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

O_3 + (α-phellandrene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.2×10^{-14}	295 ± 1	Grimsrud et al., 1975	F-CL
Relative Rate Coefficients			
$(2.14 \pm 0.48) \times 10^{-15}$	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 $k(O_3 + \alpha\text{-phellandrene})/k(O_3 + \text{terpinolene})$ is placed on an absolute basis using $k(O_3 + \text{terpinolene}) = 1.6 \times 10^{-15}$ cm^3 molecule^{-1} 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 $k(O_3 + \alpha\text{-phellandrene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene})$ is placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.9×10^{-15}	298
Reliability		
$\Delta \log k$	± 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 O_3 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 C_{10} 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 ± 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 $(1.0 \pm 0.7) \times 10^{-16}$ cm^3 $molecule^{-1}$ 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 ± 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.