IUPAC Task group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.11 HET_H2OL_11

$HCl + H_2O(l) \rightarrow$ products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Accommodation coefficients: α_b			
$(1.77^{+2.4}_{-1.7}) \times 10^{-1}$	274	Van Doren et al., 1990	DT-LAS (a)
$(6.4^{+1.2}_{-0.8}) \times 10^{-2}$	294		
$0.01 - 0.02$	296.7	Kirchner et al., 1990	LJ-HPLC (b)
0.24 ± 0.02	263	Schweitzer et al., 2000	DT-MS (c)
0.13 ± 0.01	281		
0.24 ± 0.02	273	Li et al., 2002	DT-MS (d)
0.10 ± 0.01	293		

Comments

(a) Droplets (200 μm diameter) crossing a laminar flow tube in transverse geometry. Trace gas analysis is by IR diode laser absorption at total pressures of 6.7-26.6 mbar. [HCl] was typically 7.3 x 10^{12} molecule cm^{-3}. Values listed are corrected for gas phase diffusion and distortion of velocity vector due to rapid uptake.

(b) Uptake experiment involving the interaction of HCl (about 223 ppm) in synthetic air with a liquid jet of pure water. The uptake kinetics was studied by analyzing the liquid water content for Cl$^-$ using ion chromatography. The jet diameter was 90 μm, the jet length between 0.2 and 6 mm leading to contact times of 0.03 to 1.0 ms. The uptake coefficient was interpreted as a bulk accommodation coefficient. The results are regarded as lower limits due to uncertainties in the velocity distribution of the liquid jet. The bulk accommodation coefficient showed a weak dependence on the mean speed of the jet (10-750 cm s^{-1}) and was independent of the relative humidity (0 to 48%) of the gas phase.

(c) Droplets of 80-150 μm diameter with a gas-liquid interaction time of 0-20 ms. The HCl concentrations were in the range $10^{12} - 10^{14}$ molecule cm^{-3}, with most experiments performed at 10^{13} molecule cm^{-3}. Rate of uptake was time-independent as well as independent on pH in the range 7-14. Diffusion-corrected uptake coefficient is interpreted as a bulk accommodation coefficient α_b having a significant negative temperature dependence.

(d) Droplet train experiment with ethylene glycol / water mixtures. Droplet size was in the range 70 to 300 μm, 2.7-25.3 mbar of (mostly) He in flow tube with trace gas species concentrations in the range 2x10^{13} to 3x10^{14} molecule cm^{-3}. The value of α_b was independent of the interaction time in the range 2.5 to 17 ms and had a significant negative temperature dependence. α_b varies continuously with increasing mole fraction of H_2O from a high (pure glycol) to a low (pure H_2O) value which has been successfully modelled using surface tension data for glycol/H_2O solutions of variable composition.

<div align="center">**Preferred Values**</div>

Parameter	Value	T/K
α_b	7.4×10^{-2}	298
α_b	$4.4 \times 10^{-6} \exp(2898/T)$	272-294

Reliability

$\Delta \log(\alpha)$	± 0.2	298
$\Delta (E/R)$	± 500 K	272-294

Comments on Preferred Values

Van Doren et al. (1990) interpret their diffusion corrected uptake coefficients as mass accommodation coefficients. The effective Henry's law constant for aqueous dissolution of HCl is large enough to make the characteristic phase relaxation time significantly longer than the time scale for the droplet train uptake experiment, typically one to a few ms such that there is no surface saturation of the gas-water interface. A surprising result is that both the absolute values of α_b as well as its strong negative temperature dependence were found for HCl, HNO_3, N_2O_5, H_2O_2 and others that were investigated using the same experimental technique. This strongly points towards physical solvation as the rate-determining process whose absolute rate is not accessible as the bulk accommodation coefficient only describes the overall (complex) process and is therefore not an elementary reaction parameter.

The preferred values are taken from Van Doren et al. (1990), Schweitzer et al. (2000) and Li et al. (2002), despite the rather large uncertainty in the Van Doren et al. (1990) study. This fact is due in part to the use of the droplet train apparatus in transverse geometry which affords a restricted range of gas-liquid contact times and therefore a low dynamic range of the measurements. All three studies were performed using the same experimental technique, and the individual α_b values are within the experimental uncertainties of the cited studies. The activation energy of α_b is E = -24.1 kJ/Mol.

The liquid jet technique used by Kirchner et al. (1990) that combines the measurement of the HCl uptake kinetics with the numerical simulation of the convective diffusion towards the thin H_2O jet resulted in a best fit value $0.02 \geq \alpha_b \geq 0.01$ of the mass accommodation coefficient which is in agreement with the recommendation when regarded as a lower limiting value. The sensitivity of the experimental technique used on α_b is low in the range $1 \geq \alpha_b \geq 0.05$ and seems most suited for the measurement of values $\alpha_b \leq 0.01$. Moreover, the careful study of the pressure dependence of γ in the Li et al. (2002) study enabled an easy separation of α_b from the measured uptake coefficients γ_{obs}.

<div align="center">**References**</div>

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