IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet V.A1.14 HI14

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N_2O_5 + ice

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Experimental uptake coefficients: γ, γ_{ss}			
$\gamma = 0.028 \pm 0.011$	195	Leu, 1988	CWFT-MS (a)
$\gamma > 1 \times 10^{-3}$	185	Tolbert et al., 1988	Knudsen-MS (b)
$\gamma = 0.034 \pm 0.008$	188	Quinlan et al., 1990	Knudsen-MS (c)
$\gamma = 0.023 \pm 0.008$			
$\gamma = 0.024 \pm 0.007$	201	Hanson and Ravishankara, 1991	CWFT-CIMS (d)
$\gamma = 0.01 - 0.02$	191	Hanson and Ravishankara, 1992, 1993	CWFT-CIMS (e)
$\gamma = 0.02 \pm 0.002$	200	Seisel et al., 1998	Knudsen-MS (f)
$\gamma_{ss} = (7 \pm 3) \times 10^{-4}$	185	Zondlo et al., 1998	Knudsen-MS/FTIR (g)

Comments

(a) Flow reactor at 0.36 - 0.67 mbar. The ice film was made by vapour deposition. N_2O_5 (initial concentration $\approx 1 \times 10^{13}$ molecule cm^{-3}) detected as its NO_2^+ ion-fragment. HNO_3 found to build up on the surface. γ calculated using geometric ice surface area.

(b) N_2O_5 (initial concentration $\approx 10^{13}$ molecule cm^{-3}) detected as its NO^+ and NO_2^+ ion-fragments. Surface adsorbed HNO_3 (reaction product) was detected by thermal desorption spectrometry. Coincidence of fragment ions from HNO_3 (reaction product) and N_2O_5 enabled only an upper limit to the uptake coefficient (calculated using geometric ice surface area) to be determined.

(c) N_2O_5 (initial concentration $\approx 10^{13}$ molecule cm^{-3}) detected as its NO^+ and NO_2^+ ion-fragments. Gas-phase HNO_3 reaction product was detected following thermal desorption, TD, as its HNO_3^+, NO^+ and NO_2^+ ion-fragments. γ (calculated using geometric ice surface area) showed a pronounced time dependence, maximising after several seconds of exposure, and then decreasing again. The value of γ quoted in the Table is the maximum value observed. The two values quoted represent results obtained on ice made from freezing a bulk solution (0.034 ± 0.008) or vapour deposited ice (0.023 ± 0.008). The TD yield of HNO_3 was found to match the amount of N_2O_5 lost to the surface (3-7 x 10^{16} cm^{-2}), suggesting that the uptake is purely reactive.

(d) Low initial N_2O_5 concentration (10^9-10^{10} molecule cm^{-3}) measured using I$^-$ chemi-ionisation. The 7-15 μm thick ice film was made by vapour deposition. Deactivation of the surface was seen to take place during exposures of several minutes duration. γ was calculated from first-order decay constants at low exposure times, using the geometric surface area of the ice.

(e) Same experimental procedure as (d), but with the ice film thickness varied between ≈ 1 and 40 μm. γ was found to vary between ≈ 0.01 and 0.02.

(f) The ice surface was formed by either vapour deposition or by freezing liquid water. The N_2O_5 concentration was 1.5×10^{11} molecule cm^{-3}.

(g) The ice surface was formed by vapour deposition, $[N_2O_5]$ was varied between $\approx 2 \times 10^{10}$ and 3×10^{11} molecule cm^{-3}. The uptake coefficient reported represents a steady-state value, presumably for an HNO_3 contaminated ice surface. Surface analysis was performed using reflection-absorption infra-red spectroscopy and revealed the presence of H_3O^+ and NO_3^- ions in an H_2O / HNO_3 amorphous solution at 185 K and the loss of crystalline structure of the ice.

Preferred Values

Parameter	Value	T/K
γ	0.02	190 - 200

Reliability

$\Delta \log (\gamma)$	± 0.15	190 - 200

Comments on Preferred Values

The preferred value of γ is taken from the works of Hanson and Ravishankara (1991, 1992, 1993) who used very low N_2O_5 concentrations, and applies to a pure (i.e. non passivated) ice surface. The less detailed study of Seisel et al. (1998) at 200 K is in accord with this recommendation. Hanson and Ravishankara (1991) observed deactivation of the surface after a few minutes of exposure to N_2O_5, whereas Quinlan et al (1990) observed increasing reactivity with time. This is most likely due to the use by Quinlan et al. (1990) of high concentrations of N_2O_5 at the surface, causing surface melting by HNO_3.

Evidence for an efficient hydrolysis of N_2O_5 to HNO_3 (probably present mainly in ionised form at the surface) is provided by the observation of surface deactivation for N_2O_5 uptake (Hanson and Ravishankara, 1991), thermal desorption experiments Quinlan et al. (1990) and infrared surface analysis of ions such as NO_3^- and H_3O^+ (Zondlo et al, 1998; Horn et al., 1994; Koch et al., 1997). At appropriate combinations of N_2O_5 concentration and temperature, NAT is formed (Hanson and Ravishankara, 1991).

References

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