

IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet iIOx17

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$$\Delta H^\circ(1) = -170 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -18 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -48 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(8.0 \pm 1.8) \times 10^{-11}$	298	Laszlo, Kurylo, and Huie, 1995 ¹	(a)
$(9.9 \pm 1.5) \times 10^{-11}$	250-320	Harwood <i>et al.</i> , 1997 ²	(b)
$(1.0 \pm 0.3) \times 10^{-10}$	295	Atkinson, Hudgens, and Orr-Ewing, 1999 ³	(c)
$(9.3 \pm 1.0) \times 10^{-11}$	295	Ingham <i>et al.</i> , 2000 ⁴	(d)
$4.54 \times 10^{-11} \exp[(182 \pm 122)/T]$	250-320	Bloss <i>et al.</i> , 2001 ⁵	(e)
$(8.2 \pm 1.0) \times 10^{-11}$	298		
$(9.3 \pm 1.0) \times 10^{-11}$	296	Vipond, 2002 ⁶	(f)
<i>Branching Ratios</i>			
$k_1/k < 0.05$	298	Sander, 1986 ⁷	(g)
$(k_2 + 0.5k_3)/k = 0.45$ at 28 mbar	298		
$(k_2 + 0.5k_3)/k = 0.18$ at 870 mbar	298		
$k_1/k < 0.05$	298	Laszlo, Kurylo, and Huie, 1995 ¹	(a)
$(0.5k_3 + k_4)/k = 0.78$ at 1 bar	298	Harwood <i>et al.</i> , 1997 ²	(h)
$k_1/k < 0.30$	298		
$k_1/k < 0.05$	298	Bloss <i>et al.</i> , 2001 ⁵	(i)
$k_2/k = 0.11 \pm 0.04$	298		
$k_3/k = 0.38 \pm 0.08$	298		
$k_4/k = 0.46 \pm 0.06$	298		
$k_2/k = 0.56 \pm 0.20$	296	Vipond, 2002 ⁶	(f)

Comments

- (a) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using the 4-0 band of the A-X system at 427.2 nm, for which a cross-section of $(2.8 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was measured. The total pressure was 78 mbar to 789 mbar of N₂. No prompt I₂ formation from IO decay was observed.
- (b) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using the 4-0 band of the A-X system at 427.2 nm, for which a temperature-independent cross-section of

- $(3.6 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was measured. The total pressure was 78 mbar to 789 mbar of N_2 . No statistically significant temperature dependence of either k or σ was observed over the temperature range studied.
- (c) Pulsed laser photolysis with detection of IO radicals by cavity ring-down spectroscopy using the 2-0 bandhead of the A-X system at 445.02 nm, for which an absorption cross-section of $(7.3 \pm 0.7) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was used. This was determined relative to $\sigma = (3.6 \pm 0.7) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ measured by Harwood *et al.*². The total pressure was 12.4 mbar to 40.2 mbar of Ar.
- (d) Pulsed laser photolysis (248 nm) of $\text{O}_3\text{-I}_2$ mixtures, with detection of IO radicals by time-resolved absorption spectroscopy at 427.2 nm. A cross-section of $(3.6 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was used to determine k . The total pressure was 78 mbar N_2 . OIO product detected by absorption spectroscopy.
- (e) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using time-resolved charge-coupled detection (CCD) in the A-X system at 400 nm to 470 nm. The cross-section at 427.2 nm was measured to be $(1.9 \pm 0.17) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (1.13 nm resolution). The differential cross section used to determine [IO] decreased by ~45% on increasing the temperature from 220 K to 335 K. The total pressure was 130 mbar to 1000 mbar of N_2 .
- (f) Discharge flow system with RF detection of I atoms after titration of IO radicals with NO. The total pressure was 2.5 mbar of He. Branching ratio k_2/k from analysis of I atom measurements in the absence of NO.
- (g) Flash photolysis system with detection by absorption spectroscopy. The pressure dependence of the branching ratio to produce I atoms was based on the pressure dependence of k in the presence of excess O_3 .
- (h) Based on I_2 formation at short reaction times, and on comparison of rate coefficients measured in the presence and absence of O_3 , with $k(\text{presence of } \text{O}_3)/k(\text{absence of } \text{O}_3) = 0.73$ at 1 bar.
- (i) Based on product absorptions due to I_2 , OIO and an unknown broad-band absorption at $\lambda \leq 400 \text{ nm}$ assigned to I_2O_2 . The value of $\sigma(\text{OIO})$ used was based on the branching ratio for the reaction $\text{IO} + \text{BrO} \rightarrow \text{Br} + \text{OIO}$ determined by Bedjanian *et al.*⁸

Preferred Values

$k = 9.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.4 \times 10^{-11} \exp(180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250 K to 320 K.

$k_1/k \leq 0.05$ at 298 K.

$k_3/k = 0.38$ at 298 K and 1bar.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

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

$\Delta(k_3/k) = \pm 0.1$ at 298 K and 1bar.

Comments on Preferred Values

The recently reported¹⁻⁶ values of k show good agreement for the overall rate coefficient at room temperature, which is higher than previously reported by Sander⁷, Jenkin and Cox,⁹ and by Barnes *et al.*¹⁰ (who used a discharge flow technique). When the different values of the absorption cross-sections are taken into account, there is excellent agreement in the values of $k/\sigma(427\text{nm})$ obtained by Laszlo *et al.*,¹ Harwood *et al.*,² Bloss *et al.*,⁵ and Ingham *et al.*⁴

Using a value of $\sigma(\text{IO}) = 3.6 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 427 nm from the IUPAC evaluation (see data sheet on IO photolysis), and the mean value of $k/\sigma(427\text{nm}) = 2.75 \times 10^6 \text{ cm s}^{-1}$ from these studies, gives the preferred value at 298 K of $k = 9.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The results of Vipond *et al*⁶ and Atkinson *et al*.³ are consistent with this value.

All studies agree that the overall rate coefficient in the absence of excess O_3 is independent of pressure over the range 1 mbar to 1000 mbar. The fraction of the $\text{IO} + \text{IO}$ reaction leading to I atom production from studies at higher pressures^{2,3,7} appears to be ~20% to 30%, with $(k_2 + 0.5k_3)/k \sim 0.2-0.3$ consistent with the quantum yield for I_2 -photosensitized decomposition of O_3 .¹¹ However, Sander⁷ and Jenkin and Cox¹⁰ observed a falloff in k with decreasing pressure in the presence of excess O_3 , *i.e.*, when the I atom products are recycled to form IO, suggesting that the fractional I atom yield increases as pressure decreases. This is consistent with the higher branching ratio k_2/k reported by Vipond *et al*.⁶ Bloss *et al*⁵ observed OIO formation with a branching ratio of k_3/k in the range 0.30 to 0.48, based on an OIO absorption cross-section of $\sigma(\text{OIO}) = 1.07 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 524 nm deduced from the OIO yield in the $\text{IO} + \text{BrO}$ reaction.^{8,12}

All studies show that I_2 formation is minor, with $k_1/k < 0.05$.^{1,2,5,7} Most authors have assumed that I_2O_2 is the other major product formed, although evidence for I_2O_2 formation is not unequivocal. Both Sander⁷ and Bloss *et al*⁵ report products which absorb in the UV near 300 nm but no direct identification of the absorbing species has been reported.

Temperature-dependent rate coefficients have been reported by Sander,⁷ Harwood *et al*.² and Bloss *et al*⁵. The high value of $E/R = -(1020 \pm 200) \text{ K}$ reported by Sander⁷ reflects the large temperature coefficient obtained for σ . When the much weaker changes in σ are used (see data sheet on IO photolysis), the temperature dependence of k disappears. On balance the results of Bloss *et al*⁵, which take into account the changes in the yield of IO radicals from the $\text{O} + \text{CF}_3\text{I}$ reaction used to calibrate the absorptions, are preferred. The temperature dependence of Bloss *et al*⁵ is used and the pre-exponential factor, A , is adjusted to fit the preferred 298 K rate coefficient. The error reflects the possibility of a zero E/R .

References

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