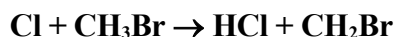


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oBrOx24; VII.A3.9

Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This data sheet last evaluated: June 2015; last change in preferred values: June 2014.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.55 \times 10^{-11} \exp[-(1070 \pm 50)/T]$	222-393.5	Gierczak et al., 1994	PLP-RF (a)
$(4.38 \pm 0.55) \times 10^{-13}$	298		
$1.66 \times 10^{-11} \exp[-(1072 \pm 46)/T]$	273-363	Kambanis et al., 1997	VLPR-MS (b)
$(4.83 \pm 0.12) \times 10^{-13}$	303		
$1.02 \times 10^{-15} T^{1.42} \exp(-605/T)$	213-697	Piety et al., 1998	PLP-RF (c)
4.5×10^{-13}	298		
<i>Relative Rate Coefficients</i>			
$1.26 \times 10^{-11} \exp(-1565/T)$	273-368	Tschuikow-Roux et al., 1988	RR (d)
6.6×10^{-14}	298		
$1.07 \times 10^{-11} \exp(-935/T)$	231-295	Orlando et al., 1996	RR (e)
4.5×10^{-13}	295		
$9.04 \times 10^{-12} \exp(-886/T)$	298-527	Gola et al., 2010	RR (f)
4.5×10^{-13}	298		

Comments

- The reaction rate coefficients were measured by generating Cl atoms via 308 nm laser photolysis of Cl_2 and measuring their temporal profiles via resonance fluorescence detection. Experiments were performed in approximately 50 Torr (66.7 mbar) of helium diluent.
- The reaction rate coefficients were measured using a very low pressure reactor, employing a microwave discharge in Cl_2 for the generation of Cl atoms with mass spectrometric detection of reactants and products. Experiments were performed in approximately 1 mTorr (1.33 mbar) of helium diluent.
- The reaction rate coefficients were measured by generating Cl atoms via 266 nm laser photolysis of Cl_2CO (or Cl_2 at 355 nm in a few experiments) and measuring their temporal profiles via resonance fluorescence detection. Experiments were performed at 161 – 697 K in 20 - 250 Torr (27 - 270 mbar) of nitrogen diluent. At temperatures in the range 161 – 177 K reversible addition of Cl atoms to give the CH_3BrCl adduct was observed. For $T \geq 213$ K where hydrogen abstraction is the dominant reaction pathway the Arrhenius expression given in the table above was obtained.
- Cl atoms were generated by the photolysis of Cl_2 at 424 nm, and the concentrations of the reactions products CH_2ClBr and CH_3Cl measured by GC. The measured rate coefficient ratio of

$k(\text{Cl} + \text{CH}_3\text{Br})/k(\text{Cl} + \text{CH}_4) = (1.91 \pm 0.09) \exp[-(325 \pm 10)/T]$ is placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).

- (e) Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. Experiments were performed in approximately 700 Torr (933 mbar) of N_2 diluent. The measured rate coefficient was placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).
- (f) Cl atoms were generated by the photolysis of Cl_2 in the 100 Torr (133 mbar) of N_2 diluent. The decays of the reactant and reference (CH_4) organic were measured by GC. The measured rate coefficient ratios were placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4.5×10^{-13}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.38 \times 10^{-11} \exp(-1020/T)$	210-300
<i>Reliability</i>		
$\Delta \log k$	0.05	298
$\Delta(E/R)$	± 100	

Comments on Preferred Values

The preferred value at 298 K is an average of the results reported by Gierczak et al., Kambanis et al., Piety et al., Orlando et al., and Gola et al. The expression for the temperature dependence is derived from the fit to the data of these studies below 300 K. The values reported by Tschuikow-Roux et al. are not used for the recommendation because they seem to be systematically higher than the results of the other measurements. At temperatures of 161 – 177 K the reaction leads to the reversible formation of the adduct CH_3BrCl . For temperatures above 213 K there is no experimental evidence for formation of the adduct and reaction proceeds via hydrogen abstraction (Piety et al., 1998; Enami et al., 2005). For temperatures above 298 K there is some disagreement between the results from Piety et al. and Gola et al. A fit of the modified Arrhenius expression to the entire data set from Gierczak et al., Kambanis et al., Piety et al., Orlando et al., and Gola et al. gives $k = 1.78 \times 10^{-17} T^2 \exp(-396/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and is recommended for $550 \text{ K} > T > 298 \text{ K}$.

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: *Atmos. Chem. Phys.*, 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>
- Enami, S., Hashimoto, S., Kawasaki, M., Nakano, Y., Ishiwata, T., Wallington, T. J.: *J. Phys. Chem. A*, 109, 1587, 2005.
- Gierczak, T., Goldfarb, L., Sueper, D. and Ravishankara, A. R.: *Int. J. Chem. Kinet.*, 26, 719, 1994.
- Gola, A.A., Sarzyński, D., Dryś, A. and Jodkowski, J.T.: *Chem. Phys. Lett.*, 486, 7, 2010.
- Kambanis, K. G., Lazarou, Y. G. and Papagiannakopoulos, P.: *J. Phys. Chem. A*, 101, 8496, 1997.
- Orlando, J. J., Tyndall, G. S., Wallington, T.J. and Dill, M.: *Int. J. Chem. Kinet.*, 28, 433, 1996.
- Piety, C. A., Soller, R., Nicovich, J. M., McKee, M. L. and Wine, P. H.: *Chem. Phys.*, 231, 155, 1998.
- Tschuikow-Roux, E., Faraji, F., Paddison, S., Niedzielski, J. and Miyokawa, K.: *J. Phys. Chem.*, 92, 1488, 1988.

