IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A5.12 HNDT12

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$ClONO_2 + H_2O$ (NAT) → $HNO_3 + HOCl$

Uptake coefficient data

Parameter	Temp/K	Reference	Comment
Uptake Coefficients			
$\gamma_{ss} = (6.0\pm2.0)\times10^{-3}$	201	Hanson and Ravishankara, 1991	CWFT-CIMS(a)
$\gamma_{ss} = 1.0\times10^{-5}$	196	Leu, Moore and Keyser, 1991	CWFT-MS(b)
$\gamma_{ss} = (2.0\pm0.8)\times10^{-3}$	191	Hanson and Ravishankara, 1992	CWFT-CIMS(c)
$\gamma_{ss} = (4.0\pm1.6)\times10^{-3}$	201		
$\gamma_{ss} = (8.0\pm3.2)\times10^{-3}$	211		
$\gamma_{ss} = (2.0\pm0.8)\times10^{-3}$ 100% rh	202	Abbatt and Molina, 1992	CWFT-MS(d)
$\gamma_{ss} = (5.0\pm2.5)\times10^{-5}$ 25% rh			
$\gamma_{ss} = (1.0\pm0.3)\times10^{-3}$	191	Hanson and Ravishankara, 1993a	CWFT-CIMS(e)
$\gamma_{ss} = 2.0\times10^{-3}$ 90% rh	191	Hanson and Ravishankara, 1993	CWFT-CIMS(f)
$\gamma_{ss} = 0.5\times10^{-3}$ 50% rh	194		
$\gamma_{ss} = 0.3\times10^{-3}$ 25% rh	198		
$\gamma_{ss} = (2.0\pm0.3)\times10^{-3}$ 100%rh	195	Zhang, Jayne and Molina, 1994	CWFT-MS(g)
$\gamma_0 = (5\pm3)\times10^{-4}$ NAD, β-NAT	185	Barone *et al*., 1997	Knud-MS(h)
$\gamma_0 = (4\pm2)\times10^{-4}$ α-NAT			
$\gamma_0 = (7\pm3.5)\times10^{-3}$ NAD, α-NAT, β-NAT			

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. [$ClONO_2$] ~ 0.5-3 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. The film surface areas and bulk densities were measured ex situ in addition to by their FTIR absorption spectra. γ on samples of varying HNO_3/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 γ given in the Table correspond to a vapour deposited film of 10 mμ thickness. p(H_2O) added to He flow from upstream ice film to prevent evaporation of film, i.e.high rh. γ varied by a factor of ≤ 3 when the thickness was varied from 2 to 20 mμ., showing reaction occurred on external surface of film. [$ClONO_2$] ~ 0.5-3 x 10^{10} molecule cm^{-3}

(d) Uptake of $ClONO_2$ on NAT with P_{ClONO2} ranging from 2.7 to 26.7x10^{-6} mbar. The NAT films were prepared starting from 10 mμ thick ice films exposed to small pressures of HNO3 over long periods of time resulting in a 0.1 mμ thick NAT layer on top of the ice film. The steady-state uptake coefficient γ increases exponentially with p(H_2O) over the NAT surface, reaching a similar value to that on ice at the ice vapour pressure of pure ice; p($ClONO_2$) = (0.27-2.67) x 10^{-5} mbar (~1-10 x 10^{11} molecule cm^{-3})

(e) Details under (a and c). p(H_2O) 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 HNO_3-doped (NAT) surfaces to further confirm the independence of γ on the substrate thickness.

(f) A 0.05 mμ thick NAT film was grown on a 0.5 mμ thick H_2O ice undercoat by flowing HNO_3 at 1.3x10^{-6} mbar. Subsequently the ice undercoat was evaporated. p(H_2O) 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 mμ, and were subsequently exposed to gas phase HNO_3 in order to generate NAT. [$ClONO_2$] ~ 1.5-2.5 x 10^9 molecule cm^{-3} ; mean of 11 experiments at p(H_2O) = 6.4 x10^{-4} mbar.

(h) Uptake study performed in a Knudsen flow reactor interfaced with MS and FTIR-RAS. Total pressure ranged between 0.67 to 27x10^{-5} mbar. Smooth films of NAD, α- and β-NAT were grown by co-deposition of $ClONO_2$ and H_2O at 150K and annealing the resulting films at 185K at a rate of 10K 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
γ_{rxn}	7.1 x 10^{-3}exp(-2940/T)	185 - 210
Reliability		
Δ log (γ_{rxn})	± 0.2	185 - 210

Comments on Preferred Values

As with ice films, the uptake of $ClONO_2$ on NAT films is followed by reaction with H_2O to form HOCl and HNO_3 in a surface reaction. At stratospheric temperatures HOCl partitions into the gas phase, but 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 γ with p(H_2O) 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 $p(H_2O)$ and they observed less dependence of γ compared to Abbatt and Molina who varied $p(H_2O)$ at constant T; the latter used higher $[ClONO_2]$ which could have led to more influence of 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 γ to the $p(H_2O)$, and the state of the surface.

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 low RH. For uptake on surfaces with HNO_3 present in the NAT stability region a parameterisation for γ 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 $ClONO_2$ on NAT surfaces as a function of relative humidity. Temperature range 185 – 211 K.

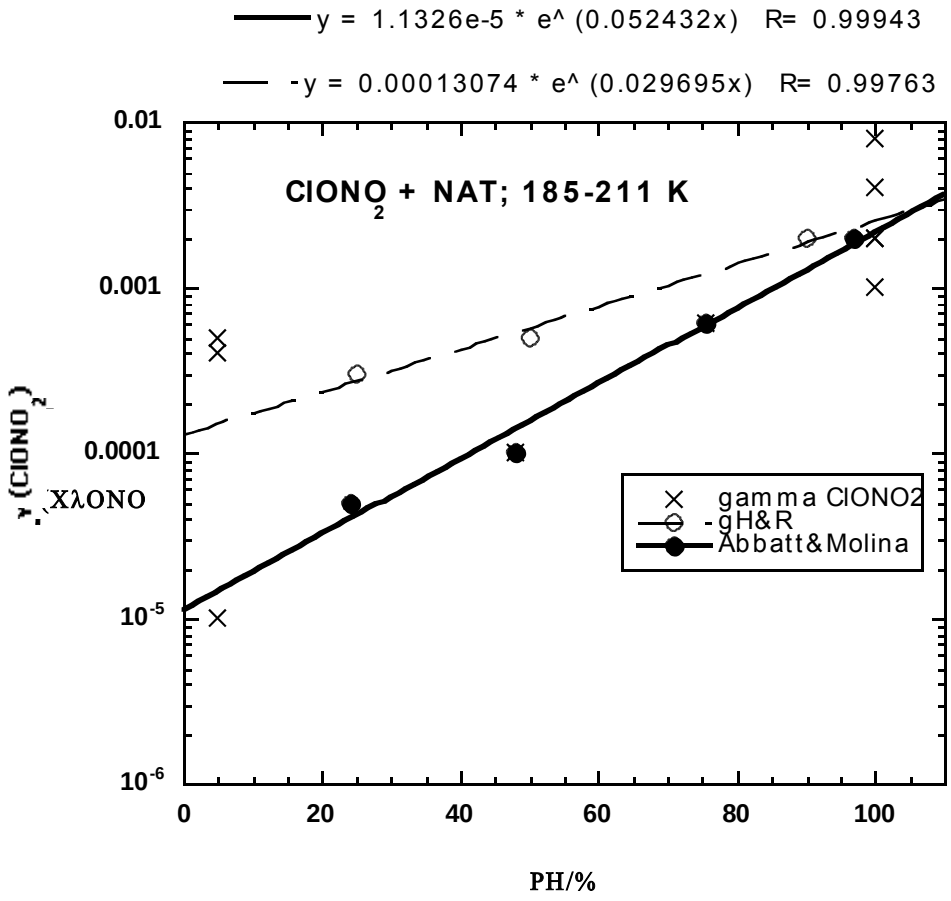

Figure 2. The temperature dependence of the uptake coefficient of $ClONO_2$ on water-rich NAT surfaces.

ψ = μ1 + μ2*M0		
	ςαλυε	Ερρορ
μ1	8.8752	4.1394
μ2	–2936.4	815.72
Χηισθ	0.72617	NA
P	0.84946	NA