IUPAC Task Group on Atmospheric Chemical kinetic Data Evaluation – Data Sheet V.A1.50 HI50

The citation for this data sheet is: IUPAC Subcommittee for Gas Kinetic Data Evaluation, http://iupac.pole-ether.fr.
This data sheet last evaluated: February 2008; last change in preferred values: February 2008.

$BrONO_2 + H_2O$ (ice surfaces) $\rightarrow$ HOBr + HNO_3

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Experimental uptake coefficients: γ			
> 0.3	200 ± 10	Hanson and Ravishankara, 1993	CWFT-CIMS (a)
0.25 ± 0.07	190	Allanic et al., 1997	Knudsen-MS (b)
0.33 ± 0.10	200		
$1.08 \times 10^{-3} \exp[(1040 \pm 130)/T]$ (ice type 1)	180-210	Aguzzi and Rossi, 2002	Knudsen-MS (c)
$5.32 \times 10^{-4} \exp[(1125 \pm 130)/T]$ (ice type 2)			
$1.16 \times 10^{-9} \exp[(3540 \pm 130)/T]$ (ice type 3)			

Comments

(a) Ice surface prepared by vapour deposition and the geometric surface area was used to calculate the uptake coefficient. The formation of HOBr was observed as gas-phase product of the surface hydrolysis of $BrONO_2$. and displayed the same kinetics as $BrONO_2$ loss.

(b) $\approx$20 µm thick ice film made by vapour deposition and located in a Knudsen reactor operated in either continuous flow or pulsed mode. Uptake coefficients reported were from pulsed experiments which suffered less from an interference by Br_2O (formed by the reaction of $BrONO_2$ with HOBr). At the prevailing $BrONO_2$ concentrations ($\approx 1 \times 10^{11}$ molecule cm^{-3}) and reaction times, no passivation of the ice surface was observed and HOBr formation was prompt.

(c) Ice surfaces formed by vapour deposition (type 1) freezing bulk solutions of distilled water either rapidly (type 2) or slowly (type 3), the latter with the intention of forming single-crystalline ice. The temperature dependencies listed in the table were obtained by weighted, least squares fitting to tabulated data of Aguzzi and Rossi, 2002.

Preferred Values

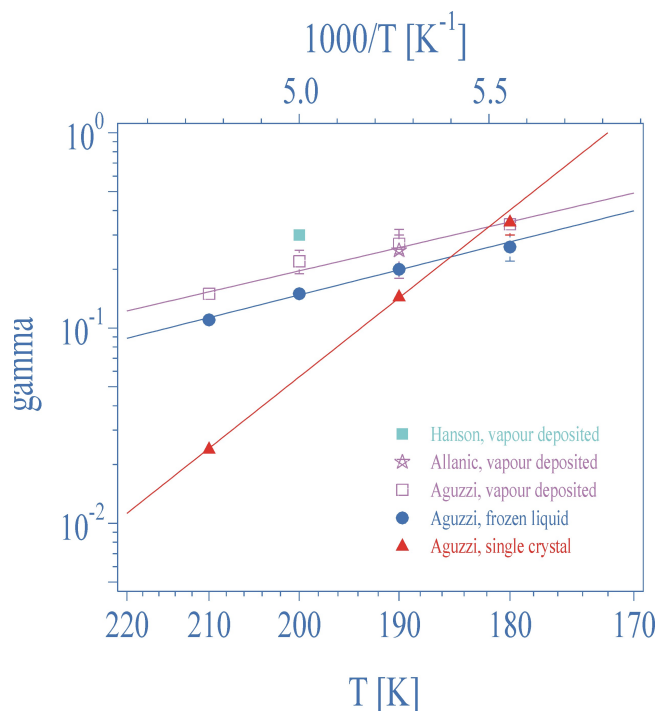| Parameter	Value	T/K
γ	$5.3 \times 10^{-4} \exp(1100/T)$	180 - 210
Reliability		
$\Delta(E/R)$ / K	± 250	210 - 250

Comments on Preferred Values

There is good agreement between the various groups (and different methods) on the uptake coefficient at 190 and 200 K. All studies agree that the reaction of $BrONO_2$ on an ice surface proceeds efficiently to form HOBr, which can be released into the gas-phase. The co-product, HNO_3, was not detected in these studies.

The most comprehensive dataset of Aguzzi et al. (2002) shows that the uptake coefficient on morphologically different ice surfaces displayed a negative dependence on temperature, indicative of a precursor mechanism in which a $H_2OBr^+ \cdot NO_3^-$ complex is formed (Gane et al., 2001; McNamara and Hillier, 2001) prior to dissociation to HOBr and HNO_3. The preferred expression for the temperature dependent uptake coefficient is that obtained by Aguzzi and Rossi (2002) obtained using ice films of type 2 (presumably polycrystalline). The assumption that the geometric surface area is equal to that available for reaction should be good for this surface and the temperature dependence is rounded down slightly. The considerably steeper temperature dependence obtained using "single crystal" ice leads to a much lower value of the uptake coefficient at higher temperatures (factor of ≈ 5), though the agreement with the type 1 and type 2 ices at 190 K is satisfactory. The yield of HOBr released to the gas-phase was close to 100 % at 200 and 210 K, decreasing to 10-20 % at lower temperatures. The "lost" HOBr was released to the gas phase when the ice film was subsequently warmed. The rate of HOBr release was reduced in the presence of nitric acid on the surface. This observation could be attributed to the reduction in surface H_2O or enhanced stabilisation of the complex when high levels of surface nitrate are present. The uptake coefficient was however found to be independent of HNO_3 adsorbed onto the ice, enabling a simple parameterisation .

References

Aguzzi, A. and Rossi, M. J.: J. Phys. Chem. A 106, 5891-5901, 2002.
Allanic, A., Oppliger, R. and Rossi, M. J.: J. Geophys. Res. 102, 23529-23541, 1997.
Gane, M. P., Williams, N. A. and Sodeau, J. R.: J. Phys. Chem. A 105, 4002-4009, 2001.
Hanson, D. R. and Raivshankara, A. R. Reactions of halogen species on ice surfaces. In *The tropospheric chemistry of ozone in the polar regions*; Niki, H., Becker, K. H., Eds.; Springer-Verlag, Berlin-Heidelberg:, 1993.
McNamara, J. P. and Hillier, I. H.: J. Phys. Chem. A 105, 7011-7024, 2001.

Uptake coefficients for $BrONO_2$ + ice. Solid lines are Arrhenius-type fits to the three data sets of Aguzzi et al. (2002).