Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A5.15 HNDT15

N_2O_5 + HCl (NAT) → products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
γ			
3.2×10^{-3}	200	Hanson and Ravishankara, 1991	CWFT-CIMS (a)

Comments

(a) Ice surfaces (7-15 μm thick) were made by vapour deposition and doped with HNO_3 formed during the N_2O_5 uptake (the amount of HNO_3 was not given). The geometric surface area was used to calculate the uptake coefficient. Experiments were conducted with [N_2O_5] and [HCl] at $\approx 10^9 - 10^{10}$ molecule cm^{-3}. HCl was generally in excess, but first oder loss of N_2O_5 was still observed when [N_2O_5] / [HCl] = 2. Variation of [N_2O_5] over a factor of 10 did not change the uptake coefficient, a dependence of γ on [HCl] was not reported.

Preferred Values

Parameter	Value	T/K
γ_{gs}	4×10^{-3}	190 - 210 K
θ_{HCl}	7.3×10^{-17} exp(2858/T) [HCl] / (7.3×10^{-17} exp(2858/T) [HCl] +1)	190 - 210 K

Reliability

$\Delta \log(\gamma)$	0.5	190 - 210 K

Comments on Preferred Value

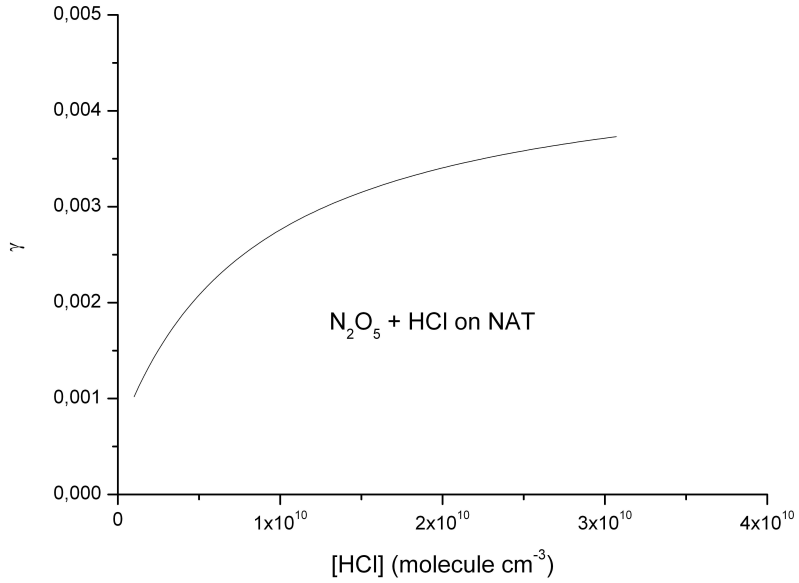
The single study (Hanson and Ravishankara, 1991) of the reaction of N_2O_5 and HCl on a NAT surface shows that the N_2O_5 uptake proceeds more efficiently than on NAT alone (for which a value of $\gamma = 6 \times 10^{-4}$ was obtained), indicating that a surface reaction tkes place presumably to form HNO_3 and $ClNO_2$, though these products were not seen. Application of the reported value of γ to the atmosphere requires parameterisation of the HCl surface coverage on NAT. We assume that this is the same as for pure ice to derive the expression for θ_{HCl} (see HCl + ice datasheet), which can be combined with a value of γ_{gs} of 4×10^{-3} to give net uptake coefficients in line with those observed by Hanson and Ravishankara, 1991.

$\gamma = \gamma_{gs}\theta_{HCl} + 6 \times 10^{-4}$

This expression assumes that the reaction is driven by the availability of surface HCl and the temperature dependence is controlled only by HCl coverage. As HCl $\rightarrow$ 0, the uptake coefficient should approach than on pure NAT (i.e. 6×10^{-4}). The ratio of $ClNO_2$ formation to the overall uptake is given by (γ - 6×10^{-4}) / γ .

References

Hanson, D. R. and Ravishankara, A. R.: J. Geophys. Res. 96, 5081-5090, 1991.



Uptake coefficients for N_2O_5 reaction on a HCl doped NAT surface according to the expression given in the datasheet. The single experimental dataset is consistent with this parameterisation, but does not confirm it.