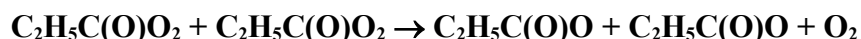


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_47

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

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



Rate coefficient data

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

Comments

- (a) k is defined by $-d[\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2]/dt = 2k [\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2]^2$.
- (b) Flash photolysis of $\text{Br}_2\text{-C}_2\text{H}_5\text{CHO-O}_2\text{-N}_2$ 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 $\text{C}_2\text{H}_5\text{O}_2$ 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 $\text{Cl}_2\text{-C}_2\text{H}_5\text{CHO-O}_2\text{-N}_2$ mixtures. k was determined simultaneously with the rate coefficient and branching ratio for the reaction of $\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2$ with $\text{C}_2\text{H}_5\text{O}_2$. Absorption cross sections for $\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2$ were derived in the same study, with $\sigma(207 \text{ nm}) = 6.71 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ and $\sigma(240 \text{ nm}) = 3.30 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ applied.

Preferred Values

Parameter	Value	T/K
k	$1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	298
<i>Reliability</i> $\Delta \log k$	± 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, $\text{CH}_3\text{C}(\text{O})\text{O}_2$. 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.