IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet AROM_RAD8

This data sheet last evaluated: January 2009; last change in preferred values: January 2009.

$HO_2 + C_6H_5CH_2O_2 \rightarrow C_6H_5CH_2OOH + O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.09 \pm 0.32) \times 10^{-11}$	300	Nozière et al., 1994	FP-AS (a)
$3.75 \times 10^{-13} \exp[(980 \pm 230)/T]$	273-450		
$(1.25 \pm 0.20) \times 10^{-11}$	298	El Dib et al., 2006	PLP-AS (b)
$5.7 \times 10^{-14} \exp[1649/T]$	298-353		

Comments

(a) Photolysis of Cl_2-toluene-CH_3OH-O_2-N_2 mixtures. Progress of the reaction was followed by time-resolved UV absorption measurements at 250 nm. Values of k were derived by simulation of, and optimisation to, the absorption profiles using a mechanism which took account of the formation of absorbing products, and removal of $C_6H_5CH_2O_2$ via its self-reaction, which was characterised in the same study. A UVP-FTIR smog chamber product study of the same chemical system was also carried out, with $C_6H_5CH_2OOH$ formation inferred from observation of a typical hydroperoxide band in the 3575–3625 cm^{-1} region. Measurements were hampered by aerosol formation, and yield determination was not possible.

(b) Photolysis of Cl_2-toluene-CH_3OH-O_2-N_2 mixtures. Progress of the reaction was followed by time-resolved UV absorption measurements at 250 nm (where $C_6H_5CH_2O_2$ absorbs strongly) and 225 nm (where HO_2 absorption makes a contribution). Values of k were derived by simulation of, and optimisation to, the absorption profiles using a mechanism which took account of the formation of absorbing products, and removal of $C_6H_5CH_2O_2$ via its self-reaction, which was characterised in the same study.

Preferred Values

Parameter	Value	T/K
k	1.2×10^{-11} cm^3 molecule^{-1} s^{-1}	298
k	$1.5 \times 10^{-13} \exp(1310/T)$ cm^3 molecule^{-1} s^{-1}	270-450
Reliability		
$\Delta \log k$	± 0.3	298
$\Delta E/R$	± 500 K	

Comments on Preferred Values

The two kinetics studies of this reaction report values of *k* which are in reasonable agreement over the common temperature range, despite differences in the UV spectra of $C_6H_5CH_2O_2$ and C_6H_5CHO, and in the kinetics of the competing self-reaction used in the analyses. The preferred rate coefficient at 298 K is taken to be the mean of the reported values at 300 K in the study of Nozière et al. (1994) and at 298 K in the study of El Dib et al. (2006). The recommended temperature coefficient is also based on the mean of the values reported in the two studies, with the pre-exponential factor adjusted to give the recommended value of *k* at 298 K. Further kinetics studies are required to reduce the uncertainties.

The FTIR product study of Nozière et al. (1994) provides evidence for the formation of the hydroperoxide product, $C_6H_5CH_2OOH$, at room temperature, although it was not possible to quantify its yield. Further quantitative product studies are required.

References

El Dib, G., Chakir, A., Roth, E., Brion, J. and Daumont, D.: J. Phys. Chem. A, 110, 7848, 2006.

Nozière, B., Lesclaux, R., Hurley, M. D., Dearth, M. A. and Wallington, T. J.: J. Phys. Chem., 98, 2864, 1994.