

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_23

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$$\Delta H^\circ(1) = -27.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -378 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (8.8 \pm 1.5) \times 10^{-12}$	298	Roehl, Bauer, and Moortgat, 1996 ¹	PLP-UVAS (a)
$k_2 = (1.0 \pm 0.5) \times 10^{-12}$	298		
$8.5 \times 10^{-13} \exp[(726 \pm 25)/T]$	209-358	Maricq and Szente, 1996 ²	PLP-UVAS (b)
$(1.0 \pm 0.2) \times 10^{-11}$	298		
$(8.2 \pm 0.6) \times 10^{-12}$	298	Villenave and Lesclaux, 1996 ³	FP-UVAS (c)

Comments

- (a) Acetyl radicals were produced from the photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-O}_2$ mixtures. CH_3O_2 radicals were produced as secondary products, or through added CH_4 . k depends on $\sigma[\text{CH}_3\text{C(O)O}_2]$ for which values of $3.21 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 240 nm and $6.67 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 207 nm were obtained, relative to the UV spectrum of $\text{C}_2\text{H}_5\text{O}_2$ [$\sigma(240 \text{ nm}) = 4.36 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$]. A value of $k_1/k = 0.9$ was used in the data analysis.
- (b) Technique as for (a) but with UV spectra recorded on a gated diode array spectrometer. $\sigma[\text{CH}_3\text{C(O)O}_2] = 6.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 206 nm and $2.9 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 250 nm. On the basis of the HCHO kinetics observed it was concluded that Channel (2) was dominant over the entire temperature range covered (209 K to 358 K). A value of $k_1/k = 0$ was used in the data analysis.
- (c) CH_3O_2 radicals were generated simultaneously with $\text{CH}_3\text{C(O)O}_2$ radicals from the flash photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-CH}_4\text{-O}_2$ mixtures. In the derivation of k , the branching ratio, $\alpha_c (=k_1/k)$ was assumed to be 0.65 but k was found to vary by less than 15% upon varying α between 0.5 and 1.0. Overall uncertainty was estimated to be 42% from error propagation analysis. A value of $k_1/k = 0.65$ was used in the data analysis.

Preferred Values

$k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.0 \times 10^{-12} \exp(500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200 K to 350 K.

$k_1/k = 0.9$; $k_2/k = 0.1$ at 298 K.

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 250 \text{ K.}$$

$$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The three cited studies, which all used UV spectroscopy with similar values of the relevant absorption cross-sections to monitor the progress of the reaction are, apparently, in good agreement. However, the values of k derived depend upon the value of k_1/k used in the data analysis and since the three studies used values ranging from 0 to 0.9 their close agreement must be, to some degree, fortuitous. Tyndall *et al.*⁴ show that, using our preferred value for k_1/k , the studies of Roehl *et al.*,¹ Maricq and Szente² and Villenave and Lesclaux,³ give values of k in the range $(0.98\text{-}2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We accept the analysis of Tyndall *et al.*⁴ and take the value of k which they recommend, based on the studies of Villenave and Lesclaux³ and Roehl *et al.*,¹ as our preferred value at 298 K. The temperature dependence is based on that observed for analogous reactions.

There is conflicting evidence on the branching ratios. At 298 K Moortgat *et al.*⁵ estimate that $k_1/k = 0.5$, whilst Roehl *et al.*¹ find that $k_1/k = 0.9$ and Maricq and Szente² conclude that, essentially, the reaction proceeds entirely by Channel (2). Further information comes from a study of Crawford *et al.*⁶ on the $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$ reaction in which the yields of the products $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and $\text{CH}_3\text{C}(\text{O})\text{OH}$ were monitored. Tyndall *et al.*⁴ have reanalysed the results reported by Crawford *et al.*⁶ and have shown that the product yields observed require that the $\text{CH}_3\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$ reaction, which could also contribute to the $\text{CH}_3\text{C}(\text{O})\text{OH}$ in the experiments of Crawford *et al.*,⁶ must occur with k_1/k close to unity. Based on the studies of Moortgat *et al.*,⁵ Horie and Moortgat,⁷ and Roehl *et al.*,¹ Tyndall *et al.*⁴ recommend values of $k_1/k = 0.9$ and $k_2/k = 0.1$ at 298 K. These are adopted as our preferred values for the branching ratios. Moortgat *et al.*⁵ have reported values for the temperature dependence of k_1 and k_2 but they imply a difference in activation energy for the two channels of 32 kJ mol^{-1} which is much greater than found for analogous peroxy radical reactions. No recommendation is made for the temperature dependences of the branching ratios at this stage.

References

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- ⁴ G. S. Tyndall, R. A. Cox, C. Granier, R. Lesclaux, G. K. Moortgat, M. J. Pilling, A. R. Ravishankara, and T. J. Wallington, *J. Geophys. Res.* **106**, 12157 (2001).
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