IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_25

This data sheet updated: 12th November 2002.

$$HOCH_2O_2 + HOCH_2O_2 \rightarrow HC(O)OH + CH_2(OH)_2 + O_2 \quad (1)$$
$$\rightarrow 2\ HOCH_2O + O_2 \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$k_1 = 5.65 \times 10^{-14} \exp[(750 \pm 400)/T]$	275-323	Veyret *et al.*, 1989[1]	FP-UVA (a,b)
$k_1 = (7.0 \pm 2.1) \times 10^{-13}$	295		
$k_1 = (5.6 \pm 2.8) \times 10^{-13}$	298	Burrows *et al.*, 1989[2]	MM-IR-AS (a,c)
Relative Rate Coefficients			
$k_2 = (5.5 \pm 1.1) \times 10^{-12}$	298	Burrows *et al.*, 1989[2]	MM-IR-AS (a,c)

Comments

(a) k is defined by $-d[HOCH_2O_2]/dt = 2k[HOCH_2O_2]^2$.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2, with time-resolved absorption spectroscopy for the detection of HO_2 and $HOCH_2O_2$ radicals. The rate coefficient k_1 was obtained from a computer fit of the absorption profiles of $HOCH_2O_2$ radicals at 250 nm. Channel (2) leads to the regeneration of HO_2 radicals and was thus not observable in this system.

(c) Molecular modulation study of Cl_2-HCHO-O_2 mixtures with diode laser infrared spectroscopy for the detection of HO_2 radicals and UV spectroscopy for $HOCH_2O_2$ radicals. The rate coefficient, k_2, was obtained from a computer simulation of quantum yields for HC(O)OH formation.

Preferred Values

$k_1 = 7.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 5.7 \times 10^{-14} \exp(750/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270 K to 330 K.
$k_2 = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta(E_1/R) = \pm 750$ K.
$\Delta \log k_2 = \pm 0.3$ at 298 K.

Comments on Preferred Values

The parallel studies of Veyret *et al.*[1] and Burrows *et al.*[2] confirm that the interaction of $HOCH_2O_2$ radicals involves two channels. The two reports[1,2] of the rate coefficient, k_1, at room temperature are in good agreement, and indicate that this channel is a factor of ~3 to 4

faster than that for the analogous interaction of CH_3O_2 radicals. The rate coefficient, k_2, is even larger than k_1, with a value ~50 times greater than that for the analogous reaction of CH_3O_2 radicals. Confirmation of the temperature coefficient of k_1 is needed, as well as a determination of the temperature coefficient of k_2.

References

[1] B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, J. Phys. Chem. **93**, 2368 (1989).

[2] J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G. D. Hayman, and B. Veyret, J. Phys. Chem. **93**, 2375 (1989).