625/T)$	290-320
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	± 300	290-320

Comments on Preferred Values

The preferred value of E/R is based on the sole temperature dependence study of Kim et al. (2011). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1990), Witter et al. (2002) and Kim et al. (2011), corrected to 298 K where necessary using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value. The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for β -ocimene, and also for several other terpenes, appear to be systematically high

The reaction may proceed by initial addition of O_3 to any of the three $\text{C}=\text{C}$ bonds in β -ocimene. Comparison of k for the reaction of O_3 with β -ocimene with that reported for the reaction of O_3 with the β -ocimene oxidation product 4-methyl-hexa-3,5-dienal, which retains the conjugated diene structure (Baker et al., 2004), suggests that the reaction of O_3 with β -ocimene occurs predominantly ($\approx 90\%$) at the isolated $\text{C}=\text{C}$ bond.

The addition of O_3 to the isolated $\text{C}=\text{C}$ bond in β -ocimene forms a “primary ozonide (POZ)” which rapidly decomposes to form two sets of “primary” carbonyl product plus Criegee intermediate, as shown in the following schematic:



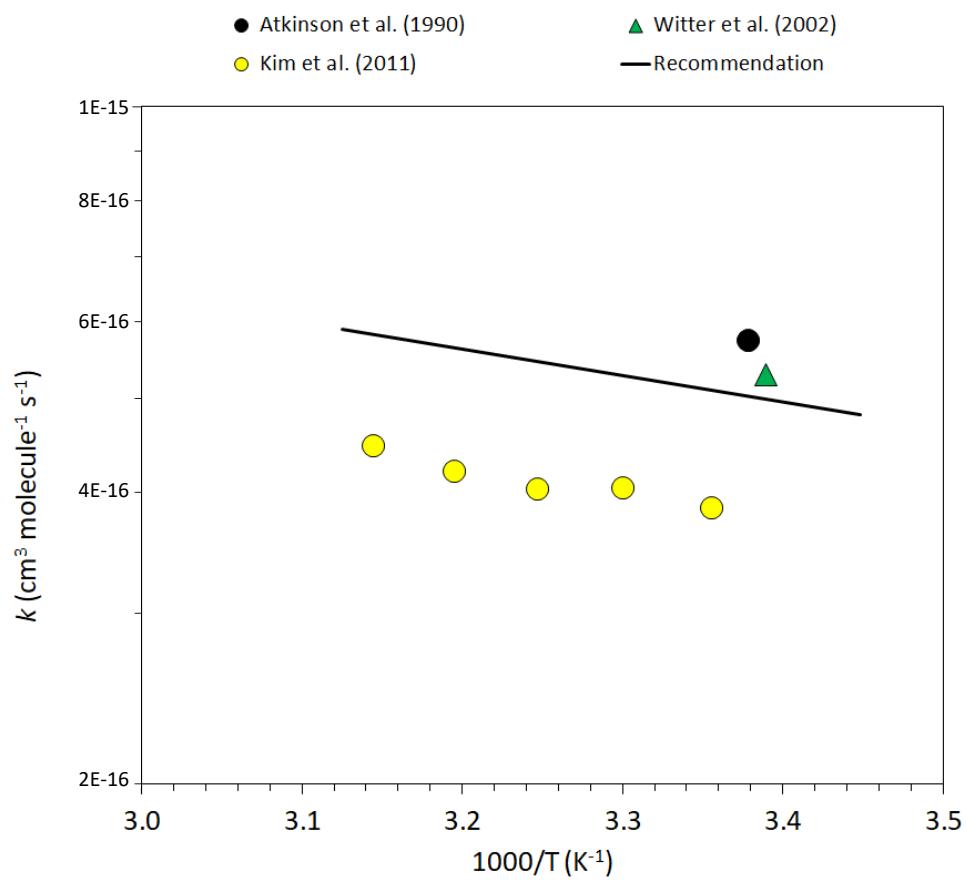
Acetone has been reported to be formed with a yield of (23 ± 2) % (Reissell et al., 1999; 2002), and 4-methyl-hexa-3,5-dienal with a yield of (33 ± 6) % (Reissell et al., 2002). This suggests important contributions from both decomposition channels, (a) and (b), as shown in the schematic, but with other unidentified pathways also contributing. These are partly accounted for by the products potentially formed from addition of O_3 to the C=C bonds in the conjugated diene system, which are not represented in the schematic (and for which there are no reported yields).

The dimethyl-substituted Criegee intermediate $(CH_3)_2COO$ decomposes almost exclusively to form HO radicals and the acetyl radical (see discussion in data sheet Ox_VOC41), the further chemistry of which potentially leads to the formation of a number of products, e.g. hydroxyacetone, methylglyoxal and formaldehyde. HO radicals have been reported to be formed with a yield of (55 ± 9) % from the reaction of O_3 with β -ocimene (Aschmann et al., 2002).

The *Z*- conformer of Criegee intermediate (I), formed in channel (b), may also decompose to form HO radicals and the β -oxo-dienyl radical shown in the schematic. HO formation via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) is unavailable for the *E*- conformer. If stabilized, this is likely to react predominantly with H_2O under atmospheric conditions, potentially forming additional 4-methyl-hexa-3,5-dienal and H_2O_2 , or 4-methyl-hexa-3,5-dienoic acid.

References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Baker, J., Arey, J. and Atkinson, R.: J. Atmos. Chem., 48, 241, 2004.
Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: Int. J. Chem. Kinet., Symp. 1, 183, 1975.
Kim, D., Stevens, P. S. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.
Reissell, A., Aschmann, S.M., Atkinson, R. and Arey, J.: J. Geophys. Res., 107 (D12), 4138, doi:10.1029/2001JD001234, 2002.
Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: Int. J. Chem. Kinet., 34, 394, 2002.



Ox_VOC26: α -phellandrene

Last evaluated: August 2020; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.2×10^{-14}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(2.14 \pm 0.48) \times 10^{-15}$	296 ± 2	Atkinson et al., 1990	RR-GC (a)
$(2.90 \pm 0.09) \times 10^{-15}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b)

 α -phellandrene is 2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene**Comments**

- (a) The concentrations of a series of alkenes (including α -phellandrene and terpinolene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \alpha\text{-phellandrene})/k(\text{O}_3 + \text{terpinolene})$ is placed on an absolute basis using $k(\text{O}_3 + \text{terpinolene}) = 1.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (b) The concentrations of α -phellandrene and 2,3-dimethyl-but-2-ene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \alpha\text{-phellandrene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene})$ is placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.9×10^{-15}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.20	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on the determination of Shu and Atkinson (1994), which supersedes that of Atkinson et al. (1990). The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for α -phellandrene, and also for several other terpenes, appear to be systematically high.

The reaction is expected to proceed by initial addition of O₃ to each of the C=C bonds in conjugated cyclic diene system, to form a pair of “primary ozonides”. These rapidly decompose to form four C₁₀ carbonyl-substituted Criegee intermediates, each of which has two stereo-conformers. HO radicals may potentially be formed (in conjunction with a number of β -oxo-alkenyl radicals) from the appropriate conformer of three of the Criegee intermediates, via the well-established decomposition mechanism involving a 1,4-H atom migration to form a vinyl hydroperoxide intermediate (e.g. see Johnson and Marston, 2008). In addition, HO formation via a rapid 1,6-allyl H atom migration is available for a further conformer (Vereecken et al., 2017), forming a conjugated vinyl hydroperoxide intermediate. Accordingly, formation of HO radicals has been quantified in chamber studies (Herrmann et al., 2010; Mackenzie-Rae et al., 2017), with a preferred yield of (32 \pm 10) % based on these observations. Mackenzie-Rae et al. (2017; 2018) reported evidence for formation of a number of products that can be formed from the subsequent chemistry of some of the β -oxo-alkenyl radicals and by other routes. These included low yields of a number of identified small products, including formaldehyde (5 – 9 %), glyoxal (6 – 23 %), methyl glyoxal (2 – 9 %), formic acid (22 – 37 %) and acetic acid (9 – 22 %). Reissell et al. (1999) have also reported an upper limit yield of acetone of < 2 %, suggesting that it is not formed as a first-generation product.

Mackenzie-Rae et al. (2017) also reported an average rate coefficient of $(1.0 \pm 0.7) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ for bulk ozonolysis of the first-generation suite of unsaturated products (which each contains a residual double bond), based on simulations of the time-dependence of the system using a detailed mechanism. Associated HO radical yields of 8 – 11 % and 15 \pm 7 % were also determined by Herrmann et al. (2010) and Mackenzie-Rae et al. (2017), respectively.

References

- Atkinson, R., Hasegawa, D. and Aschmann, S. M.: *Int. J. Chem. Kinet.*, 22, 871, 1990.
Atkinson, R. and Arey, J.: *Chem. Rev.*, 103, 4605, 2003.
Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: *Int. J. Chem. Kinet., Symp.* 1, 183, 1975.
Herrmann, F., Winterhalter, R., Moortgat, G. K. and Williams, J.: *Atmos. Environ.*, 44, 3458, 2010.
Johnson, D. and Marston, G.: *Chem. Soc. Rev.*, 37, 699, 2008.
Mackenzie-Rae, F. A., Liu, T., Deng, W., Saunders, S. M., Fang, Z., Zhang, Y., and Wang, X.: *Atmos. Chem. Phys.*, 17, 6583, 2017.
Mackenzie-Rae, F. A., Wallis, H. J., Rickard, A. R., Pereira, K. L., Saunders, S. M., Wang, X., and Hamilton, J. F.: *Atmos. Chem. Phys.*, 18, 4673, 2018.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: *J. Geophys. Res.*, 104, 13869, 1999.
Shu, Y. and Atkinson, R.: *Int. J. Chem. Kinet.*, 26, 1193, 1994.
Vereecken, L., Novelli, A. and Taraborrelli, D.: *Phys. Chem. Chem. Phys.*, 19, 31599, 2017.

Ox_VOC27: β -phellandrene

Last evaluated: August 2018; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.8×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(5.22 \pm 1.35) \times 10^{-17}$	297 ± 2	Shorees et al., 1991	RR-GC (a)

 β -phellandrene is 3-isopropyl-6-methylene-cyclohexene**Comments**

- (a) The concentrations of β -phellandrene and α -pinene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 6400 L all Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \alpha\text{-phellandrene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-pinene}) = 9.53 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation). β -phellandrene concentrations were corrected to account for the presence of a co-eluting limonene impurity, initially present at ~10 % of the β -phellandrene concentration.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.2×10^{-17}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.30	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shorees et al. (1991), but with wide uncertainty limits to reflect complications in the measurements of β -phellandrene concentrations (see comment (a)). The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for β -phellandrene, and also for several other terpenes, appear to be systematically high.

There has been only limited product and mechanistic information reported in the literature. Atkinson et al. (1992) reported a yield of HO radicals of $(14^{+7}_{-5})\%$, and Hakola et al. (1993) a yield of 4-isopropylcyclohex-2-enone of $(29 \pm 6)\%$ from the ozonolysis of β -phellandrene. The reaction is likely to proceed

by initial addition of O_3 to each of the endocyclic and exocyclic $C=C$ bonds in conjugated diene system, to form a pair of "primary ozonides". That formed from addition to the exocyclic $C=C$ bond partly decomposes to form 4-isopropyl-cyclohex-2-enone and CH_2OO ; and partly to form $HCHO$ and a complex Criegee intermediate of molecular formula $C_9H_{14}OO$, which (if stabilized) may form additional 4-isopropyl-cyclohex-2-enone following reaction with water vapour. HO radicals may be formed from the Z - conformer of $C_9H_{14}OO$ by the accepted HO -forming mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (e.g. see Johnson and Marston, 2008).

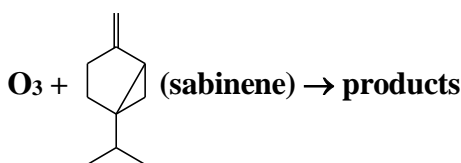
The primary ozonide formed from addition of O_3 to the endocyclic double bond is expected to decompose to form two carbonyl-substituted C_{10} Criegee intermediates. One of these is unlikely to form HO , owing to the absence of β -hydrogen atoms, with the accepted HO -forming mechanism only being available for the Z - conformer of the other Criegee intermediate. The low yield HO from the reaction of O_3 with β -phellandrene is therefore generally consistent with expectations.

References

- Atkinson, R., Aschmann, S. M., Arey, J. and Shorees, B.: *J. Geophys. Res.*, 97, 6065, 1992.
Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: *Int. J. Chem. Kinet., Symp.* 1, 183, 1975.
Hakola, H., Shorees, B., Arey, J. and Atkinson, R.: *Environ. Sci. Technol.*, 27, 278, 1993.
Johnson, D. and Marston, G.: *Chem. Soc. Rev.*, 37, 699, 2008.
Shorees, B., Atkinson, R. and Arey, J.: *Int. J. Chem. Kinet.*, 23, 897, 1991.

Ox_VOC28: sabinene

Last evaluated: August 2018; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(8.07 \pm 0.83) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990a	S-CL/GC (a)
$(6.2 \pm 2.1) \times 10^{-17}$	297 ± 1	Bernard et al., 2012	F-CL (b)
<i>Relative Rate Coefficients</i>			
$(9.55 \pm 1.04) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990b	RR-GC (c)
$(9.03 \pm 0.77) \times 10^{-16}$	303 ± 1	Bernard et al., 2012	RR-IR (d,e)
$(8.40 \pm 1.15) \times 10^{-16}$	303 ± 1		RR-IR (d,f)

sabinene is 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of sabinene (measured by GC-FID). Experiments were carried out at a total pressure of 980 mbar in a 160 L Teflon chamber.
- (b) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of sabinene, in a flow reactor at a total pressure of ~1 bar.
- (c) The concentrations of a series of alkenes (including sabinene and α -pinene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \text{sabinene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-pinene}) = 9.46 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (d) The concentrations of sabinene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O₃ - sabinene - reference compound - cyclohexane (HO radical scavenger) - air mixtures in a 7300 L Teflon chamber at ~1 bar pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \text{sabinene})/k(\text{O}_3 + \text{cyclohexene}) = 1.05 \pm 0.09$, and $k(\text{O}_3 + \text{sabinene})/k(\text{O}_3 + \text{cis-cyclooctene}) = 0.22 \pm 0.03$, are placed on an absolute basis using $k(\text{O}_3 + \text{cyclohexene}) = 8.60 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + \text{cis-cyclooctene}) = 3.82 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K (Atkinson and Arey, 2003).
- (e) Relative to $k(\text{O}_3 + \text{cyclohexene})$.
- (f) Relative to $k(\text{O}_3 + \text{cis-cyclooctene})$.

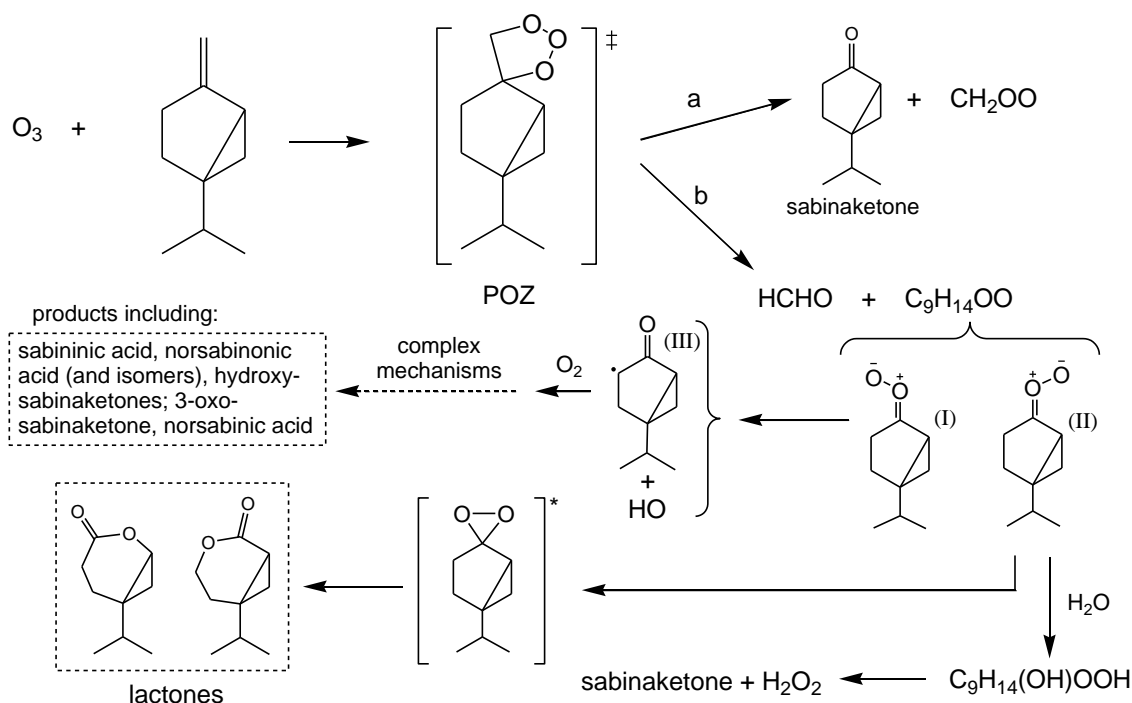
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	8.3×10^{-17}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is the average of the determinations of Atkinson et al. (1990a; 1990b) and Bernard et al. (2012), which are in good agreement.

The reaction proceeds by initial addition of O_3 to the $\text{C}=\text{C}$ bond to form a “primary ozonide (POZ)” which rapidly decomposes to form two sets of “primary” carbonyl product plus Criegee intermediate, as shown in the following schematic:



Sabinaketone (5-isopropyl-bicyclo[3.1.0]hexan-2-one) has been reported to be formed with yields in the range (35 – 50) % (Hakola et al., 1994; Yu et al., 1999; Chiappini et al., 2006), and HCHO with a yield of (52 ± 9) % (Chiappini et al., 2006), providing evidence for the significant participation of both decomposition channels, (a) and (b).

The Criegee intermediate, CH_2OO (formed from channel (a)), is expected to be almost fully stabilised at atmospheric pressure, by analogy with the β -pinene system (Nguyen et al., 2009). Its reaction with H_2O partially forms HCOOH (see data sheet Ox_VOC5), which has been reported to be formed with a yield of (17 ± 7) % from the ozonolysis of sabinene (Chiappini et al., 2006). The reported HO production from sabinene ozonolysis (Atkinson et al., 1992; Aschmann et al., 2002), preferred yield 33 ± 5 %, is expected to result mainly from reactions of the Criegee intermediate $\text{C}_9\text{H}_{14}\text{OO}$ formed in channel (b), which has the two conformers, (I) and (II). In practice, formation of HO via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide

intermediate) may only be possible for conformer (I), owing to the relevant β -hydrogen in conformer (II) being at the bridgehead of a constrained bicyclic structure, as discussed for a structurally similar Criegee intermediate formed from β -pinene by Rickard et al. (1999) and Nguyen et al. (2009); and this would help explain the relatively low HO yield from sabinene ozonolysis. The alternative well-documented decomposition route for conformer (II), via a dioxirane intermediate (e.g. Johnson and Marston, 2008), leads to the formation of lactones (6-isopropyl-2-oxa-bicyclo[4.1.0]heptan-3-one and/or 6-isopropyl-3-oxa-bicyclo[4.1.0]heptan-2-one), the detection of which has been reported by Griesbaum and Miclaus (1998) and Chiappini et al. (2006). Conformer (II) may also potentially react with H_2O under atmospheric conditions, forming H_2O_2 and additional sabinaketone.

The generation of HO from conformer (I) is accompanied by the formation of β -oxo alkyl radical (III), the further chemistry of which may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (Yu et al., 1999; Warscheid and Hoffmann, 2001; Chiappini et al., 2006).

References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
- Atkinson, R., Aschmann, S. M. and Arey, J.: Atmos. Environ., 24A, 2647, 1990a.
- Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990b.
- Atkinson, R., Aschmann, S. M., Arey, J. and Shorees, B.: J. Geophys. Res., 97, 6065, 1992.
- Bernard, F., Fedioun, I., Peyroux, F., Quilgars, A., Daële, V. and Mellouki, A.: J. Aerosol Sci., 43, 14, 2012.
- Chiappini, L., Carrasco, N., Temine, B., Picquet-Varrault, B., Durand-Jolibois, R., Wenger, J. C. and Doussin, J. F.: Environ. Chem., 3, 286, 2006.
- Griesbaum, K. and Miclaus, V.: Environ. Sci. Technol., 32, 647, 1998.
- Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
- Johnson, D. and Marston, G.: Chem. Soc. Rev., 37, 699, 2008.
- Nguyen, T. L., Peeters, J. and Vereecken, L.: Phys. Chem. Chem. Phys., 11, 5643, 2009.
- Rickard, A. R., Johnson, D., McGill, C. D. and Marston, G.: J. Phys. Chem. A, 103, 7656, 1999.
- Warscheid, B. and Hoffmann, T.: Rapid Commun. Mass Spectrom., 15, 2259, 2001.
- Yu, J., Cocker III, D. R., Griffin, R. J., Flagan, R. C., Seinfeld, J. H.: J. Atmos. Chem., 34, 207, 1999.

Ox_VOC29: α -terpinene

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
8.8×10^{-14}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(9.82 \pm 2.64) \times 10^{-15}$	296 ± 2	Atkinson et al., 1990	RR-GC (a)
$(2.62 \pm 0.88) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(c)
$(2.18 \pm 0.23) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(d)
$(1.60 \pm 0.43) \times 10^{-14}$	296 ± 2	Witter et al., 2002	RR-GC (e)

 α -terpinene is 1-isopropyl-4-methyl-cyclohexa-1,3-diene**Comments**

- (a) The concentrations of a series of alkenes (including α -terpinene and terpinolene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio, $k(\text{O}_3 + \alpha\text{-terpinene})/k(\text{O}_3 + \text{terpinolene}) = (6.14 \pm 1.24)$, is placed on an absolute basis using $k(\text{O}_3 + \text{terpinolene}) = 1.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (b) The concentrations of α -terpinene and 2,3-dimethyl-but-2-ene or β -caryophyllene (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratios, $k(\text{O}_3 + \alpha\text{-terpinene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = (24.0 \pm 8.0)$ and $k(\text{O}_3 + \alpha\text{-terpinene})/k(\text{O}_3 + \beta\text{-caryophyllene}) = (1.82 \pm 0.06)$, are placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + \beta\text{-caryophyllene}) = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendations). The final value of k quoted by the authors was based on the more precise measurement relative to β -caryophyllene.
- (c) Relative to 2,3-dimethyl-but-2-ene.
- (d) Relative to β -caryophyllene.
- (e) The concentrations of α -terpinene and 2,3-dimethyl-but-2-ene (the reference compound) were monitored by GC in reacting O_3 - α -terpinene - 2,3-dimethyl-but-2-ene - m -xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio, $k(\text{O}_3 + \alpha\text{-terpinene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = (14.7 \pm 0.7)$, is placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC current recommendation).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.9×10^{-14}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.20	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is the average of the more precise determination of Shu and Atkinson (1994), as favoured by the authors (see comment (c)), and the determination of Witter et al. (2002). The more approximate determination of Atkinson et al. (1990) is superseded by the study of Shu and Atkinson (1994). The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for α -terpinene, and also for several other terpenes, appear to be systematically high. The assigned uncertainty in k reflects the range of values reported in the relative rate studies.

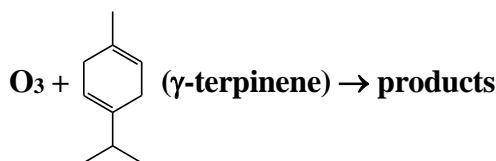
There has been only limited product and mechanistic information reported in the literature. Aschmann et al. (2002) and Herrmann et al. (2010) reported respective HO radical yields of $(38 \pm 5) \%$ and $(24 - 28) \%$; and Reissell et al. (1999) a yield of acetone of $(3 \pm 1) \%$. The reaction is likely to proceed by initial addition of O_3 to each of the C=C bonds in the cyclic conjugated diene system, to form a pair of “primary ozonides” which rapidly decompose to form four carbonyl-substituted Criegee intermediates. HO radicals may be formed (in conjunction with a number of β -oxo-alkenyl radicals) from decomposition of the Criegee intermediates, via the accepted mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (e.g. see Johnson and Marston, 2008). Acetone is most likely to be formed as a first-generation product from the further reactions of one of the β -oxo-alkenyl radicals.

References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
 Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
 Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: Int. J. Chem. Kinet., Symp. 1, 183, 1975.
 Herrmann, F., Winterhalter, R., Moortgat, G. K. and Williams, J.: Atmos. Environ., 44, 3458, 2010.
 Johnson, D. and Marston, G.: Chem. Soc. Rev., 37, 699, 2008.
 Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.
 Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.
 Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: Int. J. Chem. Kinet., 34, 394, 2002.

Ox_VOC30: γ -terpinene

Last evaluated: August 2018; Last change in preferred values: August 2018

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
2.8×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(1.55 \pm 0.17) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (a)

 γ -terpinene is 1-isopropyl-4-methyl-cyclohexa-1,4-diene**Comments**

- (a) The concentrations of a series of alkenes (including γ -terpinene and α -pinene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \gamma\text{-terpinene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-pinene}) = 9.46 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.6×10^{-16}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.30	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Atkinson et al. (1990). The absolute rate coefficient determination reported by Grimsrud et al. (1975) is about a factor of two higher, but within the upper uncertainty bound assigned to the preferred value. The Atkinson et al. (1990) value is preferred, because those reported by Grimsrud et al. (1975) for a series of terpenes appear to be systematically high.

There has been only limited product and mechanistic information reported in the literature. Aschmann et al. (2002) reported a yield of HO radicals of $(81 \pm 11) \%$; and Reissell et al. (1999) a yield of acetone of $(11 \pm 2) \%$. The reaction is likely to proceed by initial addition of O_3 to each of the endocyclic C=C bonds, to form a pair of “primary ozonides” which rapidly decompose to form four

carbonyl-substituted Criegee intermediates. HO radicals may be formed (in conjunction with a number of β -oxo-alkenyl radicals) from decomposition of all of the Criegee intermediates, via the accepted mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (e.g. see Johnson and Marston, 2008). Acetone is most likely to be formed as a first-generation product from the further reactions of one of the β -oxo-alkenyl radicals, which contains a *gem*-dimethyl substituent at the radical centre.

References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: Int. J. Chem. Kinet., Symp. 1, 183, 1975.
Johnson, D. and Marston, G.: Chem. Soc. Rev., 37, 699, 2008.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.

Ox_VOC31: terpinolene

Last evaluated: August 2018; Last change in preferred values: September 2013

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.3 \pm 2.2) \times 10^{-16}$	298	Japar et al., 1974	S-CL
1.0×10^{-14}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(1.46 \pm 0.26) \times 10^{-15}$	296 ± 2	Atkinson et al., 1990	RR-GC (a)
$(1.83 \pm 0.04) \times 10^{-15}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b)
$(1.74 \pm 0.46) \times 10^{-15}$	295 ± 0.5	Witter et al., 2002	RR-GC (c)
$(1.41 \pm 0.40) \times 10^{-15}$	298 ± 2	Stewart et al., 2013	RR-GC (d)

terpinolene is 4-isopropylidene-1-methyl-cyclohexene

Comments

- (a) The concentrations of a series of alkenes (including terpinolene and limonene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \text{terpinolene})/k(\text{O}_3 + \text{limonene})$ is placed on an absolute basis using $k(\text{O}_3 + \text{limonene}) = 2.16 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (b) The concentrations of terpinolene and 2,3-dimethyl-but-2-ene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \text{terpinolene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene})$ is placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (c) The concentrations of terpinolene and 2,3-dimethyl-but-2-ene (the reference compound) were monitored by GC in reacting O₃ - terpinolene - 2,3-dimethyl-but-2-ene - *m*-xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \text{terpinolene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.60 \pm 0.06$ is placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (d) The concentrations of terpinolene and limonene (the reference compound) were monitored by GC-FID in flowing mixtures of O₃, terpinolene, limonene, cyclohexane (the HO radical scavenger) and air at 760 Torr (1.013 bar) pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \text{terpinolene})/k(\text{O}_3 + \text{limonene}) = 6.41 \pm 0.08$ is placed on an absolute basis using $k(\text{O}_3 + \text{limonene}) = 2.2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

Preferred Values

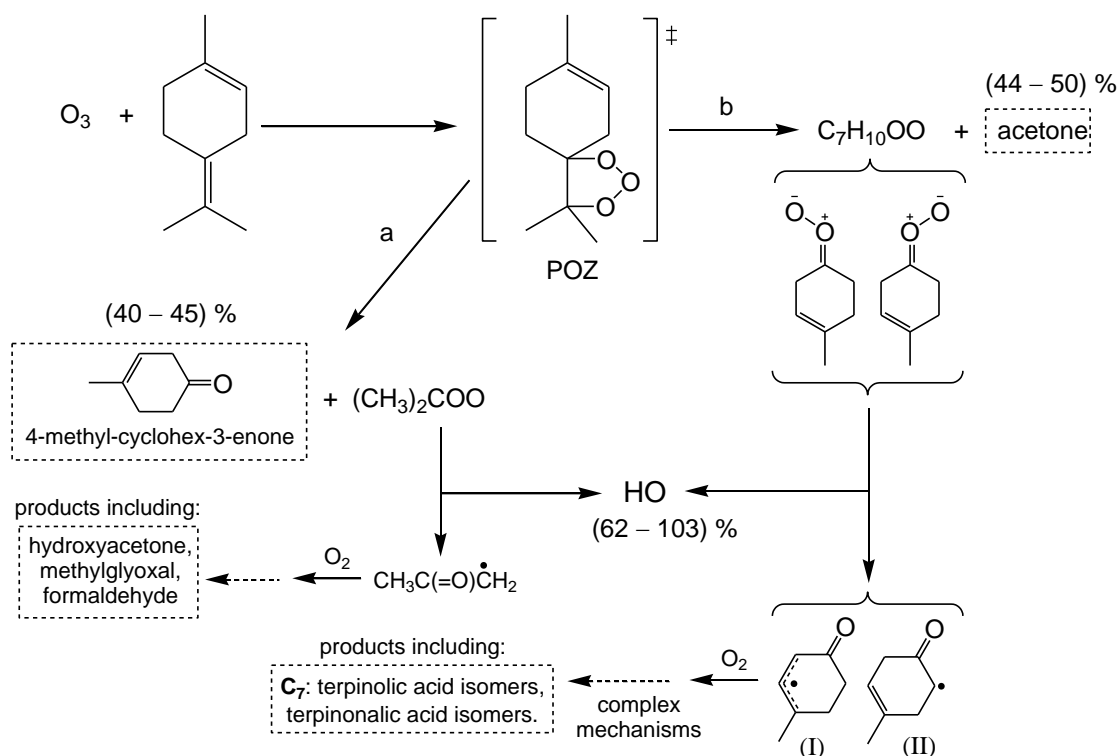
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.6×10^{-15}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is an average of the relative rate coefficient determinations of Atkinson et al. (1990), Shu and Atkinson (1994), Witter et al. (2002) and Stewart et al. (2013), which are in good agreement.

The reaction may proceed by initial addition of O_3 to either of the endocyclic or exocyclic $\text{C}=\text{C}$ bonds in terpinolene. Comparison of k for the reaction of ozone with terpinolene with that reported for the reaction of ozone with the terpinolene oxidation product, 4-methylcyclohex-3-en-1-one, which retains the endocyclic $\text{C}=\text{C}$ bond (Baker et al., 2004), suggests that the reaction of O_3 with terpinolene occurs predominantly ($\approx 95\%$) at the exocyclic bond. Support for this comes from the distribution of products reported in a number of studies.

The addition of O_3 to the exocyclic $\text{C}=\text{C}$ bond in terpinolene forms a “primary ozonide (POZ)” which rapidly decomposes to form two sets of “primary” carbonyl product plus Criegee intermediate, as shown in the following schematic:



Acetone has been reported to be formed with a yield of (44 – 50) % (Reissell et al., 1999; Orlando et al., 2000; Lee et al., 2006), and 4-methylcyclohex-3-en-1-one with a yield of (40 – 45) % (Hakola et al., 1994; Reissell et al., 1999; Ma and Marston, 2009). This suggests approximately equal contributions from each of the decomposition channels, (a) and (b), as shown in the schematic.

The dialkyl-substituted Criegee intermediates ((CH₃)₂COO and both conformers of C₇H₁₀OO) are expected to decompose mainly to form HO radicals and a number of organic co-radicals, as shown in the schematic. Accordingly, high HO radical yields in the range (62 – 103) % have been reported from the reaction of O₃ with terpinolene (Atkinson et al., 1992; Aschmann et al., 2002; Herrmann et al., 2010), preferred value 70 ± 8 %. The decomposition of (CH₃)₂COO is expected to form HO in conjunction with the acetonyl radical (see discussion in data sheet Ox_VOC41), the further chemistry of which potentially leads to the formation of a number of products, including formaldehyde, which has been reported to be formed with a yield of (29 ± 3) % from the ozonolysis of terpinolene (Lee et al., 2006). Decomposition of the two conformers of the more complex Criegee intermediate, C₇H₁₀OO, by the accepted HO-forming mechanism (involving abstraction of a β-hydrogen via a vinyl hydroperoxide intermediate), produces a resonant β-/δ-oxo-alkenyl radical (I) and a β-oxo-alkenyl radical (II), the further chemistry of which may form a number of multifunctional organic products containing hydroxy, carbonyl and acid functionalities, including the terpinolic and terpinonic acids reported and discussed by Ma and Marston (2009).

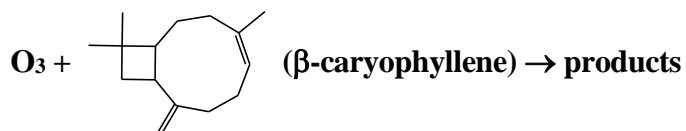
References

- Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
- Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
- Atkinson, R., Aschmann, S. M., Arey, J. and Shorees, B.: J. Geophys. Res., 97, 6065, 1992.
- Baker, J., Arey, J. and Atkinson, R.: J. Atmos. Chem., 48, 241, 2004.
- Grimsrud, E. P., Westberg, H. H. and Rasmussen, R. A.: Int. J. Chem. Kinet., Symp. 1, 183, 1975.
- Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
- Herrmann, F., Winterhalter, R., Moortgat, G. K. and Williams, J.: Atmos. Environ., 44, 3458, 2010.
- Japar, S. M., Wu, C. H. and Niki, H.: Environ. Lett., 7, 245, 1974.
- Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: J. Geophys. Res., 111, D07302, doi:10.1029/2005JD006437, 2006.
- Ma, Y. and Marston, G.: Phys. Chem. Chem. Phys., 11, 4198, 2009.
- Orlando, J. J., Noziere, B., Tyndall, G. S., Orzechowska, G. E., Paulson, S. E. and Rudich, Y.: J. Geophys. Res., 105(D9), 11,561, 2000.
- Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.
- Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.
- Stewart, D. J., Almarok, S. H., Lockhart, J. P., Mohamed, O. M., Nutt, D. R., Pfrang, C., Marston, G.: Atmos. Environ., 70, 227, 2013.
- Witter, M., Berndt, T., Böge, O., Stratmann, F. and Heintzenberg, J.: Int. J. Chem. Kinet., 34, 394, 2002.
- Zhang, J., Wilson, W. E., and Liou, P. J.: Environ. Sci. Technol., 28, 1975, 1994.

A3. Data sheets for reactions of O₃ with sesquiterpenes

Ox_VOC32: β-caryophyllene

Last evaluated: August 2018; Last change in preferred values: June 2015



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 1.0) \times 10^{-14}$	295 ± 2	Richters et al., 2015	S-IR/UVA (a)
<i>Relative Rate Coefficients</i>			
$(8.71 \pm 1.23) \times 10^{-15}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(c)
$(1.09 \pm 0.07) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(d)
$(1.02 \pm 0.03) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(e)
$(2.7 \pm 1.9) \times 10^{-15}$	366 ± 2	Ghalaieny et al., 2012	RR-GC (f)
$(1.39 \pm 0.38) \times 10^{-14}$	295 ± 2	Richters et al., 2015	RR-GC-MS (g)
$(1.19 \pm 0.21) \times 10^{-14}$	295 ± 2	Richters et al., 2015	RR-MS (h)

β-caryophyllene is 4,11,11-trimethyl-8-methylene-bicyclo[7.2.0]undec-4-ene

Comments

- (a) k determined from the observed rate of ozone decay (measured by UVA at 254 nm) in the presence of known starting concentrations of β-caryophyllene (measured by FT-IR), in stopped-flow experiments at a total pressure of ~1 bar, with sufficient propane to scavenge >99 % of HO radicals. It was not possible to temporally-resolve the ozone decay under pseudo-first order conditions for highly-reactive sesquiterpenes such as β-caryophyllene. The experiments were therefore carried out with comparable starting concentrations of ozone and β-caryophyllene, and the results were solved numerically using an extrapolation method connected with a Newton-technique for parameter estimation.
- (b) The concentrations of β-caryophyllene and 2-methyl-but-2-ene, 2,3-dimethyl-but-2-ene or terpinolene (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O₃. The measured rate coefficient ratios, $k(\text{O}_3 + \beta\text{-caryophyllene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = (22.0 \pm 3.1)$, $k(\text{O}_3 + \beta\text{-caryophyllene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = (9.98 \pm 0.60)$ and $k(\beta\text{-caryophyllene})/k(\text{O}_3 + \text{terpinolene}) = (6.40 \pm 0.20)$, are placed on an absolute basis using $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.96 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003); $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K and $k(\text{O}_3 + \text{terpinolene}) = 1.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendations). The final value of k quoted by the authors was based on the more precise measurements relative to 2,3-dimethyl-but-2-ene and terpinolene.
- (c) Relative to 2-methyl-but-2-ene.

- (d) Relative to 2,3-dimethyl-but-2-ene.
- (e) Relative to terpinolene.
- (f) The concentrations of β -caryophyllene and 2,3-dimethyl-but-2-ene (the reference compound), with excess cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 123 L Teflon-coated chamber at 780 Torr (1040 mbar) pressure of N_2 , with repeated injections of O_3/O_2 . The measured rate coefficient ratio, $k(O_3 + \beta\text{-caryophyllene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 2.04$, is placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.32 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 366 K (IUPAC, current recommendation). It is noted that the authors used a much lower value of $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 2.89 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, based on a relative rate measurement reported in the same study, leading to a reported value of $k = (5.9 \pm 4.2) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 366 K.
- (g) The concentrations of β -caryophyllene and α -terpinene (the reference compound), with 2-methylpropene to scavenge HO radicals, were monitored by GC-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(O_3 + \beta\text{-caryophyllene})/k(O_3 + \alpha\text{-terpinene}) = (0.73 \pm 0.04)$, is placed on an absolute basis using $k(O_3 + \alpha\text{-terpinene}) = 1.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (h) The concentrations of β -caryophyllene and 2,3-dimethyl-but-2-ene (the reference compound), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(O_3 + \beta\text{-caryophyllene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = (10.9 \pm 0.8)$, is placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, current recommendation).

Preferred Values

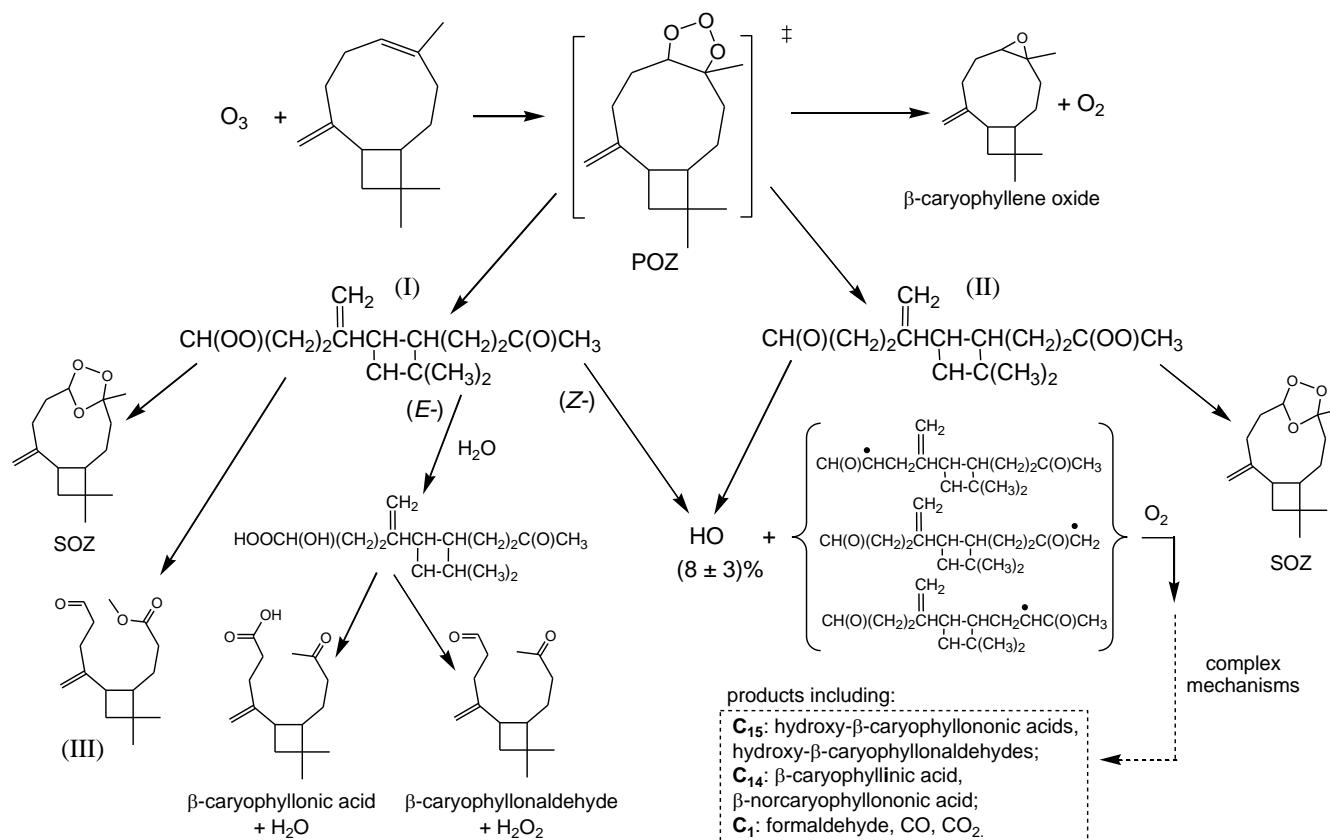
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.2×10^{-14}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on an average of the more precise determinations of Shu and Atkinson (1994), as favoured by the authors (see comment (b)), and the relative rate coefficient determinations of Richters et al. (2015), which are in good agreement and consistent with the approximate absolute rate coefficient determination of Richters et al. (2015). The preferred value of k is also consistent with that calculated theoretically by Nguyen et al. (2009), who predicted that the reaction has a weak negative temperature dependence near room temperature described by the expression $k = 8.3 \times 10^{-24} T^{3.05} \exp(1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, such that $k = 9.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The lower approximate value reported by Ghalaiey et al. (2012) at 366 K was interpreted by the authors in terms of heterogeneous interferences of secondary organic aerosol (SOA) formation, leading to overestimates in previously-reported room temperature determinations. However, the more recent consistent results of Richters et al. (2015) using low reagent concentrations in the absence of SOA formation appear to disprove this hypothesis.

The reaction may proceed by initial addition of O_3 to either of the endocyclic or exocyclic C=C bonds in β -caryophyllene. Comparison of k for the reaction of ozone with β -caryophyllene with that reported for the suite of oxidation products that retain the originally exocyclic C=C bond (Winterhalter et al., 2009), suggests that the reaction of O_3 with β -caryophyllene occurs predominantly ($\approx 99\%$) at the endocyclic bond. Support for this comes from the distribution of products reported in a number of studies.

The addition of O₃ to the endocyclic C=C bond in β -caryophyllene forms a “primary ozonide (POZ)”. Although minor (~1 %) formation of β -caryophyllene oxide has been reported (Calogirou et al., 1997; Jaoui et al., 2003), it is likely that POZ mainly decomposes to form the two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the schematic below.



The Criegee intermediates can decompose to form HO radicals, which are expected to be formed in conjunction with a number of β -oxo alkenyl radicals. Comparatively low HO radical yields in the range 6 % – 10 % have been reported (Shu and Atkinson, 1994; Winterhalter et al., 2009; Jenkin et al., 2012), preferred value 8 \pm 3 %. The further chemistry of the β -oxo alkenyl radicals may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (e.g., Calogirou et al., 1997; Jaoui et al., 2003; Kanawati et al., 2008; Winterhalter et al., 2009; Li et al., 2011), and also formaldehyde, CO and CO₂, which have been reported to be formed with respective molar yields of (7.7 \pm 4.0) %, (2.0 \pm 1.8) % and (3.8 \pm 2.8) % by Winterhalter et al. (2009) from ozonolysis of the more reactive endocyclic double bond.

Products likely to be produced from alternative reactions of the Criegee intermediates (I) and (II) have also been detected. The formation of β -caryophyllon aldehyde and/or β -caryophyllonic acid has been positively identified in a number of studies (e.g., Calogirou et al., 1997; Kanawati et al., 2008; Winterhalter et al., 2009; Li et al., 2011; Jenkin et al., 2012), with respective molar yields of 17.3 % and 13.0 % reported by Jaoui et al. (2003) at ~80% relative humidity, in the absence of an HO scavenger. The theoretical calculations of Nguyen et al. (2009) propose an important role for a thermally-stable secondary ozonide (SOZ), which is potentially formed by ring-closure of either of the Criegee intermediates (I) and (II), and suggest it should be the dominant gas phase ozonolysis product (molar yield \geq 65 %). The experimental study of Winterhalter et al. (2009) provided some qualitative support for SOZ formation, and established that its yield apparently decreases with increasing relative humidity, consistent with its formation occurring at least partially in competition with the bimolecular reactions of the Criegee intermediates with H₂O. Detection of the multifunctional ester (III), which can potentially be formed from

rearrangement of (I) or (II), has also been reported by Kanawati et al. (2008) and Winterhalter et al. (2009). The CIR-TOF-MS product study of Jenkin et al. (2012) also confirmed significant collective formation of SOZ and its isomers β -caryophyllonic acid and the multifunctional ester (III). Further experimental quantification of product yields is clearly required, particularly in relation to formation, stability and further reaction of the secondary ozonide, SOZ.

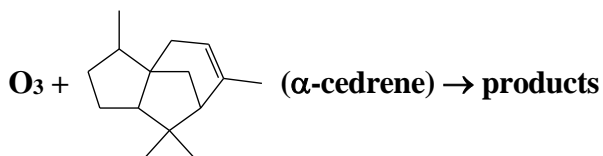
Winterhalter et al. (2009) also determined an HO yield of $(16.4 \pm 3.6) \%$ for bulk ozonolysis of the first-generation suite of products containing the originally exocyclic double bond. This was facilitated by their reactivity with O_3 being lower than that of β -caryophyllene by a factor of about 100, allowing temporal separation of the oxidation steps.

References

- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
- Calogirou, A., Kotzias, D., and Kettrup, A.: Atmos. Environ., 31, 283, 1997.
- Ghalaieny, M., Bacak, A., McGillen, M., Martin, D., Knights, A. V., O'Doherty, S., Shallcross, D. E. and Percival, C. J.: Phys. Chem. Chem. Phys., 14, 6596, 2012.
- Jaoui, M., Leungsakul, S., and Kamens, R. M.: J. Atmos. Chem., 45, 261, 2003.
- Jenkin, M. E., Wyche, K. P., Evans, C. J., Carr, T., Monks, P. S., Alfarra, M. R., Barley, M. H., McFiggans, G. B., Young, J. C., and Rickard, A. R.: Atmos. Chem. Phys., 12, 5275, 2012.
- Kanawati, B., Herrmann, F., Joniec, S., Winterhalter, R., and Moortgat, G. K.: Rapid Commun. Mass Spectrom., 22, 165, 2008.
- Li, Y. J., Chen, Q., Guzman, M. I., Chan, C. K., and Martin, S. T.: Atmos. Chem. Phys., 11, 121, 2011.
- Nguyen, T. L., Winterhalter, R., Moortgat, G., Kanawati, B., Peeters, J., and Vereecken, L.: Phys. Chem. Chem. Phys., 11, 4173, 2009.
- Richters, S., Herrmann, H. and Berndt, T.: Phys. Chem. Chem. Phys., 17, 11658, 2015.
- Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.
- Winterhalter, R., Herrmann, F., Kanawati, B., Nguyen, T. L., Peeters, J., Vereecken, L., and Moortgat, G. K.: Phys. Chem. Chem. Phys., 11, 4152, 2009.

Ox_VOC33: α -cedrene

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.3) \times 10^{-16}$	295 ± 2	Richters et al., 2015	S-IR/UVA (a)
<i>Relative Rate Coefficients</i>			
$(2.87 \pm 0.85) \times 10^{-17}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(c)
$(2.90 \pm 0.14) \times 10^{-17}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(d)
$(1.4 \pm 0.9) \times 10^{-15}$	366 ± 2	Ghalaiey et al., 2012	RR-GC (e)
$(1.22 \pm 0.19) \times 10^{-16}$	295 ± 2	Richters et al., 2015	RR-MS (f),(c)
$(1.42 \pm 0.38) \times 10^{-16}$	295 ± 2	Richters et al., 2015	RR-MS (f),(d)

 α -cedrene is 2,6,6,8-tetramethyl-tricyclo[5.3.1.0^{1,5}]undec-8-ene**Comments**

- (a) k determined from the observed pseudo-first order rate of ozone decay (measured by UVA at 254 nm) in the presence of known excess concentrations of α -cedrene (measured by FTIR), in stopped-flow experiments at a total pressure of ~ 1 bar, with sufficient propane to scavenge $>99\%$ of HO radicals.
- (b) The concentrations of α -cedrene and 2-methyl-but-2-ene or *cis*-but-2-ene (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratios, $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = (0.0725 \pm 0.0215)$ and $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + \textit{cis-but-2-ene}) = (0.228 \pm 0.011)$, are placed on an absolute basis using $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.96 \times 10^{-16}$ (Atkinson and Arey, 2003) and $k(\text{O}_3 + \textit{cis-but-2-ene}) = 1.27 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) at 296 K.
- (c) Relative to 2-methyl-but-2-ene.
- (d) Relative to *cis*-but-2-ene.
- (e) The concentrations of α -cedrene and 2,3-dimethyl-but-2-ene (the reference compound), with excess cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 123 L Teflon-coated chamber at 780 Torr (1040 mbar) pressure of N_2 , with repeated injections of O_3/O_2 . The measured rate coefficient ratio, $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.08$, is placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.32 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 366 K (IUPAC, current recommendation). It is noted that the authors used a much lower value of $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 2.89 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, based on a relative rate measurement reported in the same study, leading to a reported value of $k = (3.1 \pm 1.9) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 366 K.
- (f) The concentrations of α -cedrene and 2-methyl-but-2-ene or *cis*-but-2-ene (the reference compounds), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) =$

(0.310 ± 0.006) and $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + \text{cis-but-2-ene}) = (1.13 \pm 0.01)$, are placed on an absolute basis using $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.92 \times 10^{-16}$ (Atkinson and Arey, 2003) and $k(\text{O}_3 + \text{cis-but-2-ene}) = 1.26 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) at 295 K.

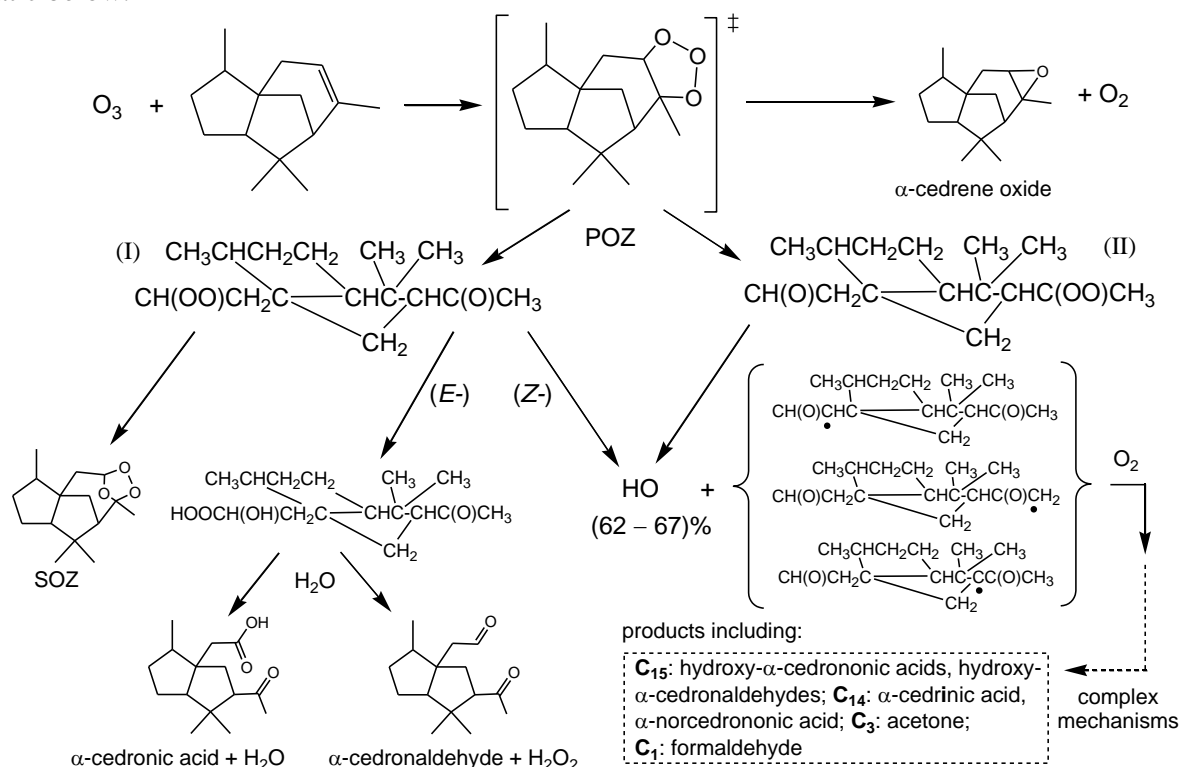
Preferred Values

No recommendation

Comments on Preferred Values

The studies tabulated above provide evidence that the reaction of O_3 with α -cedrene occurs, and that k is sufficiently high that the reaction will contribute to α -cedrene removal under atmospheric conditions. However, the level of disagreement in the reported values of k precludes recommendation of a preferred value. Further kinetics studies are required to allow the current discrepancies to be explained or reconciled.

The addition of O_3 to the C=C bond in α -cedrene forms a “primary ozonide (POZ)”. Although minor ($\sim 0.1\%$) formation of α -cedrene oxide has been reported (Jaoui et al., 2004), it is likely that POZ mainly decomposes to form the two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the schematic below.



Criegee intermediates (II) and the Z-conformer of (I) can decompose to form HO radicals, which are expected to be formed in conjunction with a number of β -oxo alkyl radicals, as shown in the schematic. HO radical yields of $67^{+34}_{-22}\%$ and $62.4 \pm 4.9\%$ have been reported Shu and Atkinson (1994) and Yao et al. (2014), preferred value $65 \pm 5\%$. The latter study reported a large decrease to $(9.0 \pm 1.6)\%$ when either $\text{CH}_3\text{C}(\text{O})\text{OH}$ or SO_2 were added to scavenge stabilized Criegee intermediates. The further chemistry of the β -oxo alkyl radicals may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (e.g., Jaoui et al., 2004; Yao et al., 2014), and also acetone and formaldehyde which have been reported to be formed by Jaoui et al. (2004).

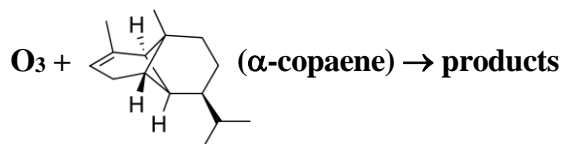
Products likely to be produced from alternative reactions of the Criegee intermediates (I) and (II) have also been detected. The formation of α -cedronaldehyde has been positively identified by Jaoui et al. (2004) and Yao et al. (2014), potentially formed from the reaction of (I) with H₂O. Jaoui et al. (2004) also detected α -cedronic acid as a possible alternative product of this reaction, although this was not confirmed by Yao et al. (2014). A thermally-stable secondary ozonide (SOZ), which can be formed by ring-closure of either of the Criegee intermediates (I) and (II), was reported as the major gas phase product of α -cedrene ozonolysis by Yao et al. (2014).

References

- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
- Ghalaieny, M., Bacak, A., McGillen, M., Martin, D., Knights, A. V., O'Doherty, S., Shallcross, D. E. and Percival, C. J.: Phys. Chem. Chem. Phys., 14, 6596, 2012.
- Jaoui, M., Sexton, K. G., and Kamens, R. M.: Atmos. Environ., 38, 2709, 2004.
- Richters, S., Herrmann, H. and Berndt, T.: Phys. Chem. Chem. Phys., 17, 11658, 2015.
- Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.
- Yao, L., Ma, Y., Wang, L., Zheng, J., Khalizov, A., Chen, M., Zhou, Y., Qi, L., and Cui, F.: Atmos. Environ., 94, 448, 2014.

Ox_VOC34: α -copaene

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(1.50 \pm 0.06) \times 10^{-16}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (a)
α -copaene is (1R,2S,6S,7S,8S)-8-isopropyl-1,3-dimethyltricyclo[4.4.0.0 ^{2,7}]dec-3-ene			

Comments

- (a) The concentrations of α -copaene and 2-methyl-but-2-ene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio, $k(\text{O}_3 + \alpha\text{-copaene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = (0.378 \pm 0.016)$, is placed on an absolute basis using $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.96 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.5×10^{-16}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on the determination of Shu and Atkinson (1994), with the uncertainty limits reflecting that this is the only reported study. Confirmatory measurements are required.

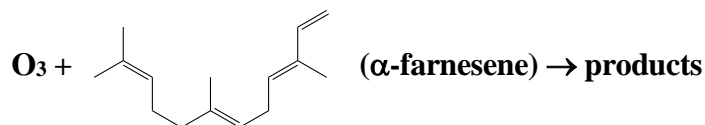
There has been only limited product and mechanistic information reported in the literature. Shu and Atkinson (1994) reported a yield of HO radicals of $(35^{+18}_{-12})\%$; and the studies of Dekermenjian et al. (1999) and Reinnig et al. (2009) provided information on the functional group content of secondary organic aerosol (SOA) formed from α -copaene ozonolysis. The mechanism is expected to proceed via addition of O_3 to the C=C bond, with the subsequent mechanism following the general framework outlined in the datasheets for other mono- and sesquiterpenes possessing endocyclic C=C bonds (e.g. α -cedrene).

References

- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
- Dekermenjian, M., Allen, D. T., Atkinson, R., and Arey, J.: Aerosol Sci. Technol., 30, 349, 1999.
- Reinnig, M.-C., Warnke, J., and Hoffmann, T.: Rapid Commun. Mass Spectrom., 23,1735, 2009.
- Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.

Ox_VOC35: α -farnesene

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$3.50 \times 10^{-12} \exp[-(2590 \pm 393)/T]$	298-318	Kim et al., 2011	RR-MS (a)
$(5.88^{+1.78}_{-1.37}) \times 10^{-16}$	298		

 α -farnesene is 3,7,11-trimethyl-dodeca-1,3,6,10-tetraene**Comments**

- (a) The concentrations of α -farnesene and *trans*-but-2-ene (the reference compound) were monitored by MS in reacting O_3 - α -farnesene - *trans*-but-2-ene - acetaldehyde - He mixtures in a 160 cm³ volume quartz vessel at ~1 bar pressure, with acetaldehyde being present to scavenge HO radicals. The measured rate coefficient ratios, $k(\text{O}_3 + \alpha\text{-farnesene})/k(\text{O}_3 + \text{trans-but-2-ene})$, are placed on an absolute basis using $k(\text{O}_3 + \text{trans-but-2-ene}) = 6.6 \times 10^{-15} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.9×10^{-16}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.5 \times 10^{-12} \exp(-2590/T)$	290-320
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298
$\Delta E/R$	± 500	290-320

Comments on Preferred Values

The preferred values of k are based on the temperature dependence expression of Kim et al. (2011), the only reported investigation of the reaction. Confirmatory studies are required.

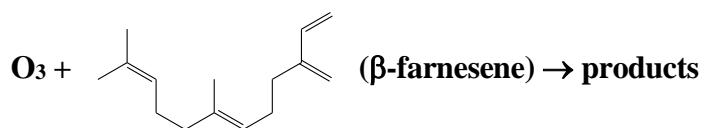
There have currently been no reported product or mechanistic investigations, and such studies are also required. However, structure-activity methods based on a summation of the rate coefficients for simple alkene and diene structures (e.g. Calvert et al., 2000) suggest that the reaction should proceed mainly via O_3 addition to the two non-conjugated methyl-substituted C=C bonds with about equal probability at 298 K, as has been reported for the structurally similar sesquiterpene, β -farnesene, by Kourtchev et al. (2009) (see data sheet Ox_VOC36).

References

- Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J., and Yarwood, G.: The mechanisms of atmospheric oxidation of alkenes, Oxford University Press, New York, ISBN 0-19-513177-0, 2000.
- Kim, D., Stevens, P. S. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.
- Kourtchev, I., Bejan, I, Sodeau, J. R., and Wenger, J. C: Atmos. Environ., 43, 3182, 2009.

Ox_VOC36: β -farnesene

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(4.12 \pm 0.17) \times 10^{-16}$	296 ± 2	Kourtchev et al., 2009	RR-FTIR (a),(b)
$(4.01 \pm 0.12) \times 10^{-16}$	296 ± 2	Kourtchev et al., 2009	RR-FTIR (a),(c)
$(4.19 \pm 0.11) \times 10^{-16}$	296 ± 2	Kourtchev et al., 2009	RR-FTIR (a),(d)
$1.80 \times 10^{-12} \exp[-(2348 \pm 329)/T]$	298-318	Kim et al., 2011	RR-MS (e)
$(6.81^{+1.70}_{-1.36}) \times 10^{-16}$	298		

 β -farnesene is (6E)-7,11-dimethyl-3-methylene-1,6,10-dodecatriene**Comments**

- (a) The concentrations of *trans*- β -farnesene and cycloocta-1,5-diene, *cis*-cyclooctene or γ -terpinene (the reference compounds), with carbon monoxide to scavenge HO radicals, were monitored by long path FTIR in a 3.91 m³ FEP chamber at 0.1–1 mbar above atmospheric pressure of purified air in the presence of O₃. The measured rate coefficient ratios, $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-farnesene})/k(\text{O}_3 + \text{cycloocta-1,5-diene}) = (2.71 \pm 0.11)$, $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-farnesene})/k(\text{O}_3 + \textit{cis}\text{-cyclooctene}) = (1.04 \pm 0.03)$ and $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-farnesene})/k(\text{O}_3 + \gamma\text{-terpinene}) = (2.79 \pm 0.07)$, are placed on an absolute basis using $k(\text{O}_3 + \text{cycloocta-1,5-diene}) = 1.52 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{O}_3 + \textit{cis}\text{-cyclooctene}) = 3.86 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Cuisick and Atkinson, 2005) and $k(\text{O}_3 + \gamma\text{-terpinene}) = 1.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendation) at 296 K. Gas phase carbonyl products were also identified as O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine derivatives (GC-MS), following collection on denuders.
- (b) Relative to cycloocta-1,5-diene.
- (c) Relative to *cis*-cyclooctene.
- (d) Relative to γ -terpinene.
- (e) The concentrations of β -farnesene and *trans*-but-2-ene (the reference compound) were monitored by MS in reacting O₃ - β -farnesene - *trans*-but-2-ene - acetaldehyde - He mixtures in a 160 cm³ volume quartz vessel at ~1 bar pressure, with acetaldehyde being present to scavenge HO radicals. The measured rate coefficient ratios, $k(\text{O}_3 + \beta\text{-farnesene})/k(\text{O}_3 + \textit{trans}\text{-but-2-ene})$, are placed on an absolute basis using $k(\text{O}_3 + \textit{trans}\text{-but-2-ene}) = 6.6 \times 10^{-15} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

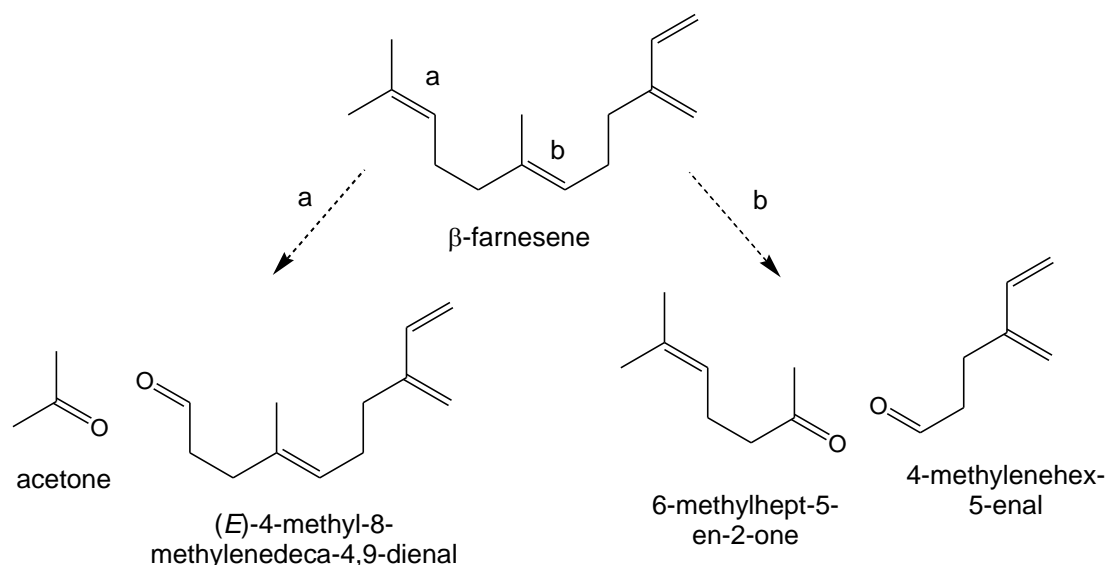
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.6×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.5 \times 10^{-12} \exp(-2350/T)$	290-320
<i>Reliability</i>		
$\Delta \log k$	± 0.25	298
$\Delta E/R$	± 500	290-320

Comments on Preferred Values

The preferred value of E/R is based on the sole temperature dependence study of Kim et al. (2011). The preferred 298 K rate coefficient is an average of those of Kourtchev et al. (2009) (corrected to 298 K using the preferred temperature dependence) and Kim et al. (2011), which are in reasonable agreement. The pre-exponential factor is adjusted to fit the 298 K preferred value. Confirmatory studies of the temperature dependence are required.

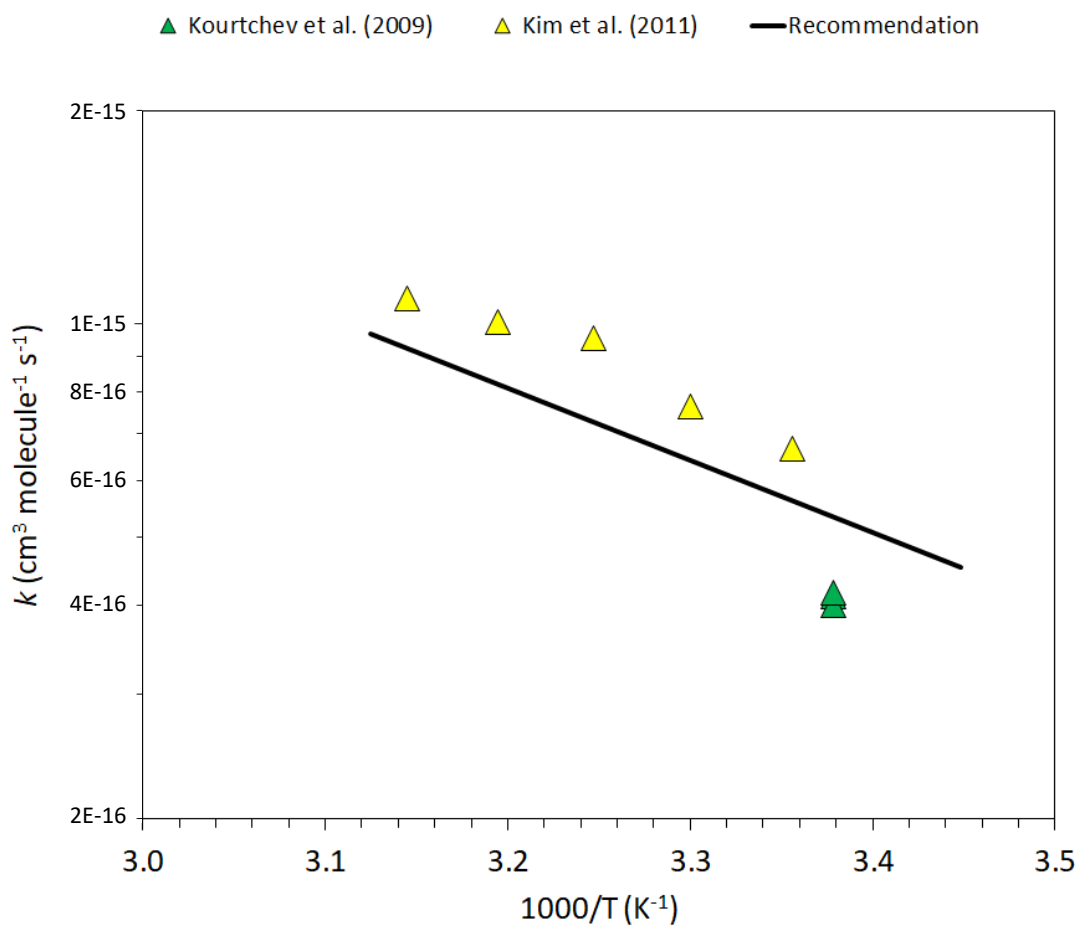
Structure-activity methods based on a summation of the rate coefficients for simple alkene and diene structures (e.g. Calvert et al., 2000) predict a rate coefficient that agrees with the preferred value to within a factor of 1.5. These methods also predict that the reaction should proceed mainly via O_3 addition to the two non-conjugated methyl-substituted $\text{C}=\text{C}$ bonds ("a" and "b") with about equal probability at 298 K. Some support for this has been provided by the product study of Kourtchev et al. (2009), who detected the formation of the corresponding primary carbonyl products (acetone, (*E*)-4-methyl-8-methylenedeca-4,9-dienal, 4-methylenehex-5-enal, 6-methylhept-5-en-2-one), as shown below.



Kourtchev et al. (2009) also reported detection of 4-oxopentanal, which may be formed from the secondary ozonolysis of both (*E*)-4-methyl-8-methylenedeca-4,9-dienal and 6-methylhept-5-en-2-one; and methylglyoxal, which may be formed from reactions of the Criegee intermediate $(\text{CH}_3)_2\text{COO}$, the expected initial co-product of (*E*)-4-methyl-8-methylenedeca-4,9-dienal. Further product and mechanistic studies are required.

References

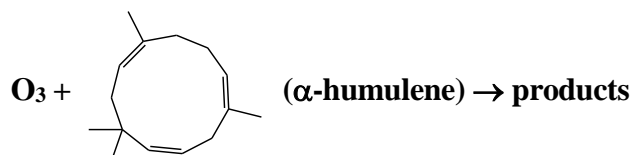
- Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J., and Yarwood, G.: The mechanisms of atmospheric oxidation of alkenes, Oxford University Press, New York, ISBN 0-19-513177-0, 2000.
- Cusick, R. D. and Atkinson, R.: Int. J. Chem. Kinet., 37, 183, 2005.
- Kim, D., Stevens, P. S. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.
- Kourtchev, I., Bejan, I., Sodeau, J. R., and Wenger, J. C: Atmos. Environ., 43, 3182, 2009.



Ox_VOC37: α -humulene

Data sheet Ox_VOC37;

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(1.12 \pm 0.17) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (a),(b)
$(1.07 \pm 0.08) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (a),(c)
$(2.9 \pm 1.9) \times 10^{-15}$	366 ± 2	Ghalaieny et al., 2012	RR-GC (d)
$(1.28 \pm 0.35) \times 10^{-14}$	295 ± 2	Richters et al., 2015	RR-GC-MS (e)
$(1.43 \pm 0.24) \times 10^{-14}$	295 ± 2	Richters et al., 2015	RR-MS (f)

 α -humulene is 2,6,6,9-tetramethyl-1,4,8-cycloundecatriene**Comments**

- (a) The concentrations of α -humulene and 2,3-dimethyl-but-2-ene or terpinolene (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratios, $k(\text{O}_3 + \alpha\text{-humulene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = (10.3 \pm 1.6)$ and $k(\alpha\text{-humulene})/k(\text{O}_3 + \text{terpinolene}) = (0.564 \pm 0.043)$, are placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K; and $k(\text{O}_3 + \text{terpinolene}) = 1.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendations).
- (b) Relative to 2,3-dimethyl-but-2-ene.
- (c) Relative to terpinolene.
- (d) The concentrations of α -humulene and 2,3-dimethyl-but-2-ene (the reference compound), with excess cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 123 L Teflon-coated chamber at 780 Torr (1040 mbar) pressure of N_2 , with repeated injections of O_3/O_2 . The measured rate coefficient ratio, $k(\text{O}_3 + \alpha\text{-humulene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 2.2$, is placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.32 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 366 K (IUPAC, current recommendation). It is noted that the authors used a much lower value of $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 2.89 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, based on a relative rate measurement reported in the same study, leading to a reported value of $k = (6.4 \pm 4.2) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 366 K.
- (e) The concentrations of α -humulene and α -terpinene (the reference compound), with 2-methylpropene to scavenge HO radicals, were monitored by GC-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(\text{O}_3 + \alpha\text{-humulene})/k(\text{O}_3 + \alpha\text{-terpinene}) = (0.75 \pm 0.04)$, is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-terpinene}) = 1.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

- (f) The concentrations of α -humulene and 2,3-dimethyl-but-2-ene (the reference compound), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(\text{O}_3 + \alpha\text{-humulene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = (11.7 \pm 0.8)$, is placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.2×10^{-14}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on an average of the relative rate determinations of Shu and Atkinson (1994) and Richters et al. (2015), which are in good agreement. The lower approximate value reported by Ghalaieny et al. (2012) at 366 K was interpreted by the authors in terms of heterogeneous interferences of secondary organic aerosol (SOA) formation, leading to overestimates in previously-reported room temperature determinations. However, the more recent consistent results of Richters et al. (2015) using low reagent concentrations in the absence of SOA formation appear to disprove this hypothesis.

The reaction potentially proceeds by initial addition of O_3 to any of the three endocyclic C=C bonds in α -humulene, although there have been no studies from which the attack distribution can be elucidated. Structure-activity methods based on a summation of the rate coefficients for simple alkene structures (e.g. Calvert et al., 2000) suggest that addition at all sites is likely to be competitive, with the methyl-substituted C=C bonds being more favoured. However, such methods also underestimate the observed value of k by an order of magnitude, suggesting a general elevating influence of ring strain on reactivity with O_3 . It is therefore not currently possible to draw firm conclusions about the attack distribution of O_3 at the three C=C bonds in α -humulene.

The initial addition of O_3 is expected to form a set of three “primary ozonides”, which rapidly decompose via ring-opening to form six carbonyl-substituted Criegee intermediates. The Criegee intermediates can decompose to form HO radicals, which are expected to be formed in conjunction with a number of β -oxo dialkenyl radicals. Comparatively low HO radical yields of $(22^{+11}_{-7})\%$ and $(10.5 \pm 0.7)\%$ have been reported by Shu and Atkinson (1994) and Beck et al. (2011), respectively. The further chemistry of the β -oxo dialkenyl co-radicals may form a large number of multifunctional organic products containing hydroxy, carbonyl and acid functionalities, some of which have been reported by Beck et al. (2011); and also formaldehyde and acetone, which have been reported to be formed with respective molar yields of $(3.5 \pm 1.1)\%$ and $(1.2 \pm 0.4)\%$ by Lee et al. (2006). Organic products likely to be produced from alternative reactions of the Criegee intermediates (e.g. C_{15} dicarbonyls and oxo-carboxylic acids from the reactions with H_2O) have also been detected, in addition to one or more “secondary ozonides” formed by intramolecular ring-closure of the Criegee intermediates (Beck et al., 2011).

Beck et al. (2011) also characterized the bulk reactivity of O_3 with the suites of first-generation products (containing two C=C bonds) and second generation products (containing one C=C bond), which were found to be lower than that of α -humulene by respective factors of about 30 and 400. The temporal separation of the oxidation steps allowed detected products to be attributed to the different generations of oxidation. An HO yield of $(12.9 \pm 0.7)\%$ was also determined for bulk ozonolysis of the first-generation suite of products.

References

- Beck, M., Winterhalter, R., Herrmann, F., and Moortgat, G. K.: Phys. Chem. Chem. Phys., 13, 10970, 2011.
- Ghalaieny, M., Bacak, A., McGillen, M., Martin, D., Knights, A. V., O'Doherty, S., Shallcross, D. E. and Percival, C. J.: Phys. Chem. Chem. Phys., 14, 6596, 2012.
- Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: J. Geophys. Res., 111, D07302, doi:10.1029/2005JD006437, 2006.
- Richters, S., Herrmann, H. and Berndt, T.: Phys. Chem. Chem. Phys., 17, 11658, 2015.
- Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.

Ox_VOC38: isolongifolene

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.8 \pm 0.8) \times 10^{-18}$	295 ± 2	Richters et al., 2015	S-IR/UVA (a)
<i>Relative Rate Coefficients</i>			
$(1.1 \pm 0.5) \times 10^{-15}$	366 ± 2	Ghalaieny et al., 2012	RR-GC (b)
$(1.57 \pm 0.29) \times 10^{-17}$	295 ± 2	Richters et al., 2015	RR-MS (c)
$(7.56 \pm 0.21) \times 10^{-18}$	295 ± 2	Richters et al., 2015	RR-MS (d)

isolongifolene is (1R)-2,2,7,7-tetramethyltricyclo[6.2.1.0^{1,6}]undec-5-ene

Comments

- (a) k determined from the observed pseudo-first order rate of ozone decay (measured by UVA at 254 nm) in the presence of known excess concentrations of isolongifolene (measured by FTIR), in stopped-flow experiments at a total pressure of ~ 1 bar, with sufficient propane to scavenge $>99\%$ of HO radicals.
- (b) The concentrations of isolongifolene and 2,3-dimethyl-but-2-ene (the reference compound), with excess cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 123 L Teflon-coated chamber at 780 Torr (1040 mbar) pressure of N_2 , with repeated injections of O_3/O_2 . The measured rate coefficient ratio, $k(\text{O}_3 + \text{isolongifolene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 0.87$, is placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.32 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 366 K (IUPAC, current recommendation). It is noted that the authors used a much lower value of $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 2.89 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, based on a relative rate measurement reported in the same study, leading to a reported value of $k = (2.5 \pm 1.1) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 366 K.
- (c) The concentrations of isolongifolene and 2-methyl-but-2-ene (the reference compound), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(\text{O}_3 + \text{isolongifolene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = (0.040 \pm 0.004)$, is placed on an absolute basis using $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson and Arey, 2003).
- (d) The concentrations of isolongifolene and *cis*-but-2-ene (the reference compound), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(\text{O}_3 + \text{isolongifolene})/k(\text{O}_3 + \text{cis-but-2-ene}) = (0.060 \pm 0.004)$, is placed on an absolute basis using $k(\text{O}_3 + \text{cis-but-2-ene}) = 1.26 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.0×10^{-17}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on a rounded average of the absolute and relative rate determinations of Richters et al. (2015), with an uncertainty that encompasses the range of values. Although Ghalaieny et al. (2012) report a comparable value of k at 366 K (see comment (c)), this was apparently based on use of an anomalously low value of the rate coefficient for the reference reaction of O_3 with 2,3-dimethyl-but-2-ene. The value tabulated above is based on the current IUPAC recommendation (see comment (c)), leading to a value of k (at 366 K) that is two orders of magnitude higher than the preferred value.

The reaction is expected to proceed via addition of O_3 to the C=C bond, with the subsequent mechanism following the general framework outlined in the datasheets for other mono- and sesquiterpenes possessing endocyclic C=C bonds (e.g. α -cedrene). However, there have apparently been no product or mechanistic studies to confirm this.

References

- Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
 Ghalaieny, M., Bacak, A., McGillen, M., Martin, D., Knights, A. V., O'Doherty, S., Shallcross, D. E. and Percival, C. J.: Phys. Chem. Chem. Phys., 14, 6596, 2012.
 Richters, S., Herrmann, H. and Berndt, T.: Phys. Chem. Chem. Phys., 17, 11658, 2015.

Ox_VOC39: longifolene

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$< 6 \times 10^{-18}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (a),(b)
$< 5 \times 10^{-19}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (a),(c)

longifolene is (1R,2S,7S,9S)-3,3,7-trimethyl-8-methylenetricyclo[5.4.0.0^{2,9}]undecane

Comments

- (a) The concentrations of longifolene and *cis*-but-2-ene or propene (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O₃. The measured coefficient ratios, $k(\text{O}_3 + \text{longifolene})/k(\text{O}_3 + \text{cis-but-2-ene})$ and $k(\text{O}_3 + \text{longifolene})/k(\text{O}_3 + \text{propene}) < 0.05$, are placed on an absolute basis using $k(\text{O}_3 + \text{cis-but-2-ene}) = 1.27 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) at 296 K.
- (b) Relative to *cis*-but-2-ene.
- (c) Relative to propene.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 5 \times 10^{-19}$	298

Comments on Preferred Values

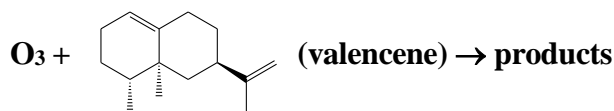
The more stringent upper limit for the value of k reported in the study of Shu and Atkinson (1994) is adopted for the preferred value. This is based on no quantifiable decay of longifolene occurring in mixtures with O₃ and propene (with cyclohexane to scavenge HO radicals), for up to 75 % decay in the propene concentration. The low value of k compared to those for other terpenes possessing methylene groups (e.g. β -pinene and sabinene) is most likely due to steric hindrance resulting from the bridged ring structure.

References

Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.

Ox_VOC40: valencene

Last evaluated: August 2018; Last change in preferred values: June 2015

**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(4.95 \pm 1.23) \times 10^{-17}$	297 ± 3	Ham, 2013	GC-MS (a),(b)
$(1.25 \pm 0.32) \times 10^{-16}$	297 ± 3	Ham, 2013	RR-MS (a),(c)

valencene is (3R,4aS,5R)-3-isopropenyl-4a,5-dimethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene

Comments

- (a) The concentrations of valencene and 3-carene or γ -terpinene (the reference compounds) were monitored by GC-FID in a 100 L Teflon chamber in purified air in the presence of O_3 . The measured rate coefficient ratios $k(\text{O}_3 + \text{valencene})/k(\text{O}_3 + 3\text{-carene}) = (1.01 \pm 0.25)$ and $k(\text{O}_3 + \text{valencene})/k(\text{O}_3 + \gamma\text{-terpinene}) = (0.78 \pm 0.20)$ are placed on an absolute basis using $k(\text{O}_3 + 3\text{-carene}) = 4.9 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + \gamma\text{-terpinene}) = 1.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendations).
- (b) Relative to 3-carene.
- (c) Relative to γ -terpinene.

Preferred Values

No recommendation

Comments on Preferred Values

The sole investigation of Ham (2013) provides evidence that the reaction of O_3 with valencene occurs, and that k is likely sufficiently high that the reaction will contribute to valencene removal under atmospheric conditions. However, the level of disagreement in the two reported determinations, and inevitable complications arising from not scavenging HO radicals in the system, preclude recommendation of a preferred value. Further kinetics studies are required.

The reaction is expected to proceed via addition of O_3 to both the endocyclic and exocyclic C=C bonds in valencene, with the subsequent mechanism following the general framework outlined in the datasheets for other mono- and sesquiterpenes. However, there have apparently been no product or mechanistic studies to confirm this.

References

Ham, J. E: Int. J. Chem. Kinet., 45, 508, 2013.

A4. Abbreviations used in data sheets

A – absorption
AS – absorption spectroscopy
CCD – charge coupled detector
CIMS – chemical ionization mass spectroscopy/spectrometry
CL – chemiluminescence
CRDS – cavity ring-down spectroscopy
DF – discharge flow
EPR – electron paramagnetic resonance
F – flow system
FP – flash photolysis
FTIR – Fourier transform infrared
FTS – Fourier transform spectroscopy
GC – gas chromatography/gas chromatographic
HPLC – high-performance liquid chromatography
IR – infrared
LIF – laser induced fluorescence
LMR – laser magnetic resonance
LP – laser photolysis
MM – molecular modulation
MS – mass spectrometry/mass spectrometric
P – steady state photolysis
PLP – pulsed laser photolysis
PR – pulse radiolysis
RA – resonance absorption
RF – resonance fluorescence
RR – relative rate
S – static system
TDLS – tunable diode laser spectroscopy
UV – ultraviolet
UVA – ultraviolet absorption
VUVA – vacuum ultraviolet absorption