IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.7 HET_H2OL_7

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$$HONO\ (g) + H_2O\ (l) \rightarrow NO\ (aqueous) + NO_2\ (aqueous) + H_2O\ (l)$$

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Bulk accommodation coefficients: α_b			
$> 5 \times 10^{-3}$	299	Kirchner et al., 1990	LJ-IC (a)
4.3×10^{-3} (wet Na_2CO_3)	298	Msibi et al., 1993	CWFT (b)
$(5^{+2}_{-1}) \times 10^{-2}$	297	Bongartz et al., 1994	LJ-IC (c)
$(5^{+4}_{-1}) \times 10^{-2}$	245		DT-IC (c)
$4 \times 10^{-3} < \alpha_b < 4 \times 10^{-2}$	278	Mertes and Wahner, 1995	LJ (d)
Solubility: H			
223 ± 11	273	Park and Lee, 1988	Bubbler-CLD (e)
121 ± 6			
60 ± 3			
38 ± 2			
$H* = 194 \pm 25$ (8.7 wt% H_2SO_4)	269	Becker et al., 1996	Static-TDLAS/IC (f)
$H* = 117 \pm 20$ (8.7 wt% H_2SO_4)	278		
$H* = 73 \pm 10$ (8.7 wt% H_2SO_4)	285		
$H* = 50 \pm 8$ (8.7 wt% H_2SO_4)	291		
$H* = 34 \pm 5$ (8.7 wt% H_2SO_4)	298		
Rate constants, k_1 [$M^{-1}\ s^{-1}$]			
3.46	283	Park and Lee, 1988	Bubbler-CLD (e)
13.4	295		
28.6	303		
Rate constants, k_{-1} [$M^{-1}\ s^{-1}$]			
1.98×10^8	283	Park and Lee, 1988	Bubbler-CLD (e)
1.58×10^8	295		
1.67×10^8	303		

Comments

(a) Interaction of HNO_2 (60 ppm) with a liquid jet of pure water. The kinetics were studied by ion chromatographic analysis of the liquid jet nitrite content. The gas phase diffusion coefficient value used was 0.13 $cm^2\ s^{-1}$, the value used for the solubility of HNO_2 in water was 60 M atm^{-1}. A kinetic model taking into account diffusion in the gas phase as well as the radially resolved flow velocity within the jet was used to simulate the data of appearance of nitrite in the aqueous phase. Agreement with the data was not very good likely due to uncertainties in the velocity distribution of the liquid jet. Taking into account dissociation of HONO in the aqueous phase did not improve the fits. Thus, the bulk accommodation coefficient is regarded as a lower limit.

(b) A flow of 6 l per min of air at 97 % relative humidity containing about 0.5 ppm NO_2 at atmospheric pressure passed an annular glass reactor, coated with a mixture of Na_2CO_3 and glycerol. Uptake of nitrous acid detected by wet extraction of reactor segments.

(c) Two experimental flow techniques, an improved version of the liquid jet and the droplet train technique, were used. Both techniques involve the measurement of the concentration of NO_2^- in the collected liquid droplets of 10 μm to 100 μm diameter at residence times of 3.7 ms to 16 ms at total pressures of 40 mbar to 80 mbar. Temperature refers to droplet surface temperature of (245 ± 5) K. A 20% uncertainty in D_g leads to the stated error intervals.

(d) Liquid jet at 298 K. Experiments were done with pure water, with 0.01 M NaOH, 33.4 g/l triethanolamine and 1g/l $NaAsO_2$ to vary the liquid phase sink. HONO was measured by DOAS in a White cell. HONO was produced indirectly by reaction of NO_2 with the glass walls upstream of the jet leading to concentrations of 10^{13} to 10^{14} cm^{-3} in presence of a factor of 50 more NO_2. Nitrite and nitrate were measured spectrophotometrically. HONO uptake was independent of pH or added sink. Within the short residence time of the jet, the liquid phase remained far from equilibrium. A kinetic model was used to obtain the likely range for α_b based on the observed loss of HONO from the gas phase (lower limit) and the appearance of nitrite in the aqueous phase (upper limit), respectively.

(e) A thermostated pyrex reactor with a fritted gas inlet. The solubility of HONO was measured by using low concentration HONO solutions $(10^{-6}$ M) and observing the purge behavior with a chemiluminescence detector. HONO decomposition experiments were performed at higher solution concentrations $> 10^{-5}$ M to allow observation of NO and NO_2 purging from the bubbler apparatus. The rate constants listed in the table for the forward (decomposition) (k_1) and backward reaction (k_{-1}) were obtained by fitting a kinetic model to the purge data. The mass transfer properties of the bubbler were calibrated using CO_2.

(f) Solubility of HONO was measured in a 11-L Pyrex glass reactor directly by monitoring both gas phase composition by tunable diode laser spectrometry and liquid phase by ion chromatography. Formation of NO_2 due to 2 HONO = NO + NO_2 + H_2O was observed. Since the NO_2 concentration equilibrated with time, this reaction was included into calculating the effective solubility.

Preferred Values

Parameter	Value	T/K
α_b	0.05	273 - 300
H^*	4.2×10^{-6} exp(4873/T) $(1 + 5.9 \times 10^{-4}$ exp(-1760 (1/T-1/298))/[H^+])	273 - 300
k_1 (M^{-1} s^{-1})	3.1×10^{14} exp(-9090/T)	273 - 300
k_{-1} (M^{-1} s^{-1})	1.7×10^8	273 - 300
Reliability		
$\Delta \log (\alpha_b)$	0.7	273 - 300
$\Delta \log (k)$	0.3	273 - 300
Δ E/R [K]	50	273 - 300

Comments on Preferred Values

Most of the attempts to measure the bulk accommodation coefficient of HONO into water or dilute aqueous solutions were done with a liquid jet experiment at relatively high pressure. Uncertainties arise from not understanding precisely the radial flow velocity distribution within the jet, which critically determines whether or not uptake runs into solubility equilibrium. The other significant issue is that especially at atmospheric pressure, transfer of the gas into the liquid is strongly affected by gas phase diffusion. We therefore adopt the value from the Bongartz et al. (1994) study performed at lower pressure than the others.

The solubility of HONO in water has been directly measured by Park and Lee (1988). Their data are also in line with the extrapolated solubility from those by Becker et al. (1996), who measured the solubility as a function of sulphuric acid composition (0.3 wt% and above). The

preferred expression is consistent with that presented in data sheet VI.A4.7 for 0 wt% H_2SO_4 and agrees well with the temperature dependence measured by Park and Lee. The acid dissociation constant used in this expression is that determined by Park and Lee, which is identical to that calculated from the standard free energies of formation of HONO(g) and HONO(aq) (Schwartz and White, 1981). We note that the acid dissociation constant determined by Riordan et al. was somewhat lower (1.6×10^{-3} (pK=2.8) at 298 K).

The rate constants for the decomposition reaction of HONO (k_1) and the reverse process (k_{-1}) has been adopted from Park and Lee (1988); for k_{-1} the average of the available rate constants at three temperatures have been taken as preferred value. They are somewhat above those of earlier studies (Schwartz and White, 1981, and references therein), but better represent the low concentrations expected under atmospheric conditions. The preferred value for k_1 is much lower than that in H_2SO_4 at about 50 wt% (320 M^{-1} s^{-1}, see data sheet VI.A4.7). Given that the back reaction is significant, an expression for gamma based on the resistance model is not appropriate.

References

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