IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.43 HI43

$ClONO_2 + H_2O$ (ice surfaces) $\rightarrow HNO_3 + HOCl$

Uptake coefficient data

Parameter	Temp/K	Reference	Comment
Uptake Coefficients			
$\gamma_{ss} = (9.0 \pm 2.0) \times 10^{-3}$	185	Tolbert et al., 1987	Knud-MS(a)
$\gamma_{ss} = (6.0 \pm 3.0) \times 10^{-2}$	200	Leu, 1988	CWFT(b)
$\gamma_{ss} = 0.3(+0.7, -0.1)$	201	Hanson and Ravishankara, 1991	CWFT(c)
$\gamma_{ss} = 5.0 \times 10^{-3} (\pm 4 \times 10^{-3})$	196	Leu, Moore and Keyser, 1991	CWFT(d)
$\gamma_0 = 0.8(+0.2, -0.3)$	191	Hanson and Ravishankara, 1992	CWFT(e)
$\gamma_{ss} = 0.30 \pm 0.10$	191	Hanson and Ravishankara, 1993a	CWFT(f)
$\gamma_{ss} > 3.0 \times 10^{-2}$	188	Chu, Leu and Keyser, 1993	CWFT(g)
$\gamma_{ss} = 0.13$			
$\gamma_{ss} = (8.0 \pm 2.0) \times 10^{-2}$	195	Zhang, Jayne and Molina, 1994	CWFT(h)
$\gamma_0 = 0.2 \pm 0.05$	180-200	Oppliger, Allanic and Rossi, 1997	Knud-MS(i)
$\gamma_{ss} = 3.0 \pm 0.5 \times 10^{-2}$			
$\gamma_0 = (9.0 \pm 2.5) \times 10^{-2}$	218	Fernandez, Hynes and Cox, 2005	CWFT-MS(j)
$\gamma_{ss} = (2.0 \pm 0.5 \times 10^{-2}$			
Partition Coefficient (cm)			
$K_{LinC}(ClONO_2) = 1.2 \times 10^4$	218/228	Fernandez, Hynes and Cox, 2005	CWFT-MS(j)

Comments

(a) γ for reactive uptake $ClONO_2$ on pure ice prepared in situ by vapour deposition was measured at typical pressures $P(ClONO_2) = 2.7 \times 10^{-5}$ and $P(H_2O) = 1.9 \times 10^{-3}$ mbar.

(b) vapour deposited ice. Significant diffusion corrections had to be made using calculated diffusion coefficients for $ClONO_2$ in He; cited standard deviation of γ includes the uncertainty in the estimation of the diffusion coefficient of $ClONO_2$ in He at 200K.

(c) Vapour deposited ice with CIMS detection. At high uptake coefficient ($\gamma \geq 0.1$) required corrections for gas-phase diffusion using calculated diffusion coefficients for $ClONO_2$ in He. Rapid saturation of the ice surface for $ClONO_2$ uptake was observed at concentrations as low as 2×10^9 molecule cm^{-3}.

(d) The substrates were prepared in situ from the gas phase by condensation at 196K resulting in film thicknesses of 70 mμ. The surface areas and bulk densities of condensed films were measured ex situ in addition to the measurement of their FTIR absorption spectra.

(e) Details under (c). Ice films (thickness 15-25 mμ) were deposited from the vapour phase at 195K. No dependence of γ on thickness.

(f) Details under (e). 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.

(g) Details under (d). Vapour deposited ice film 3.7 to 34.7 mμ thick, calibrated gravimetrically. The morphology of the ice films were layers of μ-sized granules whose internal surface was measured using BET gas adsorption measurments. Minimum $P(ClONO_2)=1.9 \times 10^{-7}$mbar.

(h) Fast flow reactor coupled to a differentially pumped beam-sampling MS. Nucleation and growth of hexagonal water ice on top of the reactant NAT film was observed for saturation ratios of $H_2O \geq 1.5$. Under these conditions the reaction efficiency increased significantly.

(i) Knudsen flow reactor using both steady-state and pulsed admission of $ClONO_2$ onto ice film (20 mμ thick) generated from vapor phase deposition. γ is extremely prone to saturation of the ice.

(j) Frozen film ice. Uptake monitored by following $ClONO_2$ loss and HOCl formation. HOCl partitioned rapidly to gas-phase. γ decreased with exposure time until surface HNO_3 product saturated according to Langmuir equilibrium surface coverage for HNO_3. The observed kinetics were best described by a Langmuir-Hinshelwood mechanism, with values of k_s and K_{LangC} at 218 K obtained by fitting to the experimental data using a numerical model. The cited value of K_{LinC} was obtained using $N_{max} = 3 \times 10^{14}$ molecule cm^{-2}.

Preferred values

Parameter	Value	T/K
α_s ($ClONO_2$)	0.5	180 - 230
γ ($ClONO_2$)	$1 / \left(\dfrac{1}{\alpha_s} + \dfrac{c}{4 k_s K_{LinC}[H_2O]_s} \right)$	180 - 230
$[H_2O]_s$/ molecule cm^{-2}	$10^{15} (1 - 0.81 \theta_{HNO3})$	
$k_s K_{LinC}$ /cm^3molecule^{-1} s^{-1}	$5.2 \times 10^{-17} \exp(2032/T)$	$180 - 230$
k_s /cm^2molecule^{-1} s^{-1}		218

Reliability

$\Delta (\alpha_s)$	± 0.3	$180 - 230$

θ_{HNO3} = dimensionless surface coverage of HNO$_3$ (calculated using IUPAC recommended K_{linC} and N_{max} = 3 x 10^{14} molecule cm^{-2})

Comments on Preferred Values

Uptake of ClONO$_2$ on ice films is followed by rapid reaction with H$_2$O to form HOCl and HNO$_3$ in a surface reaction. At stratospheric temperatures HOCl mainly partitions into the gas phase, but HNO$_3$ remains at the surface until the surface layer saturates either by physical adsorption of nitric acid molecules or by formation of ions or hydrates (NAT). The presence of HNO$_3$ on the surface inhibits the rate of reactive uptake leading to a strongly time dependent uptake coefficient of ClONO$_2$ decreasing from $\gamma > 0.1$ on a clean ice surface to a steady state uptake coefficient of <0.02 or less when HNO$_3$ product has built up to saturation. The uptake coefficients on NAD and NAT substrates at <200K are even lower and show a strong decline with decreasing relative humidity, confirming the inhibiting effect of surface HNO$_3$.

The preferred value for the surface accommodation coefficient is an average of the initial uptake coefficient measured at low p(ClONO$_2$) in the studies of Hanson & Ravishankara (1992) and Oppliger et al. (1997). using different techniques. These measurements agree reasonably well, considering the uncertainties arising from gas phase diffusion effects in the flow tube study and unavoidable inhibition by surface HNO$_3$ in the static Knudsen cell study.

For uptake on surfaces with HNO$_3$ present in the ice stability region a parameterisation for γ using a Langmuir-Hinshelwood model is recommended, based on the analysis and results of Fernandez et al. (2005). The recommended values of K_{LinC}(ClONO2) and the surface reaction rate coefficient of k_s at 218 K are those derived by Fernandez et al (2005). The surface concentration of water molecules [H$_2$O]$_s$ can be estimated assuming that the surface sites are blocked by adsorbed HNO$_3$ with an effective area of 1.23 x 10^{-15} cm^2 molecule^{-1}. Thus [H$_2$O]$_s$ = 1 x 10^{15} $-$ 3xN_{max}xθ molecule cm^{-2}, where θ is the fractional surface coverage of nitric acid and N_{max}= 2.7 x 10^{14} molecule cm^{-2} for [HNO$_3$]$_s$ at saturation, taken from this evaluation (IUPAC,2007).

The temperature dependence of the product $k_s K_{LinC}$ was obtained by fitting to experimental γ_0 values in the range 218-190 K using the Langmuir Hinshelwood expression; the resulting temperature dependence of γ_0 is shown in Fig 1. The calculated temperature dependence of γ_{ss} calculated assuming θ_{HNO3} = 1 is also shown in Fig 1. Uptake coefficients for different [HNO$_3$] can be calculated using the recommended Langmuir expression for θ_{HNO3}(see data sheet V.A1.12). The parameterisation gives a reasonable representation at $T \geq$ 200K but overestimates the uptake coefficient in the NAT stability region.

References

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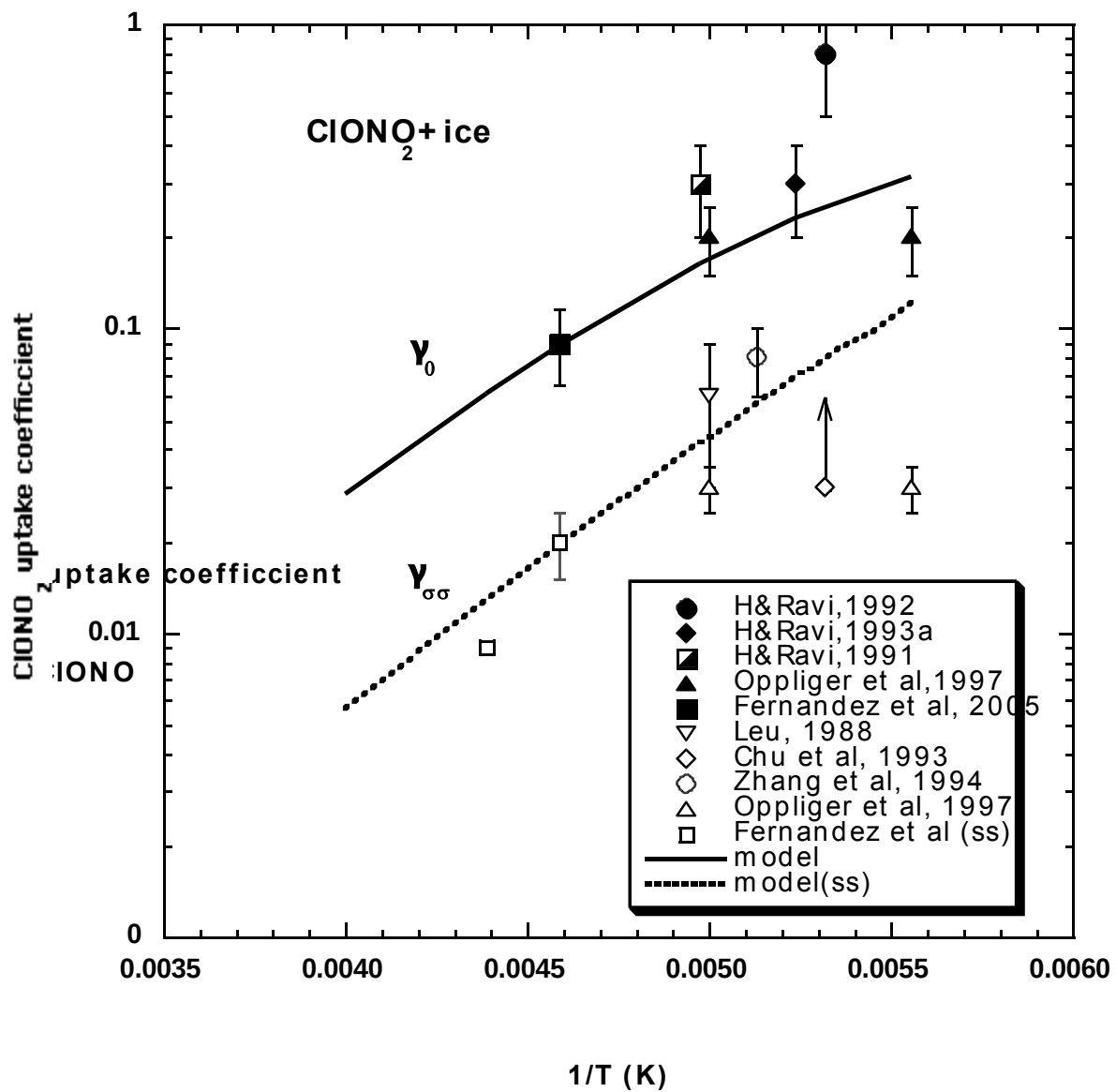
Figure 1. The recommended parameterization temperature dependence of the uptake coefficient of $ClONO_2$ on fresh ice surfaces and after steady exposure.