$$CH_3O_2 + CH_3C(O)O_2 \rightarrow CH_3O + CH_3C(O)O + O_2 \qquad \text{(1)}$$
$$\rightarrow CH_3C(O)OH + HCHO + O_2 \qquad \text{(2)}$$

$\Delta H°(1) = -27.3 \text{ kJ·mol}^{-1}$
$\Delta H°(2) = -378 \text{ kJ·mol}^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$k_1 = (8.8 \pm 1.5) \times 10^{-12}$	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 Cl_2-CH_3CHO-O_2 mixtures. CH_3O_2 radicals were produced as secondary products, or through added CH_4. k depends on $\sigma[CH_3C(O)O_2]$ for which values of 3.21×10^{-18} cm^2 molecule^{-1} at 240 nm and 6.67×10^{-18} cm^2 molecule^{-1} at 207 nm were obtained, relative to the UV spectrum of $C_2H_5O_2$ [$\sigma(240$ nm$) = 4.36 \times 10^{-18}$ cm^2 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. $\sigma[CH_3C(O)O_2] = 6.5 \times 10^{-18}$ cm^2 molecule^{-1} at 206 nm and 2.9×10^{-18} cm^2 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 $CH_3C(O)O_2$ radicals from the flash photolysis of Cl_2-CH_3CHO-CH_4-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

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-12} \exp(500/T)$ cm^3 molecule^{-1} 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
    $\Delta \log k = \pm 0.15$ at 298 K.

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

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$ at 298 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 Szente[2] and Villenave and Lesclaux,[3] give values of k in the range (0.98-2) x 10^{-11} cm^3 molecule^{-1} 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 Lesclaux[3] 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 Szente[2] conclude that, essentially, the reaction proceeds entirely by Channel (2). Further information comes from a study of Crawford *et al.*[6] on the $HO_2+CH_3C(O)O_2$ reaction in which the yields of the products $CH_3C(O)OOH$ and $CH_3C(O)OH$ 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 $CH_3O_2+CH_3C(O)O_2$ reaction, which could also contribute to the $CH_3C(O)OH$ 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.

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