IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iIOx16

This data sheet updated: 3rd February 2004.

$$\text{IO} + \text{BrO} \rightarrow \text{IBr} + \text{O}_2 \qquad (1)$$
$$\rightarrow \text{Br} + \text{I} + \text{O}_2 \qquad (2)$$
$$\rightarrow \text{Br} + \text{OIO} \qquad (3)$$
$$\rightarrow \text{I} + \text{OBrO} \qquad (4)$$
$$\text{IO} + \text{BrO} + \text{M} \rightarrow \text{IOOBr} + \text{M} \qquad (5)$$
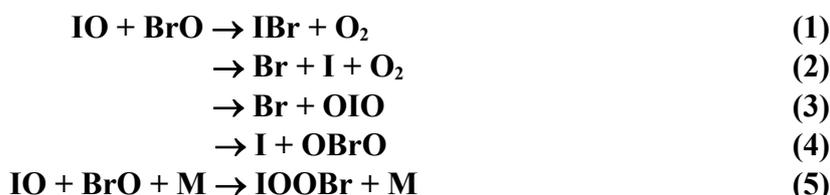
$\Delta H°(1) = -195 \text{ kJ·mol}^{-1}$
$\Delta H°(2) = -17 \text{ kJ·mol}^{-1}$
$\Delta H°(3) = -47 \text{ kJ·mol}^{-1}$
$\Delta H°(4) = 23 \text{ kJ·mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.9 \pm 2.7) \times 10^{-11}$	298	Laszlo *et al*., 1997[1]	PLP-AS (a)
$k_1 + k_3 = 2.5 \times 10^{-11} \exp[(260 \pm 100)/T]$	204-388	Gilles *et al*., 1997[2]	PLP-LIF (b)
$k_1 + k_3 = 6.0 \times 10^{-11}$	298		
$(8.5 \pm 1.5) \times 10^{-11}$	298	Bedjanian, Le Bras, and Poulet, 1998[3]	DF-MS (c)
$k_1 + k_3 = (7.5 \pm 1.0) \times 10^{-11}$	298		
$6.7 \times 10^{-12} \exp[(760 \pm 30)/T]$	210-333	Rowley *et al*, 2001[4]	(d)
$(8.5 \pm 1.4) \times 10^{-11}$	295		
Branching Ratios			
$(k_2 + k_4)/k <0.35$	298	Gilles *et al*., 1997[2]	(b)
$k_1/k <0.05$	298	Bedjanian, Le Bras, and Poulet, 1998[3]	(e)
$k_2/k <0.3$	298		
$k_3/k = 0.65$-1.0	298		
$k_4/k <0.2$	298		
$(k_2 + k_4)/k <0.3$	298		
$k_1/k <0.2$	298	Rowley *et al*, 2001[4]	(f)
$k_4/k <0.15$	298		

Comments

(a) IO and BrO radicals were monitored at 427.2 nm and 338.5 nm, respectively, using resolutions of 0.3 nm and 0.6 nm and cross-sections of 2.8 x 10^{-17} cm^2 molecule^{-1} and 1.4 x 10^{-17} cm^2 molecule^{-1}, respectively. The rate coefficient k was determined by a computer fit to complex kinetic decay curves. The total pressure was 260 mbar.

(b) IO radicals were detected by LIF. Pseudo-first order decays of IO radicals were measured in the presence of excess BrO and O$_3$. The reported rate coefficient applies only to the non-I-

atom producing channels. An upper limit of 0.35 is suggested for the fraction of the overall reaction yielding I atoms at 298 K. Total pressure was 8 mbar to 20 mbar.

(c) IO radical decays were monitored in the presence of excess BrO and O_3 to obtain the rate coefficient for the total non-I-atom forming channels. The total rate coeficient was obtained from simulations of the BrO, IO and IBr profiles. The total pressure was 1 mbar.

(d) Pulsed laser photolysis with absorption spectroscopic detection of BrO and IO radicals using a time-resolved charge coupled detector (CCD) in the A-X systems at 300 nm to 350 nm and 400 nm to 470 nm, respectively. The IO radical cross-section at 427.2 nm was measured to be (1.9 ± 0.17) x 10^{-17} cm^2 molecule^{-1} (1.13 nm resolution) and the BrO radical differential cross-sections were based on those measured by Wahner et al.,[5] but increased in magnitude by 9% as recommended by Gilles et al.[2] and adjusted for a resolution of 1.13 nm. The rate coefficient k was determined by computer simulation of IO decays in excess BrO_2. The total pressure was 100 mbar to 1000 mbar.

(e) Several experiments under varying conditions in the discharge flow system were used to establish the branching ratios. The major channel produces Br + OIO with a branching ratio in the range given. Only upper limits were obtained for I atom and IBr formation.

(f) Based on the upper limits to the formation of the products IBr and OBrO, as measured by absorption spectroscopy. OIO was shown to be the major product.

Preferred Values

$k = 8.5$ x 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5$ x 10^{-11} exp(510/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200 K to 390 K.
$k_3/k = 0.80$ at 298 K.

Reliability
    Δlog $k = \pm 0.1$ at 298 K.
    $\Delta(E/R) = \pm 350$ K.
    $\Delta(k_3/k) = 0.15$ at 298 K.

Comments on Preferred Values
    The recent kinetic studies of this reaction by Laszlo et al.,[1] Gilles et al.,[2] Bedjanian et al.[3] and Rowley et al,[4] are in remarkedly good agreement considering the experimental difficulties. Both Gilles et al.[2] and Bedjanian et al.[3] observed first-order kinetics for IO radical decays in excess BrO to obtain the rate coefficient for non-I-atom producing channels, $(k_1 + k_3) = (6.8 \pm 0.8)$ x 10^{-12} cm^3 molecule^{-1} s^{-1}. The overall rate coefficients measured by Bedjanian et al.[3] and Rowley et al,[4] which were measured under complex kinetic conditions, are nevertheless in excellent agreement, giving $k = (8.5 \pm 1.2)$ x 10^{-12} cm^3 molecule^{-1} s^{-1}. These measurements give a value of $(k_1 + k_3)/k = 0.80 \pm 0.15$ which lies in the middle of the range suggested by Bedjanian et al.[3] for the branching ratio k_3/k. Considering that the IBr measurements of Bedjanian et al.[3] give k_1/k <0.05, we recommend that $k_3/k = 0.80$ and that the total rate coefficient is that determined by Bedjanian et al.[3] and Rowley et al,[4] at 298 K. The rate coefficient measurement of Laszlo et al.[1] is less precise but agrees within the experimental error limits with the recommendation.
    The two studies of the temperature dependence[2,4] both show a negative activation energy for this radical + radical reaction. Although the temperature dependence of Gilles et al.[2] is derived from measurements of $k_1 + k_3$ over a wider temperature range, their result may not reflect the temperature dependence of the overall reaction if the branching ratio changes with temperature.   The recommended temperature dependence is the simple mean of the two determinations of Gilles et al.[2] and Rowley et al,[4] with the pre-exponential factor, A, being

adjusted to fit the preferred 298 K rate coefficient. The data do not allow a precise recommendation for the remaining branching between channels (1), (2) and (4). However, OBrO formation is not favorable on thermochemical grounds.

References

[1] B. Laszlo, R. E. Huie, M. J. Kurylo, and A. W. Miziolek, J. Geophys. Res. **102**, 1523 (1997).

[2] M. K. Gilles, A. A. Turnipseed, J. B. Burkholder, A. R. Ravishankara, and S. Solomon, J. Phys. Chem. A **101**, 5526 (1997).

[3] Y. Bedjanian, G. Le Bras, and G. Poulet, J. Phys. Chem. A **102**, 10501 (1998).

[4] D.M.Rowley, W.J.Bloss, R.A.Cox, and R.L.Jones, J.Phys.Chem. A, **105**, 7885, (2001).

[5] A. Wahner, A. R. Ravishankara, S. P. Sander, and R. R. Friedl, Chem. Phys. Lett. **152**, 507 (1988).