# Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A5.13 HNDT13

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## $ClONO_2 + HCl (NAT) \rightarrow HNO_3 + Cl_2$

### Uptake coefficient data

| Parameter | Temp/K | Reference | Comment |
|---|---|---|---|
| *Uptake Coefficients( $ClONO_2$)* | | | |
| 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) |
| $\gamma_{ss} = (3.0\pm1.0) \times 10^{-3}$ 25% RH | | | |
| $\gamma_{ss} = 0.23$ ($p_{HCl}=6.7\times10^{-8}$ mbar) 90% RH | 190 | Hanson and Ravishankara, 1993 | CWFT-CIMS(e) |
| $\gamma_{ss} = 0.20$ ($p_{HCl}\sim4.6\times10^{-7}$ mbar) 90%RH | 190 | | |
| $\gamma_{ss} = 0.03$ ($p_{HCl}\sim4.6\times10^{-7}$ mbar) 30%RH | 197 | | |

## Comments

(a) Vapour deposited ice; NAT was prepared in situ by converting $N_2O_5$ into $HNO_3$ on the ice surface well past saturation. The $HNO_3$ vapor detected at the downstream end of the flow tube was consistent within a factor of two with the expected vapor pressure over NAT/ $HNO_3$ in ice solid solution near 201K. $[HCl]_0 = 2 \times [ClONO_2]_0$, i.e. ~ 0.4-1.2 x $10^{10}$ molecule $cm^{-3}$.

(b) The films, typically 70 mμ thick, were prepared in situ by vapour condensation of $HNO_3$ and $H_2O$ at 196K. Initial $p_{HCl}$ = 0.27 to $2.7\times10^{-3}$ mbar, $P_{ClONO2}$=10.6 $\times10^{-5}$ mbar. The measured values of $\gamma$ were independent of the composition of $HNO_3$/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±0.02 if pore diffusion is taken into account.

(c) Details under (a). The uptake of $ClONO_2$, HCl and the formation of the reaction product $Cl_2$ were studied at constant HCl concentration ($10^{10}$ molecule $cm^{-3}$) and varying $ClONO_2$ concentration ranging from 0.6-3.0 x $10^{10}$ molecule $cm^{-3}$. The authors argue in favor of a direct reaction between $ClONO_2$ and HCl rather than a reaction via the intermediate HOCl in view of the high value for $\gamma$.

(d) The NAT films were prepared starting from 10 mµ thick ice films exposed to small pressures of $HNO_3$ over long periods of time resulting in a 0.1 mµ thick NAT layer on top of the ice film. pressure of $ClONO_2$ ranging from 1.3 to 12 x $10^{-6}$ mbar and HCl ranging from 5.3 to 13.3x$10^{-6}$ mbar. A factor of four increase in $\gamma$ (from 0.01 to 0.04) was noted when $p_{HCl}$ increased from 2 to 10.6 x $10^{-6}$ mbar.

(e) Details under (a and c). A 0.05 mm thick NAT film was grown on a 0.5 mm thick $H_2O$ ice undercoat by flowing $HNO_3$ at 1.3x$10^{-6}$ mbar. Subsequently the ice undercoat was evaporated. p($H_2O$) added to He flow to adjust relative humidity over the film. $\gamma$ decreased strongly with decreasing relative humidity which was varied by adjusting the temperature of the frozen phase at a constant $H_2O$ flow rate of 3.3x$10^{-4}$ mbar. $\gamma$ given by the expression: $1/\gamma = 1/\gamma_{max} + 1/A\exp(b\Delta T)$ where $\Delta T$ 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 $H_2O$ (RH=100 x $p_{H2O}/p_{ice}(T)$). For $p_{HCl} \approx$ 6.7x$10^{-8}$ mbar and $\approx$ 4.6 x$10^{-7}$ mbar ([HCl] (2.5 and 17.5 x $10^9$ molecule $cm^{-3}$ at 195 K), $\gamma_{max}$ = 0.23 and 0.20, A=0.7022 and 2.2543, b = -0.518 and -0.558 respectively.

## Preferred values

| Parameter | Value | Temp/K |
|---|---|---|
| $\gamma_{rxn}$ | $[1/\gamma_{max} + 1/A\exp(B\Delta T)]^{-1}$ | 190 -200 |
| $p_{H2O}$ (mbar ) | 3.3 x $10^{-4}$ | (RH=20-100%) |
| $\Delta T$ (K) | T - 190 | |

| $p_{HCl}$ (mbar ) | 6.7x$10^{-8}$ | 4.6 x$10^{-7}$ |
|---|---|---|
| $\gamma_{max}$ | 0.25 | 0.20 |
| A | 0.7022 | 2.2543 |
| B | -0.518 | -0.558 |

| | | |
|---|---|---|
| *Reliability* | | |
| $\Delta\log(\gamma_{rxn})$ | ±0.3 | 190 – 200 K. |

*Comments on Preferred Values*

As with ice films the uptake of $ClONO_2$ on NAT films in the presence of HCl is followed by reaction to form $Cl_2$ and $HNO_3$ in a surface reaction. At stratospheric temperatures $Cl_2$ partitions into the gas phase, but $HNO_3$ remains at the surface with formation of hydrates. The uptake coefficients of $ClONO_2$ in the presence of HCl on $H_2O$-rich NAT substrates are similar to those on pure ice, but show a strong dependence on relative humidity. Thus $\gamma$ decreases with decreasing p($H_2O$) and decreases with increasing temperature at fixed p($H_2O$).

This reflects the amounts of surface-adsorbed water and reactants, and leads to a complex dependence of $\gamma$ 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 $p(H_2O)$ and they observed less dependence of $\gamma$ compared to Abbatt and Molina who varied $p(H_2O)$ 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 $\gamma$ increases slowly with $p_{HCl}$ in the range ≈ (0.5-5) $x10^{-7}$ mbar, which is consistent with the high fractional surface coverage for HCl ($\theta$ ≈ 0.33) for these conditions. At lower RH and higher [HCl], Abbatt and Molina observed much stronger dependence of $p_{HCl}$ in the range ≈ (2-10) $x10^{-6}$

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 [HCl] and fixed $p(H_2O) = 3.3 \times 10^{-4}$ 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 $\gamma$ at lower [HCl] and absolute humidity. For uptake on NAT surfaces with at lower [HCl] and absolute humidity in the NAT stability region, a parameterisation for $\gamma$ using a Langmuir-Hinshelwood model such as used for $ClONO_2$+ 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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Hanson, D.R. and Ravishankara, A.R.: J. Geophys. Res. 96, 5081 (1991).
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Figure 1. The dependence of the steady-state uptake coefficient of $ClONO_2$ 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