IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A4.8 HSTD8

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$ClONO_2 + HCl\ (SAT) \rightarrow HNO_3 + Cl_2$

Uptake coefficient data

Parameter	Temp/K	Reference	Comment
Uptake Coefficients($ClONO_2$)			
0.125 100% RH 2.4×10^{-4} 8% RH		Hanson and Ravishankara, 1993	CWFT-CIMS(a)
0.12±0.03 100% RH 0.06±0.03 72% RH* 0.04±0.03 61% RH* 0.01±0.03 36% RH* 0.0035±0.03 18% RH* $(7.0\pm2.0) \times 10^{-4}$ 7% RH	195	Zhang, Jayne and Molina, 1994	CWFT-EIMS(b)
>0.2* 0.02*	190 208		
$<1.0 \times 10^{-4}$	200-220	Zhang, Leu and Keyser, 1995	CWFT-CIMS(c)

Comments

(a) Solid film of sulphuric acid ≥ 0.1 mm thickness made from freezing a liquid solution of composition corresponding to SAT (57.5% H_2SO_4/H_2O) on the inside of the flow tube wall to 195K. The cryogenic deposits were characterized by their vapour pressure of H_2O monitored by an ion-molecule reaction with F_2^-. The results were obtained as a function of relative humidity in the range 10 to 90%, obtained by using a fixed $p(H_2O$ and varying the temperature from 192 - 205 K. $p(ClONO_2)$ = (1.3 to 7 $x10^{-7}$) mbar. P_{HCl} was approximately held at 2×10^{-7} mbar (2-3 ppbv at 17 km) and p_{H2O} for the displayed γ values was 6.7×10^{-4} mbar. The uptake coefficients could be expressed as $\ln\gamma = -0.636-0.4802\Delta T$, where $\Delta T = T-189$. ΔT can be approximated by $T-T_{ice}$ where T_{ice} is the temperature of the ice point at a given partial pressure of water vapor and where $p_{H2O} < p_{ice}$.

(b) Solid film of sulphuric acid ≥ 0.1 mm thickness made from freezing a liquid solution of composition corresponding to SAT (57.5% H_2SO_4/H_2O) on the inside of the flow tube wall to <200 K. The thermodynamic state of the SAT sample was controlled by setting the vapour pressure of H_2O, either H_2O -rich (approaching 100% rh) or H_2SO_4-rich at constant temperature or selecting the temperature at constant $p(H_2O)$. The HCl was always in excess of $ClONO_2$ and no HOCl product was detected. γ strongly depends on the relative humidity over the SAT

surface, a trend that reflects the partitioning of HCl to the surface; its value decreases by more than two orders of magnitude at 195K, from 0.12 at 100% rh to $7x10^{-4}$ at low rh. The following expressions are provided for the uptake coefficient at typical stratospheric [HCl]: log $\gamma = 5.25 + 1.91 \log P_{H2O}$ for T=195K, P_{ClONO2} = 4 to 5.3 $x10^{-8}$ mbar, P_{HCl} = 5.3 to 10.5 x 10^{-7} mbar, P_{H2O}= 5.3 $x10^{-5}$ to 7.4 $x10^{-5}$ mbar; log $\gamma = 175.74 - 1.59 \log T + 0.0035 \log^2 T$ for T in the range 195-206K, P_{ClONO2} = 4 to $6.7x10^{-8}$ mbar, P_{HCl} = 5.3 to 10.6 x 10^{-7} mbar and P_{H2O}= $7.4x10^{-4}$ mbar.

(c) Solid film of sulphuric acid ≥ 0.1 mm thickness made from freezing a liquid solution of composition corresponding to SAM (75-85% H_2SO_4/H_2O) on the inside of the flow tube wall at 220-230 K. P_{HCl} and P_{ClONO2} were in the range 2.7 to10.6 $x10^{-7}$ mbar. The experiment was performed by first exposing SAM to HCl and subsequently measuring the uptake of $ClONO_2$ which was identical to hydrolysis on SAM with HCl absent.

Preferred Values

Parameter	Value	T/K
γ_{ER}	0.12	190 – 199
θ_{HCl}	[HCl]* 6800 * F	190 – 199
F	$(-2.47x10^{11}+3.28x10^{11}RH+3.27x10^{9}\ RH^2+2.43x10^{9}\ RH^3)/1.7x10^{14}$	190 – 199

[HCl] in molecule cm^{-3}.

Reliability

$\Delta(\gamma_{rxn})$	±0.2	185 – 210 K.

Comments on Preferred Values

As with ice films the uptake of $ClONO_2$ on SAT films is followed by reaction with HCl to form Cl_2 and HNO_3 in a surface reaction. At stratospheric temperatures HOCl partitions into the gas phase. The two studies of Hanson and Ravishankara (1993) and Zhang et al. (1994) on SAT show that reactive uptake of $ClONO_2$ on HCl-doped SAT is a strong function of relative humidity, declining as RH reduced, as was also found for NAT surfaces. In the case of SAT, Zhang et al. (1994) showed that surface coverage resulting from a given p(HCl) also declined rapidly with decreasing RH, which accounts for the effect on the surface reaction rate and hence the reactive uptake coefficient of $ClONO_2$. The γ values of Hanson and Ravishankara(1993) are in good agreement with the more extensive data Zhang et al.(1994). For H_2O-rich SAT (>90% RH) at 195 K, $\gamma = 0.12$ which is approximately a factor of 2 lower than observed for HCl doped ice (0.27±0.02) for similar p(HCl) of 7 x 10^{-7} mbar. At lower $p(H_2O)$ and higher temperatures γ reduces to ~10^{-3}, although there is some indication that γ on H_2O-rich SAT increases with decreasing temperature. Reactive uptake of $ClONO_2$ on HCl-doped SAM is very slow, $\gamma \sim 1 \times 10^{-4}$.

The IUPAC recommended upateke coefficient parameterisation for reaction of $ClONO_2$ + HCl on ice surfaces used an Ely-Rideal model. Application of this model to solid sulphuric acid films requires the surface concentration $[HCl]_s$ to be defined as a function of temperature and $p(H_2O)$. The partitioning of HCl to SAT studied by Zhang et al.(1994) forms the basis of our recommendation for K_{LinC} for HCl as a function of RH in the temperature range 190 - 199 K (IUPAC, 2009). The recommended reactive uptake coefficients for $ClONO_2$ + HCl use the IUPAC K_{LinC} to evaluate θ_{HCl} in the following expression for γ_{ClONO2}

$\gamma_s = \gamma_{ER}(ClONO_2)$ x θ_{HCl}

The uptake coefficients from this expression give a reasonable fit to results of Zhang et al. (1994) as a function of relative humidity and temperature over the temperature range 191.5 to 205 K.

References

Hanson, D.R. and Ravishankara, A.R.: J. Geophys. Res. 98, 22931 (1993).
Leu, M.-T., Moore, S.B. and Keyser, L.F.: J. Phys. Chem. 95, 7763 (1991).
Zhang, R., J. T. Jayne and Molina, M.J.: J.Phys. Chem. 98, 867 (1994).