

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.3 HET_H2OL_3

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Experimental data

<i>Parameter</i>	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>			
10^{-7} (pure water and 0.05 M NaOH)	273	Lee and Tang, 1988	(a)
$(1.5 \pm 0.6) \times 10^{-3}$ ($9 \times 10^{14} \text{ cm}^{-3} \text{ NO}_2$)	298	Ponche et al., 1993	DT-IC (b)
$(8.7 \pm 0.6) \times 10^{-5}$	298	Msibi et al., 1993	CWFT(c)
$(2.4 \pm 1.4) \times 10^{-4}$ ($9 \times 10^{14} \text{ cm}^{-3} \text{ NO}_2$)	298	Mertes and Wahner, 1995	LJ(d)
$(1.2 \pm 0.4) \times 10^{-3}$ ($5 \times 10^{15} \text{ cm}^{-3} \text{ NO}_2$)	298		
$(9.5 \pm 1.5) \times 10^{-7}$ ($3 - 6 \times 10^{14} \text{ cm}^{-3} \text{ NO}_2$)	298	Kleffmann et al., 1998	Bubbler-IR/IC (e)
$< 5 \times 10^{-4}$	273	Cheung et al., 2000	DT-MS (f)
$\leq 10^{-7}$ (pH 2 – 12)	298	Gutzwiller et al., 2002 Ammann et al., 2005	WWFT-CLD (g)
$\approx 10^{-6}$ ($6 \times 10^{14} \text{ cm}^{-3} \text{ NO}_2$, 0.01 M NaOH)	288	Komiyama and Inoue, 1980	Bubbler-UV (h)
<i>Accommodation coefficient: α_b</i>			
$(6.3 \pm 0.7) \times 10^{-4}$ ($> 10^2 \text{ M}$ hydroquinone)	273	Lee and Tang, 1988	(a)
$(4.2 \pm 0.9) \times 10^{-4}$ ($5 \times 10^2 \text{ M}$ ascorbate)	298	Msibi et al., 1993	CWFT (c)
$(2.4 \pm 1.8) \times 10^{-2}$ (deliquesced dihydroxyphenolates)	296	Sosedova et al., 2009	AFT-RC (i)
<i>$Hk_2^{1/2}$</i>			
$70 \text{ M}^{-1/2} \text{ atm}^{-1} \text{ s}^{-1/2}$	295	Lee and Schwartz, 1981	(j)
$134 \text{ M}^{-1/2} \text{ atm}^{-1} \text{ s}^{-1/2}$	284	Cape et al., 1993	(k)
$71 \pm 10 \text{ M}^{-1/2} \text{ atm}^{-1} \text{ s}^{-1/2}$	293	Cheung et al., 2000	(f)
$92 \text{ M}^{-1/2} \text{ atm}^{-1} \text{ s}^{-1/2}$	295	Park and Lee, 1988	(l)
<i>Solubility</i>			
$2.0 \times 10^{-2} \text{ M atm}^{-1}$	298	Andrew and Hanson, 1960	(m)
$2.2 \times 10^{-2} \text{ M atm}^{-1}$	288	Komiyama and Inoue, 1980	(h)

$(7.0 \pm 0.5) \times 10^{-3} \text{ M atm}^{-1}$	295	Lee and Schwartz, 1981	(i)
$(5.5 \pm 0.6) \times 10^{-2} \text{ M atm}^{-1}$	284	Cape et al., 1993	(k)
$(1.4 \pm 0.2) \times 10^{-2} \text{ M atm}^{-1}$	293	Cheung et al., 2000	(f)
$(2.3 \pm 0.3 - 0.9) \times 10^{-2} \text{ M atm}^{-1}$	276		
<i>Liquid phase rate constant</i>			
$(1.0 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	295	Lee and Schwartz, 1981	(j)
$(8.4 \pm 1.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	295	Park and Lee, 1988	(m)
$(6.0 \pm 2.0) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	284	Cape et al., 1993	(k)
$(3.0 \pm 0.9) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	293	Cheung et al., 2000	(f)
$(2.2 \pm 0.6) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	276		

Comments

- (a) Uptake experiment involving a stopped flow of NO_2 (initial concentration 10^{15} cm^{-3}) in humidified He carrier gas exposed to a circulating fluid sample of either pure water, water with 0.05 M NaOH, or water containing $(1-7) \times 10^{-2} \text{ M}$ hydroquinone sodium salt. The uptake coefficients were corrected for gas phase diffusion.
- (b) Gas uptake into a monodisperse (70 μm to 110 μm diameter) droplet train. The pH of water was adjusted to 4, 5.6 and 11.0. Uptake was determined by detecting nitrate by ion chromatography in the collected aqueous phase after addition of 0.16 M H_2O_2 to convert all nitrite to nitrate. The uptake coefficient corrected for gas phase diffusion was independent of pH. The value for the diffusion coefficient used was $0.192 \text{ cm}^2 \text{ s}^{-1}$ in the gas phase and $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in the liquid phase. The solubility was assumed to be $1.2 \times 10^{-2} \text{ M atm}^{-1}$. The observed uptake coefficient γ_{obs} was larger than expected from solubility limited uptake, independent of pH. Impurities might have been present as a liquid phase sink for NO_2 to drive reaction limited uptake.
- (c) 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 either deionised water or a mixture of 0.05 M ascorbic acid and 0.05 M NaOH (pH 9.3). NO_2 was measured using a luminol based NO_2 analyzer.
- (d) Liquid jet (50 μm diameter) in a reactor 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 for NO_2 . Nitrite and nitrate were measured spectrophotometrically. NO_2 uptake was independent of pH or added sink, but was much larger than solubility limited uptake. The authors therefore proposed a surface reaction proceeding with the uptake coefficients listed in the table.
- (e) NO_2 was circulated through a thermostated bubbler containing 125 to 500 ml of water. NO_2 and HONO were measured using tunable diode laser absorption spectrometry. Nitrate and nitrite in the liquid were measured using ion chromatography, showing that they were initially formed at equimolar amounts. The first order rate constant for NO_2 decay was not depending on the NO_2 concentration, indicating overall first-order behaviour.
- (f) Experiments were performed with both a droplet train and a bubble train apparatus. The droplet train was operated with $10^{13} - 10^{16} \text{ NO}_2 \text{ molecules cm}^{-3}$. Uptake of NO_2 was not detectable in the droplet train experiment, leading to an upper limit of $\gamma < 5 \times 10^{-4}$ at 273 K. In

the bubble train flow reactor, the NO₂(g) concentration was monitored by QMS. Loss of NO₂ from the gas phase was fitted with a model of NO₂ uptake considering both solubility limitation and reaction in the bulk. This led to both, independent values for H and

- (g) The wetted wall flow tube was operated at room temperature and with 80 ppb of NO₂ in N₂. The uptake coefficient listed in the table was obtained as blank values for pure water and water with pH adjusted to between 2 and 12 as part of a study to explore the reactivity of NO₂ with hydroxysubstituted aromatics.
- (h) NO₂ (10 to 2000 ppm) was passed either over a flat liquid surface (both gas and liquid stirred) or through a bubbler. NO₂ concentration in the gas phase and nitrate and nitrite were measured using UV absorption. The mass transfer characteristics were determined with CO₂. Nitrate and nitrite concentrations were equal over the whole NO₂ pressure range. The NO₂ absorption rate reported over the full range was proportional to the square of the NO₂ pressure at high and proportional to NO₂ at low NO₂ pressures as expected for mass transport limitation. The absorption rate reported for about $6 \times 10^{14} \text{ cm}^{-3}$ is converted to an uptake coefficient and listed in the table.
- (i) Aerosol particles were produced from nebulizing aqueous solutions of dihydroxybenzoic acid and hydroquinone sodium salts. ¹³N labeled NO₂ was used as reactant, and uptake to particles was monitored by counting radioactive decays of ¹³N associated with particles after the flow reactor with residence times between 1 and 60 s at ambient pressure and 40 % relative humidity. The observed uptake coefficients in the range of a few 10⁻³ could be well explained by bulk reaction limited uptake, which allowed deriving an estimate for α_b listed in the table.
- (j) NO₂ at partial pressures of 100 ppb to 800 ppm was passed through 10 to 70 ml of water in a fritted bubbler in a thermostated vessel. NO₂ was measured with a chemiluminescence detector. The ionic products in water were determined with a conductivity detector online. Nitrate and nitrite were measured offline with a colorimetric method. The mass transport characteristics were calibrated using CO₂, leading to mass transfer times between 1.7 and 5.3 s.
- (k) NO₂ at partial pressures of 10 to 100 ppb was passed through 1.0 l of water or aqueous solution in a fritted bubbler in a thermostated vessel. The loss of NO₂ was measured with a chemiluminescence detector. The mixing time in the reactor was 60 s based on experiments with CO₂. The authors caution that the distribution of NO₂ in the reactor may have not been uniform, leading to an overestimate of the rate constants.
- (l) Investigation of HNO₂ decomposition kinetics in water in a bubbler type apparatus. The kinetics of the hydrolysis reaction was indirectly derived from the evolution of NO and NO₂ measured with a chemiluminescence detector.
- (m) NO₂ (200 ppm to 10%) was passed through water in a bubbler type reactor. The solubility listed in the table was derived from observations of HNO₂ formation as a function of NO₂ pressure.

Preferred Values

Parameter	Value	T/K
α_b	2×10^{-2}	273 - 298
$k / \text{M}^{-1} \text{s}^{-1}$	$8.1 \times 10^9 \exp(-1630/T)$	276 - 293
$H / \text{M atm}^{-1}$	$4.4 \times 10^{-6} \exp(-2350/T)$	273 - 298
<i>Reliability</i>		
$\Delta \log(\alpha_b)$	± 0.7	273-298
$\Delta \log(k)$	± 0.08	273-298
$\Delta \log(H)$	± 0.06	273-298

Comments on Preferred Values

Uptake of NO_2 to pure water is driven by the low solubility and slow second order hydrolysis in bulk water. The study by Cheung et al. (2000) has covered the NO_2 concentration range down to atmospherically relevant levels and most carefully elaborated the associated mass transfer issues, allowing them to obtain an independent estimate for the solubility at 293 K. They also estimate a value at 276 K using arguments about the expected solubility dependence presented by Schwartz and White (1981). The recommended expression for the temperature dependence is based on these two values.

Cheung et al. also show that their value for $Hk^{1/2}$ is consistent with most earlier studies covering the lower concentration range, especially the one by Lee and Schwartz (1981). The disagreement with Cape et al. (1993) is likely due to inhomogeneous distribution of NO_2 in their reactor, as cautioned by the authors. Due to strong coupling between the liquid phase rate constant and the solubility, we calculate an average value of $Hk^{1/2}$ extracted from the Cheung et al. (2000), Lee and Schwartz (1981) and Park and Lee (1988) and use the solubility as recommended to arrive at the expression for the rate constant.

Bambauer et al. (1994) report an experiment in a cloud chamber, in which the cloud droplet seeds were NaCl, which seemed to be inconsistent with the second-order reaction of NO_2 in water. This and other evidence for apparent first order uptake with surprisingly high uptake coefficient can be discussed as due to reactions with impurities (Ponche et al. 1993; Msibi et al., 1993; Mertes and Wahner, 1995) rather than being representative of bulk accommodation limitation. Yabushita et al. (2009) suggest the formation of a surface complex with chloride ions to explain enhanced NO_2 hydrolysis in mM chloride solutions (see also data sheet VI.A2.4). Due to the low solubility of NO_2 , a strong aqueous phase scavenger is required to get into a bulk accommodation limited kinetic regime. While the CWFT study by Msibi et al. (1993) was likely affected by evaporation, Lee and Tang (1988) show evidence for the transition from reaction limited to bulk accommodation limited kinetics. Sosedova et al. (2009) used an aerosol flow tube approach, which is practically free of gas phase diffusion effects, to obtain a bulk accommodation coefficient of 0.02 for deliquesced sodium salts of hydroquinone and dihydroxybenzoate, which is used as a basis for the recommendation for α_b .

The recommended values can be used to calculate uptake coefficients for the reaction of NO_2 with dilute aqueous solutions in absence of significant aqueous phase scavengers. In this case, $1/\alpha_b$ is not rate limiting, and the uptake coefficients can be calculated using

$$\gamma = \frac{4HRT}{\bar{c}} \sqrt{D_1 \cdot k'}, \quad k' = H_{\text{NO}_2} p_{\text{NO}_2} k$$

This leads to uptake coefficients of e.g. 6×10^{-9} at 10 ppb NO_2 due to hydrolysis. Under many conditions, the reacto-diffusive length may be large compared to the diameter of the droplet, so that the geometry correction needs to be applied to this expression. On shorter time scales, it needs to be carefully evaluated whether or not $1/\Gamma_{\text{sol}}$ is rate limiting.

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