

## Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A5.12 HNNT12

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### Uptake coefficient data

Parameter	Temp/K	Reference	Comment
<b>Uptake Coefficients</b>			
$\gamma_{\text{ss}} = (6.0 \pm 2.0) \times 10^{-3}$	201	Hanson and Ravishankara, 1991	CWFT-CIMS(a)
$\gamma_{\text{ss}} = 1.0 \times 10^{-5}$	196	Leu, Moore and Keyser, 1991	CWFT-MS(b)
$\gamma_{\text{ss}} = (2.0 \pm 0.8) \times 10^{-3}$	191	Hanson and Ravishankara, 1992	CWFT-CIMS(c)
$\gamma_{\text{ss}} = (4.0 \pm 1.6) \times 10^{-3}$	201		
$\gamma_{\text{ss}} = (8.0 \pm 3.2) \times 10^{-3}$	211		
$\gamma_{\text{ss}} = (2.0 \pm 0.8) \times 10^{-3}$ 100% rh	202	Abbatt and Molina, 1992	CWFT-MS(d)
$\gamma_{\text{ss}} = (5.0 \pm 2.5) \times 10^{-5}$ 25% rh			
$\gamma_{\text{ss}} = (1.0 \pm 0.3) \times 10^{-3}$	191	Hanson and Ravishankara, 1993a	CWFT-CIMS(e)
$\gamma_{\text{ss}} = 2.0 \times 10^{-3}$ 90% rh	191	Hanson and Ravishankara, 1993	CWFT-CIMS(f)
$\gamma_{\text{ss}} = 0.5 \times 10^{-3}$ 50% rh	194		
$\gamma_{\text{ss}} = 0.3 \times 10^{-3}$ 25% rh	198		
$\gamma_{\text{ss}} = (2.0 \pm 0.3) \times 10^{-3}$ 100%rh	195	Zhang, Jayne and Molina, 1994	CWFT-MS(g)
$\gamma_0 = (5 \pm 3) \times 10^{-4}$ NAD, $\beta$ -NAT	185	Barone <i>et al.</i> , 1997	Knud-MS(h)
$\gamma_0 = (4 \pm 2) \times 10^{-4}$ $\alpha$ -NAT			
$\gamma_0 = (7 \pm 3.5) \times 10^{-3}$ NAD, $\alpha$ -NAT, $\beta$ -NAT			

### Comments

- (a) Vapour deposited ice; NAT was prepared in situ by converting  $\text{N}_2\text{O}_5$  into  $\text{HNO}_3$  on the ice surface well past saturation. The  $\text{HNO}_3$  vapor detected at the downstream end of the flow tube was consistent within a factor of two with the expected vapor pressure over NAT/ $\text{HNO}_3$ -in- ice solid solution near 201K.  $[\text{ClONO}_2] \sim 0.5\text{--}3 \times 10^{10} \text{ molecule cm}^{-3}$
- (b) The films, typically 70 nm thick, were prepared in situ by vapour condensation of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  at 196K. The film surface areas and bulk densities were measured ex situ in addition to by their FTIR absorption spectra.  $\gamma$  on samples of varying  $\text{HNO}_3/\text{NAT}$  composition was in

the range  $10^{-5}$  to  $10^{-3}$  and was observed to saturate within a few minutes. No added water vapour (low rh)

- (c) Details under (a). The values for  $\gamma$  given in the Table correspond to a vapour deposited film of 10 m $\mu$  thickness.  $p(\text{H}_2\text{O})$  added to He flow from upstream ice film to prevent evaporation of film, i.e. high rh.  $\gamma$  varied by a factor of  $\leq 3$  when the thickness was varied from 2 to 20 m $\mu$ ., showing reaction occurred on external surface of film.  $[\text{ClONO}_2] \sim 0.5\text{--}3 \times 10^{10}$  molecule  $\text{cm}^{-3}$
- (d) Uptake of  $\text{ClONO}_2$  on NAT with  $P_{\text{ClONO}_2}$  ranging from 2.7 to  $26.7 \times 10^{-6}$  mbar. The NAT films were prepared starting from 10 m $\mu$  thick ice films exposed to small pressures of  $\text{HNO}_3$  over long periods of time resulting in a 0.1 m $\mu$  thick NAT layer on top of the ice film. The steady-state uptake coefficient  $\gamma$  increases exponentially with  $p(\text{H}_2\text{O})$  over the NAT surface, reaching a similar value to that on ice at the ice vapour pressure of pure ice;  $p(\text{ClONO}_2) = (0.27\text{--}2.67) \times 10^{-5}$  mbar ( $\sim 1\text{--}10 \times 10^{11}$  molecule  $\text{cm}^{-3}$ )
- (e) Details under (a and c).  $p(\text{H}_2\text{O})$  added to He flow from upstream ice film to prevent evaporation of film. This study was undertaken to supplement the original work on ice and  $\text{HNO}_3$ -doped (NAT) surfaces to further confirm the independence of  $\gamma$  on the substrate thickness.
- (f) A 0.05 m $\mu$  thick NAT film was grown on a 0.5 m $\mu$  thick  $\text{H}_2\text{O}$  ice undercoat by flowing  $\text{HNO}_3$  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. The uptake coefficients were strongly dependent on rh.
- (g) Ice films were deposited from the vapor phase at 195K, attained a thickness of between 15–25 m $\mu$ , and were subsequently exposed to gas phase  $\text{HNO}_3$  in order to generate NAT.  $[\text{ClONO}_2] \sim 1.5\text{--}2.5 \times 10^9$  molecule  $\text{cm}^{-3}$ ; mean of 11 experiments at  $p(\text{H}_2\text{O}) = 6.4 \times 10^{-4}$  mbar.
- (h) Uptake study performed in a Knudsen flow reactor interfaced with MS and FTIR-RAS. Total pressure ranged between 0.67 to  $27 \times 10^{-5}$  mbar. Smooth films of NAD,  $\alpha$ - and  $\beta$ -NAT were grown by co-deposition of  $\text{ClONO}_2$  and  $\text{H}_2\text{O}$  at 150K and annealing the resulting films at 185K at a rate of  $10\text{K min}^{-1}$ . Crystallization of the deposits to NAT and NAD was observed to occur between 170 and 185K. The reactant films were in the range 5 to 50 nm thick.

### Preferred values

Parameter	Value	T/K
$\gamma_{\text{rxn}}$	$7.1 \times 10^{-3} \exp(-2940/T)$	185 - 210
<i>Reliability</i>		
$\Delta \log (\gamma_{\text{rxn}})$	$\pm 0.2$	185 - 210

### Comments on Preferred Values

As with ice films, the uptake of  $\text{ClONO}_2$  on NAT films is followed by reaction with  $\text{H}_2\text{O}$  to form  $\text{HOCl}$  and  $\text{HNO}_3$  in a surface reaction. At stratospheric temperatures  $\text{HOCl}$  partitions into the gas phase, but  $\text{HNO}_3$  remains at the surface with formation of hydrates (NAT). The uptake coefficients on NAD and NAT substrates are substantially lower than on pure ice and show a strong dependence on relative humidity, which is reflected in an increase in  $\gamma$  with  $p(\text{H}_2\text{O})$  and temperature. This is believed to reflect the decreasing amounts of available surface-adsorbed water.

Uptake coefficients measured on water-rich NAT (100% rh) from the different studies agree quite well. At lower RH there is more variability. The RH dependence of the uptake coefficients from various studies are shown in Fig 1. 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  $\gamma$  compared to Abbatt and Molina who varied  $p(\text{H}_2\text{O})$  at constant T; the latter used higher  $[\text{ClONO}_2]$  which could have led to more influence of  $\text{HNO}_3$  product, reducing surface water availability.

The preferred values for the reactive coefficient on water rich NAT are given by an Arrhenius fit of the uptake coefficients measured near 100% RH in the studies of Hanson & Ravishankara (1992), Abbatt and Molina, (1992), and Zhang, Jayne and Molina (1994), which are in reasonable agreement for these conditions, considering the uncertainties arising from sensitivity of  $\gamma$  to the  $p(\text{H}_2\text{O})$ , and the state of the surface.

In view of the complex dependence of the uptake coefficient on the state of the  $\text{HNO}_3$ -rich surfaces, and the lack of consistency in the reported data for these conditions, no recommendation is made for  $\gamma$  at low RH. For uptake on surfaces with  $\text{HNO}_3$  present in the NAT stability region a parameterisation for  $\gamma$  using a Langmuir-Hinshelwood model such as used for ice (IUPAC, 2007), would require a better definition of the surface water concentration than is available at present.

## References

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Figure 1. The dependence of the steady-state uptake coefficient of ClONO<sub>2</sub> on NAT surfaces as a function of relative humidity. Temperature range 185 – 211 K.

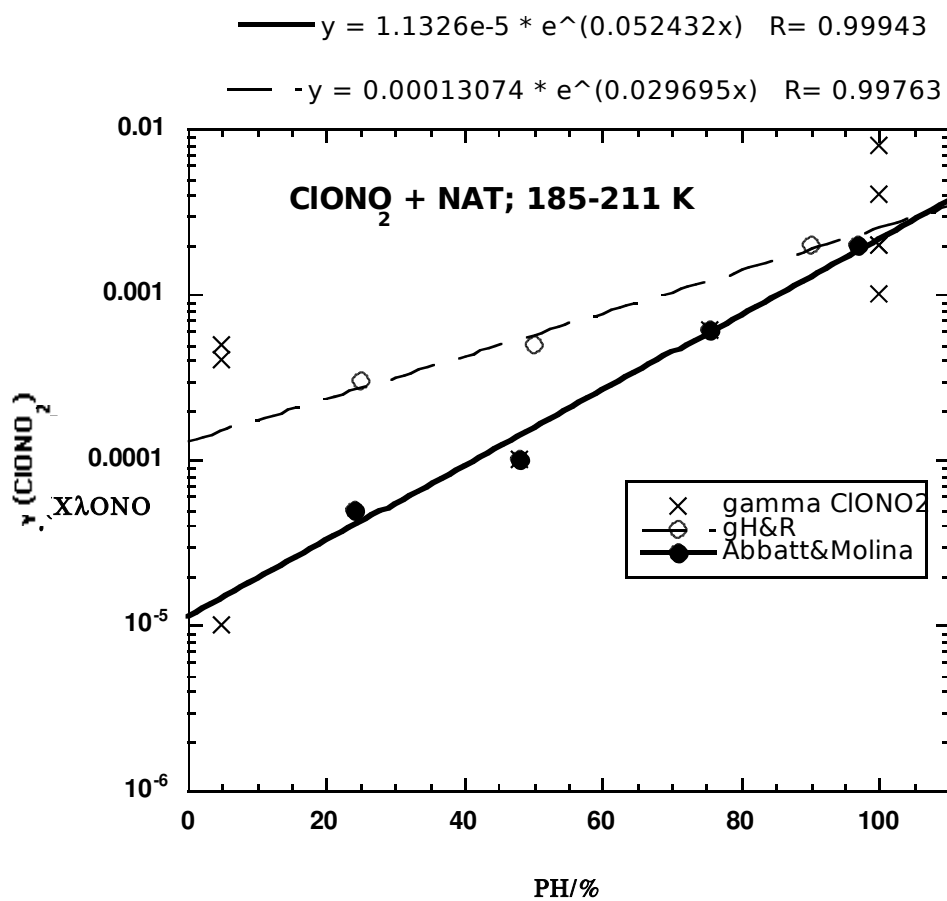


Figure 2. The temperature dependence of the uptake coefficient of ClONO<sub>2</sub> on water-rich NAT surfaces.

