IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.46 HI46

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$N_2O_5 + HCl\ (ice) \rightarrow ClNO_2 + HNO_3$

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Experimental uptake coefficients: γ			
0.028 (HCl mole fraction = 0)	195	Leu, 1988	CWFT-MS (a)
0.037 (HCl mole fraction = 0.015)			
0.063 (HCl mole fraction = 0.04)			
> 1 x 10^{-3}	185	Tolbert et al., 1988	Knudsen-MS (b)
0.0048-0.035	200	Seisel *et al.*, 1998	Knudsen-MS (c)

Comments

(a) Flow reactor at 0.36 - 0.67 mbar. The HCl containing ice film was made by vapour deposition of both gases simultaneously, resulting in HCl mole fractions of 0.015 and 0.04. N_2O_5 (initial concentration ≈ 1x10^{13} molecule cm^{-3}) detected as its NO_2^+ ion-fragment (electron impact ionisation). γ was calculated using the geometric ice surface area.

(b) The HCl containing ice film was made by vapour deposition of both gases simultaneously, resulting in HCl mole fractions of 0.07 and 0.14. N_2O_5 (initial concentration ≈ 10^{13} molecule cm^{-3}) detected as its NO^+ and NO_2^+ ion-fragments. The uptake coefficient (calculated using geometric ice surface area) is suggested to be a lower limit due to the non specific detection of N_2O_5.

(c) Uptake of N_2O_5 to ice made by vapour deposition or frozen solutions. HCl flows were varied, the concentrations were not reported by the authors. Calculations using Knudsen reactor parameters and escape rate for N_2O_5 show that the HCl concentrations were between ≈ 10^{11} and 10^{12} molecule cm^{-3}.

Preferred Values

no recommendation

Comments on Preferred Values

Leu (1988) combined the two experimental values of γ on HCl-ice with his own data on a pure ice surface to show a distinct trend in γ with HCl mole fraction. As the surface concentration of HCl is unknown in these experiments, the dependence of γ on [HCl] (gas phase) can not be extracted from the dataset. Despite the use of larger HCl mole fractions, the uptake coefficients quoted by Tolbert et al. (1988) are significantly lower than the values of Leu et al. Both Leu et al., (1988) and Tolbert et al. (1988) detected $ClNO_2$ as product, but did not quantify the yield.

Seisel *et al.* (1998) found that small amounts of HCl increased the N_2O_5 uptake coefficient slightly, the results in qualitative agreement with those of Leu (1988). At high concentrations of HCl (which induced surface melting) the uptake coefficient increased as did the yield of $ClNO_2$. The use in these studies of high concentrations of N_2O_5 and HCl and low temperatures, and the fact that N_2O_5 may hydrolyse to HNO_3 makes assessment of the true thermodynamic state of the surface difficult. However, it appears that atmospheric concentrations of HCl will not significantly affect the rate of uptake of N_2O_5 to an ice surface.
The production of $ClNO_2$ could not be confirmed in the studies of Sodeau et al. (2000), who co-deposited H_2O, N_2O_5 and HCl at 85 K and analysed the surface using RAIRS.

References

Leu, M. T.: Geophys. Res. Lett. 15, 851-854, 1988.
Sodeau, J. R., Roddis, T. B. and Gane, M. P.: J. Phys. Chem. A 104, 1890-1897, 2000.
Tolbert, M. A., Rossi, M. J., and Golden, D. M.: Science, 240, 1018-1021, 1988.