IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.48 HI48

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HOBr + HCl(ice) → BrCl + H_2O

Uptake coefficient data

Parameter	Temp./K	Reference	Technique/Comments
Experimental uptake coefficients: γ, γ_0			
0.25 (+0.10/-0.05)	228	Abbatt, 1994	CWFT-MS(a)
$(3.3\pm0.5)\times10^{-1}$	190	Allanic, Oppliger and Rossi, 1997	Knudsen –MS (b)
$(2.3\pm0.2)\times10^{-1}$	200		
5×10^{-2} – pHCl = 1.8×10^{-7} mbar	190	Chu and Chu, 1999	CWFT-MS (c)
0.23 – pHCl = 1.2×10^{-5} mbar			
4×10^{-3} – pHCl = 5.6×10^{-7} mbar	222		
0.19 – pHCl = 2×10^{-5} mbar			
0.3±0.05	180-195	Chaix, Allanic and Rossi, 2000	Knudsen –MS (b)
>0.1 ; [HCl] = 8×10^{11}	205-227	Mössinger, Hynes and Cox, 2002	CWFT-MS (e)
γ_{ss}= 0.005±0.002 ; $[HCl]_o = 5.8\times10^{11}$	227		

Comments

(a) Frozen film ice surface; [HOBr] ~ 10^{12} molecule cm^{-3}, generated in situ by reaction of Br_2 with OH. $[HCl]_o$ = (1-2) x 10^{12} molecule cm^{-3} which corresponded to a fractional surface coverage of >0.95 at 228 K, based on the recommended K_{LinC}(data sheet V.A1.27). Gas phase BrCl formation kinetics matched the HOBr decay.

(b) ≈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 cited obtained at short (0.3 s) residence time avoiding saturation effects. P_{HCl} used was sufficient to give at least 1 ML coverage and all HOBr taken up was converted to BrCl, demonstrating effective competition of HCl surface reaction with uptake of HOBr into the ice film.

(c) The ice film of typical thickness of 28 μm was grown from H_2O vapor condensation in the temperature range 190 to 240 K. Uptake coefficients were determined from HOBr loss and BrCl formation, giving comparable values. Both γHOBr amd γBrCl decreased substantially with decreasing P_{HCl} from 2×10^{-5} mbar down to 2×10^{-7}.

(d) 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 add to maintain the ice films during experiments. Both pulsed-valve and continuous flow experiments were performed on the different types of HX-doped ice samples, using two sources of HOBr. Typical flow rates of HX 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 of HX onto ice depending on the deposition time. In all cases the uptke of HOBr led to rapid and quantitative production of BrCl with the cited uptake coefficient.

(e) The ice coating was produced by freezing a liquid H_2O film and HOBr was stored as an aqueous solution at 273K. [HOBr] and [HCl] varied between (2–22)x10^{11} and (4-8)x10^{11} molecule cm^{-3}, respectively. The lower limit of γ>0.1 reflects diffusion limited uptake. For [HCl]< [HOBr] the HOBr uptake was time- and concentration dependent owing to the changing HCl surface coverage. BrCl was observed as product. Evidence for an Ely Rideal mechanism was presented.

Preferred values

Parameter	Value	T/K
γ_{ER}(HOBr)	0.25	185 – 210

Reliability		
$\Delta(\gamma_{ER})$	±0.05	185 – 210 K.

Comments on preferred values

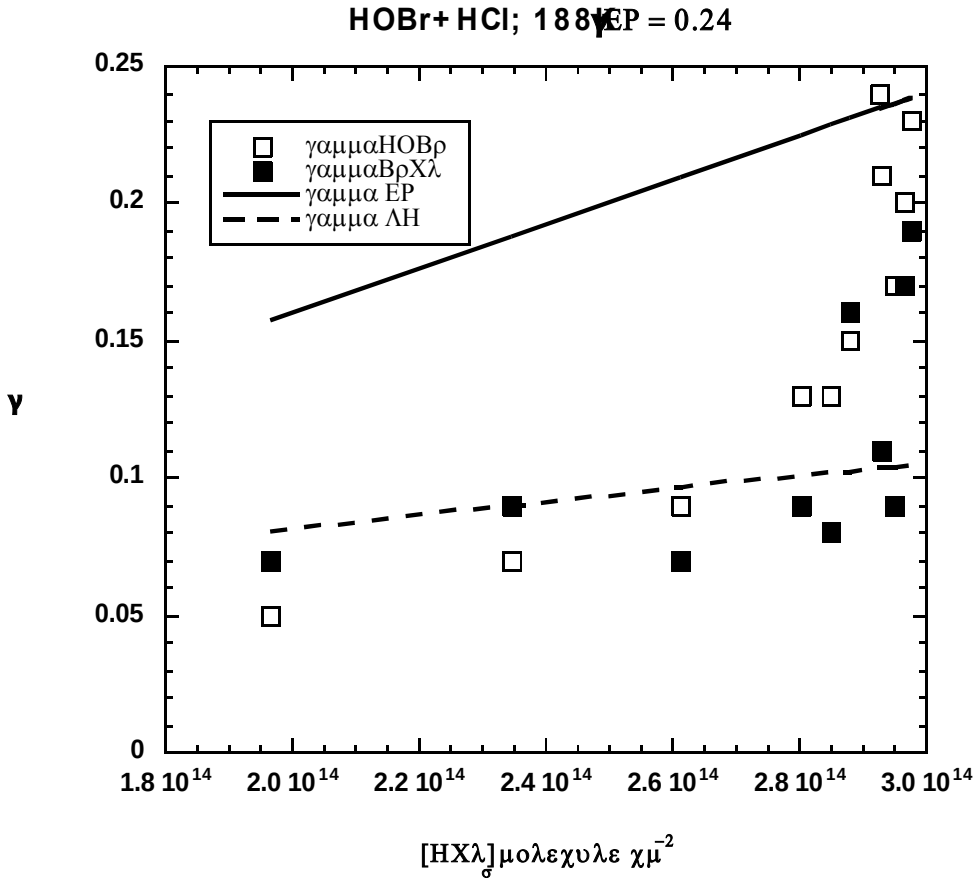
All studies report rapid uptake of HOBr onto ice films doped with HCl. BrCl is the sole product with a yield of 100%. The conditions of these experiments mostly corresponded to near maximum coverage of HCl in the ice or HCl hydrate stability region. The reported maximum values of γ at high [HCl] in the temperature range 180 – 228 K are in reasonably good agreement, with a slight tendency to increase with decreasing temperature. We recommend a temperature independent value of γ_{max}, which is a mean of the values obtained from all studies cited and the T range is extended to 220 K.

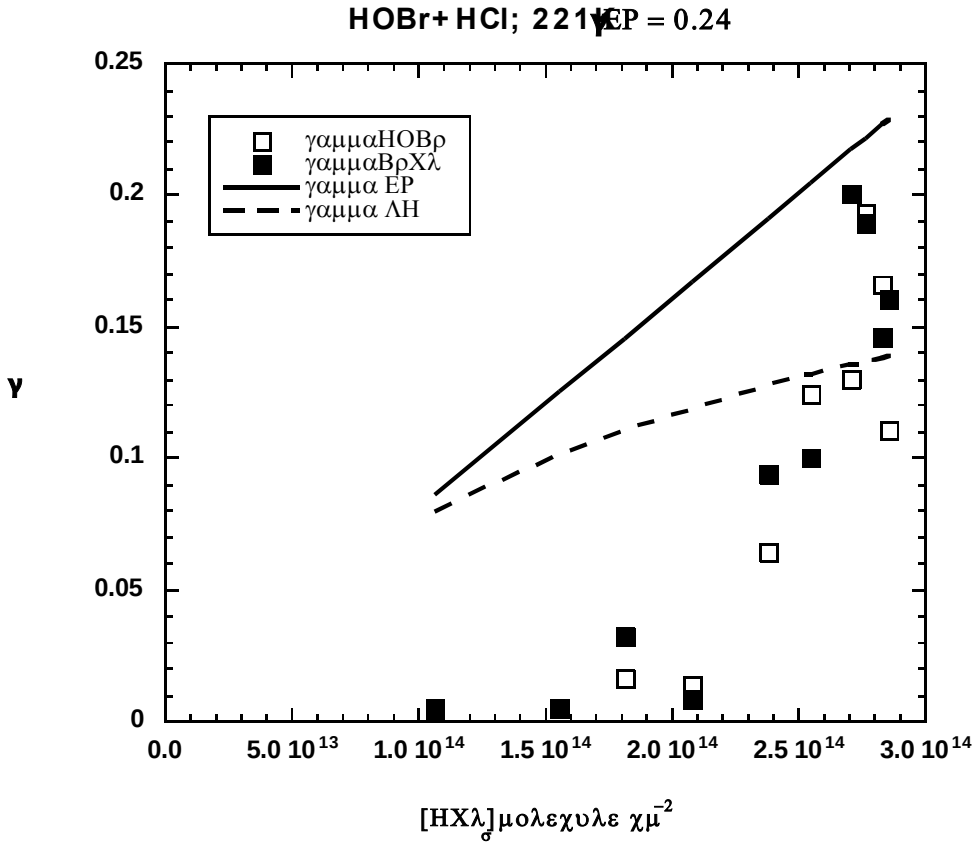
The study of Chu and Chu (1999) observed a dependence of the uptake coefficient on initial [HCl] and Mossinger et al. (2002) found evidence for surface coverage dependence of the uptake coefficient when initial [HOBr] was in excess of [HCl], leading significant HCl consumption. The kinetic dependence in both studies appears to be complex and the data are not well fitted by either an Ely-Rideal and Langmuir Hinshelwood mechanism. Fig 1 & 2 show fits to the data for HCl dependence reported by Chu and Chu (1999). In particular neither model captures the observed fall-off in γ with initial p(HCl) assuming that surface coverage of HCl is given by the recommended IUPAC value of the [HCl] partition coefficient with N_{max} = 3 x 10^{14} molecule cm^{-3}. This probably results from reagent depletion due to the surface reaction. Therefore we cannot recommend a reactive uptake coefficient for HOCl as a function of $[HCl]_g$

References

Abbatt, J.P.D.: Geophys. Res. Lett. 21, 665 (1994).

Allanic, A., Oppliger, R. and Rossi, M.J.: J. Geophys. Res. 102D, 23529 (1997).
Chaix, L., Allanic, A. and Rossi, M.J.: J. Phys. Chem. A 104, 7268 (2000).
Chu, L. and Chu, L.T.: J. Phys. Chem. A 103, 8640 (1999).
Mössinger, J.C., Hynes, R.G. and Cox, R.A.; J. Geophys. Res. 107, art. No. 4740 (2002), doi:10.1029/2002JD002151.


HOBr+ HCl; 188 K
γ EP = 0.24
γαμμαΗΟΒρ
γαμμαΒρΧλ
γαμμα ΕΡ
γαμμα ΛΗ
γ
0.25
0.2
0.15
0.1
0.05
0
1.8 10^14
2.0 10^14
2.2 10^14
2.4 10^14
2.6 10^14
2.8 10^14
3.0 10^14
[ΗΧλ]μολεχυλε χμ^-2
σ


HOBr+ HCl; 221 K
γ EP = 0.24
γαμμαΗΟΒρ
γαμμαΒρΧλ
γαμμα ΕΡ
γαμμα ΛΗ
γ
0.25
0.2
0.15
0.1
0.05
0
0.0
5.0 10^13
1.0 10^14
1.5 10^14
2.0 10^14
2.5 10^14
3.0 10^14
[ΗΧλ]μολεχυλε χμ^-2
σ