Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC27

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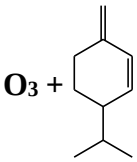

O_3 + (β-phellandrene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.8×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
Relative Rate Coefficients			
$(5.22 \pm 1.35) \times 10^{-17}$	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 $k(O_3 + \alpha\text{-phellandrene})/k(O_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(O_3 + \alpha\text{-pinene}) = 9.53 \times 10^{-17}$ cm^3 molecule^{-1} 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 /cm^3 molecule^{-1} s^{-1}	5.2×10^{-17}	298
Reliability		
$\Delta \log k$	± 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-isopropyl-cyclohex-2-enone of (29 ± 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 exocylic 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 one 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.