IUPAC Task Group on Atmospheric Chemical Kinetc Data Evaluation – Data Sheet MD9 (V.A2.9)

N_2O_5 + mineral oxide (dust) surfaces

Experimental data

Parameter	Temp./K	Reference	Technique/Comments
Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$			
$\gamma_0 = 0.08 \pm 0.003$ (Saharan dust)	298	Seisel et al., 2005	Knudsen-MS/DRIFTS (a)
$\gamma_{ss} = 0.013 \pm 0.003$ (Saharan dust)			
$\gamma_0 = 0.3 \pm 0.08$ (Saharan dust)	298 ± 2	Karagulian et al., 2006	Knudsen-MS (b)
$\gamma_{ss} = 0.2 \pm 0.05$ (Saharan dust)			
$\gamma_0 = 0.2 \pm 0.06$ (Arizona dust)			
$\gamma_{ss} = 0.11 \pm 0.03$ (Arizona dust)			
$\gamma_0 = 0.12 \pm 0.04$ ($CaCO_3$)			
$\gamma_{ss} = 0.021 \pm 0.006$ ($CaCO_3$)			
$\gamma = (1.9 \pm 0.2) \times 10^{-4}$ ($CaCO_3$)		Mogili et al., 2006	(c)
$\gamma = (13 \pm 2) \times 10^{-3}$ (Saharan dust)	296 ± 2	Wagner et al., 2007	AFT-CLD (d)
$\gamma = (37 \pm 12) \times 10^{-3}$ (Saharan dust)	296 ± 2	Wagner et al., 2007	Knudsen-MS (e)
$\gamma = (22 \pm 8) \times 10^{-3}$ (Arizona dust)			
$\gamma = (50 \pm 20) \times 10^{-3}$ ($CaCO_3$, unheated)			
$\gamma = (26 \pm 8) \times 10^{-3}$ ($CaCO_3$, heated)			
$\gamma = (4.8 \pm 0.7) \times 10^{-3}$ ($CaCO_3$, RH = 0 %)	296 ± 2	Wagner et al., 2009	AFT-CLD (f)
$\gamma = (5.3 \pm 1.0) \times 10^{-3}$ ($CaCO_3$, RH = 29 %)			
$\gamma = (11.3 \pm 1.6) \times 10^{-3}$ ($CaCO_3$, RH = 58 %)			
$\gamma = (19.4 \pm 2.2) \times 10^{-3}$ ($CaCO_3$, RH = 71 %)			
$\gamma = (9.8 \pm 1.0) \times 10^{-3}$ (Arizona dust, RH = 0 %)			
$\gamma = (7.3 \pm 0.7) \times 10^{-3}$ (Arizona dust, RH = 29 %)			
$\gamma = (8.6 \pm 0.6) \times 10^{-3}$ (quartz, RH = 0 %)			
$\gamma = (4.5 \pm 0.5) \times 10^{-3}$ (quartz, RH = 29 %)			
$\gamma = (20 \pm 10) \times 10^{-3}$ (Saharan dust, RH = 0- 67 %)	298	Tang et al., 2012	AFT-CRD (g)
$\gamma = (6.3 \pm 1.6) \times 10^{-3}$ (Arizona dust, RH = 0- 67 %)	298	Tang et al., 2014	AFT-CRD (h)
$\gamma = (91 \pm 39) \times 10^{-3}$ (Illite, RH = 0 %)			
$\gamma = (39 \pm 12) \times 10^{-3}$ (Illite, RH = 67 %)			

Comments

(a) Continuous flow and pulsed valve experiments using bulk samples (140 - 460 mg) which were prepared from an aqueous suspension of Saharan dust, and dried under vacuum before each experiment. The initial N_2O_5 concentration in the Knudsen reactor experiments was 3-100 x 10^{10} molecule cm^{-3}. No dependence of γ on sample mass was

observed and the uptake coefficients given in the table were thus calculated using the geometric surface area of the sample. The rate of uptake was seen to decrease with exposure time, leading to the steady state value of γ listed. A lower value of $\gamma = (9.1 \pm 0.7) \times 10^{-3}$ was calculated using DRIFTS measurements of the time dependence of surface nitrate formation.

(b) Continuous flow experiments using bulk samples from a slurry in water which were pre-treated by drying under vacuum at 294 K until H_2O desorption ceased ($\approx$ 30 min). Pulsed valve experiments were in good agreement. A dependence of γ on $[N_2O_5]$ was observed, those listed were obtained at the lowest N_2O_5 concentrations used (circa 4 x 10^{11} molecule cm^{-3}). Data were also obtained for kaolinite and limestone.

(c) 150 L environmental chamber with detection of N_2O_5 and HNO_3 by FTIR. $CaCO_3$ surface area was ≈ 0.25 m^2 (based on mass of $CaCO_3$ added and the known BET surface area of the sample). Uptake coefficients are cited as "apparent" and are a factor $\approx$ 160 less than a true value. This factor was derived from a comparison of N_2O_5 uptake in the chamber to literatre values of its uptake cofficient for NaCl.

(d) Atmospheric pressure aerosol flow tube (mean diameter of dust particles measured using aerodynamic sizer to be $\approx$ 1 μm) with detection of N_2O_5 (present at $\approx 10^{13}$ molecule cm^{-3}) by modified CLD (N_2O_5 measured via thermal dissociation to NO_3 and modulation of NO signal). No dependence on the uptake coefficient on RH (0-30 %) or $[N_2O_5]$ was observed.

(e) Bulk dust samples were prepared by mixing the powder to a paste with methanol and evenly spreading this onto a polished α-Al_2O_3 flat prior to drying under vacuum for $\approx$ 8 hours at room temperature. Some $CaCO_3$ samples were heated to 400 K for several hours under vacuum. The data were analysed using the geometric surface area. The initial N_2O_5 concentration was varied between 3 x 10^9 and 2 x 10^{10} molecule cm^{-3}.

(f) Atmospheric pressure aerosol flow tube (mean diameter of dust particles measured using aerodynamic sizer as $\approx$ 0.7, 1.5 and 5 μm for quartz, CaCO3 and ATD, respectively. Detection of N_2O_5 (varied between 10^{12} and 10^{13} molecule cm^{-3}) was as described in comment (d). The $CaCO_3$ uptake coefficient increased with RH (0-71 %). No dependence on $[N_2O_5]$ was observed. Values listed in the table were corrected for diffusive effects and, as suggested by the authors, carry estimated uncertainties of > factor two, stemming mainly from assumptions about particle shape.

(g) Atmospheric pressure aerosol flow tube with N_2O_5 (varied from 5×10^{11} to 3×10^{13} molecule cm^{-3}) detected as NO_3 (by cavity ring-down spectroscopy) after thermal dissociation. Gas and particle product analysis suggests formation of particulate nitrate (two nitrate groups per N_2O_5 taken up) dominates. No dependence of γ on the N_2O_5 concentration or RH was observed.

(h) Atmospheric pressure aerosol flow tube with N_2O_5 (varied from 8×10^{12} to 2.4×10^{13} molecule cm^{-3}) detected as NO_3 (by cavity ring-down spectroscopy) after thermal dissociation.

Preferred Values

Parameter	Value	T/K
γ (Saharan dust)	2×10^{-2}	290-300

Reliability

$\Delta \log (\gamma)$	0.5

Comments on Preferred Values

Despite the use of very similar experimental methods, the common assumption that the geometric surface is appropriate for determination of γ and the use of similar surfaces, the agreement in the derived uptake coefficients returned by the three Knudsen reactor studies on Saharan dust, (Seisel at al., 2005; Karagulian et al., 2006 and Wagner et al, 2007) is poor, with the reported values of γ between 0.2 and 0.037.

Both Seisel et al. (2005) and Karagulian et al. (2006) report a decrease in reactivity with exposure time, with the ratio of γ_0 to $\gamma_{ss} \approx 6$ (Seisel et al.) and ≈ 2 (Karagulian et al.). In contrast, Wagner et al. (2007) report no surface deactivation on the time scales of their Knudsen reactor experiments with $\gamma_0 = \gamma_{ss}$. Part of this difference is certainly caused by the use of much lower concentrations of N_2O_5 by Wagner et al., but may also be caused by different rates of diffusion into the sample, as Seisel et al. (2005) and Karagulian et al. (2006) report very different average diameters for the particles comprising the bulk samples. It may also be related to different amounts of water associated with the substrates.

The AFT experiments of Wagner et al (2007, 2009), report lower uptake coefficient than the Knudsen reactor experiments using similar samples. Note that, in Knudsen reactor experiments, the use of the projected surface area to calculate γ, should lead to upper limits for the uptake coefficient. No variation in γ with RH was observed by Wagner et al. (2007) or Tang et al., (2012) for Saharan dust, though the reaction with calcite appears to become more efficient at relative humidities larger than about 60 %. Tang et al showed that, for Saharan dust, not only the surface but also a substantial fraction of the bulk of the Saharan dust particles investigated interacts with N_2O_5.

Tang et al (2014) indicate how different minerals react differently with N_2O_5, both in terms of the size of the uptake coeffient (small for Arizona dust, large for Illite) and its dependence on RH. The large uptake for Illite and its reduction with increasing RH was interpreted in terms of efficient surface reaction with "internal" OH groups in Illite, which could be deactivated by surface adsorbed water.

The differences in the uptake coefficients from one mineral to the next combined with the uncertainy associated with use of the geometric area of a porous, bulk sample in the Knudsen studies leads us to prefer the results obtained using dispersed, Saharan dust aerosol, which should represent the best proxy for atmospheric mineral aerosol. The result of Tang et al (2012) supercedes the earlier work from the same group (Wagner et al., 2007, 2009) and is thus preferred.

The formation of NO_3^-, H_3O^+ and H_2O and the loss of surface OH groups during the reaction of N_2O_5 with Saharan dust has been observed using DRIFTS (Seisel et al, 2005). In Knudsen experiments using $CaCO_3$, gas-phase HNO_3, H_2O and CO_2 were observed (Karagulian et al. 2006; Wagner et al. 2007). Mogili et al. (2006) report stoichiometric conversion of N_2O_5 to HNO_3. In their aerosol flow tube studies, Tang et al (2012) report formation of particle nitrate (two nitrate groups per N_2O_5 taken up).

A mechanism has been proposed (Seisel et al., 2005; Karagulian et al. 2006) whereby N_2O_5 can either react with initially present surface-OH groups (on $CaCO_3$ these are available as $Ca(OH)(HCO_3)$) to form HNO_3 and surface-nitrate, or with adsorbed H_2O to form HNO_3. The HNO_3 product can react with surface-OH to form H_2O and surface-nitrate, or with H_2O to form the observed H_3O^+ and NO_3^- ions. The removal of surface-OH groups (or $Ca(OH)(HCO_3)$) explains the change in reactivity during exposure, whereas the steady state uptake coefficient will be dominated by the reaction of N_2O_5 with surface-H_2O. The yield of gas-phase HNO_3 depends on its reactivity with the dust substrate and is of the order of 4-5 % for reactive surfaces such as $CaCO_3$ and Saharan dust (Karagulian et al., 2006). The

irreversible nature of the reaction could be confirmed by heating exposed samples to 470 K, with no loss of surface adsorbed nitrate (Seisel et al., 2005).

References

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