

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO\_23

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This data sheet updated: 12<sup>th</sup> November 2002.



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

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

### 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 <sup>1</sup>	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 <sup>2</sup>	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 <sup>3</sup>	FP-UVAS (c)

### Comments

- (a) Acetyl radicals were produced from the photolysis of  $\text{Cl}_2\text{-CH}_3\text{CHO-O}_2$  mixtures.  $\text{CH}_3\text{O}_2$  radicals were produced as secondary products, or through added  $\text{CH}_4$ .  $k$  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)  $\text{CH}_3\text{O}_2$  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  $\alpha$  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.*<sup>4</sup> show that, using our preferred value for  $k_1/k$ , the studies of Roehl *et al.*,<sup>1</sup> Maricq and Szente<sup>2</sup> and Villenave and Lesclaux,<sup>3</sup> 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.*<sup>4</sup> and take the value of  $k$  which they recommend, based on the studies of Villenave and Lesclaux<sup>3</sup> and Roehl *et al.*,<sup>1</sup> 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.*<sup>5</sup> estimate that  $k_1/k = 0.5$ , whilst Roehl *et al.*<sup>1</sup> find that  $k_1/k = 0.9$  and Maricq and Szente<sup>2</sup> conclude that, essentially, the reaction proceeds entirely by Channel (2). Further information comes from a study of Crawford *et al.*<sup>6</sup> 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.*<sup>4</sup> have reanalysed the results reported by Crawford *et al.*<sup>6</sup> 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.*,<sup>6</sup> must occur with  $k_1/k$  close to unity. Based on the studies of Moortgat *et al.*,<sup>5</sup> Horie and Moortgat,<sup>7</sup> and Roehl *et al.*,<sup>1</sup> Tyndall *et al.*<sup>4</sup> 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.*<sup>5</sup> 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  $32 \text{ kJ mol}^{-1}$  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

- <sup>1</sup> C. M. Roehl, D. Bauer, and C. K. Moortgat, *J. Phys. Chem.* **100**, 4038 (1996).
- <sup>2</sup> M. M. Maricq and J. J. Szente, *J. Phys. Chem.* **100**, 4507 (1996).
- <sup>3</sup> E. Villenave and R. Lesclaux, *J. Phys. Chem.* **100**, 14372 (1996).
- <sup>4</sup> 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).
- <sup>5</sup> G. K. Moortgat, B. Veyret, and R. Lesclaux, *J. Phys. Chem.* **93**, 2362 (1989).
- <sup>6</sup> M. A. Crawford, T. J. Wallington, M. M. szente, M. M. Maricq, and J. S. Francisco, *J. Phys. Chem. A* **103**, 365 (1999).
- <sup>7</sup> O. Horie and G. K. Moortgat, *J. Chem. Soc. Faraday Trans.* **88**, 3305 (1992).