IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_47

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

$C_2H_5C(O)O_2 + C_2H_5C(O)O_2 \rightarrow C_2H_5C(O)O + C_2H_5C(O)O + O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.68 \pm 0.08) \times 10^{-11}$	298	Le Crâne et al., 2005	FP-AS (a,b)

Comments

(a) k is defined by $-d[C_2H_5C(O)O_2]/dt = 2k\,[C_2H_5C(O)O_2]^2$.

(b) 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 and 240 nm. The value of k was derived by simulation of, and optimisation to, the absorption profiles at these wavelengths, using a detailed chemical mechanism which took account of formation of $C_2H_5O_2$ and HO_2 in the system, and the permutation reactions of the three peroxy radicals. 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 was determined simultaneously with the rate coefficient and branching ratio for the reaction of $C_2H_5C(O)O_2$ with $C_2H_5O_2$. 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	1.7×10^{-11} cm^3 molecule^{-1} s^{-1}	298
Reliability		
$\Delta \log k$	± 0.2	298

Comments on Preferred Values

The preferred value of k is based on the results of the only study of the reaction, and is almost identical to that recommended for the self-reaction of the structurally-similar radical, $CH_3C(O)O_2$. 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.