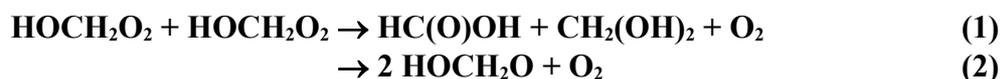


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO\_25

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This data sheet updated: 12<sup>th</sup> 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 <sup>1</sup>	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 <sup>2</sup>	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 <sup>2</sup>	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  $\text{Cl}_2$  in the presence of  $\text{HCHO}$  or  $\text{CH}_3\text{OH}$  and  $\text{O}_2$ , with time-resolved absorption spectroscopy for the detection of  $\text{HO}_2$  and  $\text{HOCH}_2\text{O}_2$  radicals. The rate coefficient  $k_1$  was obtained from a computer fit of the absorption profiles of  $\text{HOCH}_2\text{O}_2$  radicals at 250 nm. Channel (2) leads to the regeneration of  $\text{HO}_2$  radicals and was thus not observable in this system.
- (c) Molecular modulation study of  $\text{Cl}_2$ - $\text{HCHO}$ - $\text{O}_2$  mixtures with diode laser infrared spectroscopy for the detection of  $\text{HO}_2$  radicals and UV spectroscopy for  $\text{HOCH}_2\text{O}_2$  radicals. The rate coefficient,  $k_2$ , was obtained from a computer simulation of quantum yields for  $\text{HC(O)OH}$  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.*<sup>1</sup> and Burrows *et al.*<sup>2</sup> confirm that the interaction of  $\text{HOCH}_2\text{O}_2$  radicals involves two channels. The two reports<sup>1,2</sup> of the rate coefficient,  $k_1$ , at room temperature are in good agreement, and indicate that this channel is a factor of  $\sim 3$  to 4

faster than that for the analogous interaction of  $\text{CH}_3\text{O}_2$  radicals. The rate coefficient,  $k_2$ , is even larger than  $k_1$ , with a value  $\sim 50$  times greater than that for the analogous reaction of  $\text{CH}_3\text{O}_2$  radicals. Confirmation of the temperature coefficient of  $k_1$  is needed, as well as a determination of the temperature coefficient of  $k_2$ .

### References

- <sup>1</sup> B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, *J. Phys. Chem.* **93**, 2368 (1989).
- <sup>2</sup> 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).