$$C_6H_5CH_2O_2 + C_6H_5CH_2O_2 \rightarrow C_6H_5CH_2O + C_6H_5CH_2O + O_2 \qquad (1)$$
$$\rightarrow C_6H_5CH_2OH + C_6H_5CHO + O_2 \qquad (2)$$

Rate coefficient data   ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.95 \pm 1.55) \times 10^{-12}$	298	Nozière et al., 1994	FP-UVA (a,b)
$2.75 \times 10^{-14} \exp[(1680 \pm 140)/T]$	273-450		
$(4.20 \pm 0.70) \times 10^{-12}$	298	El Dib et al., 2006	PLP-UVA (a,c)
$2.5 \times 10^{-14} \exp[1562/T]$	298-353		
Branching Ratios			
$k_1/k \approx 0.4$	295	Nozière et al., 1994	UVP-FTIR (d)
$k_2/k \approx 0.4$	295		

Comments

(a) k is defined by $-d[C_6H_5CH_2O_2]/dt = 2k\,[C_6H_5CH_2O_2]^2$.

(b) Photolysis of Cl_2-toluene-O_2-N_2 mixtures. Progress of the reaction was followed by time-resolved UV absorption measurements at 250 nm, close to a maximum in the UV absorption spectrum of $C_6H_5CH_2O_2$, which was characterised over the range 220 – 300 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 secondary removal of $C_6H_5CH_2O_2$ via reaction with HO_2. Major residual product absorptions reported to be due to C_6H_5CHO, formed with a yield of ca. 45 %, in good agreement with that measured in the same study by FTIR analysis (see comment (d)).

(c) Photolysis of Cl_2-toluene-O_2-N_2 mixtures. Progress of the reaction was determined primarily by time-resolved UV absorption measurements in the range 245 – 255 nm, close to a weak maximum in the UV absorption spectrum of $C_6H_5CH_2O_2$ which was characterised over the range 220 – 280 nm. The 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 secondary removal of $C_6H_5CH_2O_2$ via reaction with HO_2, informed by the study of Nozière et al. (1994) Major residual product absorptions reported to be due to C_6H_5CHO, formed with a yield of (65 ± 5) %.

(d) UV irradiation of Cl_2-toluene-O_2-N_2 mixtures in a smog chamber fitted with an FTIR detection system, at a total pressure of 930 mbar. C_6H_5CHO, $C_6H_5CH_2OH$ and $C_6H_5CH_2OOH$ identified as products, with their yields being insensitive to variation of $[O_2]$ over the range 20 – 930 mbar. Respective yields quantified as (41 ± 4) % and (15 ± 3) % for C_6H_5CHO and $C_6H_5CH_2OH$ using calibrated spectra, and (18 ± 4) % for $C_6H_5CH_2OOH$ using a band strength in 3575–3625 cm^{-1} region inferred from that of C_2H_5OOH. Approximate values of

$k_1/k = k_2/k = 0.4$ reported, based on these yields and an appraisal of the likely reaction mechanism and secondary chemistry.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	5.5 x 10^{-12}	298
k/cm^3 molecule^{-1} s^{-1}	2.4 x 10^{-14} exp (1620/T)	298 - 450
k_1/k	0.5	298
k_2/k	0.5	298
Reliability		
$\Delta \log k$	± 0.3	298
$\Delta E/R$	± 300 K	
$\Delta k_1/k$	± 0.2	298
$\Delta k_2/k$	± 0.2	298

Comments on Preferred Values

Despite using very similar experimental methods, the two reported values of k at 298 K differ by a factor of about 1.7, apparently due to differences in the values of the UV absorption cross sections for $C_6H_5CH_2O_2$ and C_6H_5CHO used in the analyses. The preferred rate coefficient at 298 K is taken to be the mean of the reported values. The recommended temperature coefficient is also based on the mean of the values reported in the two studies, which are in reasonable agreement, 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. It is also noted that the shapes of the UV absorption spectra reported for $C_6H_5CH_2O_2$ in the two studies are not in good agreement, and further studies to resolve these differences would be of value.

The FTIR product study of Nozière et al. (1994) provides firm evidence for significant participation of channels (1) and (2) at room temperature, with approximately equal branching ratios. El Dib et al. (2006) also reported the formation of C_6H_5CHO, but with a yield a factor of about 1.5 greater than that reported by Nozière et al. (1994). Both studies discussed the possible participation of a third channel forming $C_6H_5CH_2OOCH_2C_6H_5$ and O_2, with a branching ratio of up to 0.2, although no definitive identification was possible in either study. The preferred branching ratios, k_1/k and k_2/k, are provisionally each set to a value of 0.5 at 298 K. Further product studies are required to improve the reliability of these values, and to establish whether significant formation of $C_6H_5CH_2OOCH_2C_6H_5$ and O_2 occurs.

References

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