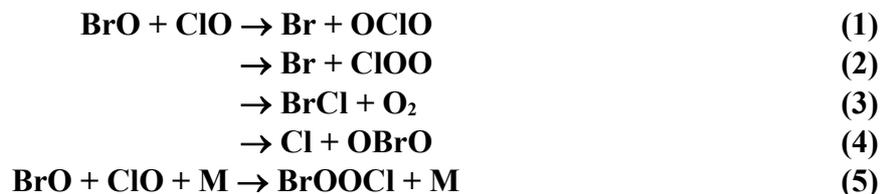


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx21

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This data sheet updated: 3rd February 2004.



$$\Delta H^\circ(1) = -14 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -12 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -207 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) = 52 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$6.1 \times 10^{-12} \exp[(240 \pm 60)/T]$	220-400	Sander and Friedl, 1988 ¹	FP-UVA (a)
$(1.29 \pm 0.18) \times 10^{-11}$	298		
$4.7 \times 10^{-12} \exp[(320 \pm 60)/T]$	220-400	Friedl and Sander, 1988 ²	DF-MS (b)
$(1.29 \pm 0.19) \times 10^{-11}$	298		
$2.59 \times 10^{-12} \exp[(445 \pm 84)/T]$	234-406	Turnipseed, Birks, and Calvert, 1991 ³	DF-MS (c)
$(1.08 \pm 0.20) \times 10^{-11}$	304		
$k_1 = 6.7 \times 10^{-13} \exp[(622 \pm 94)/T]$	234-406		
$k_2 = 2.1 \times 10^{-12} \exp[(258 \pm 56)/T]$	234-406		
$k_3 = 1.9 \times 10^{-13} \exp[(513 \pm 86)/T]$	234-406		
<i>Branching Ratios</i>			
$k_1/k = 0.68 \pm 0.10$	220	Sander and Friedl, 1988 ¹	(a)
$k_1/k = 0.59 \pm 0.10$	298		
$k_1/k = 0.55 \pm 0.07$	220	Friedl and Sander, 1988 ²	(b)
$k_1/k = 0.48 \pm 0.07$	298		
$k_1/k = 0.44 \pm 0.07$	400		
$k_2/k = 0.39 \pm 0.10$	220	Friedl and Sander, 1988 ²	(b)
$k_2/k = 0.40 \pm 0.10$	298		
$k_2/k = 0.44 \pm 0.10$	400		
$k_3/k = 0.06 \pm 0.03$	220	Friedl and Sander, 1988 ²	(b)
$k_3/k = 0.08 \pm 0.03$	298		
$k_3/k = 0.08 \pm 0.03$	400		
$k_1/k = 0.51 \pm 0.09$	250	Turnipseed, Birks, and Calvert, 1991 ³	(c)
$k_1/k = 0.48 \pm 0.07$	304		
$k_1/k = 0.39 \pm 0.07$	406		
$(k_2 + k_3)/k = 0.46 \pm 0.07$	250	Turnipseed, Birks, and Calvert, 1991 ³	(c)
$(k_2 + k_3)/k = 0.55 \pm 0.09$	304		

$(k_2 + k_3)/k = 0.61 \pm 0.11$	406		
$k_3/k = 0.10 \pm 0.02$	250	Turnipseed, Birks, and Calvert, 1991 ³	(c)
$k_3/k = 0.09 \pm 0.02$	304		
$k_3/k = 0.09 \pm 0.02$	406		
$k_1/k = 0.53 \pm 0.05$	295	Bloss, 1999 ⁴	(d)
$k_4/k < 0.02$	295		

Comments

- (a) BrO, ClO and OClO were detected using the temperature-dependent absorption cross-sections measured in the same study. BrO radical decays were monitored with $[\text{ClO}] > [\text{BrO}]$. Measurement of the rate coefficient ratio k_1/k was based on $\Delta[\text{OClO}]/\Delta[\text{BrO}]$ as a function of time.
- (b) BrO, ClO, OClO and BrCl were detected. BrO radical decays were measured in excess ClO. The branching ratios were based on the yields of OClO, Cl (after conversion to BrCl) and BrCl compared to the amounts of BrO and ClO reacted.
- (c) Discharge flow system with MS detection of BrO, ClO, OClO and BrCl. BrO radical decays were monitored in the presence of a 10 to 60 fold excess of ClO radicals. Branching ratios were based on the yields of OClO, ClO and BrCl in the presence of the Cl atom scavengers HBr and $\text{C}_2\text{H}_3\text{Br}$.
- (d) Flash photolysis system with UV absorption detection (using a coupled charge detector) of BrO, ClO, OClO and OBrO using differential absorption spectroscopy. The branching ratio k_4/k was based on the absence of characteristic OBrO absorption in the region 400 nm to 500 nm during the BrO and ClO decays.

Preferred Values

$$k_1 = 6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 6.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_3 = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 1.6 \times 10^{-12} \exp(430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220 \text{ K to } 400 \text{ K.}$$

$$k_2 = 2.9 \times 10^{-12} \exp(220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220 \text{ K to } 400 \text{ K.}$$

$$k_3 = 5.8 \times 10^{-13} \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220 \text{ K to } 400 \text{ K.}$$

Reliability

$$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E_1/R) = \Delta(E_2/R) = \Delta(E_3/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The data base for this reaction is now extensive. Friedl and Sander,² using a discharge flow-mass spectrometry system, measured the overall rate coefficient over the temperature range 220 K to 400 K and also over this temperature range determined directly the branching ratios for the reaction channels producing BrCl and OClO. In a separate study¹ the same authors, using flash photolysis-ultraviolet absorption techniques, measured the overall rate coefficient over the temperature range 220 K to 400 K and pressure range 67 mbar to 1000 mbar, and also determined the branching ratio for OClO production at 220 K and 298 K. The results by these two independent techniques^{1,2} are in excellent agreement, with the overall rate coefficient showing a negative temperature dependence. The study of Turnipseed *et al.*³ also resulted in a comprehensive set of rate coefficient and branching ratio data. The overall rate coefficients from these three studies¹⁻³ are in good agreement at room temperature (within 20%) and are in

excellent agreement at stratospheric temperatures. Toohey and Anderson,⁵ using discharge flow-resonance fluorescence/LMR techniques, reported room temperature values of the overall rate coefficient and the branching ratio for OCIO production. They also found evidence for the direct production of BrCl in a vibrationally excited π state.⁵ Poulet *et al.*,⁶ using discharge flow-mass spectrometry techniques, reported room temperature values of the overall rate coefficient and branching ratios for OCIO and BrCl production. Clyne and Watson⁷ also studied this reaction using a discharge flow-MS system.

The results of the studies of Toohey and Anderson,⁵ Sander and Friedl,¹ Friedl and Sander,² Poulet *et al.*,⁶ Turnipseed *et al.*³ and Bloss⁴ are in reasonably good agreement. The rate coefficients of Hills *et al.*,⁸ using a discharge flow-mass spectrometry technique, were independent of temperature over the range 241 K to 308 K and the room temperature rate coefficient was substantially lower than the average value from the above-mentioned studies.^{1-3,5,6} Hills *et al.*⁸ also reported no BrCl formation. In the flash photolysis study of Basco and Dogra⁹ a different interpretation of the reaction mechanism was used; the reported rate coefficients were low and are not used in the evaluation of the rate coefficient for this reaction.

The recommended Arrhenius expressions for the individual reaction channels are taken from the studies of Friedl and Sander² and Turnipseed *et al.*,³ which contain the most comprehensive sets of rate coefficient and branching ratio data. Both of these studies,^{2,3} as well as that of Sander and Friedl,¹ show that OCIO production by channel (1) becomes dominant at very low temperature. Both studies show an ~8% yield of BrCl by channel (3). The recommended expressions are consistent with the body of data from all studies except those of references 8 and 9. Quantum mechanical calculations of the transition state configurations and energy minima on the P.E. surface for this reaction confirm the mechanism involving a BrOOCl peroxide intermediate¹⁰.

References

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