IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.25 HET_SL_25

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$ClONO_2 + H_2O$ (aqueous sulphuric acid aerosol) $\rightarrow HONO_2 + HOCl$

Experimental data

Parameter	[H_2SO_4] wt%	Temp./K	Reference	Technique/ Comments
$\gamma, \gamma_{ss}, \gamma_0$ ($ClONO_2$)				
(3.2 ± 0.8) x 10^{-3}	95.6% H_2SO_4		Rossi et al, 1987	Knud-MS (a)
2.6 x 10^{-3}	65% H_2SO_4	210	Tolbert, et al,, 1988	Knud-MS
3 x 10^{-4}	75% H_2SO_4	230		(b)
0.064 ± 0.010	40% H_2SO_4.	218	Hanson and Ravishankara, 1991a	WWFT-CIMS (c)
(3.1 ± 0.5) x 10^{-3}	60% H_2SO_4	215		
(1.2 ± 0.2) x 10^{-3}	65% H_2SO_4	215		
(3.9 ± 0.7) x 10^{-4}	70% H_2SO_4	220		
(1.9 ± 0.3) x 10^{-4}	75% H_2SO_4	230		
(8.1 ± 1.3) x 10^{-2}	40% H_2SO_4	220 ± 5	Golden et al., 1992;	Knud-MS
(4.1 ± 0.7) x 10^{-3}	57.5% H_2SO_4		Williams et al., 1994;	(d)
(2.1 ± 0.35) x 10^{-4}	75% H_2SO_4		Manion et al., 1994	
(3.8 ± 1.2) x 10^{-2}	46.6% H_2SO_4	202	Hanson and Ravishankara, 1994	WWFT-CIMS (e)
(6.1 ± 2.0) x 10^{-3}	57.5% H_2SO_4			
(9.3 ± 3.0) x 10^{-4}	65% H_2SO_4			
(2.0 ± 0.6) x 10^{-2}	50% H_2SO_4	197.5	Zhang, Leu and Keyser, 1994	WWFT-CIMS (f)
(2.5 ± 0.7) x 10^{-3}	60% H_2SO_4	205		
(7.5 ± 2.5) x 10^{-4}	65% H_2SO_4	211		
(3.0 ± 1.0) x 10^{-4}	70% H_2SO_4	218		
2 x 10^{-3}	65% H_2SO_4	250	Hanson and Lovejoy, 1995	AFT-CIMS (g)
0.11	53% H_2SO_4	200	Zhang, Leu and Keyser, 1995	WWFT-CIMS (h)
0.034	29%	195		
0.021	H_2SO_4,16.4%$H NO_3$	200		
0.045		200		
0.10	5% H_2SO_4,41% HNO_3	220		
	40% H_2SO_4,10% HNO_3			
	5% H_2SO_4,41% HNO_3			
(3.7 ± 0.6) x 10^{-3}	59% H_2SO_4	241	Robinson et al., 1997	DT-TDLAS
(5.60 ± 0.84) x 10^{-2}	39% H_2SO_4	229		
(2.62 ± 0.39) x 10^{-2}	39% H_2SO_4	259		(i)
0.071 ± 0.025	36% H_2SO_4	245	Ball *et al.*, 1998	AFT-CL (j)

0.038±0.009	43% H$_2$SO$_4$	248		
0.0094±0.003	54% H$_2$SO$_4$	253		
0.113±0.023	36.5% H$_2$SO$_4$	203	Hanson, 1998	WWFT CIMS (k)
0.086±0.017	36.5% H$_2$SO$_4$	230		
0.053±0.011	45% H$_2$SO$_4$	203		
0.038±0.008	45% H$_2$SO$_4$	230		
0.011±0.002	55% H$_2$SO$_4$	203		
(1.6±0.3) x 10^{-4}	75% H$_2$SO$_4$	270		
(1.4±0.3) x 10^{-4}	75% H$_2$SO$_4$	250		
(1.1±0.2) x 10^{-4}	75% H$_2$SO$_4$	230		
(6.4±1.3) x 10^{-5}	75% H$_2$SO$_4$	217		
(2.5±1.0) x 10^{-5}	75% H$_2$SO$_4$	200		
0.019±0.004	44%	203		
0.042±0.016	H$_2$SO$_4$,4.6% HNO$_3$ 20% H$_2$SO$_4$,26% HNO$_3$	205		

Comments

(a) Simultaneous flows of H$_2$O (1.5x10^{13} molecule cm^{-3}) and ClONO$_2$ (9.4x10^{11} - 4.5x10^{13} molecule cm^{-3}) were exposed to bulk 95.6% H$_2$SO$_4$ at ambient temperature; γ is first order in [ClONO$_2$] and declines with exposure time.

(b) The H$_2$O vapor pressure in the flow reactor was 5.3x10^{-4} mbar (±30%). Uptake of ClONO$_2$ at typical pressures of 6.4x10^{-3} mbar on 65% H$_2$SO$_4$/H$_2$O.

(c) Flowing aqueous H$_2$SO$_4$ film residence time of 20-30s. p(H$_2$O) was ~ 1.3 x 10^{-3} mbar and [ClONO$_2$] was approx.10^{10} - 10^{11} molecule cm^{-3}. The temperature dependence of γ was measured for the 60% and 70% H$_2$SO$_4$ solution: none was found within the reported error limits.

(d) [ClONO$_2$] was approx.10^{12} - 10^{13} molecule cm^{-3}. The following analytical expression was obtained for the uptake/reaction probability (γ) of ClONO$_2$:   log γ =1.87-0.074x[H$_2$SO$_4$] (wt%) (±15%) valid for the range 40 to 80% H$_2$SO$_4$ /H$_2$O mixtures at 220K.

(e) Quiescent liquid H$_2$SO$_4$ surface with CIMS detection. H$_2$SO$_4$ (46.6% to 65%) was applied as a cold liquid to the inner wall of the flow tube.

(f) Walls coated with a 70% H$_2$SO$_4$ solution of approximately 0.1 mm thickness. The partial pressure of H$_2$O was held constant (5 ppm at 100 mbar pressure) throughout the temperature range 195 - 220K in order to control the acid concentration with temperature leading to [H$_2$SO$_4$] in the range 45 to 70% by weight.

(g) High pressure (0.3 to 0.8 bar) flow tube using slow flow conditions and sub micron H$_2$SO$_4$ aerosol generated by homogeneous nucleation from the reaction of SO$_3$ + H$_2$O. Particle size 60 - 250 nm diam. The uptake coefficient for the reaction of ClONO$_2$ with 60 wt% sulfuric acid aerosol increases monotonically with particle size at 250 K. The reactive-diffusive length (*l*, the effective liq. depth over which reaction occurs) derived from these experiments is 0.037 ± 0.007 μm.

(h) Two methods of film preparation of defined ternary composition H$_2$SO$_4$/H$_2$O/HNO$_3$ at low temperatures resulted in identical values of γ which does not change in the presence of HNO$_3$, even at a limiting composition of 15% HNO$_3$/30% H$_2$SO$_4$ at 195K.

(i) Fast train of 200μm H$_2$SO$_4$/H$_2$O droplets traversing a flow tube with TDLAS detection. Pressures = 13.3 mbar and droplet-gas interaction times of 2 to 20 ms. The temperature of the droplets was inferred from the water partial pressure measured by TDL absorption. A negative temperature dependence of γ$_{ss}$ was observed for T≥230K and γ$_{ss}$ slightly increased with increasing concentration of H$_2$SO$_4$ measured at 39, 54 and 69%. A model involving neutral and acid catalysed mechanism for ClONO$_2$ hydrolysis was used to extract valies of a_s and liquid phase rate constants by fitting data from several laboratories over a range of temperature and composition. The temperature dependence of a_s was given in the form $a_s /(1- a_s) = \exp(-17.89 + 4515/T)$.

(j) High pressure (0.3 to 0.8 atm) flow tube using slow flow conditions and sub micron H_2SO_4 aerosol generated by homogeneous nucleation from the reaction of $SO_3 + H_2O$. Particles of a narrow size range were selected with a DMA for each H_2SO_4 concentration used: mean size 95 nm, 104 nm and 63 nm radius for 36, 43 and 54 wt% respectively. $ClONO_2$ (30 to 200 ppb) detected by titrating with NO in a heated quartz tube, using TDLAS to monitor NO and also H_2O vapor. The average value of γ was used to derive a value of $l = 26$ nm for the reacto-diffusive length at ~43% H_2SO_4

(k) Uptake of $ClONO_2$ measured in two flow reactors: *a*: Rotating wetted wall flow tube with sulfuric acid wall film (0.2 mm thickness). The pressure was 0.5 mbar He in the wall coated tube and 240 mbar of N_2 in the aerosol flow tube. The range of $[H_2SO_4]$ investigated was 36.5 to 55% H_2SO_4/H_2O at 203K, 36.5 to 45.0% at 230K and 75% in the temperature range 200 to 270K. *b*: sub-micron aerosol (particle size 0.1 μm) 49±1% H_2SO_4/H_2O . CIMS detection for $ClONO_2$, HOCl and water vapor. Initial concentration was 5 x 10^{11} molecule cm^{-3} in both studies. The results for small sulfuric acid particles resulted in a lower limit of $\alpha_s > 0.5$. $ClONO_2$ reaction probabilities were also measured on H_2SO_4 solutions containing significant amounts of HNO_3. In contrast to previous reports, HNO_3 was found to have a significant reducing effect on γ for $ClONO_2$.

Preferred Values

Parameter	Value	T/K
α_s	1	298
k_{H2O} /s^{-1}	1.95 x 10^{10} exp(2800/T)	190 - 280
k_{H+} /$M^{-1}s^{-1}$	1.22 x 10^{12} exp(6200/T)	190 - 280
H_{ClONO2}/M.bar^{-1}	1.6 x 10^{-6} exp(4710/*T*).exp[(-0.306 + 24.0/T).M_{H2SO4}]	200 - 280
D_l /cm^2s^{-1}	5 x $10^{-8}T/\eta$	180 - 240

M_{H2SO4}= molarity H_2SO_4(Mol dm^{-3}); wt = weight% H_2SO_4; X= mole fraction H_2SO_4

Reliability

$\Delta \log (\alpha)$	± 0.1	298
$\Delta \log (\gamma)$	±0.2	200 -280

Comments on Preferred Values

There is a large body of experimental data on the uptake of $ClONO_2$ on H_2SO_4/H_2O surfaces covering a relevant temperatures, humidity and sulphuric acid aerosol composition for the atmosphere between the surface and the lower stratosphere. The results are generally consistent between the different studies which used both bulk and dispersed (aerosol) surfaces. The uptake leads to hydrolysis of $ClONO_2$ and formation of HOCl and HNO_3 which both transfer to the gas phase. The presence of HNO_3 in the H_2SO_4/H_2O solutions leads to a reduction in the uptake rate (Hanson, 1998; Zhang et.al, 1995). Based on uptake measurements of Hanson (1998) on $HNO_3/H_2SO_4/H_2O$ solutions corresponding to conditions in the polar lower stratosphere (~5 ppb HNO_3 in the gas phase), the γ values would be approximately a factor of 2 lower than for H_2SO_4/H_2O solutions.

Uptake rates show strong dependence on H_2O content of the sulphuric acid solution/aerosol, γ_{ClONO2} decreasing in the range 20 - 70 wt% H_2SO_4. H_2O content depends on both temperature and relative humidity and consequently there is a complex variation of γ for atmospheric

conditions: generally low temperature and high RH favour rapid reactive uptake with γ values ~ 0.1 in 40% H_2SO_4 falling off to ~10^{-4} in 75% H_2SO_4. At low temperature the effects of composition dominates leading to weak negative T dependence of γ.

These characteristics indicate that uptake is determined by chemical reaction in the liquid droplet and can be interpreted in terms of the resistance model. Thus the overall uptake coefficient is given by eq.(2)

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_b} \qquad (1)$$

$$\Gamma_b = 4RTH(D_l k^I)^{1/2}/c \qquad (2)$$

where H is the Henry's solubility constant of $ClONO_2$, D_l is the diffusion coefficient of $ClONO_2$, and k^I the first order rate constant for hydrolysis of $ClONO_2$ in H_2SO_4/H_2O solutions.

Robinson et al.(1977) presented a phenomenological model addressing solubility, diffusion and chemical reactivity of $ClONO_2$,which accounts for the observed dependence of the uptake coefficients on concentration and temperature. Two hydrolysis pathways are proposed, a direct reaction with H_2O and an acid-catalysed reaction involving H^+ ions to promote the dissociation: $ClONO_2 + H^+ \rightarrow HOCl + NO_2^+$. The hydrolysis rate coefficient representing the two pathways was given in the form: $k^I = k_{H2O} a_w + k_{H+} a_{H+}$; here a_w and a_{H+} are the activities of H_2O and H^+ in solution respectively. They extracted temperature and composition dependencies for the individual parameters, α_s and k^I from a fit of their experimental γ values using this model, together with a parameterisation of H based on solubility data given by Huthwelker et al (1995) for HOCl as a proxy for $ClONO_2$. D_l was parameterized using the expression: $D_l = CT/\eta$, with C evaluated from viscosity data for H_2SO_4/H_2O solutions obtained by Williams and Long(1995).

Hanson (1998) has used a similar model, which gives γ values as a function of mole fraction of H_2SO_4, X, which is defined for a given temperature and water activity (RH). Only a single direct hydrolysis reaction was used for k^I. Composition dependent values of Γ_b were obtained from a fit of eq(1) to experimental X-dependent γ values for 200-205K, assuming $\alpha_s =1.0$: $\Gamma_b = \exp(-0.392-13.13X-50.914X^2)$ (3). This simple expression can be used to calculate γ from eq.1 with reasonable acuracy for specified values of H_2SO_4 wt% in the range 40 - 65% in and for temperatures near 200 K; at $\geq$70 wt% the observed γ values are seriously underpredicted. Thus this formula only applies for only for a limited range of lower stratospheric conditions. Hanson also derived individual parameterisations for variation of H, D_l, H_2SO_4 acidity (a_{H+}, a_{H2O}) as a function of mole fraction of H_2SO_4, X, at temperatures near 200 K.

Shi et al (2001) have reported further analysis using these models for representation of uptake coefficients for $ClONO_2$ hydrolysis and reaction with HCl in H_2SO_4 solutions. They adopt a general mechanism involving both a direct and an acid-catalyzed channel for $ClONO_2$ reaction with H_2O and HCl, with the reactive species controlled by following equilibrium:

$$ClONO_2(liq) + H^+ \Leftrightarrow HClONO_2^+(liq) \qquad\qquad K_{eq}$$
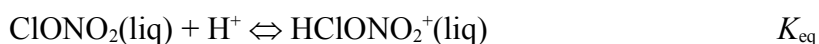
The hydrolysis rate constant is given by:

$$k^I = k_{H2O} a_w + k_{H+} a_{H+} a_w , \qquad\qquad (3)$$

where the acid catalysed rate constant, k_{H+}, includes the term K_{eq}, arising from the assumption that protonated species are in equilibrium. The values of D_l, H, H_2SO_4 acidity and water activity(a_{H+}, a_w) were parameterized independently of the experimental uptake measurements.

The thermodynamic model of Carslaw et al. (1995) was used to derive a parameterization of a_w in terms of the mole fraction (X) of H_2SO_4, (X = wt%/(wt% + (100 – wt%)98/18):

$$a_w = \exp[(-69.775X - 18253.7X^2 + 31072.2X^3 - 25668.8X^4)(1/T - 26.9033/T^2)].$$

Note however that for atmospheric modelling a_w is usually calculated from the local H_2O mixing ratio and temperature. For the acid activity 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%):

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

$$+ (-805.89 + 253.05wt\%^{0.076})/T^{0.5}.$$

Diffusion coefficients, D_l were estimated using the expression: $D_l = CT/\eta$, with C = 5 x 10^{-8} cm^{2}cP K^{-1}s^{-1} (taken from Klassen et al., 1998). Viscosity data for H_2SO_4/H_2O obtained by Williams and Long (1995) was re-parameterized to give a more general formulation covering the temperature range 200 – 300 K and 0 – 80wt% H_2SO_4:

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

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

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

The variations of H and k_1 with acid strength are constrained by the experimental values of $H(k_1)^{1/2}$, which is determined from experimental uptake coefficients using eq (2) for defined D_l. Following Robinson et al.,(1997), the solubility of HOCl was used as proxy for $ClONO_2$, and is given in the functional form:

$$H = H_o \exp(B/T).\exp(-S_t M_{H2SO4}) \qquad (4)$$

$$S_t = c + d/T \qquad (5)$$

H(HOCl) was re-parameterized taking into account the higher temperature and wt% H_2SO_4 data of Donaldson et al (1997) which extended and improved that of Huthwelker et al (1995). The Setchenow coefficient, S_t, was assumed to depend on the *molarity* (rather than molality) of the H_2SO_4 solution. H was derived from indirect analysis of aerosol kinetics measurements of Hanson and Lovejoy (1995), which provided uptake coefficient, γ, and reacto-diffusive length, l, for hydrolysis of $ClONO_2$ on 60% H_2SO_4 at 250 K. This provides a value for H_{ClONO2} at a single temperature and to obtain the temperature dependence of H (and also of k^1), use was made of the kinetic data for the $ClONO_2$ + HCl reaction, for which the temperature dependence includes that of H_{ClONO2} and k^1_{HCl}. Assuming the latter is diffusion limited (following Hanson, 1998) its temperature dependence is fixed, allowing extraction of the following parameters for calculation of the solubility of $ClONO_2$: H^0 = 1.6 x 10^{-6}, B = 4710, c = 0.306, and d = 24.0 in equations (4) and (5).

The rate coefficients for the direct and acid catalysed hydrolysis were expressed in Arrhenius form:

$$k_{H2O} = A_{H2O}. \exp(-E_{H2O}/T)$$

$$k_{H+} = A_{H+}. \exp(-E_{H+}/T)$$

The values of k^1 for experimental conditions were calculated from eq 3, using the parameterisations for a_{H+}, a_{H2O} given above. The A and E values for the temperature dependence of k_H and k_{H2O} were determined from a global fit to experimental uptake coefficients for both the $ClONO_2$ hydrolysis and HCl reaction data, assuming the reaction $ClONO_2$ + HCl is diffusion limited, in the same procedure as the determination of H_{ClONO2} over a range of temperature. The values obtained from fitting of the data from [Hanson, 1998, Ball et al.,

1998, Robinson et al. 1997, Hanson and Lovejoy, 1995, Zhang et al., 1994, Manion et al. 1994, Hanson and Ravishankara, 1991, 1994] were:

$A_{H2O} = 1.95 \times 10^{10} \, s^{-1}$ $\qquad$ $E_{H2O} = 2800$ K

$A_{H+} = 1.22 \times 10^{12} \, M^{-1}s^{-1}$ $\qquad$ $E_{H+} = 6200$ K

All three models give a good description of the experimental γ values for the range of conditions used to derive the parameters. However the parameterisations for H, D_l, k_1 and the other data on which they are based, differ considerably. The simpler parameterisation for Γ_b (eq.3) obtained by Hanson gives a reasonable representation of observed γ values as a function [H_2SO_4], but only up to 65 wt%, and at temperatures around 200 K. The more complex parameterisation of Shi et al (2001) gives an excellent description of the experimentally observed data over a range of temperature 190 - 260 K at [H_2SO_4] in the range 35 - 75 wt%, as can be seen in the figure. The standard deviation of this model with respect to all experimental data used in the global fit was 32%(1σ) The parameters of Shi et al., given in the Table above, are recommended as the preferred values for hydrolysis of ClONO$_2$ covering most atmospheric conditions.

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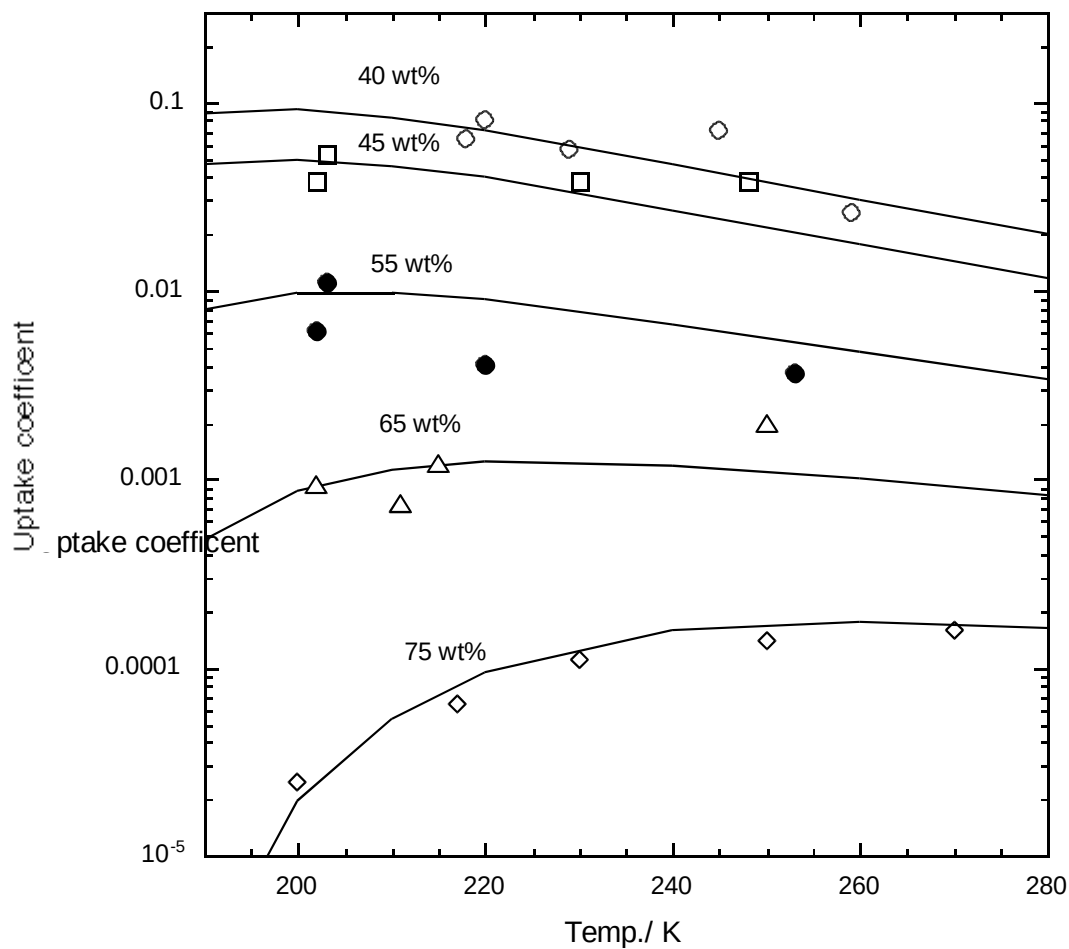Zhang, R., Leu, M.-T. and Keyser, L.F.: J. Phys. Chem. 98, 13563, 1994.

Figure 1: Temperature dependence of uptake coefficients for uptake of ClONO$_2$ \by H$_2$SO$_4$/H$_2$O surfaces plotted as a function of acid wt% in H$_2$SO$_4$/H$_2$O solutions Lines show values calculated using parameters recommended in this evaluation, based on Shi et al.(2001). Points show selected experimental data taken from the table given in this datasheet, grouped in approximate acid wt% bands.