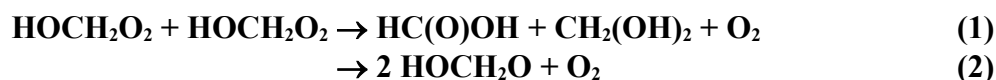


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_25

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 12th November 2002.



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>			
$k_1 = 5.65 \times 10^{-14} \exp[(750 \pm 400)/T]$	275-323	Veyret <i>et al.</i> , 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 <i>et al.</i> , 1989 ²	MM-IR-AS (a,c)
<i>Relative Rate Coefficients</i>			
$k_2 = (5.5 \pm 1.1) \times 10^{-12}$	298	Burrows <i>et al.</i> , 1989 ²	MM-IR-AS (a,c)

Comments

- (a) k is defined by $-d[\text{HOCH}_2\text{O}_2]/dt = 2k[\text{HOCH}_2\text{O}_2]^2$.
- (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

$k_1 = 7.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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

$k_2 = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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).