

## Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox\_VOC27

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>)

This datasheet 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>			
$1.8 \times 10^{-16}$	$295 \pm 1$	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(5.22 \pm 1.35) \times 10^{-17}$	$297 \pm 2$	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<sub>3</sub>. 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
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$5.2 \times 10^{-17}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.30$	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  $\beta$ -phellandrene concentrations (see comment (a)). The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for  $\beta$ -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  $(29 \pm 6)\%$  from the ozonolysis of  $\beta$ -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 from the *Z*-conformer of  $C_9H_{14}OO$  by the accepted HO-forming mechanism involving abstraction of a  $\beta$ -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  $\beta$ -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  $\beta$ -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.