

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A5.13 HNNT13

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Uptake coefficient data

| Parameter | Temp/K | Reference | Comment |
|---|--------|-------------------------------|--------------|
| <i>Uptake Coefficients(ClONO₂)</i> | | | |
| 0.3(+0.7, -0.1) | | Hanson and Ravishankara, 1991 | CWFT-CIMS(a) |
| 0.27±0.04 | 196 | Leu, Moore and Keyser, 1991 | CWFT-MS(b) |
| 0.3(+0.7, -0.1) | 191 | Hanson and Ravishankara, 1992 | CWFT-CIMS(c) |
| $\gamma_{ss} \geq 0.20$ 100% RH | 202 | Abbatt and Molina, 1992 | CWFT-MS(d) |
| $\gamma_{ss} = (3.0 \pm 1.0) \times 10^{-3}$ 25% RH | | | |
| $\gamma_{ss} = 0.23$ ($p_{\text{HCl}} = 6.7 \times 10^{-8}$ mbar) | 190 | Hanson and Ravishankara, 1993 | CWFT-CIMS(e) |
| 90% RH | 190 | | |
| $\gamma_{ss} = 0.20$ ($p_{\text{HCl}} \sim 4.6 \times 10^{-7}$ mbar) | 197 | | |
| 90%RH | | | |
| $\gamma_{ss} = 0.03$ ($p_{\text{HCl}} \sim 4.6 \times 10^{-7}$ mbar) | | | |
| 30%RH | | | |

Comments

- (a) Vapour deposited ice; NAT was prepared in situ by converting N₂O₅ into HNO₃ on the ice surface well past saturation. The HNO₃ vapor detected at the downstream end of the flow tube was consistent within a factor of two with the expected vapor pressure over NAT/ HNO₃ in ice solid solution near 201K. $[\text{HCl}]_0 = 2 \times [\text{ClONO}_2]_0$, i.e. $\sim 0.4\text{-}1.2 \times 10^{10}$ molecule cm⁻³.
- (b) The films, typically 70 μm thick, were prepared in situ by vapour condensation of HNO₃ and H₂O at 196K. Initial $p_{\text{HCl}} = 0.27$ to 2.7×10^{-3} mbar, $P_{\text{ClONO}_2} = 10.6 \times 10^{-5}$ mbar. The measured values of γ were independent of the composition of HNO₃/NAT in the range 41.8 to 60.4% and of the HCl content (0.0375% to 3.91% HCl). The authors give a corrected value of $\gamma = 0.10 \pm 0.02$ if pore diffusion is taken into account.
- (c) Details under (a). The uptake of ClONO₂, HCl and the formation of the reaction product Cl₂ were studied at constant HCl concentration (10^{10} molecule cm⁻³) and varying ClONO₂ concentration ranging from $0.6\text{-}3.0 \times 10^{10}$ molecule cm⁻³. The authors argue in favor of a direct

reaction between ClONO₂ and HCl rather than a reaction via the intermediate HOCl in view of the high value for γ .

- (d) The NAT films were prepared starting from 10 μm thick ice films exposed to small pressures of HNO₃ over long periods of time resulting in a 0.1 μm thick NAT layer on top of the ice film. pressure of ClONO₂ ranging from 1.3 to 12 $\times 10^{-6}$ mbar and HCl ranging from 5.3 to 13.3 $\times 10^{-6}$ mbar. A factor of four increase in γ (from 0.01 to 0.04) was noted when p_{HCl} increased from 2 to 10.6 $\times 10^{-6}$ mbar.
- (e) Details under (a and c). A 0.05 mm thick NAT film was grown on a 0.5 mm thick H₂O ice undercoat by flowing HNO₃ at 1.3 $\times 10^{-6}$ mbar. Subsequently the ice undercoat was evaporated. $p(\text{H}_2\text{O})$ added to He flow to adjust relative humidity over the film. γ decreased strongly with decreasing relative humidity which was varied by adjusting the temperature of the frozen phase at a constant H₂O flow rate of 3.3 $\times 10^{-4}$ mbar. γ given by the expression: $1/\gamma = 1/\gamma_{\text{max}} + 1/A\exp(b\Delta T)$ where ΔT is (T-190), the difference between the temperature of interest and the ice point temperature at which RH is 100% at the chosen flow rate of H₂O (RH=100 $\times p_{\text{H}_2\text{O}}/p_{\text{ice}}(T)$). For $p_{\text{HCl}} \approx 6.7 \times 10^{-8}$ mbar and $\approx 4.6 \times 10^{-7}$ mbar ([HCl] (2.5 and 17.5 $\times 10^9$ molecule cm^{-3} at 195 K), $\gamma_{\text{max}} = 0.23$ and 0.20, A=0.7022 and 2.2543, b = -0.518 and -0.558 respectively.

Preferred values

| Parameter | Value | | Temp/K |
|------------------------------------|---|----------------------|--------------|
| γ_{rxn} | $[1/\gamma_{\text{max}} + 1/A\exp(B\Delta T)]^{-1}$ | | 190 -200 |
| $p_{\text{H}_2\text{O}}$ (mbar) | 3.3×10^{-4} | | (RH=20-100%) |
| ΔT (K) | T - 190 | | |
| p_{HCl} (mbar) | 6.7×10^{-8} | 4.6×10^{-7} | |
| γ_{max} | 0.25 | 0.20 | |
| A | 0.7022 | 2.2543 | |
| B | -0.518 | -0.558 | |
| <i>Reliability</i> | | | |
| $\Delta \log(\gamma_{\text{rxn}})$ | ± 0.3 | | 190 – 200 K. |

Comments on Preferred Values

As with ice films the uptake of ClONO₂ on NAT films in the presence of HCl is followed by reaction to form Cl₂ and HNO₃ in a surface reaction. At stratospheric temperatures Cl₂ partitions into the gas phase, but HNO₃ remains at the surface with formation of hydrates. The uptake coefficients of ClONO₂ in the presence of HCl on H₂O-rich NAT substrates are similar to those on pure ice, but show a strong dependence on relative humidity. Thus γ decreases with decreasing $p(\text{H}_2\text{O})$ and decreases with increasing temperature at fixed $p(\text{H}_2\text{O})$. This reflects the amounts of surface-adsorbed water and reactants, and leads to a complex dependence of γ with conditions.

Uptake coefficients measured on water-rich NAT (100% rh) from the different studies agree quite well. At lower RH there is more variability. Only Hanson and Ravishankara and Abbatt and Molina did a systematic study of the water dependence; in the former study RH was varied by changing T at constant $p(\text{H}_2\text{O})$ and they observed less dependence of γ compared to Abbatt

and Molina who varied $p(\text{H}_2\text{O})$ at constant T ; the latter used higher reactant concentrations which could have led to more influence of HNO_3 product, reducing surface water availability. On H_2O -rich NAT substrates Hanson and Ravishankara observed that γ increases slowly with p_{HCl} in the range $\approx (0.5-5) \times 10^{-7}$ mbar, which is consistent with the high fractional surface coverage for HCl ($\theta \approx 0.33$) for these conditions. At lower RH and higher $[\text{HCl}]$, Abbatt and Molina observed much stronger dependence of p_{HCl} in the range $\approx (2-10) \times 10^{-6}$

The preferred values for the reactive uptake coefficient on NAT under stratospheric conditions are given by the parameterisation of Hanson & Ravishankara (1993), which gives the reactive uptake coefficient for specified $[\text{HCl}]$ and fixed $p(\text{H}_2\text{O}) = 3.3 \times 10^{-4}$ mbar, as a function of temperature in the range 190 -200 K. This corresponds to RH in the range 20-100%.

In view of the complex dependence of the uptake coefficient on the state of the HNO_3 -rich surfaces, and the lack of consistency in the reported data for these conditions, no recommendation is made for γ at lower $[\text{HCl}]$ and absolute humidity. For uptake on NAT surfaces with at lower $[\text{HCl}]$ and absolute humidity in the NAT stability region, a parameterisation for γ using a Langmuir-Hinshelwood model such as used for $\text{ClONO}_2 + \text{HCl}$ on ice (IUPAC, 2009), would require a better definition of the surface concentration of water and HCl on NAT than is available at present.

References

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Figure 1. The dependence of the steady-state uptake coefficient of ClONO₂ on NAT surfaces as a function of temperature range 190 – 200 K. Prediction for p(HCl) = 6.7x10⁻⁸ mbar and ≈ 4.6 x10⁻⁷ mbar

