IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_48

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

$$C_2H_5O_2 + C_2H_5C(O)O_2 \rightarrow C_2H_5O + C_2H_5C(O)O + O_2 \quad (1)$$
$$\rightarrow CH_3CHO + C_2H_5C(O)OH + O_2 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.20 \pm 0.06) \times 10^{-11}$	298	Le Crâne et al., 2005	FP-AS (a)
Branching Ratios			
$k_1/k = 0.82 \pm 0.04$	298	Le Crâne et al., 2005	FP-AS (a)

Comments

(a) Flash photolysis of Br_2-C_2H_5CHO-O_2-N_2 mixtures. The progress of the reaction was followed by time-resolved UV absorption measurements at 207 nm (where $C_2H_5C(O)O_2$ absorbs strongly) and 240 nm (where both radicals absorb strongly). The values of k and k_1/k were derived by simulation of, and optimisation to, the absorption profiles at these wavelengths, using a detailed chemical mechanism which took account of the permutation reactions of $C_2H_5C(O)O_2$, $C_2H_5O_2$ and HO_2 in the system. Support for the mechanism was obtained from FTIR product measurements during the UV photolysis of Cl_2-C_2H_5CHO-O_2-N_2 mixtures. k and k_1/k were determined simultaneously with the rate coefficient for the self-reaction of $C_2H_5C(O)O_2$. Sensitivity to k_1/k results from channel (1) leading to no net loss of $C_2H_5O_2$. Absorption cross sections for $C_2H_5C(O)O_2$ were derived in the same study, with $\sigma(207\text{ nm}) = 6.71 \times 10^{-18}$ cm^2 molecule^{-1} and $\sigma(240\text{ nm}) = 3.30 \times 10^{-18}$ cm^2 molecule^{-1} applied.

Preferred Values

Parameter	Value	T/K
k	1.2×10^{-11} cm^3 molecule^{-1} s^{-1}	298
k_1/k	0.8	298
k_2/k	0.2	298
Reliability		
$\Delta \log k$	± 0.3	298
$\Delta k_1/k$	± 0.2	298
$\Delta k_2/k$	± 0.2	298

Comments on Preferred Values

The preferred values of k and k_1/k are based on the results of the only study of the reaction, with the balance of the reaction assigned to channel (2). The values are close to those recommended for the reaction of the structurally-similar radicals $CH_3C(O)O_2$ and CH_3O_2. Independent confirmatory studies are required, as are measurements as a function of temperature.

References

Le Crâne, J-P., Villenave, E., Hurley, M. D., Wallington, T. J. and Ball J. C: J. Phys. Chem. A, 109, 11837, 2005.