

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

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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>			
1.8×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(5.10 \pm 1.32) \times 10^{-17}$	297 ± 2	Shorees et al., 1991	RR-GC (b)

Comments

- (a) 3-isopropyl-6-methylene-cyclohexene.
- (b) 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 O₃. 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 $k(\text{O}_3 + \alpha\text{-pinene}) = 9.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.0×10^{-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 (b)). 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 $\approx 14\%$, and Hakola et al. (1993) a yield of 4-isopropyl-cyclohex-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 may form additional 4-isopropyl-cyclohex-2-enone following reaction with water vapour. HO radicals may be formed in low yield from further reactions of $[CH_2OO]^*$ (see datasheets Ox_VOC3 and Ox_VOC5), and from the *syn*- 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 Criegee intermediates. One of these is unlikely to form HO, owing to the absence of β -hydrogens, with the accepted HO-forming mechanism only being available for the *syn*- 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

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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.
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