IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.15 HET_SL_15

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ClO + H_2SO_4 (l) → products

Experimental data

Parameter	[H_2SO_4] /wt %	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ				
$(2.0\pm1) \times 10^{-5}$	90	295	Martin et al., 1980	CWFT-EPR (a)
$(1.5\pm1) \times 10^{-4}$	85	260		
$(2.2\pm1) \times 10^{-4}$	80	240		
$<1.0 \times 10^{-4}$	60-70	213	Abbatt, 1996	CWFT-RF (b)

Comments

(a) Measurement of the uptake kinetics in a fast flow tube with EPR detection of ClO. Pure Cl_2 at 0.67 mbar was discharged in a μ-wave cavity and combined downstream with an excess of O_3 in order to generate ClO. The quartz flow tube was coated with halocarbon wax and the discharge tube with solid B_2O_3 in order to minimize wall losses of ClO. The inside of the flow tube was coated with H_2SO_4 and the H_2O vapor pressure was held constant throughout the temperature range at $6.7x10^{-4}$ mbar leading to a changing composition of the H_2SO_4/H_2O mixture as the temperature was changed (96% at 300K, 80% at 240K).

(b) Uptake rates measured in a coated wall flow tube at 1.3 mbar total pressure of He coupled to a resonance fluorescence (RF) detector after chemical conversion. ClO was generated from the reaction Cl + O_3 → ClO + O_2 by discharging Cl_2/He in a microwave cavity and adding O_3 downstream at typical [O_3] in the range from 1 to 3 x 10^{13} molecule cm^{-3}. After ClO interacted with the active surface it was converted to Cl in the reaction ClO + NO → Cl + NO_2 which was detected using a RF-excited Cl_2/He lamp emitting in the VUV at 119 nm in conjunction with a flowing O_2 filter. The sensitivit of the RF lamp was measured using the reaction H + Cl_2 → HCl + Cl. The ClO concentrations used in this work were on the order of 1 to 2 x 10^{11} molecule cm^{-3}.

Preferred Values

Parameter	Value	T/K
γ	No recommendation	

Comments on Preferred Values

In the work of Martin et al. (1980) no separation between the effects of changing composition of the cryogenic phase (considered to be negligible) and the temperature dependence of γ was performed. All kinetic results were obtained from the full numerical integration of the parabolic flow system including axial diffusion and resulted in a pronounced negative temperature dependence of the uptake coefficient γ_{SS}. The unexpected product of the heterogeneous reaction was HCl and no effect of irradiation by simulated sunlight on γ was found within a ± 20% variation of γ. Martin et al. (1980) report a higher sensitivity for ClO-detection compared to Abbatt (1996). In the light of the disagreement between the two datasets we make no recommendations, but note that uptake of ClO to H_2SO_4 at stratospheric temperatures and composition is inefficient.

References

Martin, L.R., Judeikis, H.S., Wun, M.: J. Geophys. Res. 85, 5511-5518, 1980.
Abbatt, J.P.D.: Geophys. Res. Lett. 23, 1681-1684, 1996.