IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet iBrOx9

This data sheet updated: 25th September 2003.

$Br + Cl_2O \rightarrow BrCl + ClO$
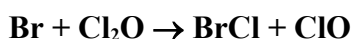
$\Delta H° = -72.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
2.1 x 10^{-11} exp[-(520 ± 260)/T]	220-298	Sander and Friedl, 1989[1]	FP-AS (a)
(3.79 ± 0.38) x 10^{-12}	298		
2.1 x 10^{-11} exp[-(435 ± 30)/T]	233-402	Stevens and Anderson, 1992[2]	DF-RF
(4.8 ± 0.2) x 10^{-12}	298		

Comments

(a) Flash photolysis (λ >300 nm) of Br$_2$ in the presence of an excess of Cl$_2$O at 130 mbar pressure of Ar. ClO radical concentrations were monitored by long-path UV absorption at 275.2 nm.

Preferred Values

$k = 4.3$ x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.1$ x 10^{-11} exp(-470/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220 K to 410 K.

Reliability
Δlog $k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
The studies of Sander and Friedl[1] and Stevens and Anderson,[2] which used totally different techniques, are in excellent agreement. The preferred values are based on the results of these two studies.[1,2] The significantly lower value (by a factor of 4) reported earlier by Basco and Dogra[3] is not used in the evaluation. In the same study, Basco and Dogra[3] reported a value for k(Cl + Cl$_2$O) more than two orders of magnitude less than that recommended in the present evaluation, suggesting errors in their method of determining the ClO radical concentration which was used to monitor the progress of the reaction.

References

[1]   S. P. Sander and R. R. Friedl, J. Phys. Chem. **93**, 4764 (1989).
[2]   P. S. Stevens and J. G. Anderson, J. Phys. Chem. **96**, 1708 (1992).
[3]   N. Basco and S. K. Dogra, Proc. Roy. Soc. London **A323**, 401 (1971).