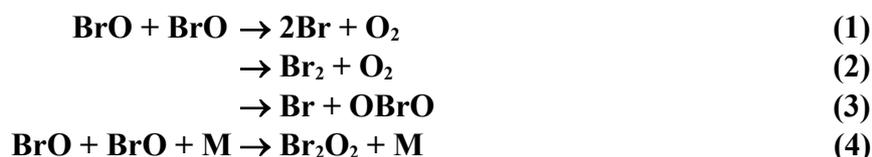


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx22

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This datasheet updated: 3rd February 2004.



$$\Delta H^\circ(1) = -16 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -209 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = 24 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) = -59 \text{ kJ}\cdot\text{mol}^{-1}$$

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>			
$(3.17 \pm 0.67) \times 10^{-12}$	298	Clyne and Watson, 1975 ¹	DF-MS
$9.58 \times 10^{-13} \exp[(255 \pm 195)/T]$	223-388	Sander and Watson, 1981 ²	(a)
$(2.17 \pm 0.68) \times 10^{-12}$	298		
$(3.2 \pm 0.5) \times 10^{-12}$	298	Lancar <i>et al.</i> , 1991 ³	(b)
$k_2 = (4.7 \pm 1.5) \times 10^{-13}$	298		
$(2.75 \pm 0.57) \times 10^{-12}$	298	Mauldin, Wahner	(c)
$k_2 = (4.45 \pm 0.82) \times 10^{-13}$	298	and Ravishankara, 1993 ⁴	
$k_1 = (2.49 \pm 0.42) \times 10^{-12}$	298	Rowley <i>et al.</i> , 1996 ⁵	(d)
$k_2 = (4.69 \pm 0.68) \times 10^{-13}$	298		
$(2.8 \pm 0.5) \times 10^{-12}$	298	Laszlo <i>et al.</i> , 1997 ⁶	(e)
$1.70 \times 10^{-12} \exp[(215 \pm 50)/T]$	204-388	Gilles <i>et al.</i> , 1997 ⁷	(f)
$(3.51 \pm 0.35) \times 10^{-12}$	298		
$k_1 = 5.31 \times 10^{-12} \exp[-(211 \pm 59)/T]$	250-298	Harwood <i>et al.</i> , 1998 ⁸	(g)
$k_2 = 1.13 \times 10^{-14} \exp[(983 \pm 111)/T]$	250-298		
$k_4 = (8.2 \pm 1.1) \times 10^{-32} [\text{M}]$	222		
<i>Branching Ratios</i>			
$k_1/k = 0.84 \pm 0.03$	298	Sander and Watson, 1981 ²	(a)
$k_1/k = 0.84 \pm 0.01$	298	Mauldin, Wahner	(c)
$k_1/k = 0.68 \pm 0.05$	220	and Ravishankara, 1993 ⁴	
$k_1/k = 0.85 \pm 0.02$	298	Rowley <i>et al.</i> , 1996 ⁵	(d)

Comments

- (a) Flash photolysis study with absorption spectroscopic detection of BrO radicals using the 7-0 band of the A-X system at 339 nm, for which a cross-section of $(1.14 \pm 0.14) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ was measured. The total pressure was 65 mbar to 789 mbar of N₂. The branching ratio was determined from measurements with and without excess O₃ present, using two methods which gave the same result.
- (b) Discharge flow-mass spectrometry study, in which rate coefficients were determined from measurements with and without excess O₃ present. The rate coefficient, k_2 was obtained from BrO radical decays and Br₂ formation.
- (c) Flash photolysis-longpath absorption technique. Measurements were made at 298 K and 220 K over a pressure range of 100 mbar to 800 mbar of He, N₂, and SF₆. The overall rate coefficient was found to be independent of pressure at 298 K, but at 220 K to increase from $2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 133 mbar to $3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 530 mbar. The branching ratio was found to be independent of pressure at 298 K and 220 K. An additional transient absorption feature was observed at 220 K and was tentatively attributed to Br₂O₂. BrO concentrations were determined using the absorption cross-sections of Wahner *et al.*;⁹ the cross-section at 338.5 nm was $1.71 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 298 K and $2.21 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 220 K (0.2 nm resolution). The following expressions were recommended for atmospheric modeling: $k_1 = 4.0 \times 10^{-12} \exp(-190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = 4.2 \times 10^{-14} \exp(660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) Flash photolysis-UV absorption technique, with detection of BrO radicals using time-resolved CCD detection in the A-X system at 400 nm to 470 nm. BrO radical concentrations were determined using the absorption cross-sections of Wahner *et al.*⁹ compensated for the change in resolution. Rate coefficients were obtained from measurements with and without excess O₃ present. OBrO was observed in the presence of high concentrations of O₃, apparently due to the BrO + O₃ reaction and not to channel (3). The total pressure was 1000 mbar.
- (e) Pulsed laser photolysis of N₂O-Br₂-N₂ mixtures, with absorption spectroscopic detection of BrO radicals. An absorption cross-section of $(1.41 \pm 0.15) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 338.5 nm was measured.
- (f) Pulsed laser photolysis of N₂O-Br₂-N₂ mixtures, with absorption spectroscopic detection of BrO radicals. An absorption cross-section of $1.63 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 338.5 nm (0.5 nm resolution) was measured at 298 K. A similar temperature dependence of the absorption cross-section as observed by Wahner *et al.*⁹ was obtained.
- (g) Flash photolysis-absorption spectroscopy technique with detection of BrO radicals using time-resolved CCD detection in the A-X system at 400 nm to 470 nm. BrO concentrations were determined using the absorption cross-sections of Wahner *et al.*⁹ compensated for change in resolution and for temperature dependence. Rate coefficients were obtained from measurements with and without excess O₃ present. The total pressure was in the range 130 mbar to 1000 mbar. In the presence of O₃ and below 250 K, departure from second-order kinetics for BrO was observed and a transient absorption attributed to Br₂O₂ was observed. The overall rate coefficient was pressure dependent in this temperature regime and the results were analyzed to yield a value for the rate coefficient for dimer formation [channel (4)] at 222 K. The formation of the dimer apparently replaced the bimolecular channels at low temperature, and the expressions for k_1 and k_2 only apply to temperatures >250 K.

Preferred Values

$k_1 = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250 K to 390 K.

$k_2 = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 = 2.9 \times 10^{-14} \exp(840/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250 K to 390 K.

$k = 1.6 \times 10^{-12} \exp(210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200 K to 390 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.1$ at 298 K.

$\Delta(E_1/R) = \Delta(E_2/R) = \pm 200$ K.

Comments on Preferred Values

The total rate coefficient for the BrO + BrO reaction has been studied by a variety of techniques, including discharge flow-mass spectrometry and flash photolysis-ultraviolet absorption spectroscopy. The results from the latter technique depend on the value used for the absorption cross-section of BrO at the monitoring wavelength, usually 338.5 nm (the (7-0) band of the A←X transition). The absorption cross-section of BrO was remeasured by Gilles *et al.*,⁷ with the values obtained being given by the expression $\sigma(\text{BrO}) = [3.29 - (5.58 \times 10^{-3})T] \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 338.5 nm. At a comparable resolution this expression gives values of $\sigma(\text{BrO}) \sim 10\%$ larger than those of Wahner *et al.*⁹ and employed by most of the earlier studies. When this difference is taken into account, the 298 K rate coefficients from the flash photolysis-absorption spectroscopy studies are in excellent agreement with the discharge flow studies (to within 10%), except for the study of Turnipseed *et al.*¹⁰ The mean 298 K rate coefficient is $3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of pressure.

The branching ratio between the bimolecular channels has been measured directly in the studies cited,^{1,4,5} and by Turnipseed *et al.*¹⁰ and indirectly by Jaffe and Mainquist¹¹ from 258 K to 333 K, Cox *et al.*¹² from 278 K to 348 K, and by Rattigan *et al.*¹³ at 298 K. All studies are in agreement that $k_1/k = 0.85 \pm 0.03$ at 298 K and that the termolecular channel increases in importance with decreasing temperature. Recent *ab initio* calculations¹⁴ have confirmed the existence of stable Br₂O₂ isomers and the endothermicity of channel (3) forming OBrO.

The temperature dependence is complicated by a pressure dependence of the rate coefficients at low temperatures (<250 K), as observed by Mauldin *et al.*⁴ and Harwood *et al.*⁸ The rate coefficients at <250 K increase with pressure, which Harwood *et al.*⁸ associated with the formation of an unstable Br₂O₂ dimer which was observed spectroscopically by both Mauldin *et al.*⁴ and Harwood *et al.*⁸ The study of Gilles *et al.*,⁷ which covers the largest temperature range and was conducted at low total pressures, shows a small negative temperature dependence for the overall rate coefficient. The preferred values are based on the above 298 K rate coefficient of $k = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an $(E/R) = -210$ K, resulting in $k = 1.6 \times 10^{-12} \exp(210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The recommended channel-specific rate coefficients are based on the values of $k_1/k = 0.85$ at 298 K and $k_1/k = 0.68$ at 220 K.

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