IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_27

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$$C_2H_5O_2 + CH_3C(O)O_2 \rightarrow C_2H_5O + CH_3C(O)O + O \quad (1)$$
$$\rightarrow CH_3CHO + CH_3C(O)OH + O_2 \quad (2)$$

$\Delta H°(1) = -23.6$ kJ·mol^{-1}
$\Delta H°(2) = -398.5$ 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			
$(1.0 \pm 0.3) \times 10^{-11}$	298	Villenave and Lesclaux, 1996[1]	FP-UVAS (a)
$5 \times 10^{-13} \exp[(1070 \pm 200)/T]$	220-440	Maricq and Szente, 2000[2]	PLP-UVAS (b)
2.2×10^{-11}	295		

Comments

(a) Flash photolysis of Cl_2-C_2H_6-CH_3CHO-O_2 mixtures. $CH_3C(O)O_2$ and $C_2H_5O_2$ radical concentrations were determined by fitting absorption-time data at 207 nm and 240 nm, using cross- sections recommended in Lightfoot *et al.*[3] Complex reaction mechanism with $\alpha_c(=k_1/k)$ assumed to be 0.82. The overall uncertainty was estimated as 54%.

(b) Pulsed laser photolysis at 351 nm of CH_3CHO-C_2H_6-Cl_2-O_2-N_2 mixtures at total pressures of 166 mbar to 190 mbar (126 Torr to 144 Torr). The reaction progress was monitored by time-resolved UV absorption over the range 200 nm to 300 nm. Values of k were derived by fitting the spectral profiles using a detailed model. The cross-sections for the principal absorbing radicals ($CH_3C(O)O_2$, $C_2H_5O_2$, and CH_3O_2) were taken from the studies of Maricq and Szente[4] and Maricq and Wallington.[5] A satisfactory fit to the spectra could be obtained using values of $\alpha_c(=k_1/k)$ in the range 1.0-0.80.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.4 \times 10^{-13} \exp(1070/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220 K to 440 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 500$ K

Comments on Preferred Values

The two available experimental studies of this reaction report values of the rate coefficient at 298 K differing by a factor of 2. In both cases substantial error limits were assigned

reflecting the difficulties in deconvoluting overlapping UV spectra and in accounting for complex secondary chemistry in deriving the rate coefficient. Villenave and Leclaux[1] based their results on absorption measurements at only two wavelengths, whereas Maricq and Szente[2] used spectra covering the range 200 nm to 300 nm but, until more definitive measurements are available, the preferred value at 298 K is taken as the mean of the studies of Villenave and Lesclaux[1] and of Maricq and Szente,[2] with substantial error limits. The only determination of the temperature dependence of k is that of Maricq and Szente[2] who obtained a value of E/R of –1070 K, which is consistent with values found for analogous reactions. The preferred expression for k is obtained by combining the temperature dependence found by Maricq and Szente[2] with an A-factor chosen to fit the preferred value of k at 298 K. Channel (1) is likely to be the main reaction channel at 298 K.

References

1 E. Villenave and R. Lesclaux, J. Phys. Chem. **100**, 14372 (1996).
2 M. M. Maricq and J. J. Szente, J. Phys. Chem. A **104**, 7239 (2000).
3 P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).
4 M. M. Maricq and J. J. Szente, J. Phys. Chem. **100**, 4507 (1996).
5 M. M. Maricq and T. J. Wallington, J. Phys. Chem. **96**, 986 (1992).