

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.5 HET_H2OL_5

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This data sheet evaluated: October 2008; last change in preferred values: October 2008.

N₂O₅ + H₂O (water droplets)

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>			
$\gamma = 0.040 \pm 0.005$	282	Van Doren et al., 1990	DT-TDLAS (a)
$\gamma = 0.061 \pm 0.004$	271		
> 0.005	293	Kirchner et al, 1990	LJ-IC (b)
$\gamma = 0.030 \pm 0.002$	262	George et al., 1994	DT-FTIR/HPLC (c)
$\gamma = 0.013 \pm 0.008$	277		
$\gamma = 0.018 \pm 0.003$	262-278	Schweitzer, Mirabel, George, 1998	DT-FTIR/MS (d)
$\gamma = 0.011 + 0.012/-0.006$	293	Schütze and Herrmann, 2002	DT-UV/Vis (e)

Comments

- Fast train of monodisperse 200 μ m H₂O droplets traversing a flow tube with TDLAS detection. The temperature of the droplet was controlled by varying partial pressure of H₂O in the carrier gas and hence evaporation rate. The temperature reported is the mean temperature in the vicinity of the droplet. Total pressures = 5.02 Torr at 271 K and 9.26 Torr at 282 K. [N₂O₅] ~ 2 x 10¹⁴ molecule cm⁻³. γ determined from measured fractional uptake with and without droplets present, with (small, <10%) correction for gas phase diffusion and distortion of molecular velocity distribution.
- Interaction of N₂O₅ (116 ppm in 1 bar air, measure by UVA) with a 90 mm dia. liquid jet of pure water with contact time 0.03 - 1.0 ms. Uptake coefficients were deduced by comparing NO₃⁻ concentrations in the absorbing liquid, which are measured as a function of contact time, with numerical solutions of the convective diffusion equation. γ is regarded as a lower limit due to its sensitivity to the value of $D_g(\text{N}_2\text{O}_5)$ and uncertainties in the velocity distribution of the liquid jet.
- Fast train of water droplets (80-150 m μ diameter) inside a flow tube at total pressures of 27-80 mbar synthetic air with 4-16 ms contact time. The temperature of the droplet was controlled by varying partial pressure of H₂O in the carrier gas and hence evaporation rate. N₂O₅ (20 to 2000 ppm) monitored by FTIR, and the extent of uptake was followed by measuring the NO₃⁻ concentration in the collected droplets using hplc.
- Experimental configuration as (b). FTIR absorption and ion-trap mass spectrometry for used for detection of changes in gas phase N₂O₅ on exposure to droplets. No products were detected. The uptake coefficients were independent of temperature in the stated range.
- Uptake onto static single drop monitored by time-resolved UV/Vis absorption spectroscopy in the range 240 to 800 nm. Uptake coefficient determined from absorbance-time profiles of the product NO₃⁻ at two different wavelengths (302, 345 nm) after diffusion correction. [N₂O₅] = (2.3 to 4.6) x 10¹³ molecule cm⁻³ at a total pressure (He) of 100 mbar.

Preferred Values

Parameter	Value	T/K
γ	$2.7 \times 10^{-5} \exp(1800/T)$	265 - 300
	<i>Reliability</i>	
$\Delta \log(\gamma)$	± 0.3	298
$\Delta(E/R)$	$\pm 1000 \text{ K}$	265 - 305

Comments on Preferred Values

Except for the liquid jet experiment of Kirchner et al (1990), the reported studies all used similar experimental configurations involving uptake onto large water droplets, but with different methods used for measurement of uptake rate, i.e. loss of N_2O_5 from gas phase (Van Doren et al (1990); Schweitzer et al.(1997) and accumulation of hydrolysis product NO_3^- in the droplets (George et al. (1992) and Schütze and Herrman, 2002). Corrections for effects of gas phase diffusion on uptake rates were necessary in all cases, and are a particular source of uncertainty in the liquid drop experiment. The values of γ from the different studies are broadly consistent with each other, and show a negative temperature dependence, although the γ values of Van Doren et al (1990) are higher than in the other studies. There are potential sources of systematic error in these studies but there is no obvious explanation of the differences in the results. The recommended expression for γ is a least squares fit to all the cited data from the droplet train experiments, plotted in Arrhenius form, with large error limits reflecting the possible systematic errors.

It has been suggested the measured uptake coefficient represents the mass accommodation coefficient for N_2O_5 on an aqueous surface, which by definition gives the maximum rate of reactive uptake. Maximum uptake coefficients for N_2O_5 on aqueous electrolyte aerosols (e.g. NaCl, malonic acid, H_2SO_4) at room temperature and high RH often exceed those measured on pure water by a factor of ~ 2 to 3. The mass accommodation coefficient for N_2O_5 at 298 K is thus likely to be at least 0.03.

References

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$\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ droplets

