

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet HO_x_VOC84

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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>			
$(3.53 \pm 0.39) \times 10^{-10}$	294 \pm 1	Atkinson et al., 1986	RR (a)
$(3.4 \pm 0.4) \times 10^{-10}$	290	Peeters et al., 1999	FT-MS (b)

α -terpinene is 1-isopropyl-4-methyl-cyclohexa-1,3-diene.

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. Correction made to the α -terpinene loss rate due to reaction with NO₂ was 24 to 65 % (generally \approx 30%). α -terpinene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, $k(\text{OH} + \alpha\text{-terpinene}) / k(\text{OH} + 2,3\text{-dimethyl-2-butene}) = 3.21 \pm 0.35$ is placed on an absolute basis by $k(\text{OH} + 2,3\text{-dimethyl-2-butene}) = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 -terpinene and isoprene (reference reactant) were monitored by mass spectrometry in excess of OH radicals. The rate constant ratio obtained, $k(\text{OH} + \alpha\text{-terpinene}) / k(\text{OH} + \text{isoprene})$ is not provided by the authors. The rate coefficient value was placed on an absolute basis using $k(\text{OH} + \text{isoprene}) = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

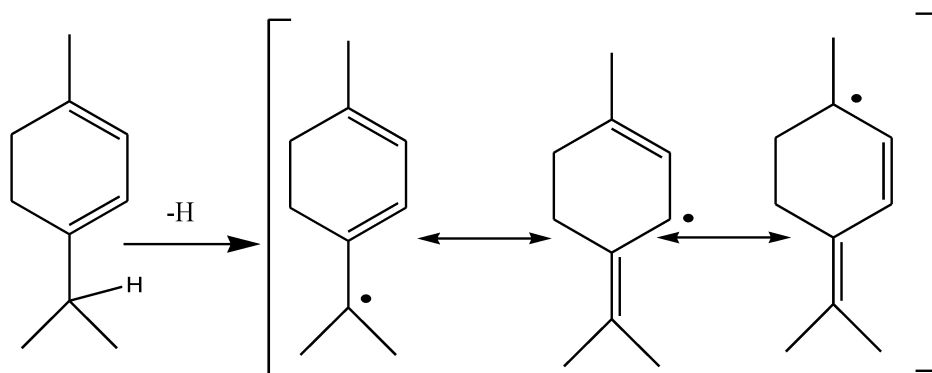
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3.5×10^{-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 addition of the OH radical to the $>C=C<$ double bonds and by H-atom abstraction from the various C-H bonds with the OH radical addition channel expected to be the dominant channel. Reissell et al. (1999) have observed acetone ($\approx 10\%$) 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) reported a yield of $(30\pm 8)\%$ for H-atom abstraction from all of the non-vinyl C-H bonds in the α -terpinene molecule. The hydrogen abstraction is facilitated by stabilization of the resulting radical by “super allyl” resonance delocalizing the unpaired electron over three C-atoms as shown in the scheme below (Vereecken and Peeters, 2001). Aschmann et al. (2011) suggested that H-abstraction from α -terpinene and γ -terpinene occur at similar rates. In their study of the OH reaction with γ -terpinene, they have shown that this reaction leads to p-cymene formation at least partly from H-atom abstraction from the two CH_2 groups in the 6-member ring. Lee et al. (2006) reported the following molar product yields from the HO-initiated oxidation of α -terpinene in the presence of NO_x : α -terpinaldehyde ($19\pm 2\%$), HCHO ($7.8\pm 2\%$), CH_3CHO ($0.7\pm 0.1\%$), HCOOH ($6.1\pm 1\%$), $CH_3C(O)CH_3$ ($3.1\pm 4\%$) and $CH_3C(O)OH$ ($2\pm 0.3\%$).



References

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