IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_29

This data sheet updated: 12th November 2002.

$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow 2CH_3C(O)O + O_2$

$\Delta H° = -71$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.8 \times 10^{-12} \exp[(530 \pm 100)/T]$	253-368	Moortgat, Veyret and Lesclaux, 1989[1]	FP-UVAS (a,b)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
$(1.36 \pm 0.19) \times 10^{-11}$	298	Roehl, Bauer and Moortgat, 1996[2]	PLP-UVAS (a,c)
$3.0 \times 10^{-12} \exp[(504 \pm 114)/T]$	209-358	Maricq and Szente, 1996[3]	PLP-UVAS (a,d)
1.5×10^{-11}	298		

Comments

(a) k is defined by $-d[CH_3C(O)O_2]/dt = 2k\,[CH_3C(O)O_2]^2$.

(b) k was determined using absorption cross-sections for $CH_3C(O)O_2$ and CH_3O_2 radicals approximately 20% higher than later consensus values. $CH_3C(O)O_2$ radicals were produced by photolysis of Cl_2-CH_3CHO-O_2 mixtures.

(c) k was determined using an absorption cross-section of $\sigma = 6.67 \times 10^{-18}$ cm^2 molecule^{-1} at 207 nm for $CH_3C(O)O_2$. Source of $CH_3C(O)O_2$ radicals as in (b). Detailed analysis of secondary chemistry.

(d) Based on $\sigma(CH_3C(O)O_2) = 6.5 \times 10^{-18}$ cm^2 molecule^{-1} at 206 nm. Source of $CH_3C(O)O_2$ radicals as in (b). Detailed analysis of secondary chemistry.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9 \times 10^{-12} \exp(500/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200 K to 370 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

All three studies,[1,2,3] taking proper account of the complex secondary chemistry following recombination of $CH_3C(O)O_2$ radicals and of the magnitude and overlap of the UV absorptions due to acetylperoxy, methylperoxy and hydroperoxy radicals, now give results in good agreement for k and its temperature dependence. The recommendation is thus based on the data of Moortgat *et al.*,[1] Roehl *et al.*[2] and Maricq and Szente.[3]

References

[1] G. K. Moortgat, B. Veyret, and R. Lesclaux, J. Phys. Chem. **93**, 2362 (1989).
[2] C. M. Roehl, D. Bauer, and G. K. Moortgat, J. Phys. Chem. **100**, 4038 (1996).
[3] M. M. Maricq and J. J. Szente, J. Phys. Chem. **100**, 4507 (1996).