IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A4.9 HNDT9

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HCl + NAT

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Experimental uptake coefficients: γ, γ₀			
$\gamma > 0.2$	202	Abbatt and Molina, 1992	CWFT-MS (a)
Partition coefficients: K(cm)			
27.5 (at $p_{H2O} = 6.7 \times 10^{-4}$ mb)	202	Abbatt and Molina, 1992	CWFT-MS (a)
534 (at $p_{H2O} = 16.6 \times 10^{-4}$ mb)			
3×10^4 (at $p_{H2O} \sim 3 \times 10^{-4}$ mb)	191	Hanson & Ravishankara, 1992	CWFT-CIMS (b)
2.57×10^4 (at $p_{H2O} = 1 \times 10^{-4}$ mb)	188	Chu, Leu and Keyser, 1993	CWFT-MS (c)

Comments

(a) The NAT films were prepared from 10 μm thick ice films exposed to ~1 x 10⁻⁴ mbar HNO₃ to form a NAT layer a few μm thick on top of the ice film. p_{H2O} was varied to provide water-rich or HNO₃-rich NAT films. At $p_{HCl} = (0.67 - 14) \times 10^{-5}$ mbar the HCl uptake is reversible and saturates, the amount adsorbed increasing with p_{HCl} and p_{H2O}. At higher p_{HCl} (>2 x 10⁻⁴ mbar) irreversible uptake occurs above a threshold value which depends on p_{H2O}, suggested due to formation of a liquid surface by HCl. The cited uptake coefficient refers to these conditions. The surface coverage increased from 0.05 to 1.7 x 10¹⁴ molecules cm⁻² in the reversible adsorption region depending on p_{HCl} and p_{H2O} The value of K_{linC} at low $p_{H2O} = 6.7 \times 10^{-4}$ mb was obtained from a linear plot of surface coverage against [HCl]. At higher p_{H2O} and fixed [HCl] (= 2.3 x 10¹⁰ molecules cm⁻³) partition coefficients were calculated from observed surface coverages assuming $N_{max} = 3 \times 10^{14}$ molecules cm⁻².

(b) The NAT films were prepared from 10 μm thick ice films exposed to HNO₃. p_{H2O} was set at the ice pressure which provided water-rich NAT films. [HCl] ~ 1 x 10¹⁰ molecules cm⁻³. The HCl uptake is reported to be reversible and saturates at a surface coverage of (2 - 3) x 10¹⁴ molecules cm⁻², which was 50±10% of the coverage achieved on ice at the same [HCl]. No dependence on p_{HCl} is given, but the partition constant is calculated assuming $N_{max} = 3 \times 10^{14}$ molecules cm⁻² and a fractional surface coverage of $\theta = 0.5$ (1.5 x 10¹⁴ molecules cm⁻²) at [HCl] = 1 x 10¹⁰ molecules cm⁻³.

(c) The NAT films were prepared by freezing vapours from 54% aqueous HNO3 solutions at 188K. They consistedof a mixture of NAT and water ice and were ~1.6 μm thick. p_{H2O} was set at the ice pressure which provided water-rich NAT films. Uptake was fully reversible at low [H_2O]/[HNO_3] and increased with p_{H2O}. Partition coefficient calculated from the surface coverage of ~2 x 10^{14} molecules cm^{-2} at [HCl] = 2.33 x 10^{10} molecules cm^{-3} assuming N_{max} = 3 x 10^{14} molecules cm^{-2}.

Preferred Values

Parameter	Value	T/K
α_s	0.3	190 - 210
N_{max} / molecule cm^{-2}	3 x 10^{14}	190 - 230
K_{LinC} / cm	3 x 10^{4}	191
Reliability		
$\Delta \log (\alpha_s)$	± 0.3	190 - 210
$\Delta (K_{LinC})$ / cm	± 0.3	205 - 230

Comments on Preferred Values

The three studies which addressed uptake of HCl on NAT surfaces show that uptake is strongly dependent on the state of the NAT surface, and in particular the water vapour partial pressure. At low [HCl] on HNO_3-rich NAT films (low p_{H2O}) uptake is reversible, saturates and is much weaker than on water ice surfaces. However H_2O-rich NAT films take up HCl in amounts similar to water ice surfaces. At high p_{HCl} (> 1.33 x 10^{-4} mb) very much greater uptake by both H_2O-rich and HNO_3-rich NAT films is observed, which is indicates surface melting occurs in these cases.

Only the study of Abbatt and Molina using HNO_3-rich NAT films showed an [HCl] dependence of uptake that could be used to derive partition coefficients at low coverage. Their data (*taken from Fig 4 of Abbatt and Molina, 1992*) is plotted in Fig 1, was used to obtain the cited value of K_{linC}. At higher surface coverages partition coefficients were calculated from observed surface coverages assuming N_{max} = 3 x 10^{14} molecules cm^{-2} The K_{linC} values as a function of p_{H2O} (*obtained from data in Fig 4 of Abbatt and Molina, 1992*) were fitted to a power law function : K_{linC} = 3.75 x 10^{12} x $(p_{H2O})^{3.73}$ The extrapolated value at p_{H2O} = 0.0017 (ice vapour pressure at 202 K) is K_{linC} =1.75 x 10^{3} cm, which is substantially lower than that for HCl uptake on water ice at this temperature, ~3.0 x 10^{4} cm. The K_{linC} values calculated from uptakes on H_2O-rich NAT films observed by Hanson and Ravishankara and Chu et al. at lower temperatures were in reasonable agreement, and are only a factor of 2 or so lower than they observed on ice at the same conditions. There appears to be some inconsistency in the results at this stage, which may arise from complications from using the higher [HCl] used by Abbatt and Molina. We make a recommendation for K_{linC} only at 191 K for H_2O-rich NAT films based on the results of Hanson and Ravishankara (1992). The temperature dependence for partition coefficients for HCl on H_2O-rich NAT is likely to be similar to that on ice.

References

Abbatt, J.P.D. and Molina, M.J.: J. Phys. Chem. 96, 7674 (1992).

Chu, L.T., Leu, M.-T. and Keyser, L.F.: J. Phys. Chem. 97, 7779 (1993).
Hanson, D.R. and Ravishankara, A.R.: J. Phys. Chem. 96, 2682 (1992).

Fig 1 Plot of p(H$_2$O) dependence of K_{linC} derived from surface coverages measured at 202K (Abbatt and Molina, 1992)

HCl+NAT_202K_PH2Odep

y = 3.7548e+13 * x^ (3.7313)   R= 0.99267