IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC81

This data sheet last evaluated: June 2011; last change in preferred values: June 2011.

$HOC_5H_8O_2 + HO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients $(1.74 \pm 0.25) \times 10^{-11}$	298	Boyd et al., 2003	PLP-UVA (a,b)

Comments

(a) $HOC_5H_8O_2$ is used here to represent the set of isomeric peroxy radicals formed from sequential addition of HO and O_2 to isoprene (2-methyl-buta-1,3-diene).

(b) PLP-UV absorption study of H_2O_2-isoprene-O_2-N_2 mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO_2 was in excess, with initial concentration ratios $[HO_2]/[C_5H_8O_2]$ in the range 4 - 10. k was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by $C_5H_8O_2$ absorption, with its decay being almost entirely due to the reaction with HO_2. The signal at 210 nm or 220 nm was mainly due to HO_2 absorption, with its self-reaction making the major contribution to its removal.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	1.7×10^{-11}	298
Reliability $\Delta \log k$	± 0.3	298

Comments on Preferred Values

The sequential addition of HO and O_2 to isoprene generates a set of six structurally isomeric peroxy radicals, of which four possess β–hydroxy groups and two possess δ–hydroxy groups. Each of the δ–hydroxy peroxy radicals may also exist in E⁻ and Z⁻ forms. The sole reported determination of k (Boyd et al., 2003) considered reaction of HO_2 with the entire population of $HOC_5H_8O_2$ radicals formed following addition of HO to isoprene.

The preferred value of k is based on the results Boyd et al. (2003), in which the decay in absorption (due mainly to the time dependence of the $HOC_5H_8O_2$ isomer population) was monitored directly under pseudo-first order conditions. The lack of reported evidence of differential reactivity for the $HOC_5H_8O_2$ isomers suggests that the preferred value of k can reasonably be assigned to the reactions of each of the individual isomers. This is also generally consistent with the wider kinetics database, which demonstrates a similar reactivity for reactions of HO_2 with other similar sized alkyl$^-$ and β–hydroxy$^-$ RO_2 radicals. For example, an empirical parameterisation of such data, reported by Saunders et al. (2003), predicts a value of $k = 1.6$ x 10^{-11} cm^3 molecule^{-1} s^{-1} for C_5 peroxy radicals in these classes. However, further kinetics studies are required to reduce the uncertainty on k, to confirm the lack of differential reactivity among the $HOC_5H_8O_2$ isomers, and to provide a temperature dependence of the reaction(s).

The results of product studies of isoprene oxidation under NOx-free conditions have confirmed production of HOC_5H_8OOH isomers (Ruppert and Becker, 2000; Paulot et al., 2009); with the CIMS study of Paulot et al. (2009), at elevated $[HO_2]/[C_5H_8O_2]$, reporting a collective yield of >70%. Dillon and Crowley (2008) have investigated the formation of HO from the reactions of HO_2 with selected RO_2 radicals. In the case of the structurally similar peroxy radicals, $HOCH_2CH_2O_2$ and $CH_3CH(OH)CH_2O_2$, respective upper limits of 0.04 and 0.06 were reported for the propagating channels forming HO, O_2 and the corresponding oxy radical. It is therefore probable that the title reactions are also mainly (or exclusively) terminating, with formation of HOC_5H_8OOH and O_2 being the dominant channel(s).

References

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