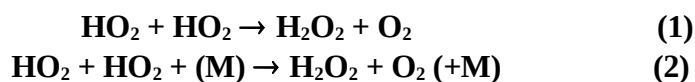


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx14

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: 2<sup>nd</sup> October 2001.



$$\Delta H^\circ(1) = \Delta H^\circ(2) = -165.5 \text{ kJ}\cdot\text{mol}^{-1}$$

## 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>			
$3.8 \times 10^{-14} \exp[(1250 \pm 200)/T]$	273-339	Cox and Burrows, 1979 <sup>1</sup>	MM (a)
$(2.35 \pm 0.2) \times 10^{-12}$	298		
$2.4 \times 10^{-13} \exp[(560 \pm 200)/T]$	298-359	Thrush and Tyndall, 1982 <sup>2</sup>	FP-TDLS (b)
$(1.6 \pm 0.1) \times 10^{-12}$	298		
$2.5 \times 10^{-12}$ (760 Torr N <sub>2</sub> )	296	Simonaitis and Heicklen, 1982 <sup>3</sup>	FP-UVA
$k_1 = (1.4 \pm 0.2) \times 10^{-12}$	296		
$k_1 = 2.2 \times 10^{-13} \exp(620/T)$	230-420	Kircher and Sander, 1984 <sup>4</sup>	FP-UVA (c)
$k_1 = (1.7 \pm 0.22) \times 10^{-12}$	298		
$k_2 = 1.9 \times 10^{-33} [\text{N}_2] \exp(980/T)$	230-420	Kircher and Sander, 1984 <sup>4</sup>	FP-UVA (c)
$k_2 = (5.4 \pm 3.1) \times 10^{-32} [\text{N}_2]$	298		
$k_1 = 1.88 \times 10^{-12}$	298	Kurylo, Ouellette and Laufer, 1986 <sup>5</sup>	FP-UVA (d)
$k_2 = 4.53 \times 10^{-32} [\text{O}_2]$	298		
$k_2 = 5.95 \times 10^{-32} [\text{N}_2]$	298		
$k_1 = 2.0 \times 10^{-13} \exp[(595 \pm 120)/T]$	253-390	Takacs and Howard, 1986 <sup>6</sup>	DF-LMR
$k_1 = (1.54 \pm 0.07) \times 10^{-12}$	294		
$(3.3 \pm 0.9) \times 10^{-12}$	298	Lightfoot, Veyret and Lesclaux, 1988 <sup>7</sup>	FP-UVA
$(1.5 \pm 0.5) \times 10^{-12}$	418		
$(8.8 \pm 1.2) \times 10^{-13}$	577		
$(8.2 \pm 2.0) \times 10^{-13}$	623		
$(8.1 \pm 1.5) \times 10^{-13}$	677		
$(7.6 \pm 1.4) \times 10^{-13}$	723		
$(9.1 \pm 2.5) \times 10^{-13}$	777		
$(2.44 \pm 0.20) \times 10^{-12}$ (1000 mb O <sub>2</sub> )	298	Crowley <i>et al.</i> , 1991 <sup>8</sup>	MMS
$(2.84 \pm 0.30) \times 10^{-12}$ (1000 mb N <sub>2</sub> )	298		
$(3.5 \pm 1.0) \times 10^{-12}$ (1000 mb SF <sub>6</sub> )	295	Sehested <i>et al.</i> , 1997 <sup>9</sup>	PR-UVA

## Comments

- (a) HO<sub>2</sub> radicals were monitored by molecular modulation spectrometry. The data cited refer to a total pressure of 760 Torr and absence of H<sub>2</sub>O.

- (b) HO<sub>2</sub> radicals were monitored by diode laser spectroscopy. Pressure = 9-27 mb (7-20 Torr) of O<sub>2</sub>.
- (c) Pressure range was 0.133-0.933 bar (100-700 Torr) of Ar and N<sub>2</sub>. Enhancement of  $k$  by added water was observed, in a linear fashion independent of the pressure of other gases, according to the equation  $k_{\text{obs}} = k \times (1 + 1.4 \times 10^{-21} \exp(2200/T) [\text{H}_2\text{O}])$ .
- (d) Total pressure range was 0.033-1.01 bar (25-760 Torr).

### Preferred Values

$k_1 = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2 = 5.2 \times 10^{-32} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2 = 4.5 \times 10^{-32} [\text{O}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_1 = 2.2 \times 10^{-13} \exp(600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-420 K.

$k_2 = 1.9 \times 10^{-33} [\text{N}_2] \exp(980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-420 K.

In the presence of H<sub>2</sub>O the expressions for  $k_1$  and  $k_2$  should be multiplied by the factor:  $\{1 + 1.4 \times 10^{-21} [\text{H}_2\text{O}] \exp(2200/T)\}$ , where [H<sub>2</sub>O] is in molecule cm<sup>-3</sup> units.

### Reliability

$\Delta \log k_1 = \Delta \log k_2 = 0.15$  at 298 K.

$\Delta(E_1/R) = \pm 200 \text{ K}$ .

$\Delta(E_2/R) = \pm 300 \text{ K}$ .

### Comments on Preferred Values

The preferred values given here are identical with the values derived by Kircher and Sander<sup>4</sup> and also recommended in the review by Wallington *et al.*<sup>8</sup>

At temperatures close to 298 K, the reaction proceeds by two channels, one bimolecular and the other termolecular. The preferred values for  $k_1$  are based on the work of Cox and Burrows,<sup>1</sup> Thrush and Tyndall,<sup>2</sup> Kircher and Sander,<sup>4</sup> Kurylo *et al.*,<sup>5</sup> Takacs and Howard<sup>6</sup> and Lightfoot *et al.*<sup>7</sup> The work of Kurylo *et al.*<sup>5</sup> and of Lightfoot *et al.*<sup>7</sup> has confirmed quantitatively the effects of pressure previously observed by Simonaitis and Heicklen<sup>3</sup> and Kircher and Sander.<sup>4</sup> The recommendations for  $k_2$  are based on the work of Kircher and Sander<sup>4</sup> and Kurylo *et al.*,<sup>5</sup> with the temperature coefficient of  $k_2$  being taken from Kircher and Sander<sup>4</sup> and Lightfoot *et al.*<sup>7</sup> At higher temperatures,  $T > 600 \text{ K}$ , Hippler *et al.*<sup>14</sup> and Lightfoot *et al.*<sup>7</sup> observe a sharp change in the temperature coefficient with upward curvature of the Arrhenius plot.

The marked effect of water on this reaction was established in the work of Lii *et al.*<sup>15</sup> and Kircher and Sander.<sup>4</sup> The recommended multiplying factor for  $k_1$  and  $k_2$  in the presence of water is based on these two studies.<sup>4,15</sup>

Mozurkewich and Benson<sup>16</sup> have considered the HO<sub>2</sub> + HO<sub>2</sub> reaction theoretically and conclude that the negative temperature dependence, the pressure dependence, and the observed isotope effects can most reasonably be explained in terms of a cyclic hydrogen bonded, HO<sub>2</sub> O<sub>2</sub>H, intermediate to alternative structures suggested by others.

Sahetchian *et al.*<sup>17</sup> reported the formation of H<sub>2</sub> (~10% at 500 K) in the reaction system but this is contrary to earlier evidence of Baldwin *et al.*<sup>18</sup> and the more recent and careful study of Stephens *et al.*<sup>19</sup> who find less than 0.01 fractional contribution from the channel leading to H<sub>2</sub> + 2O<sub>2</sub>. Keyser *et al.*<sup>20</sup> have measured a yield of O<sub>2</sub>(b<sup>1</sup>Σ) of  $< 3 \times 10^{-2}$  per HO<sub>2</sub> consumed.

### References

- <sup>1</sup> R. A. Cox and J. P. Burrows, *J. Phys. Chem.* **83**, 2560 (1979).
- <sup>2</sup> B. A. Thrush and G. S. Tyndall, *Chem. Phys. Lett.* **92**, 232 (1982).
- <sup>3</sup> R. Simonaitis and J. Heicklen, *J. Phys. Chem.* **86**, 3416 (1982).
- <sup>4</sup> C. C. Kircher and S. P. Sander, *J. Phys. Chem.* **88**, 2082 (1984).
- <sup>5</sup> M. J. Kurylo, P.A. Ouellette, and A. H. Laufer, *J. Phys. Chem.* **90**, 437 (1986).
- <sup>6</sup> G. A. Takacs and C. J. Howard, *J. Phys. Chem.* **90**, 687 (1986).
- <sup>7</sup> P. D. Lightfoot, B. Veyret, and R. Lesclaux, *Chem. Phys. Lett.* **150**, 120 (1988).
- <sup>8</sup> J. N. Crowley, F. G. Simon, J. P. Burrows, G. K. Moortgat, M. E. Jenkin, and R. A. Cox, *J. Photochem. Photobiol. A: Chem.* **60**, 1 (1991).
- <sup>9</sup> J. Sehested, T. Mogdeberg, K. Fagerstrom, G. Mahmoud, and T. J. Wallington, *Int. J. Chem. Kinet.* **29**, 673 (1997).
- <sup>10</sup> T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).
- <sup>11</sup> B. A. Thrush and G. S. Tyndall, *J. Chem. Soc. Faraday Trans. 2* **78**, 1469 (1982).
- <sup>12</sup> S. P. Sander, *J. Phys. Chem.* **88**, 6018 (1984).
- <sup>13</sup> S. P. Sander, M. Peterson, R. T. Watson, and R. Patrick, *J. Phys. Chem.* **86**, 1236 (1982).
- <sup>14</sup> H. Hippler, J. Troe, and J. Willner, *J. Chem. Phys.* **93**, 1755 (1990).
- <sup>15</sup> R.-R. Lii, M. C. Sauer, Jr., and S. Gordon, *J. Phys. Chem.* **85**, 2833 (1981).
- <sup>16</sup> M. Mozurkewich and S. W. Benson, *Int. J. Chem. Kinet.* **17**, 787 (1985).
- <sup>17</sup> K. A. Sahetchian, A. Heiss, and R. Rigny, *Can. J. Chem.* **60**, 2896 (1982).
- <sup>18</sup> R. R. Baldwin, C. E. Dean, M. R. Honeyman, and R. W. Walker, *J. Chem. Soc. Faraday 1*, **80**, 3187 (1984).
- <sup>19</sup> S. L. Stephens, J. W. Birks, and R. J. Glinski, *J. Phys. Chem.* **93**, 8384 (1989).
- <sup>20</sup> L. F. Keyser, K. Y. Choo, and M. T. Leu, *Int. J. Chem. Kinet.* **17**, 1169 (1985).