

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.24 HET_SL_24

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ClONO₂ + HCl (aqueous sulphuric acid aerosol) → HONO₂ + Cl₂

Experimental data

Parameter	[H ₂ SO ₄] (wt%)	[HCl] / [HNO ₃] M	Temp./K	Reference	Technique/ Comments
$\gamma(\text{ClONO}_2)$					
3×10^{-3}	65%		210	Tolbert, Rossi and Golden, 1988	Knud-MS (a)
2×10^{-3}	40		218	Hanson and Ravishankara, 1991	WWFT-CIMS (b)
2×10^{-4}	60		215		
$<1 \times 10^{-4}$	65		215		
$<2 \times 10^{-5}$	70		220		
$<2 \times 10^{-5}$	75		230		
0.038	46.6	$< 10^{-4}$	202	Hanson and Ravishankara, 1994	WWFT-CIMS (c)
0.10	46.6	10^{-3}			
0.30	46.6	6×10^{-3}			
0.16 ± 0.06	49	5.8×10^{-3}	197	Zhang, Leu and Keyser, 1994	WWFT-CIMS (d)
0.10 ± 0.05	51	2.2×10^{-3}	198.5		
0.04 ± 0.013	55	3.3×10^{-4}	201		
$(9.5 \pm 3.2) \times 10^{-3}$	60	2.5×10^{-5}	205.5		
$(1.8 \pm 1.6) \times 10^{-3}$	65	2.5×10^{-6}	211		
0.3	43	8.2×10^{-4}	194	Elrod et al., 1995	WWFT-MS(e)
0.083	47	1.4×10^{-4}	196		
0.038	51	2.4×10^{-5}	198		
0.01	55.2	3×10^{-6}	201		
0.11	20.2	4.88×10^{-4} (28.35% HNO ₃)	195		
0.058	44		197		
0.021	50.3	6.18×10^{-5} (6.1% HNO ₃)	199		
		1.38×10^{-5} (2.26% HNO ₃)			
0.07	45	10^{-8} mbar	203-205	Hanson, 1998	WWFT-CIMS (f)
0.6	45	10^{-6} mbar			
0.03	51	10^{-8} mbar			
0.019	51	10^{-6} mbar			
0.011	55	10^{-8} mbar			
0.043	55	10^{-6} mbar			
0.18 ± 0.10	44	10^{-6} mbar, 4.4% HNO ₃	205		
	20.3				
0.25 ± 0.15		10^{-6} mbar, 25.6% HNO ₃			
0.38 ± 0.1	49 ± 1	1.1×10^{-7} mbar	240	Hanson, 1998	AFT-CIMS(g)

Comments

- (a) The H₂O vapor pressure in the flow reactor was 5.3x10⁻⁴ mbar (±30%). Before ClONO₂ uptake at typical pressures of 6.4x10⁻³ mbar, the 65% H₂SO₄/H₂O solution was exposed to 1.7x10⁻³ mbar HCl for an hour to result in an estimated mole fraction ratio HCl:H₂O=2x10⁻⁴. More than 85% of the HCl is recoverable as Cl₂ from the 65% H₂SO₄ solution at 210K. Resulting γ values are very similar to experiments without added HCl.
- (b) The cold aqueous solution of H₂SO₄ was flowed down the walls of the vertical flow tube with a liquid film residence time of 20-30s. p(H₂O) was generally around 1.3 x 10⁻³ mbar, [HCl] for the experiments on the 40% solution was 2 x 10¹¹, for the 60 to 75% solution was in the range 1 to 3 x 10¹¹ molecule cm⁻³. The error limits are reported to be (+100%,-50%) except for the 40 and the 60% solution. The uptake of ClONO₂ in the presence of HCl is not accelerated compared to experiments without HCl. A number of experiments were performed at high HCl concentrations with the result that γ is significantly enhanced at comparable ClONO₂ concentrations: for a 60% solution γ was 2 x 10⁻⁴ (215K), 0.006 (215K) and ~0.01 (238K) for gas phase HCl concentrations of 2 x 10¹⁰, 7 x 10¹² and ~5 x 10¹² molecule cm⁻³.
- (c) Liquid H₂SO₄ (46.6% to 65%) was applied as a cold liquid to the inner wall of the flow tube. The HCl was either added to the liquid (46.6 and 51%) or taken up from the gas phase (55.6, 57.5, 58.5, 59.8 and 65%). No significant temperature dependence of the uptake coefficient in the temperature range 192 to 208 K was observed. The uptake coefficient increased with increasing p(HCl) and increasing H₂O activity. Significant uptake was observed at [HCl] → 0 which was attributed to the ClONO₂ hydrolysis reaction. It was found from fitting experimental data over a wide range that a surface-mediated reaction between Cl⁻ and ClONO₂ scaling with p(HCl) was required in addition to the competitive bulk reaction to account for the observed uptake rates.
- (d) Total pressure of He 0.67 mbar and flow velocity 890 cm s⁻¹ linear. The partial pressure of H₂O (5ppm at 100mbar) was held constant throughout the range of 195 to 220K in order to control [H₂SO₄] between 45 and 70% as a function of temperature. p(ClONO₂) and p(HCl) were varied between (1 - 2.5) x 10⁻⁷ and (2.7 - 27) x 10⁻⁷ mbar, respectively. The value of γ increases by a factor of ten with increasing [HCl] in the given range. Identical values of γ were measured on liquid sulfuric acid containing up to 5% of HNO₃ and 5 ppm. H₂O
- (e) Reactive uptake experiment using a vertically-mounted wetted-wall flow reactor coupled to a differentially-pumped beam-sampling quadrupole MS. The substrates were bulk ternary or quaternary solutions of H₂SO₄-H₂O-HCl-HNO₃. The uptake measurements were performed at 203 K, and the composition of the solutions selected to correspond to various atmospheric equilibrium temperatures in the range 194-201K. p(HCl) over the solutions was measured at temperatures in the range 208 - 233K to determine H*(HCl) and p(ClONO₂) was of the order of 1.3 x 10⁻⁶ mbar. It was established that γ_{ss} was essentially independent of temperature at a given composition and that it was controlled by the HCl solubility in the condensed phase.
- (f) Uptake experiment in rotating wetted wall flow tube using CIMS detection for ClONO₂, Cl₂, HOCl and water vapor. HCl was doped into the 49.5, 51, 53 and 55% H₂SO₄/H₂O solutions from the gas phase. For 45% sulfuric acid solutions HCl was added by mixing pure with sulfuric acid containing known amounts of HCl. The measured uptake is the sum of the reactions of ClONO₂ with HCl and the hydrolysis with H₂O. The parametrization of the total

uptake contains an interfacial term for $\text{ClONO}_2 + \text{HCl}$ which is important for $[\text{HCl}] > 10^{-3} \text{ M}$. For liquid ternary solutions containing HNO_3 the uptake was significantly lower compared to pure sulfuric acid solutions: for partial pressures corresponding to 5 ppm H_2O and 5 ppb HNO_3 at 19 km altitude γ_{ss} was typically lower by a factor of two.

- (g) Uptake on sub-micron aerosol particles of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ (49±1 wt %) doped with HCl, measured at 240K and 120 mbar total pressure to determine surface accommodation coefficient, α_s . The surface-area-weighted mean diameter was 160 nm and the number density (2 - 5) $\times 10^5 \text{ cm}^{-3}$. The particles were doped with HCl ($p(\text{HCl}) = 1.1$ and $2.0 \times 10^4 \text{ mbar}$), resulting in an HCl content of 9.6×10^{-3} and $1.7 \times 10^{-2} \text{ M}$, respectively. The weak dependence of γ on $p(\text{HCl})$ suggests that reaction rate is not quite fast enough to force the measured γ to the value of α_s . A best estimate for α_s based on a crude analysis gave 0.72 ± 0.1 but a value of $\alpha_s = 1$ is consistent with the measurements.

Preferred Values

Parameter	Value	T/K
α_s	1.0	298
$b_0 / \text{M}^2 \text{cm}^{-2}$	7.9×10^{-11}	
$k_{\text{H}_2\text{O}} / \text{s}^{-1}$	$1.95 \times 10^{10} \exp(2800/T)$	190 - 280
$k_{\text{H}^+} / \text{M}^{-1} \text{s}^{-1}$	$1.22 \times 10^{12} \exp(6200/T)$	190 - 280
Γ_s	$66.12 \exp(-1374/T) \times H_{\text{ClONO}_2} \times M_{\text{HCl}}$	
$H_{\text{ClONO}_2} / \text{M} \cdot \text{bar}^{-1}$	$1.6 \times 10^{-6} \exp(4710/T) \exp[(-0.306 + 24.0/T) M_{\text{H}_2\text{SO}_4}]$	200 - 280
$D_l / \text{cm}^2 \text{s}^{-1}$	$5 \times 10^{-8} T / \eta$	180 - 240
.		
<i>Reliability</i>		
$\Delta \log(\alpha)$	± 0.1	298
$\Delta \log(\gamma)$	± 0.3	200 - 280

$M_{\text{H}_2\text{SO}_4}$ = molarity H_2SO_4 (Mol dm^{-3}); M_{HCl} = molarity HCl (Mol dm^{-3}) = $p(\text{HCl}) \times H_{\text{HCl}}^*$.

Comments on Preferred Values

There is a large body of experimental data on the reactive uptake of ClONO_2 in the presence of HCl on $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ surfaces, mainly covering the range of temperature and humidity, and acid composition relevant for the upper troposphere and lower stratosphere. The uptake leads to efficient formation of HNO_3 and Cl_2 products both of which transfer rapidly to the gas phase. At low $p(\text{HCl})$, when hydrolysis of ClONO_2 contributes, HOCl is also observed as a product.

The kinetic results are generally consistent between the different studies which used both bulk and dispersed (aerosol) surfaces, although the uptake coefficients measured on bulk surfaces often required large correction for gas phase diffusion effects, because of fast reactive uptake of ClONO_2 (or HCl) at the surface. The reactive uptake coefficient increases strongly with H_2O content of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions in the corresponding range 40 - 70 wt% at constant $p(\text{HCl})$, which reflects the increasing solubility of HCl in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ as relative humidity increases. The uptake coefficient shows only a very weak dependence on temperature.

The uptake coefficient also shows a complex dependence on $p(\text{HCl})$, or on $[\text{HCl}]_l$ in experiments where the solutions were specifically prepared. At intermediate $[\text{HCl}]$ Elrod et al

(1997) found γ proportional to $[\text{HCl}]^{1/2}$, whilst Zhang et al (1994) who used higher $p(\text{HCl})$, gave close to linear dependence on $[\text{HCl}]$. Hanson and Ravishankara (1994) covered a wider range of $p(\text{HCl})$, and found that for intermediate and high HCl amounts, γ values were proportional to $p(\text{HCl})^{1/2}$ and $p(\text{HCl})$ respectively, attaining a γ value of 0.3 at 1.3×10^{-4} mbar HCl at 202 K. At low $p(\text{HCl})$, γ tends to a constant value of ~ 0.01 , which is due to the additional contribution of hydrolysis of ClONO_2 to the overall γ . The observed effects of temperature can also be rationalised by its effect on HCl solubility in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution of varying mole fraction, together with compensating effects on the rate coefficient of the liquid phase reaction. At low temperatures the presence of HNO_3 in the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions leads to significantly lower γ relative to solutions without HNO_3 (Hanson,1998). The effect increases with $[\text{HNO}_3]/[\text{H}_2\text{SO}_4]$ and at equal wt% amounts to a 50% reduction in γ at 205 K.

Hanson and Ravishankara (1994) suggested that two pathways control the rate of heterogenous reaction of ClONO_2 with HCl: a direct surface reaction; and a bulk phase reaction involving reaction of solvated ClONO_2 with Cl^- , leading to the distinct kinetic dependencies on $p(\text{HCl})$. Hanson (1998) has reanalysed their earlier data, and those of Elrod et al.(1997) and Zhang et al.(1994) in the light of improved measurements of HCl solubility, and has formulated a parameterisation for overall γ taking into account the different reactive processes, using a resistance-model formulation, eq (1):

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\frac{1}{\frac{1}{\Gamma_b} + \frac{1}{\alpha_s \frac{k_{sol}}{k_{des}}}} + \Gamma_s} \quad (1)$$

Hanson's parameterisation gives overall γ for uptake of chlorine nitrate as a function of mole fraction of H_2SO_4 and $p(\text{HCl})$ for stratospheric conditions near 200 K, using an empirical representation of the composition-dependent liquid phase resistance due to chemical reaction.

Shi et al. (2001) have adopted the Hanson model and extended the parameterisation to include temperature dependence, using re-evaluated $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ composition and temperature dependent expressions for HCl solubility, H^*_{HCl} (see VI.A4.14), chlorine nitrate solubility, H_{ClONO_2} , and resistance term Γ_b for the $\text{ClONO}_2 + \text{H}_2\text{O}$ reaction (see VI.A4.25). Shi et al. (2001) assumed that the $\text{ClONO}_2 + \text{HCl}$ reaction is H^+ catalysed and its rate is diffusion controlled, as deduced by Hanson (1998). They also assume that the direct surface reaction of ClONO_2 with HCl depends on bulk-liquid $[\text{ClONO}_2]$ and $[\text{HCl}]$ through their respective T - and composition-dependent H values. Overall the deviation from the experimental data was 40% for the Shi model compared to 46% for the Hanson (1998) parameters. We adopt the Shi et al. (2001) parameters in this recommendation.

The preferred value α_s is based on the measured uptake coefficients on HCl-doped aerosols reported by Hanson (1998), which support a surface accommodation coefficient near unity ($\alpha_s = 1$. see comment *g* above). It follows that the term $\alpha_s k_{sol}/k_{des}$ which is equivalent to the surface to bulk resistance term, Γ_{sb} , must also be close to unity, and equation (1) reduces to:

$$\frac{1}{\gamma} = 1 + \frac{1}{(\Gamma_b + \Gamma_s)} \quad (2)$$

The resistance term Γ_b for the bulk reaction probability is given by: $\Gamma_b = 4RTH(D_1k^I)^{1/2}/c$ where D_1 and H are respectively the diffusion coefficient and Henry's constant for ClONO₂. k^I is the sum of the first order rate coefficients for reaction of ClONO₂ with Cl⁻ (k'_{HCl}) and H₂O (k'_{H2O}) in the bulk. Combining the resistance terms for these two processes acting in parallel gives:

$$\Gamma_b = \Gamma_{H2O} \sqrt{1 + \frac{k'_{HCl}}{k'_{H2O}}} \quad (3)$$

Here $\Gamma_{H2O} = 4RTH(D_1k'_{H2O})^{1/2}/c$ and the recommended temperature and composition dependence of the first order rate coefficient, k'_{H2O} , and solubility of ClONO₂, H , are given in the functional forms described in the data sheet for the ClONO₂ + H₂O reaction (see VI.A4.25). The overall hydrolysis rate constant is given by the expression:

$$k'_{H2O} (s^{-1}) = (k_{H2O} + k_{H^+} a_{H^+}) a_w$$

where a_w = activity water; a_{H^+} = acid activity (Mol dm⁻³). a_w is calculated from: $a_w = \exp[(-69.775X - 18253.7X^2 + 31072.2X^3 - 25668.8X^4)/(1/T - 26.9033/T^2)]$ where wt = weight% H₂SO₄.

The diffusion controlled rate coefficient for the ClONO₂ + HCl reaction is given by the expression:

$$k'_{HCl} (s^{-1}) = b_0 D_1 a_{H^+} H^*_{HCl} p(HCl) \quad (4)$$

The recommended value for the constant b_0 ($= 7.9 \times 10^{-11} \text{ M}^2\text{cm}^2$), was determined from the experimental measurement of the reacto-diffusive length at 250 K at high [HCl] (Hanson 1998). The value of H^*_{HCl} is given as a function of H₂SO₄ mole fraction, X , by the expression:

$$H^*_{HCl} = (0.094 - 0.61X + 1.2X^2) \exp(-8.68 + (8515 - 10718X^{0.7})/T) \quad (5)$$

as given in data sheet for HCl solubility VI.A4.14. The acid activity is derived from the data from the thermodynamic model of Carslaw et al.(1997). For the expression for a_{H^+} in the table the Carslaw model was extended to include the acidity of pure water, to provide values of a_{H^+} as a function of acid wt% (wt) in units of M dm⁻³ extending to dilute solution (wt ~ 0%):

$$a_{H^+} = \exp[60.51 - 0.095\text{wt} + 0.0077\text{wt}^2 - 1.61 \times 10^{-5}\text{wt}^3 - (1.76 + 2.52 \times 10^{-4}\text{wt}^2)T^{0.5} + (-805.89 + 2.53.05\text{wt}^{0.076})/T^{0.5}]$$

Diffusion coefficients, D_i , are calculated using the expression: $D_i = CT/\eta$, with $C = 5 \times 10^{-8} \text{ cm}^2\text{cP K}^{-1}\text{s}^{-1}$ (taken from Klassen et al., 1998). Viscosity data for H₂SO₄/H₂O obtained by Williams and Long(1995) was reparameterized to give a more general formulation for D_i covering the temperature range 200 – 300 K and 0 – 80wt% H₂SO₄:

$$\eta = AT^{1.43} \exp(448/T - T_0)$$

$$A = 169.5 + 5.18\text{wt} - 0.0825\text{wt}^2 + 3.27 \times 10^{-3}\text{wt}^3$$

$$T_0 = 144.11 - 0.166\text{wt} + 0.015\text{wt}^2 - 2.18 \times 10^{-4}\text{wt}^3$$

The resistance term Γ_s for the surface reaction probability was parameterised by Shi et al (2001) as follows:

$$\Gamma_s = 66.12 \exp(-1374/T) H_{\text{ClONO}_2} H_{\text{HCl}}^* P_{\text{HCl}} \quad (6)$$

which assumes a dependence of surface reaction rate on liquid phase concentrations of reactants, which is determined by their solubilities. An Arrhenius temperature dependence is assumed and the recommended constant term was evaluated by fitting to the ClONO₂ uptake rate data at high [HCl]. This expression gave a better representation of the temperature dependence of the surface reaction component than that used by Hanson (1998).

The figure shows a comparison of γ values calculated using eq (2) for a large range of p(HCl) and at different acid wt% H₂SO₄, with experimental data obtained mainly at temperatures near 200 K. The model gives a good fit to the data over the range of conditions employed and will give reasonably accurate values of $\gamma(\text{ClONO}_2)$ for UTLS conditions. Overall the deviation reported by Shi et al. (2001) from experimental data used for the fit was 40%, compared with 46% for the parameters reported by Hanson (1998). These form the basis of the recommended uncertainty in γ over the temperature range 200 – 280 K. The temperature dependence of the γ_r is in fact rather small due to compensating effects of the temperature dependence of D_1 and H_{HCl}^* . For detailed discussion of the model/measurement comparison the Shi et al paper (2001) should be consulted.

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Figure 1: Plot of $p(\text{HCl})$ dependence of uptake coefficient at different H_2SO_4 wt%. Symbols show experimental data: open circles = 45-47%; closed circles = 49-49.5%; open squares = 51%; triangles = 55%; half filled squares = 60%; square cross = 65%. Lines show predicted uptake coefficients using recommended parameters for each wt%. Temperature = 197 - 205 K, except data collected for $p(\text{HCl}) = \sim 10^{-7}$ bar on aerosols by Hanson (1998) at 240 K

