

IUPAC Task group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.44 HI44

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Uptake coefficient data

Parameter	Temp/K	Reference	Comment
<i>Uptake coefficients (ClONO₂)</i>			
$\gamma_{\text{SS}} = 0.27(+0.73,-0.13)$	200	Leu, 1988	CWFT-MS(a)
$\gamma_{\text{SS}} = 0.3(+0.7, -0.1)$	191	Hanson and Ravishankara, 1992	CWFT-CIMS(b)
$\gamma_{\text{SS}} = 0.27 \pm 0.19$	188	Chu, Leu and Keyser, 1993	CWFT-MS(c)
$\gamma_0 = 0.64 \pm 0.07$	180	Oppliger, Allanic and Rossi, 1997	Knud-MS(d)
$\gamma_0 = 0.27 \pm 0.07$	200		
$\gamma_0 > 0.3$ ($P_{\text{HCl}} = (0.26 - 10.6) \times 10^{-6}$ mbar)	201	Lee et al., 1999	CWFT-CIMS (e)
$\gamma_0 > 0.1$ ($P_{\text{HCl}} = (1.3 - 2.6) \times 10^{-6}$ mbar)	210	Lee et al., 1999	Aerosol FT-CIMS(f)
$\gamma_{\text{SS}} > 0.1$ ($P_{\text{HCl}} = 1.33 \times 10^{-6}$ mbar)	218, 228	Fernandez, Hynes and Cox, 2005	CWFT-MS (g)
$\gamma_{\text{SS}} = 0.023 \pm 0.012$ ($P_{\text{HCl}} = 1.33 \times 10^{-7}$ mbar)*	218		
$\gamma_{\text{SS}} = 0.078 \pm 0.025$ ($P_{\text{HCl}} = 8.11 \times 10^{-7}$ mbar)*	228		
$\gamma_{\text{SS}} = 0.020 \pm 0.004$ ($P_{\text{HCl}} = 5.85 \times 10^{-7}$ mbar)*	228		
$\gamma_{\text{SS}} = 0.040 \pm 0.007$ ($P_{\text{HCl}} = 1.46 \times 10^{-6}$ mbar)*			
* ice doped with 1.33×10^{-6} mbar HNO ₃			
$\gamma_{\text{SS}} > 0.1$ ($P_{\text{HCl}} = 1.33 \times 10^{-6}$ mbar)	196	McNeil et al, 2006	CWFT-CIMS(h)
$\gamma_{\text{SS}} = 0.014 \pm 0.005$ ($P_{\text{HCl}} = 1.33 \times 10^{-6}$ mbar)	218		

Comments

- (a) Ice was condensed from the vapour phase onto the cold wall of the flow tube (1 gr total) together with HCl vapor to obtain mole fractions X_{HCl} in the range 0.37 to 7.1% relative to H₂O. The reaction probability γ increased from 0.06, the value obtained for the reaction $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCl}$ to a constant value of 0.27 independent of X_{HCl} for the range

1.5 to 7.1% (see Table). Significant diffusion corrections had to be made using calculated diffusion coefficients for ClONO₂ in He.

- (b) Vapour deposited ice with CIMS detection. The uptake of ClONO₂, HCl and the formation of the reaction product Cl₂, were studied at constant [HCl] (2×10^{10} molecule cm⁻³) and varying ClONO₂ concentration ranging from 6×10^9 to 3×10^{10} molecule cm⁻¹. 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 . The high uptake coefficient ($\gamma \geq 0.1$) required corrections for gas-phase diffusion using calculated diffusion coefficients for ClONO₂ in He.
- (c) Ice film deposited He-H₂O vapour mixture to thicknesses ranging from 3.7 to 34.7 μm which were both calculated and calibrated gravimetrically. The morphology of the ice films were layers of μm-sized granules whose internal surface was measured using BET gas adsorption measurements. p_{ClONO_2} ranged from 8.6×10^{-8} to $\sim 1.3 \times 10^{-6}$ mbar and p_{HCl} from 2.1×10^{-7} to 3.1×10^{-6} mbar. The diffusion correction amounted to a factor exceeding ten in some cases.
- (d) Both steady-state and real-time pulsed valve admission of ClONO₂ to Knudsen flow reactor coupled to MS detector. The ice samples were generated from vapor phase deposition of approximately 2×10^6 monolayers of H₂O (20 μm thickness). Pulses of 10^{14} molecules interacting with HCl-doped ice at excess HCl conditions resulted in prompt formation of Cl₂ thus pointing to a direct mechanism of product formation. γ has a negative temperature dependence that parallels the change in solubility of HCl in ice with temperature.
- (e) Uptake experiment in a laminar flow tube with both vapour-deposited and frozen film ice. Comparable amounts of HCl were taken up on smooth as well as on rough ice films on the order of 1 to 4×10^{14} molecules cm⁻² for HCl ranging from 1.3×10^{-7} to 5×10^{-6} mbar, with only a weak dependence on p_{HCl} for these conditions. The measured uptake coefficient of ClONO₂ is only a lower limit because of diffusion limitations but this showed practically no dependence on P_{HCl} . An ionic reaction mechanism was proposed, which assumes significant mobility of the reactants close to the surface of the condensed phase in a liquid-like layer of HCl/H₂O.
- (f) Uptake experiment conducted at 1 bar in an aerosol flow tube equipped with CIMS detection for reactant and product. Aerosols consisted of 1-5 μm single ice crystals. Similar conditions to (e) and similar results were obtained, i.e no dependence of γ on P_{HCl} , within experimental error.
- (g) Uptake of chlorine nitrate in the presence of HCl was measured on a frozen-film of pure ice and ice doped with continuous flow of HNO₃ ($P_{\text{HNO}_3} = 1.33 \times 10^{-6}$ mbar) in the temperature range 208 – 228 K, with $P_{\text{ClONO}_2} < 1 \times 10^{-6}$ mbar. On pure ice uptake was diffusion limited and gas phase Cl₂ was formed with a yield of 100%. On HNO₃-doped ice at low P_{HCl} , γ_{max} was linearly dependent on surface coverage of HCl which was related to P_{HCl} by a 2-species (HCl/HNO₃) Langmuir isotherm. At low P_{HCl} , HOCl was observed as a product in addition to Cl₂, indicating competition between reaction of ClONO₂ with surface water and HCl. Kinetics of Cl₂ formation were consistent with an Ely-Rideal mechanism.
- (h) The ice surfaces were hollow cylinders of zone-refined ice prepared externally and inserted into the flow tube. The zone refining formed ice with few large crystals which were amenable to probing of surface phase change induced by HCl adsorption by ellipsometry.

The uptake coefficient was measured at constant reactant conditions ($P_{\text{HCl}} = 1.33 \times 10^{-6}$ mbar, $P_{\text{ClONO}_2} = 6 \times 10^{-7}$ mbar) at two temperatures corresponding to surface disorder (196 K) and no surface disorder (218 K). Reactive uptake was found to be enhanced at the lower temperature and this is attributed to HCl being more readily available for reaction in the quasi liquid layer formed by HCl near its phase boundary.

Preferred values

Parameter	Value	T/K
$\gamma_{\text{ER}}(\text{ClONO}_2)$	0.24	185 – 230
$\gamma_{\text{s}}(\text{ClONO}_2)$	$\gamma_{\text{ER}} \times \theta_{\text{HCl}}$	185 – 230

Reliability

$\Delta(\gamma_{\text{ER}})$	± 0.1	K.
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Comments on Preferred Values

Heterogeneous reaction of ClONO_2 with HCl occurs rapidly on ice surfaces at all atmospherically relevant temperatures. Cl_2 is the sole product of this reaction, and is released promptly to the gas phase (Oppliger et al, 1997). Most earlier studies were at temperatures < 200 K and HCl concentrations corresponding to stability regions of the phase diagram for either HCl hydrate or supercooled HCl/ H_2O solutions, which McNeill et al. (2006) have shown can be formed by surface melting induced by exposure to HCl. All studies under these conditions with $p_{\text{HCl}} > p_{\text{ClONO}_2}$ gave a reactive uptake coefficient ≥ 0.3 , which was practically independent of p_{HCl} . The lower limit for γ results from the large correction needed for the influence of gas phase diffusion on the measured loss rate coefficients. The Knudsen cell results (Oppliger et al, 1997), which do not require correction for gas phase diffusion, are considered the most accurate and these data show a small negative temperature dependence. An Arrhenius fit to these data give: $\gamma_0 = 1.14 \times 10^{-4} \exp(1553/T)$, which gives values consistent with the upper limits from flow tube studies at comparable p_{HCl} and temperature. However in view of the uncertainties and the spread of reported values a temperature independent value is recommended for γ_{max} .

At higher temperatures, at low p_{HCl} and at $p_{\text{HCl}} \leq p_{\text{ClONO}_2}$ uptake coefficients decline and depend on p_{HCl} (Oppliger et al, 1997; Fernandez et al, 2005). Also it is established that the presence of HNO_3 in/on the surface layer of ice, either added or produced by surface reaction of ClONO_2 , reduces the uptake rate (Hanson and Ravishankara, 1992; Oppliger et al, 1997; Fernandez et al, 2005). Fernandez et al. (2005) showed that this is due to reduced HCl surface coverage in the presence of HNO_3 . The mechanism of the reaction has been discussed in several of the cited studies. Hanson and Ravishankara, 1992 showed that formation of HOCl was not intermediate in the fast reaction forming Cl_2 , which occurred by a direct surface reaction. Oppliger et al (1997) also concluded that reaction involved a direct surface reaction of ClONO_2 with Cl^- ions.

Carslaw and Peter (1997) described the reaction rate for $\text{ClONO}_2 + \text{HCl}$ and related stratospheric reactions on ice particles in terms of surface coverage of HCl, using a modified

Langmuir-Hinshelwood model. This approach was used by Fernandez et al (2005) to model their reactive uptake coefficients measured on HNO₃-doped ice, but their results were best described in terms of an Ely-Rideal mechanism without competitive adsorption of ClONO₂ prior to surface reaction. This forms the basis of the recommended parameterisation of the reactive uptake coefficient for ClONO₂ as a function of [HCl]_g given by the product of γ_{max} and the dimensionless surface coverage θ_{HCl} . In the ice stability region ($T \geq 200K$) this coverage can be calculated for a fresh ice surface and in the presence of co-adsorbed HNO₃ using a single site Langmuir model with the appropriate partition coefficients for HCl and HNO₃:

$$\theta_{HCl} = \frac{K_{LangC}[HCl]}{1 + K_{LangC}[HCl] + K_{LangC}[HNO_3]}$$

Values of γ given by this parameterisation for $p_{HCl} = 10^{-6}$ and 10^{-7} Torr are shown on Fig 1. Fig 2 shows calculated and experimental values of γ for reactive uptake of ClONO₂ in as a function of p_{HCl} on nitric acid doped ice at 218 and 228 K; θ_{HCl} was calculated using the partition coefficient expression: $K_{LinC} = 1.3 \times 10^{-5} \exp(4600/T)$ cm with $N_{max} = 3 \times 10^{14}$ molecule cm⁻², derived from the same experimental study (Fernandez et al (2005)). γ was assumed to have 2 components due to reaction of ClONO₂ with H₂O and HCl.

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Figure 1. The recommended parameterization for temperature dependence of the initial uptake coefficient of ClONO₂ on ice in the presence of HCl.

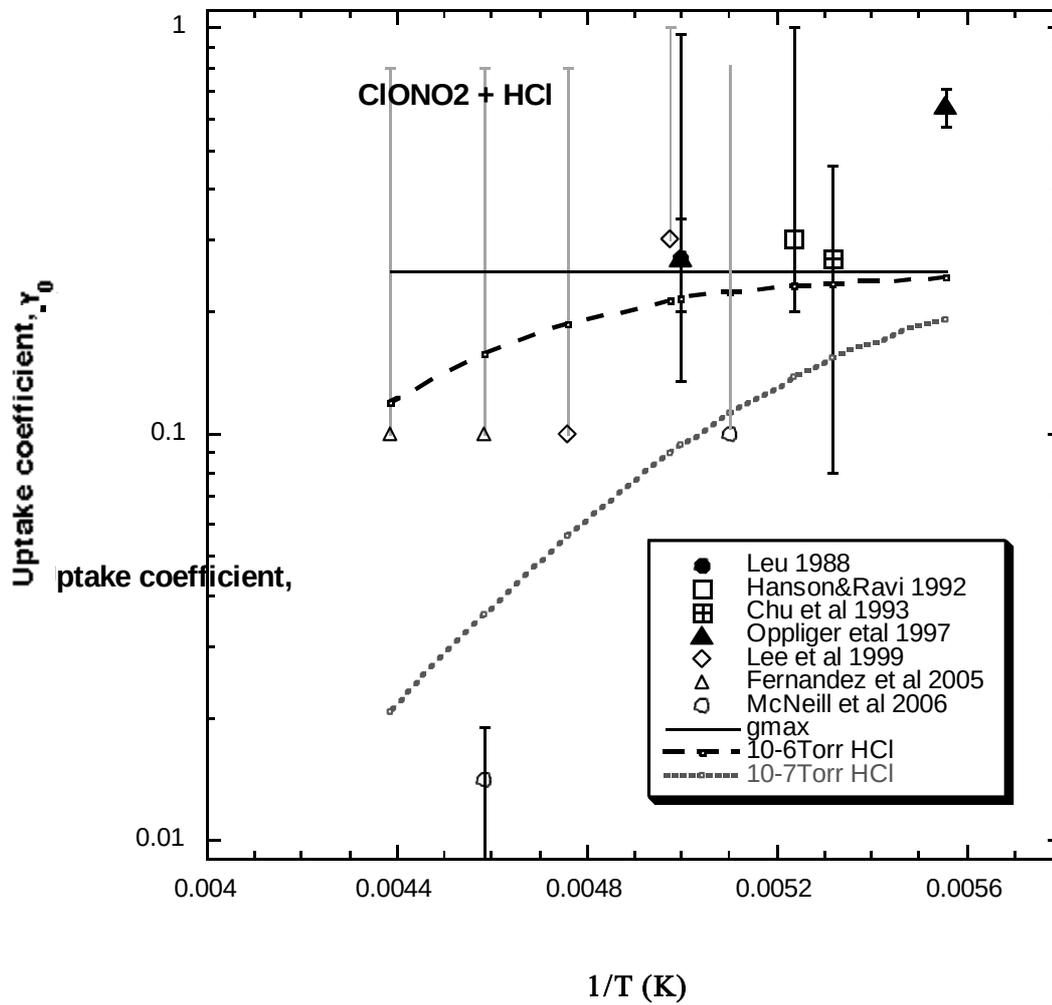


Figure 2. The recommended parameterization for P(HCl) dependence of the uptake coefficient of ClONO₂ on HNO₃ doped ice in the presence of HCl.

