IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.22 HET_SL_22

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HOCl + HCl (aqueous sulphuric acid aerosol)→ H_2O + Cl_2

Experimental data

Parameter	p_{HOCl} /mbar	p_{HCl} /mbar	$[H_2SO_4]$ /wt%	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ						
$\gamma_{HOCl} = 1 \times 10^{-3}$		7×10^{-6}	60	263	Hanson and Ravishankara, 1991	WWFT-CIMS (a)
$\gamma_{HCl} = 6 \times 10^{-3}$	1.5×10^{-5}	9×10^{-6}	60	215		
$\gamma_{HOCl} = 0.02 - 0.15$		10^{-8}-10^{-6}	59.6	200-205	Hanson and Ravishankara, 1993	WWFT-CIMS (b)
$\gamma_{HOCl} = 0.45$		4×10^{-7}	50	198	Zhang et al., 1994	WWFT-MS (c)
$\gamma_{HOCl} = 7 \times 10^{-2}$		4×10^{-7}	60	205		
$\gamma_{HOCl} = 4 \times 10^{-3}$		4×10^{-7}	68	214		
$\gamma_{HOCl} = 0.1$		4×10^{-7}	57	202		
$\gamma_{HOCl} = 0.2$		8×10^{-7}	50	198		
$\gamma_{HOCl} = 0.5$		2×10^{-6}	60	205		
$\gamma_{HOCl} = 4.5 \times 10^{-3}$		2×10^{-6}	59.6	251	Hanson and Lovejoy, 1996	RWFT-CIMS (d)
$\gamma_{HOCl} = 1.3 \times 10^{-2}$		2×10^{-5}				
$\gamma_{HOCl} = 2.7 \times 10^{-2}$		7×10^{-5}				
$\gamma_{HOCl} = 2.5 \times 10^{-2}$ (70nm)		3×10^{-3}	59.5	251	Hanson and Lovejoy, 1996	AFT-CIMS (d)
$\gamma_{HOCl} = 7.5 \times 10^{-2}$ (200nm)		3×10^{-3}		251		
$\gamma_{HOCl} = 1.0 \times 10^{-1}$ (400nm)		3×10^{-3}				
$\gamma_{HOCl} = 0.07$ ($a_{H2O} = 0.10$)		3×10^{-3}				
$\gamma_{HOCl} = 0.4$ ($a_{H2O} = 0.28$)		3×10^{-3}				
$\gamma_{HOCl} = 0.86$ ($a_{H2O} = 0.56$)		3×10^{-3}				
$\gamma_{HCl} = 0.1$ (38 nm)	1.5×10^{-3}		34	274		
$\gamma_{HCl} = 0.32$ (160 nm)	1.5×10^{-3}		34			
$\gamma_{HCl} = 0.58$ (420 nm)	1.5×10^{-3}		34			
$\gamma_{HCl} = 0.08$ ($a_{H2O} = 0.58$)	1.5×10^{-3}			272-276		
$\gamma_{HCl} = 0.44$ ($a_{H2O} = 0.69$)	1.5×10^{-3}					

γ_{HCl} = 0.75 (a_{H2O} = 0.79)	1.5×10^{-3}				
γ_{HOCl} =0.013	5×10^{-7} -	52	250	Donaldson et al., 1997	RWFT-CIMS (e)
γ_{HOCl} =0.09	2×10^{-5}	52			
γ_{HOCl} =0.011	2×10^{-5} –	62.5	250		
γ_{HOCl} =0.045	2×10^{-4}	62.5			
γ_{HOCl} =0.0048	4×10^{-5} -	67	250		
γ_{HOCl} =0.018	1×10^{-3}	67			
γ_{HOCl} =0.043	5×10^{-7} -	58	220		
γ_{HOCl} =0.15	1×10^{-5}	58			
γ_{HOCl} =0.05	2×10^{-6} -	60	220		
γ_{HOCl} =0.12	4×10^{-5}	60			
γ_{HOCl} =0.023	1×10^{-6} -	63	220		
γ_{HOCl} =0.070	2×10^{-5}	63			
γ_{HOCl} = 2.0×10^{-3} (70 nm)	10^{-3}	67	250		AFT-CIMS (e)
γ_{HOCl} = 5.5×10^{-3} (180 nm)	10^{-3}				
γ_{HOCl} = 1.3×10^{-2} (400 nm)	10^{-3}				
γ_{HOCl} = 1.3×10^{-2} (680 nm)	10^{-3}				
Reacto-diffusive parameters					
$H_{HOCl}(D_l k_b H^*_{HCl})^{1/2}$ = 4.0×10^4 M cm s^{-1} atm$^{-3/2}$		59.6	251	Hanson and Lovejoy, 1996	RWFT-CIMS (d)
l_{HOCl} = 1.2×10^{-5} cm		59.5	251	Hanson and Lovejoy, 1996	AFT-CIMS (d)
l_{HCl} = 1.2×10^{-4} cm		34	274		
$(k_b H_{HOCl})^{1/2}$ = 1.1×10^4 (atm s)$^{-1/2}$		34	274		

Comments

(a) The cold aqueous solution of H_2SO_4 flowed down the walls of the vertical flow tube. p(H_2O) was generally around 1.3 x 10^{-3} mbar, [HCl] for the experiments on the 40% solution was 2 x 10^{11}, for the 60 to 75% solution it was in the range 1 to 3 x 10^{11} molecule cm-3.

(b) First order loss of HOCl was observed in a cylindrical flow tube with H_2SO_4 applied as a coating for the 200-205 K measurements or contained in a boat for the measurement at 219 K. HOCl was generated by reacting HF with $Ca(OCl)_2$ powder. HCl was added via uptake from the gas phase at pressures > 3 x 10^{-7} mbar, leading to [Cl$^-$] > 10^{-5} M, in excess of HOCl. The value for k_b reported and listed in the table was obtained by estimates of the diffusion coefficients and solubilities as reported from the same study.

(c) Wetted wall flow tube with water vapour pressure maintained constant at 1.5×10^{-3} Torr, to give 45 – 70 wt% H_2SO_4 solutions for 195 K < T < 220 K. Detection limits were 5×10^{-8} Torr for HOCl 5×10^{-7} Torr for HCl. Production of Cl_2 matched the loss of HOCl or HCl. Experiments with both excess of HCl and HOCl were performed. Uptake coefficients were consistent between

analysis of reactant loss and Cl_2 formation. Kinetics were not affected by the presence of HNO_3 at 6.5×10^{-7} mbar.

(d) Bulk measurements of first-order loss of either HOCl or HCl under conditions of mutual excess of the other, respectively. HOCl, HCl and Cl_2 were detected using SF_6^- reactant ion. The parameter listed in the table is the slope of a plot of $1/\gamma$ vs. the square root of the HCl pressure. Aerosol flow tube experiment operated at 180 Torr of N_2, 10 STP cm^3 s^{-1} and 251-276 K. The aerosol mode diameter was 200nm with a geometric standard deviation of 1.2. Under the conditions of the experiment, for both HOCl and HCl diffusion controlled loss to the flow tube walls occurred.

(e) Rotating wetted wall and aerosol flow tube experiments identical to those done by Hanson and Lovejoy (1996). The total pressure in the wetted wall flow tube was at maximum a few mbar (mostly He), with a flow rate of 3-4 STP cm^3 s^{-1}.

Preferred Values

Parameter	Value	T/K
$\alpha_{b,HCl}$	see datasheet VI.A4.14	
$\alpha_{b,HOCl}$	1	
k_b (M^{-1} s^{-1})	80 [H$^+$] T/η	$190 - 273$
Reliability		
Δ log (k_b)	0.3	

Comments on Preferred Values

HOCl reacts efficiently with HCl under acidic conditions (Eigen and Kustin, 1962). Most of the kinetic data covering tropospheric and lower stratospheric conditions were obtained by one group using coated wall and aerosol flow tubes. The measured uptake coefficients clearly established that kinetics is driven by reaction in the bulk (Lovejoy and Hanson, 1996). Donaldson et al. (1997) suggested protonated HOCl, H_2OCl^+, being the reactive species, based on the strong sensitivity of the first order loss rate constant in the bulk on acidity and on theoretical evidence (Koch et al., 1997; Francisco and Sander, 1995; and references therein). Shi et al. (2001) suggested the expression adopted here for the second order rate constant to explicitly include the proton molarity and assumed that the rate constant is limited by diffusion of HOCl (leading to a dependence of the apparent rate constant on viscosity). As already pointed out by Shi et al., taking the revised parameterizations for H_{HOCl} (datasheet VI.A4.13) and H^*_{HCl} (datasheet VI.A4.14), this leads to good agreement with all available data of γ_{HOCl} for a wide range of conditions, including those by Zhang et al. (1994), another flow tube experiment at low temperature.

The recommended parameterisation reproduces the available data of γ_{HCl} reasonably well and notably also the size dependence for both measured by Hanson and Lovejoy (1996) and Donaldson et al. (1997), since the reacto-diffusive length is in the range of 0.1 to 1 μm, as well as the dependence of the uptake as a function of water activity.

Therefore, the uptake coefficients of HOCl and HCl on sulphuric acid in presence of HCl or HOCl, respectively, can be obtained from:

$$\frac{1}{\gamma_{HOCl}} = \frac{1}{\alpha_{b,HOCl}} + \frac{\bar{c}_{HOCl}}{4H_{HOCl}RT\sqrt{D_{l,HOCl} \cdot k_b p_{HCl} H^*_{HCl}}\left[\coth\left(\frac{r_p}{l_{HOCl}}\right) - \left(\frac{l_{HOCl}}{r_p}\right)\right]}$$

$$\frac{1}{\gamma_{HCl}} = \frac{1}{\alpha_{b,HCl}} + \frac{\bar{c}_{HCl}}{4H^*_{HCl}RT\sqrt{D_{l,HCl} \cdot k_b p_{HOCl} H_{HOCl}}\left[\coth\left(\frac{r_p}{l_{HCl}}\right) - \left(\frac{l_{HCl}}{r_p}\right)\right]}$$

$\alpha_{b,HOCl}$ is assumed to be one (see datasheet (VI.A4.13). For $\alpha_{b,HCl}$ we recommend the parameterization given on datasheet VI.A4.14, which leads to slightly better agreement with data

than assuming $\alpha_{b,HCl} = 1$: $\alpha_{b,HCl} = k_{sol}/(k_{des} + k_{sol})$ with $k_{sol} = 7.84 \times 10^{10}$ /η and $k_{des} = 8.0 \times 10^{17}$ exp(-5000/T).

We suggest using the parameterisation of Shi et al. for the proton concentration:

$[H^+]$ = exp [60.51 – 0.095$wt\%$ + 0.0077$wt\%^2$ – 1.61× $10^{-5}wt\%^3$ – (1.76 + 2.52× 10^{-4} $wt\%^2$)$T^{0.5}$ + (-805.89 + 253.05$wt\%^{0.076}$)/$T^{0.5}$]

We take the preferred expression for the solubility of HOCl from datasheet VI.A4.13,

H_{HOCl} = 1.91 × 10^{-6} exp(5862.4/T) exp (-(0.0776+59.18/T)[H_2SO_4])

and that for HCl from datasheet VI.A4.14:

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

The mole fraction, X, of sulfuric acid is given by X = $wt\%$/($wt\%$ + (100 – $wt\%$)98/18 and [H_2SO_4] in mol L^{-1} can be calculated from the sulfuric acid content using density data provided by Shi et al.

The diffusion coefficients for HOCl and HCl are parameterized by $D_{l,X} = C_X \times 10^{-8}$ T /η; with C_{HOCl} = cm^2 cP K^{-1} s^{-1} (see datasheet VI.A4.13) and C_{HCl} = 7.8 × 10^{-8} cm^2 cP K^{-1} s^{-1} (see datasheet VI.A4.14). For the viscosity, we suggest using the parameterization presented by Shi et al. (2001), which fits well to data by Williams and Long (1995) but extends into tropospherically more relevant dilute solutions at high T:

$\eta = A$T$^{-1.43}$ exp(448K /(T-T$_0$)),

with A = 169.5 + 5.18 (wt%) – 0.0825 (wt%)^2 +3.27 × 10^{-3} (wt%)^3,

and T_0 = 144.11 + 0.166 (wt%) – 0.015 (wt%)^2 + 2.18 × 10^{-4} (wt%)^3

The reacto-diffusive lengths needed to account for finite particle sizes are given by:

l_{HOCl} = ($D_{l,HOCl}$/($k_b p_{HCl}$ H^*_{HCl}))$^{0.5}$

l_{HCl} = ($D_{l,HCl}$/($k_b p_{HOCl}$ H_{HOCl}))$^{0.5}$

References

Eigen, M., and Kustin, K. J.: J. Am. Chem. Soc., 84, 1355-1361, 1962.

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Zhang, R. Y., Leu, M. T., and Keyser, L. F.: J. Phys. Chem., 98, 13563-13574, 1994.

Donaldson, D. J., Ravishankara, A. R., and Hanson, D. R.: J. Phys. Chem. A, 101, 4717-4725, 1997.

Koch, T. G., Banham, S. F., Sodeau, J. R., Horn, A. B., McCoustra, M. R. S., and Chesters, M. A.: J. Geophys. Res., 102, 1513-1522, 1997.

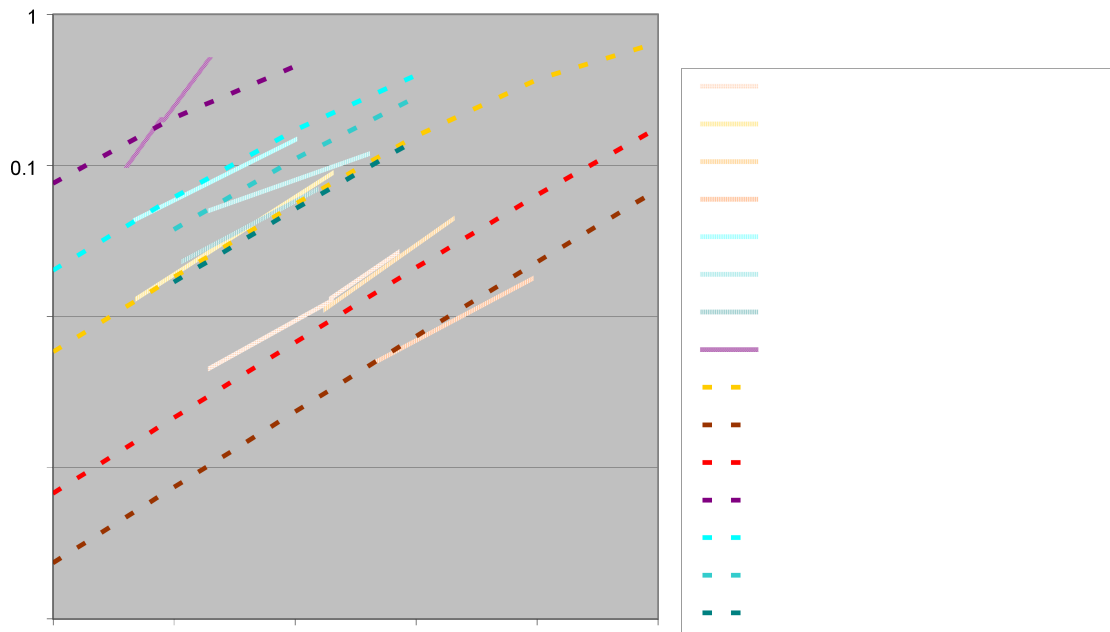Francisco, J. S., and Sander, S. P.: J. Chem. Phys., 102, 9615-9618, 1995.

Figure 1: Uptake coefficient of HOCl on sulphuric acid solutions as a function of HCl partial pressure. Dotted bars denote the range of experimental data. Dotted lines present recommended values calculated for the composition and temperatures of the experimental data.
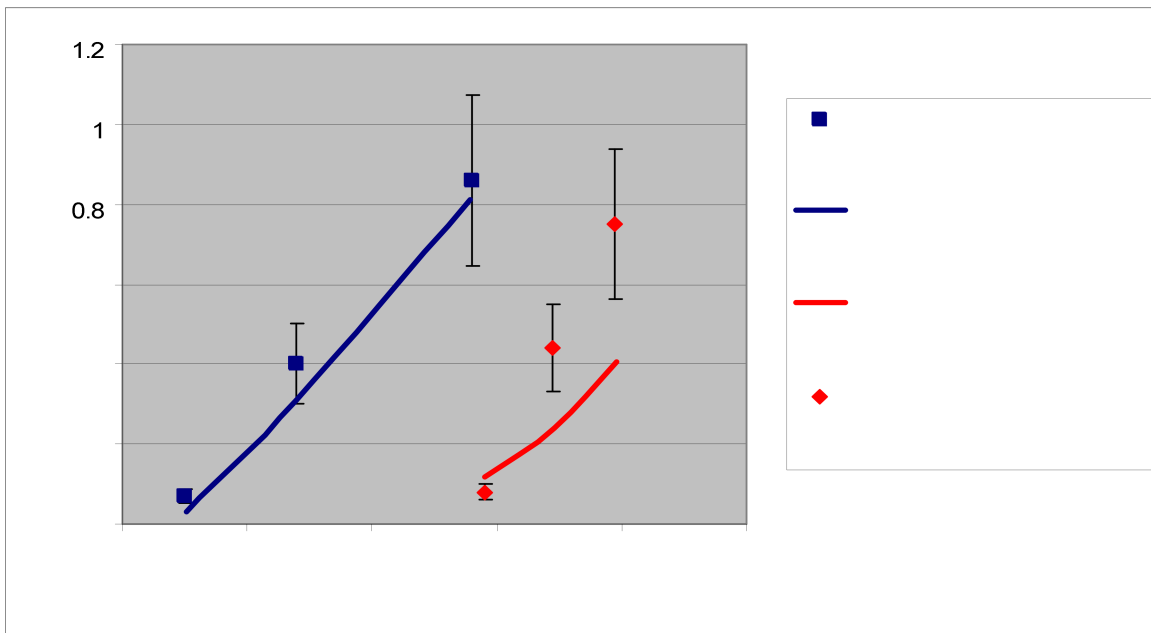

Figure 2: Uptake coefficient of HCl (red) and HOCl (blue) as a function of water activity. Symbols denote experimental data, lines represent the recommendation.
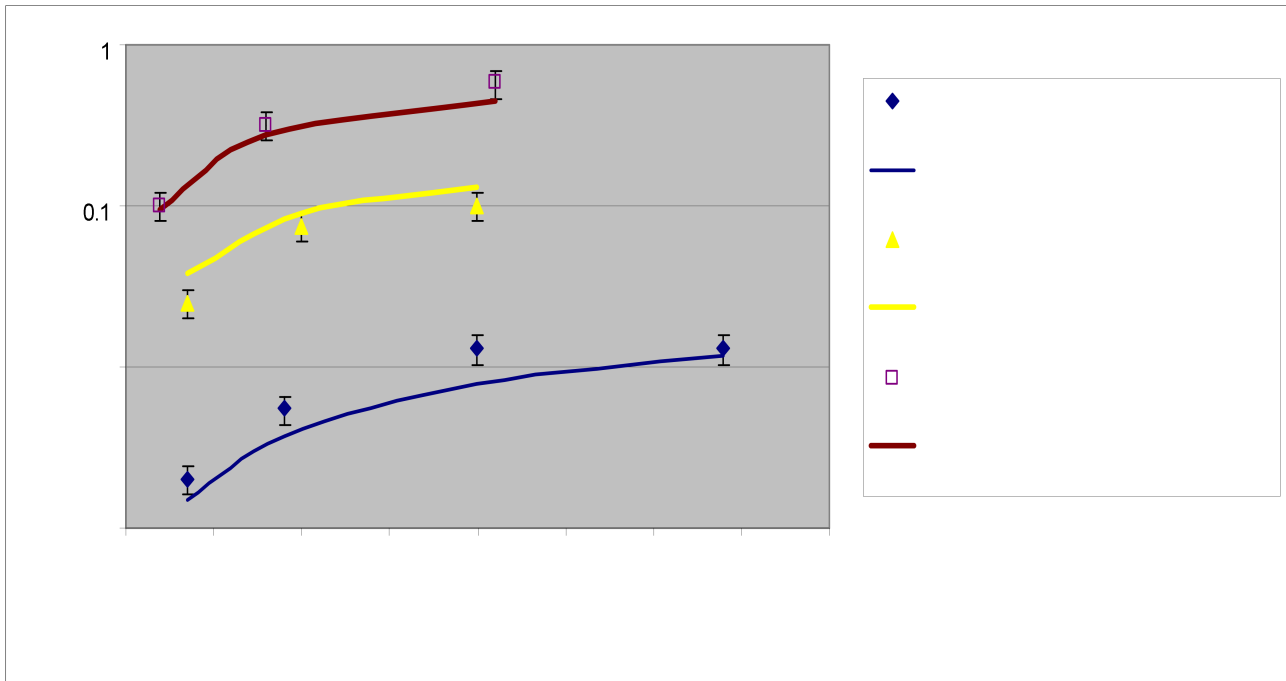
Figure 3: Uptake coefficient of HOCl and HCl as a function of particle size. Symbols denote experimental data, lines are calculated uptake coefficients based on the recommended parameters.