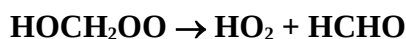


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC59

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This data sheet updated: 17<sup>th</sup> February 2005.



$$\Delta H^\circ = 68.1 \text{ kJ}\cdot\text{mol}^{-1}$$

## Rate coefficient data

<i>k</i> /s <sup>-1</sup>	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
20 <sup>+20</sup> <sub>-10</sub>	273	Barnes et al., 1985	S-FTIR (a)
2.0 x 10 <sup>12</sup> exp[-(7000±2000)/T]	275-333	Veyret et al., 1989	FP-AS (b)
100 ± 50	295		

## Comments

- (a) FTIR spectroscopic study in a 420 L reaction chamber. HO<sub>2</sub> radicals were generated from thermal decomposition of HO<sub>2</sub>NO<sub>2</sub> in the presence of HCHO, NO<sub>2</sub> and synthetic air at a total pressure of 533 mbar (400 Torr). The rate coefficient, *k*, was derived from a computer simulation of the rates of decay of HCHO and rates of formation of HCOOH and HOCH<sub>2</sub>O<sub>2</sub>NO<sub>2</sub> based on a reaction scheme consisting of nine elementary reactions.
- (b) Flash photolysis of Cl<sub>2</sub> in the presence of HCHO or CH<sub>3</sub>OH and O<sub>2</sub> with long-path absorption measurements of [HO<sub>2</sub>] and [HOCH<sub>2</sub>O<sub>2</sub>] at total pressures of 113 mbar to 227 mbar (85 Torr to 170 Torr). The rate coefficient, *k*, was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

## Preferred Values

$$k = 1.5 \times 10^2 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.4 \times 10^{12} \exp(-7000/T) \text{ s}^{-1} \text{ over the temperature range } 275 \text{ K to } 330 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 2000 \text{ K.}$$

### Comments on Preferred Values

The studies of Barnes et al. (1985) and of Veyret et al. (1989) are in good agreement regarding the rate coefficient of this reaction. The preferred rate equation has been obtained by taking the average of the rate coefficients at 273 K to 275 K from these studies together with the *E/R* determined by Veyret et al. (1989). It should be pointed out that the value of the equilibrium constant, *K*<sub>1</sub>, for the reaction HO<sub>2</sub> + HCHO ⇌ HOCH<sub>2</sub>O<sub>2</sub> (1,-1), *K*<sub>1</sub> = 5.0 x 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> at 298 K, derived from the kinetic study of Veyret et al. (1989) (which is identical to the value obtained from our recommended data for *k*<sub>1</sub> and *k*<sub>-1</sub>), is in excellent agreement with the value of *K*<sub>1</sub> = 4.0 x 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> at 298 K obtained

independently by Burrows et al. (1989) from molecular modulation studies. The above value of  $K_1$  is, however, considerably smaller than the value of  $K_1 = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}$  at 298 K reported by Zabel et al. (1987) from EPR spectroscopic measurements of the ratio of concentrations of  $\text{HO}_2$  and  $\text{HOCH}_2\text{O}_2$  radicals in the photolysis of  $\text{HCHO-O}_2$  mixtures.

### References

- Barnes, I., Becker, K. H., Fink, E. H., Reimer, A., Zabel, F. and Niki, H.: Chem. Phys. Lett., 115, 1, 1985.
- Burrows, J. P., Moortgat, G. K., Tyndall, G. S., Cox, R. A., Jenkin, M. E., Hayman, G. D. and Veyret, B.: J. Phys. Chem., 93, 2375, 1989.
- Veyret, B., Lesclaux, R., Rayez, M.-T., Rayez, J.-C., Cox, R. A. and Moortgat, G. K.: J. Phys. Chem., 93, 2368, 1989.
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