

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC26

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
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.

There has been only limited product and mechanistic information reported in the literature. Herrmann et al. (2010) reported a yield of HO radicals of (26 – 31) %, and Reissell et al. (1999) a yield of acetone of < 2 %. The reaction is likely 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” which rapidly decompose to form four carbonyl-substituted Criegee intermediates. HO radicals may potentially be formed (in conjunction with a number of β -oxo-alkenyl radicals) from three of the Criegee intermediates, via the accepted decomposition mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (e.g. see Johnson and Marston, 2008).

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.
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.