IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.49 HI49

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$HOBr + HBr(ice) \rightarrow Br_2 + H_2O$

Uptake coefficient data

Parameter	Temp./K	Reference	Technique/Comments
Experimental uptake coefficients for HOBr: γ, γ_0			
0.12±0.03	228	Abbatt, 1994	CWFT-MS(a)
≥ 1.5	230-240	Kirchner, Benter and Schindler, 1997	CWFT-MS(b)
0.44	180	Chaix, Allanic and Rossi, 2000	Knudsen –MS (c)
0.39	185		
0.37	190		
0.305	195		
0.205	200		
0.16	205		

Comments

(a) Frozen film ice surface; [HOBr] ~ 10^{12} molecule cm^{-3}, generated in situ by reaction of Br_2 with OH. $[HBr]_o$ = (1-2) x 10^{12} molecule cm^{-3} which corresponded to a surface coverage of at least 10 formal ML at 188 K, based on the recommended K_{LinC}(data sheet V.A1.27). Gas phase Br_2 formation kinetics matched the HOBr decay. Continuous steady state uptake rate observed.

(b) Reflectron Time-of-Flight mass spectrometer used. The total pressure was in the range 5 to 20 mbar He. Ice films were produced by spraying water or aqueous solutions of HBr onto the interior walls of the cold flow tube. [HOBr] was in the range 0.7 to 1.2x10^{13} molecules cm^{-3}.

(c) Ice surfaces formed by vapour deposition (type C) freezing bulk solutions of distilled water either rapidly (type B) or slowly (type SC), the latter with the intention of forming single-crystalline ice. Water vapour was continuously added to maintain the ice films during experiments. Both pulsed-valve and continuous flow experiments were performed on the different types of HBr-doped ice samples, using two sources of HOBr. Typical flow rates of HBr used to dope the surface of ice ranged from 10^{14} to 10^{16} molecule s^{-1} leading to the deposition of 0.5 to 10 formal monolayers onto ice depending on the deposition time. In all cases the uptke of HOBr led to production of Br_2. The cited uptake coefficients are the mean of values reported for type C and type B ice surfaces at each temperature, which were very similar.

Preferred values

Parameter	Value	T/K
γ_s(HOBr)	4.8 x 10^{-4}exp(1240/T)	180 – 230

Reliability

$\Delta \log(\gamma_{ER})$	±0.15	185 – 210

Comments on preferred values

All studies report rapid and continuous uptake of HOBr onto ice films doped with gaseous HBr. Under the conditions of these experiments both HBr and HOBr form stable hydrates on ice surfaces and no dependence of γ(HOBr) on [HBr] wasfound. Br_2 is the sole product observed. The reported γ values in the temperature range 180 – 228 K are in reasonably consistent and show a negative temperature dependence. The recommended expression for γ_{max}, is an Arrhenius fit to the data of Abbatt at 229 K and the mean of the values reported by Chaix et al. on vapour-deposited and frozen film ice at each temperature in the range 180 – 205 K. These values can be assumed to be independent of [HBr] provided $[HBr]_o > [HOBr]_o$.

References

Abbatt, J.P.D.: Geophys. Res. Lett. 21, 665 (1994).
Chaix, L., Allanic, A. and Rossi, M.J.: J. Phys. Chem. A 104, 7268 (2000).
Kirchner, U., Benter, Th. and Schindler, R.N.: Ber. Bunsenges. Phys. Chem. 101, 975 (1997).

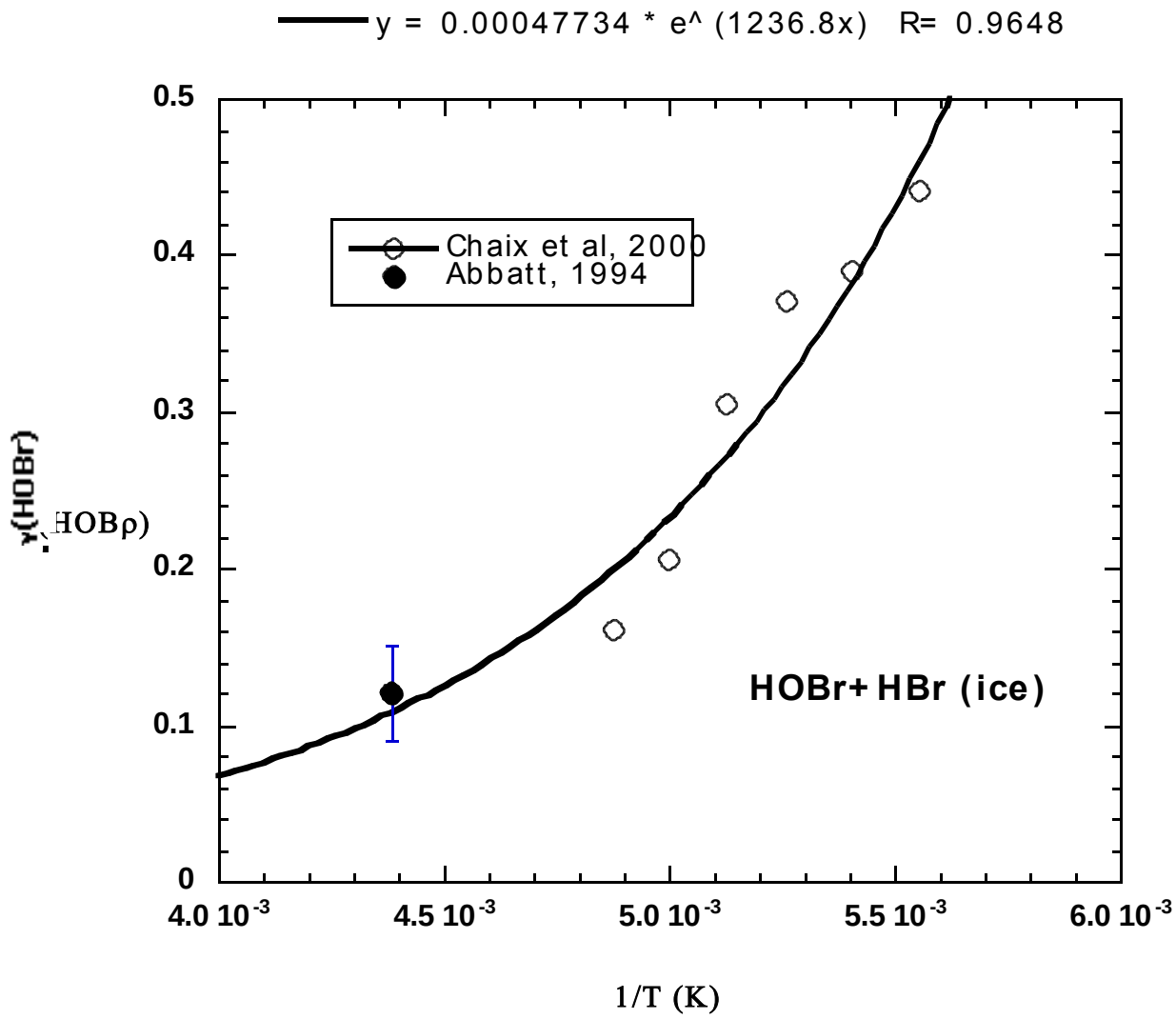

Figure 1 Arrehius plot of uptake coefficient for HOBr on ice doped with HBr