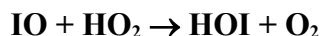


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iIOx13

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This data sheet updated: 25<sup>th</sup> September 2003.



$$\Delta H^\circ = -200 \text{ kJ}\cdot\text{mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(6.4 \pm 0.7) \times 10^{-11}$	298	Jenkin, Cox and Hayman, 1991 <sup>1</sup>	MM (a)
$(1.03 \pm 0.13) \times 10^{-10}$	298	Maguin <i>et al.</i> , 1992 <sup>2</sup>	DF-MS (b)
$9.3 \times 10^{-12} \exp[(680 \pm 110)/T]$	274-373	Cronkhite <i>et al.</i> , 1999 <sup>3</sup>	FP-UVA/IR (c)
$(9.7 \pm 2.9) \times 10^{-11}$	298		
$(7.1 \pm 1.6) \times 10^{-11}$	296	Canosa-Mas <i>et al.</i> , 1999 <sup>4</sup>	DF-RF (d)
$2.2 \times 10^{-11} \exp[(400 \pm 80)/T]$	273-353	Knight and Crowley, 2001 <sup>5</sup>	DF-MS (e)
$(8.9 \pm 0.9) \times 10^{-11}$	298		(f)
$(8.00 \pm 0.15) \times 10^{-11}$	298		(g)

## Comments

- Molecular modulation technique with UV absorption detection of HO<sub>2</sub> radicals at 220 nm and visible absorption detection of IO radicals at 427 nm. The radicals were produced by photolysis of O<sub>3</sub>-CH<sub>3</sub>OH-I<sub>2</sub>-O<sub>2</sub> mixtures at 254 nm with HO<sub>2</sub> in excess over IO. The rate coefficient, *k*, was derived from a non-linear least-squares analysis of absorption wave-forms. The error limits do not include possible systematic errors.
- Discharge flow system with MS detection of HO<sub>2</sub> and IO radicals and HOI. IO and HO<sub>2</sub> radicals were produced by the O(<sup>3</sup>P) + I<sub>2</sub> and Cl + CH<sub>3</sub>OH + O<sub>2</sub>, reactions, respectively. Pseudo first-order decays of IO radicals were measured in the presence of excess HO<sub>2</sub>. The cited value of *k* is the average of 25 experiments. HOI was shown to be a major product. The uniqueness of the HOI + O<sub>2</sub> forming channel could not be established, although no evidence was found for O<sub>3</sub> formation by the alternative HI + O<sub>3</sub> channel.
- Pulsed laser photolysis of Cl<sub>2</sub>-CH<sub>3</sub>OH-O<sub>2</sub>-I<sub>2</sub>-NO<sub>2</sub>-SF<sub>6</sub>-N<sub>2</sub> mixtures at 308 nm with simultaneous time-resolved detection of HO<sub>2</sub> radicals (by infrared TDLS) and IO radicals (by visible absorption spectroscopy). HO<sub>2</sub> radicals were generated by the reaction of Cl atoms (from photolysis of Cl<sub>2</sub>) with CH<sub>3</sub>OH in the presence of O<sub>2</sub>, and IO radicals were generated by the reaction of O(<sup>3</sup>P) atoms (from photolysis of NO<sub>2</sub>) with I<sub>2</sub>.
- IO generated from O(<sup>3</sup>P) + CF<sub>3</sub>I (following discharge of O<sub>2</sub>). HO<sub>2</sub> generated from Cl + CH<sub>3</sub>OH in the presence of O<sub>2</sub>. IO and HO<sub>2</sub> concentrations were monitored by titration to I and OH by the respective reactions with NO. Experiments carried out at 1.7-2 Torr.
- IO generated from O(<sup>3</sup>P) + CF<sub>3</sub>I or O(<sup>3</sup>P) + I<sub>2</sub> (following discharge of O<sub>2</sub>). HO<sub>2</sub> generated from Cl+CH<sub>3</sub>OH in the presence of O<sub>2</sub>. IO and HO<sub>2</sub> concentrations were monitored directly at their parent peaks. Experiments carried out at 1.3-2.3 mbar.

- (f) IO from O(<sup>3</sup>P) + CF<sub>3</sub>I.  
(g) IO from O(<sup>3</sup>P) + I<sub>2</sub>.

### Preferred Values

$k = 8.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.4 \times 10^{-11} \exp(540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270 K to 380 K.

#### Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 300$  K.

#### Comments on Preferred Values

The preferred value at 298 K is the average of the reported room temperature data<sup>1-5</sup>. The preferred Arrhenius expression is based on the  $E/R$  values from the temperature dependence studies of Cronkhite *et al.*<sup>3</sup> and Knight and Crowley<sup>5</sup>, combined with a pre-exponential factor adjusted to give the preferred value of  $k$  at 298 K.

The studies of Maguin *et al.*<sup>2</sup> and Knight and Crowley<sup>5</sup> provide strong evidence that the formation of HOI and O<sub>2</sub> is the dominant pathway. On the basis of current thermochemical data for the IO radical, the channel forming HI + O<sub>3</sub> is endothermic by *ca.* 40 kJ mol<sup>-1</sup>, and a limit of  $\leq 10\%$  has been reported for this channel<sup>5</sup>, based on no detectable formation of O<sub>3</sub>. As pointed out by Knight and Crowley<sup>5</sup>, a channel forming OH + OIO is exothermic by 12 kJ mol<sup>-1</sup>, but no firm evidence for this channel has been reported.

### References

- <sup>1</sup> M. E. Jenkin, R. A. Cox, and G. D. Hayman, *Chem. Phys. Lett.* **177**, 272 (1991).
- <sup>2</sup> F. Maguin, G. Laverdet, G. Le Bras, and G. Poulet, *J. Phys. Chem.* **96**, 1775 (1992).
- <sup>3</sup> J. M. Cronkhite, R. E. Stickel, J. M. Nicovich, and P. H. Wine, *J. Phys. Chem. A* **103**, 3228 (1999).
- <sup>4</sup> C. E. Canosa-Mas, M. L. Flugge, D. Shah, A. Vipond and R. P. Wayne, *J. Atmos. Chem.* **34**, 153, 1999.
- <sup>5</sup> G. P. Knight and J. N. Crowley, *Phys. Chem. Chem. Phys.*, **3**, 393 (2001).