IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet AROM_RAD11

$$HO_2 + C_6H_5C(O)O_2 \rightarrow O_2 + C_6H_5C(O)OOH \qquad (1)$$
$$\rightarrow O_3 + C_6H_5C(O)OH \qquad (2)$$
$$\rightarrow O_2 + HO + C_6H_5C(O)O \qquad (3)$$
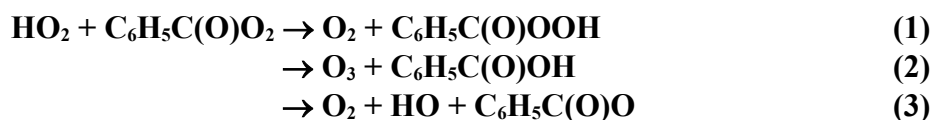
Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.82 \pm 1.10) \times 10^{-11}$	295	Roth et al., 2010	PLP-UVA (a)
$1.1 \times 10^{-11} \exp[(364 \pm 200)/T]$	295-357		
Branching Ratios			
$k_3/k \approx 0.2$	298	Dillon and Crowley, 2008	PLP-LIF (b)
$k_2/k = (0.15 \pm 0.10)$	295	Roth et al., 2010	PLP-UVA (a)
$k_2/k = (0.2 \pm 0.1)$	316		
$k_2/k = (0.3 \pm 0.1)$	337		
$k_2/k = (0.4 \pm 0.1)$	357		
$k_3/k = (0.20 \pm 0.05)$	295-357		

Comments

(a) $C_6H_5C(O)O_2$ and HO_2 generated from the pulsed laser photolysis of Cl_2-benzaldehyde-CH_3OH-O_2-N_2 mixtures at 107-160 mbar (80-120 Torr). k, k_2/k and k_3/k were determined from simulation of the transient decay traces recorded at 245-260 nm, for a range of $[HO_2]$/ $[C_6H_5C(O)O_2]$. Sensitivity to the branching ratios reported to be due to the variable impacts of channels (2) and (3) on the production and removal of absorbing species, i.e. O_3 production in channel (2) and $C_6H_5O_2$ production and secondary removal of benzaldehyde in channel (3).

(b) Pulsed laser photolysis of Cl_2-benzaldehyde-CH_3OH-O_2-N_2 mixtures to generate the reagent radicals with HO_2 in large excess. The production and removal of HO radicals was followed using direct detection by LIF. k_3/k determined from simulation of the time dependence of the HO radical concentration, using a detailed chemical mechanism.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	3.7×10^{-11}	298
k/cm^3 molecule^{-1} s^{-1}	1.1×10^{-11} exp(364/T)	295-360
k_1/k	0.65	298
k_2/k	0.15	298
k_3/k	0.20	295-360
k_1/k	0.8 - (k_2/k)	295-360
k_2/k	47 exp(-1700/T)	295-360
Reliability		
$\Delta \log k$	± 0.3	298
ΔE/R	± 300 K	
$\Delta k_1/k$	± 0.2	298
$\Delta k_2/k$	± 0.2	298
$\Delta k_3/k$	± 0.1	295-360
$\Delta(E_2$/R $- E$/R)	± 500 K	

Comments on Preferred Values

The preferred values of k are based on the sole kinetics study of Roth et al. (2010). It is noted that the values are about a factor of $2 - 3$ greater than those recommended for the reaction of HO_2 with the structurally-similar peroxy radical, $CH_3C(O)O_2$, suggesting a relative activating influence of the C_6H_5- substituent. However, confirmatory studies are required to reduce the recommended uncertainty limits on both k and E/R.

The preferred values of the branching ratios are also based on those finally reported by Roth et al. (2010). It is noted that an alternative interpretation of the 295 K results, with $k_3/k = 0$, is also presented by Roth et al. (2010), and it therefore not clear how well determined their final values of k_3/k tabulated above are. However, Dillon and Crowley (2008) also report a value of $k_3/k \approx 0.2$ at 298 K from direct observation of HO production (albeit using a much lower value of k in their analysis); and the interpretation of the Roth et al. (2010) data with this branching ratio is therefore provisionally recommended. Additional product studies are clearly required to reduce the uncertainties on these branching ratios.

References

Dillon, T. J. and Crowley, J. N.: Atmos. Chem. Phys., 8, 4877, 2008.
Roth, E., Chakir, A. and Ferhati, A.: J. Phys. Chem. A, 114, 10367, 2010.