IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet III.A3.77 iBrOx20

This data sheet last evaluated: March 2005.

$BrO + NO_2 + M \rightarrow BrONO_2 + M$

$\Delta H° = -106$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(5.0 \pm 1.0) \times 10^{-31}$ [N_2]	298	Sander, Ray and Watson, 1981	DF-MS/FP-UVA (a)
$(4.2 \pm 0.8) \times 10^{-31}$ $(T/300)^{-2.0}$ [O_2]	263-343	Danis et al., 1990	PLP-MS (b)
5.4×10^{-31} $(T/298)^{-3.2}$ [N_2]	248-346	Thorn, Daykin and Wine, 1993	PLP-UVA (c)

Comments

(a) DF-MS study over the pressure range 1.3-8 mbar, and FP-UVA study from 57-933 mbar. In the DF-MS study, BrO radicals were produced by the reaction $Br + O_3 \rightarrow BrO + O_2$, and in the FP-UVA study BrO radicals were formed by the reaction of $O(^3P)$ atoms (from the photolysis of O_2) with Br_2. A major portion of the falloff curve was observed and analyzed with a fitted value of $F_c = 0.4$ at 298 K.

(b) BrO radicals were produced by the photolysis of O_3 at 248 nm in the presence of Br_2. Rate coefficients were measured at total pressures below 16 mbar. Falloff curves were extrapolated using $F_c = \exp(-T/325)$.

(c) BrO radicals were generated by the photolysis of Br_2-NO_2-N_2 mixtures at 351 nm, and were monitored by long-path (550 cm) absorption at 338.3 nm. The total pressure was varied over the range 21-1060 mbar. The data were analyzed with $F_c = \exp(-T/327)$, based on the fitted value of $F_c = 0.4$ of Sander et al. (1981). If a value of $F_c = 0.6$ is used, a rate coefficient of $k_0 = 5.2 \times 10^{-31}$ $(T/300)^{-3.2}$ [N_2] cm^3 molecule^{-1} s^{-1} is obtained.

Preferred Values

$k_0 = 4.7 \times 10^{-31}$ $(T/300)^{-3.1}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 240-350 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the data of Sander et al. (1981), Danis et al. (1990) and Thorn et al. (1993). The reverse dissociation reaction $BrONO_2 + M \rightarrow BrO + NO_2 + M$ was measured by Orlando and Tyndall (1996) over the temperature range 320-340 K and at pressures of 133-1330 mbar. Their rate data were combined with the present preferred values for the reverse reaction leading to $\Delta H° = -118$ kJ · mol^{-1}. Ab initio calculations of the bond strength have also been reported by Rayez and Destriau (1993) and Parthiban and Lee (1998).

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(2.0± 0.5) x 10^{-11}	298	Sander, Ray and Watson, 1981	DF-MS/FP-UVA (a)
1.4 x 10^{-11} (T/300)$^{-1.2}$	248-346	Thorn, Daykin and Wine, 1993[3]	PLP-UVA (b)

Comments

(a) See comment (a) for k_0. Extrapolation of falloff curve with a fitted value of $F_c = 0.4$.

(b) See comment (c) for k_0. Evaluated with $F_c = \exp(-T/327)$. If $F_c = 0.6$ is employed, $k_\infty = 6.9 \times 10^{-12}$ (T/300)$^{-2.9}$ cm^3 molecule^{-1} s^{-1} is fitted.

Preferred Values

$k_\infty = 1.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 240-350 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the data of Thorn et al. (1993) which are in good agreement with the data of Sander et al. (1981) at 298 K. A temperature-independent $F_c = 0.4$ is used for representing the falloff curve which leads to the given practically temperature-independent k_∞. The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k:

=((4.7e-31*(T/300)^-3.1)*M*(1.8e-11))/((4.7e-31*(T/300)^-3.1)*M+(1.8e-11))*10^(log10(0.4)/(1+(log10((4.7e-31*(T/300)^-3.1)*M/(1.8e-11))/(0.75-1.27*log10(0.4)))^2))

The molecular density, $M = 7.243 \times 10^{21} P(bar)/T(K)$

References

Danis, R., Caralp, F., Masanet, J. and Lesclaux, R.: Chem. Phys. Lett., 167, 450, 1990.
Orlando, J. J. and Tyndall, G. S.: J. Phys. Chem., 100, 19398, 1996.

Parthiban, S. and Lee, T. J.: J. Chem. Phys., 109, 525, 1998.
Rayez, M. T. and Destriau, M.: Chem. Phys. Lett., 206, 278, 1993.
Sander, S. P., Ray, G. W. and Watson, R. T.: J. Phys. Chem., 85, 199. 1981.
Thorn, R. P., Daykin, E. P. and Wine, P. H.: Int. J. Chem. Kinet., 25, 521, 1993.