IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A4.7 HSTD7

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$ClONO_2 + H_2O$ (SAT) → $HNO_3 + HOCl$

Uptake coefficient data

Parameter	Temp/K	Reference	Comment
Uptake Coefficients($ClONO_2$)			
2.0×10^{-3} (RH = 90%) 2.0×10^{-3} (RH = 30%) 5.0×10^{-4} (RH = 16%) 1.0×10^{-4} (RH = 7%)	191.5 196 200 205	Hanson and Ravishankara, 1993	CWFT-CIMS(a)
0.016±0.4 (RH = 100%) 5.6×10^{-3} (RH = 72%)* 2×10^{3} (RH = 36%)* 9×10^{-4} (RH = 18%)* $(5.0\pm1.3) \times 10^{-4}$ 8% RH	195 195 195 195 195	Zhang, Jayne and Molina, 1994	CWFT-EIMS(b)
0.02 (RH = 100%)* 4×10^{-3} (RH = 52%)* 1.5×10^{-3} (RH = 28%)* 0.85×10^{-3} (RH = 13%)*	192 196 200 205		
$<1.0 \times 10^{-4}$	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 $p(H_2O)$ ~3.3 $x10^4$ mbar and varying the temperature from 192 - 205 K. $p(ClONO_2)$ = (1.3 to 7 $x10^{-7}$) mbar. Uptake slower than onto liquid sulphuric acid surfaces.

(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 $p(H_2O)$ for the cited data are

given in terms of relative humidity expressed relative to $p(H_2O)$ for pure ice at the experimental temperature. Data marked* were extracted from graphs. The dependence of γ on P_{H2O} (Torr) and on temperature (K) was expressed in parametric form: $\log \gamma = 10.12 + 5.75\log P + 0.62\log^2 P$ for T=195K, [P= $p(H_2O)$]]; $p(ClONO_2)$ = 3 to $5x10^8$ Torr, $p(H_2O)$ = $4x10^{-5}$ to $5.6x10^{-4}$ Torr; $\log \gamma = 318.67 - 3.13\log T + 0.0076\log^2 T$ for T in the range 192-206K, $p(ClONO_2)$ = 2 to $4x10^{-8}$ Torr and $p(H_2O)$=$3.4x10^{-4}$ Torr.

(c) Uptake experiment on solid sulphuric acid monohydrate ($H_2SO_4 \cdot H_2O$, SAM) using a fast flow tube reactor coupled either to MS (most data) or CIMS. The thickness of the crystalline SAM films was approximately 0.1 mm, $p(H_2O) = (1.3 - 5.2) \times 10^{-4}$ mbar at 220-240 K. $ClONO_2$ uptake was much slower than onto liquid sulphuric acid surfaces.

Preferred values

parameter	value	Temp/K
γ	$1 \times 10^{-4} + 4 \times 10^{-5}$ RH + 4.7×10^{-7} RH^2	195 – 205

RH = $p(H_2O)/p(ice)$

Reliability

$\Delta(\log \gamma)$	0.3	195 - 205

Comments on Preferred Values

Uptake of $ClONO_2$ on solid sulphuric acid films is followed by rapid reaction with H_2O to form HOCl and HNO_3 in a surface reaction. HOCl partitions into the gas phase, but HNO_3 can remain on the surface. The two studies on SAT show that uptake is slower than on liquid sulphuric acid and is a strong function of relative humidity. Thus the uptake coefficient depends on the thermodynamic state of the surface. The γ values of Hanson and Ravishankara are significantly lower than the more extensive data of Zhang et al (1994), especially at low RH. The γ value of Zhang et al. (1993) for H_2O-rich SAT (>90% RH) is intermediate between that observed for ice (0.08±0.02) and H_2O-rich NAT (~0.002). At lower $p(H_2O)$ and higher temperatures the reaction becomes very slow, although there is some indication that γ on H_2O-rich SAT increases with decreasing temperature. The origin of the apparent discrepancy in the two studies at low RH is unclear. Hanson and Ravishankara reported time-dependent γ, characteristic of inhibition of uptake by surface HNO_3, whilst Zhang et al. (1994) report γ constant with exposure time.

The IUPAC recommended parameterisation for hydrolysis of $ClONO_2$ on ice surfaces used a Langmuir-Hinshelwood model. Application of this model to solid sulphuric acid films requires the surface concentration of water molecules $[H_2O]_s$ to be defined. If $[H_2O]_s$ is related directly to $p(H_2O)$ (i.e low coverage of available H_2O molecules) γ_{LH} should be linearly dependent on RH (or $p(H_2O)$ at a fixed temperature). The experimental γ values of Zhang et al. at 195 K show higher order dependence on RH, indicating a more complex model is needed. Note that if surface saturation at high RH occurs the opposite trend would result.

The recommended expression for γ_{ClONO2} is a second order polynomial fit as a function of relative humidity to results of Zhang et al. (1994) over the temperature range 191.5 to 205 K. An alternate parameterisation based on the Langmuir-Hinshelwood model fit to the data for 195K :

$$\frac{1}{g} = \frac{1}{\alpha_s} + \frac{A}{RH(\,)}$$

where α_s = 1 and A = (1.68±0.22) x 10^4. This gives a reasonable representation of the uptake coefficient at RH < 60% but underestimates the uptake coefficient 100% RH. The factor A in the γ_{LH} part of the expression contains usual $\bar{c}$, k_s and K_{LinC} terms for $ClONO_2$, as well as the conversion between $[H_2O]_s$ (molecule cm^{-2}) and relative humidity (i.e. $p(H_2O)/p(ice)$ [= 7.4 x 10^{-4} mbar at 195K). The temperature dependence of these terms is needed if the expression is applied to other temperatures.

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).