

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet HO_x_VOC87

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This datasheet last evaluated: June 2014; last change in preferred values: June 2014.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(3.05 \pm 0.70) \times 10^{-10}$	294 \pm 1	Atkinson et al., 1986	RR (a)
$(3.3 \pm 0.4) \times 10^{-10}$	290	Peeters et al., 1999	FT-MS (b)

α -phellandrene is 2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene.

Comments

- (a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. OH radical was generated by the photolysis of CH₃ONO at wavelengths > 300 nm. α -phellandrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. Correction made to the α -phellandrene loss rate due to reaction with NO₂ was 15 to 59 % (generally \approx 50%). The rate constant ratio, $k(\text{OH} + \alpha\text{-phellandrene}) / k(\text{OH} + 2,3\text{-dimethyl-2-butene}) = 2.77 \pm 0.63$ is placed on an absolute basis using $k(\text{OH} + 2,3\text{-dimethyl-2-butene}) = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson and Arey, 2003).
- (b) Flow tube at \approx 2.7 mbar (2 Torr) of He. OH was generated by the reaction H+NO₂. α -phellandrene and isoprene (reference reactant) were monitored by mass spectrometry in excess of OH radicals. The rate constant ratio obtained, $k(\text{OH} + \alpha\text{-phellandrene}) / k(\text{OH} + \text{isoprene})$ is not provided by the authors. The rate coefficient value was placed on an absolute basis using $k(\text{OH} + \text{isoprene}) = 1.0 \pm 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

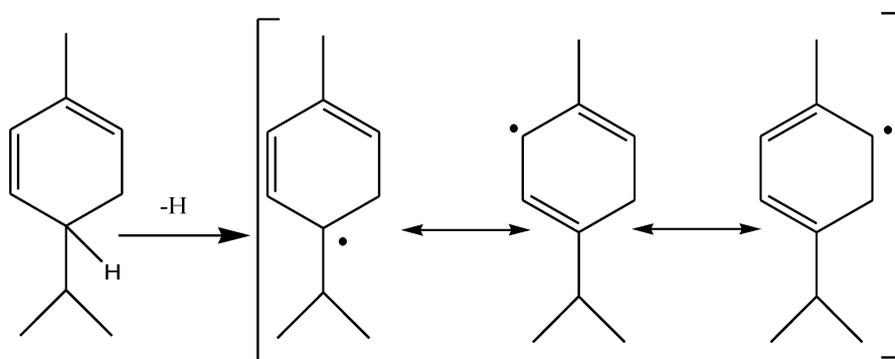
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3.2×10^{-10}	298
<i>Reliability</i>		
$\Delta \log k$	0.08	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate studies of Atkinson et al. (1986) and Peeters et al. (1999).

The reaction proceeds by initial addition of the OH radical to the carbon atoms of the C=C bonds and by H-atom abstraction from the various C-H bonds with the OH radical addition channel being expected to be dominant. Reissell et al. (1999) have observed acetone ($8\pm 4\%$) as a reaction product but could not ascribe the reaction pathways leading to its formation. Both, OH-addition and H-abstraction could be involved. Peeters et al. (1999) have reported a yield of $(27\pm 10)\%$ for H-atom abstraction through the direct observation of H_2O as reaction product. H-atom abstraction is expected to occur mainly from the non-vinylic C-H bonds and CH_2 group in the ring with H-atom abstraction from the methyl and isopropyl substituent groups being of minor importance since the tertiary C-H bond in the isopropyl group is not allylic. The hydrogen abstraction is facilitated by stabilization of the formed radical by “super allyl” resonance delocalizing the unpaired electron over three C-atoms as shown in the scheme (Vereecken and Peeters, 2001, Aschmann et al., 2011).



References

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