IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC80

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

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$HO_2 + (CH_3)_2C(OH)CH_2O_2 \rightarrow$ products

Rate coefficient data

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k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.30 \pm 0.05) \times 10^{-11}$	306	Boyd et al., 1996	FP-UVA (a)
$5.6 \times 10^{-14} \exp[(1650 \pm 130)/T]$	306-398		
2.01×10^{-11}	298	Chakir et al., 2004	MM-UVA (b)
1.00×10^{-11}	349		
$1.42 \times 10^{-13} \exp[(1490 \pm 120)/T]$	298-349		

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Comments

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(a) $(CH_3)_2C(OH)CH_2O_2$ and HO_2 generated from the flash photolysis of Cl_2-*t*-butanol-CH_3OH-O_2-N_2 mixtures at 1013 mbar (760 Torr). Kinetics experiments were performed for a range in initial $[(CH_3)_2C(OH)CH_2O_2]/[HO_2]$. k was determined from simulation of the transient decay traces recorded at 260 nm and 220 nm (where both HO_2 and $(CH_3)_2C(OH)CH_2O_2$ absorb significantly) for the entire set of experiments, using a chemical mechanism informed by a companion FTIR product study. This involved an iterative procedure in which the rate coefficient and branching ratios for the self-reaction of $(CH_3)_2C(OH)CH_2O_2$ were also determined.

(b) $(CH_3)_2C(OH)CH_2O_2$ generated from the modulated photolysis of Cl_2-*t*-butanol-O_2-N_2 mixtures, using blacklights. k was determined (in conjunction with that of the self-reaction of $(CH_3)_2C(OH)CH_2O_2$,) from analysis of the steady state absorption due to $(CH_3)_2C(OH)CH_2O_2$ and HO_2 in the latter part of the light-on phase of the modulated waveform, following correction for the steady accumulation of stable absorbing products. Confirmatory simulations of the modulated waveforms carried out using a detailed reaction scheme.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	1.4×10^{-11}	298
k/cm^3 molecule^{-1} s^{-1}	5.6×10^{-14} exp(1650/T)	298-400
Reliability		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	± 300 K	

Comments on Preferred Values

The preferred values of k are based on the temperature dependence expression of Boyd et al. (1996), which is the more direct study of the reaction kinetics and $(CH_3)_2C(OH)CH_2O_2$ absorption spectrum. Although the study of Chakir et al. (2004) is much more indirect, it nevertheless provides a similar temperature dependence for k, with values consistently higher by a factor of about 1.5 over the measured temperature range. The uncertainty assigned to the preferred values therefore encompasses the results of Chakir et al. (2004).

By analogy with the reaction of HO_2 with $HOCH_2CH_2O_2$, it is likely that the reaction mainly yields $(CH_3)_2C(OH)CH_2OOH$ and O_2. Indeed, the FTIR product study of Boyd et al. (1996) reported residual bands characteristic of an organic hydroperoxide, during the Cl initiated oxidation of *t*-butanol, attributed to the reaction of $(CH_3)_2C(OH)CH_2O_2$ with HO_2; and Chakir et al. (2004) were able to characterise a UV spectrum attributed to $(CH_3)_2C(OH)CH_2OOH$, based on stable product absorptions in their MM experiments. However, further product studies are clearly required to quantify the branching ratio for $(CH_3)_2C(OH)CH_2OOH$ and O_2 formation. 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 reaction is also mainly (or exclusively) terminating.

References

Boyd, A.A., Lesclaux, R., Jenkin, M.E. and Wallington, T.J.: J. Phys. Chem., 100, 6594, 1996.
Chakir, A., Ganne, J.P., Roth, E., Brion, J. and Daumont, D.: Phys. Chem. Chem. Phys., 6 , 3389, 2004.
Dillon, T. J. and Crowley, J. N.: Atmos. Chem. Phys., 8, 4877, 2008.

HO$_2$ + (CH