IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_34

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$$\mathbf{CH_3C(O)CH_2O_2 + CH_3C(O)CH_2O_2 \rightarrow CH_3C(O)CH_2OH + CH_3C(O)CHO + O_2} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow 2\ CH_3C(O)CH_2O + O_2} \quad \mathbf{(2)}$$

$\Delta H°(1) = -314$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$\leq 8.3 \times 10^{-12}$	298	Cox et al., 1990	PR-UVA (a,b)
$(8.0 \pm 0.2) \times 10^{-12}$	298	Bridier et al., 1993	FP-UVA (a,c)
Branching Ratios			
$k_2/k = (0.75 \pm 0.1)$	298	Bridier et al., 1993	FP-UVA (d)
$k_2/k = (0.50 \pm 0.05)$	298	Emrich and Warneck, 2003	UVP-GC (e)

Comments

(a) k is defined by $-d[CH_3C(O)CH_2O_2]/dt = 2k[CH_3C(O)CH_2O_2]^2$.

(b) Derived value of $k_{obs} = (8.3 \pm 1.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K is an upper limit due to secondary reactions producing possible enhanced decay of $CH_3C(O)CH_2O_2$ radicals.

(c) Flash photolysis of Cl_2 in the presence of $CH_3C(O)CH_3$-O_2-N_2 mixtures at a total pressure of 1013 mbar (760 Torr). The rate coefficient, k, was derived from a kinetic analysis of absorption-time profiles at 230 nm and 260 nm, taking account of the information on the mechanism of the overall reaction obtained from the product study of Jenkin et al. (1993).

(d) Technique as in Comment (c). The branching ratio was obtained on the basis of absorption due to radicals formed in channel (2) and subsequent reactions.

(e) Continuous photolysis of Cl_2 at 330 nm, in the presence of $CH_3C(O)CH_3$-O_2-NO_2-N_2 mixtures at a total pressure of 1020 mbar (765 Torr). The branching ratio, k_2/k, was determined from the observed formation of peroxyacetyl nitrate (PAN), which is generated in the system from chemistry subsequent to the thermal decomposition of $CH_3C(O)CH_2O$, using simulations with an explicit chemical mechanism. PAN was measured by GC coupled with indirect analysis, which involved conversion to NO in a heated molybdenum catalytic converter, followed by detection of NO by its chemiluminescent reaction with O_3.

Preferred Values

$k = 8.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2/k = 0.63$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(k_2/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The rate coefficients for $CH_3C(O)CH_2O_2$ radical decay obtained in the two studies (Cox et al., 1990; Bridier et al., 1993) are in reasonable agreement, and the more rigorous analysis carried out by Bridier et al. (1993), on the basis of the product study of Jenkin et al. (1993), provides the basis for the preferred rate coefficient. The value of k_2/k reported more recently by Emrich and Warneck (2003) is somewhat lower than that derived by Bridier et al. (1993), but the two determinations are in reasonable agreement, given the complexity of the chemical systems and the indirect nature of the determinations. The preferred branching ratio is the mean of the values reported in those two studies. Further verification of the overall rate coefficient and branching ratio is required, as are studies as a function of temperature.

References

Bridier, I., Veyret, B., Lesclaux, R. and Jenkin, M. E.: J. Chem. Soc. Faraday Trans.. 89, 2993, 1993.

Cox, R. A., Munk, J., Nielsen, O. J., Pagsberg, P. and Ratajczak, E.: Chem. Phys. Lett., 173, 206, 1990.

Emrich, M. and Warneck, P.: Z. Naturforsch. 58a, 429, 2003.

Jenkin, M. E., Cox, R. A., Emrich, M. and Moortgat, G. K.: J. Chem. Soc. Faraday Trans., 89, 2983, 1993.