

N₂O₅ hydrolysis on the components of mineral dust and sea salt aerosol: Comparison study in an environmental aerosol reaction chamber

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Abstract

The kinetics of the heterogeneous hydrolysis of N₂O₅ on some of the major components of mineral dust and sea salt aerosol have been investigated in an environmental aerosol chamber. Gas-phase N₂O₅ undergoes heterogeneous reaction to form HNO₃ on carbonate, clay and oxide minerals. The nitric acid hydrolysis product was promptly detected in the gas phase concomitant with the decay of N₂O₅ over time. The N₂O₅ decay kinetics were measured and analyzed assuming first-order reaction kinetics. When normalized for surface area, heterogeneous decay of N₂O₅ on the different minerals followed the reactivity trend; kaolinite > hematite > montmorillonite > calcite > quartz. N₂O₅ decay was faster on all of the mineral dust aerosol components relative to NaCl, a major component of sea salt, at a relative humidity (RH) below the NaCl deliquescence point. The measured heterogeneous uptake coefficients were over an order of magnitude larger on several of the mineral dust aerosol compared to NaCl. The uptake coefficient was found to increase with RH.

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1. Introduction

Heterogeneous uptake and reaction of NO₃ and N₂O₅ on aerosol particles can have a large influence on the concentrations of important atmospheric oxidants, such as NO_x, O₃, and OH (Dentener and Crutzen, 1993). N₂O₅ is formed by the oxidation of

NO₂ by O₃ via the following steps:



where reaction R1 is the rate-controlling step (Mentel et al., 1999). Subsequent loss of N₂O₅ will result in a decrease in NO_x and O₃ concentrations. One of the major reaction pathways that accounts for the removal of N₂O₅ is the hydrolysis reaction (Evans and Jacob, 2005). N₂O₅ is known to readily hydrolyze on aqueous surfaces (Wahner et al., 1998). The HNO₃ formed in the heterogeneous

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hydrolysis contributes significantly to HNO_3 concentration at night (Johnson and Grassian, 2005; Wahner et al., 1998). In theory, N_2O_5 can hydrolyze on any surface with adsorbed water. It has been proposed by Hoffman et al. (2003) that N_2O_5 can auto-ionize to NO_2^+ and NO_3^- in an adsorbed water film on an aerosol surface. These ions can react with H_2O to yield HNO_3 according to R3;



Mineral dust aerosol is abundant in the troposphere and provides a reactive surface for the uptake and reaction of trace atmospheric gases (Usher et al., 2003). Several studies have shown that including heterogeneous reactions of nitrogen oxides on mineral dust aerosol improves the ability of atmospheric chemistry models to match field measurements (Geyer and Stutz, 2004). The importance of the hydrolysis reaction in determining the atmospheric concentrations of O_3 and OH is well established. Predicted global tropospheric concentrations of O_3 and OH decrease when N_2O_5 hydrolysis reactions are included in model calculations (Martin et al., 2003; Tie et al., 2003). For example, when hydrolysis on mineral dust aerosol is included, ozone loss is calculated to be as high as 10–20% (Zhang and Carmichael, 1999) even when direct ozone dissociation on mineral dust aerosol is not taken into account. In Zhang and Carmichael (1999), an uptake coefficient of 0.1 was assumed for N_2O_5 hydrolysis. In another modeling study, it was determined that N_2O_5 hydrolysis accounts for 0.8% of global ozone loss, when a value of 0.02 (at RH of 70%) is used as the uptake coefficient.

It can be seen from the above modeling studies that an accurate value of the uptake coefficient is important in determining tropospheric concentrations of trace gases. However, model predictions remain uncertain due to the lack of experimental uptake coefficients for mineral dust and the lack of detail regarding the heterogeneous kinetics (Bauer et al., 2004; Dentener et al., 1996). Currently, values for uptake coefficients used in modeling studies for N_2O_5 on mineral dust aerosol range from 0.001 to 0.1. When a value of 0.1 is used, the models over predict the removal of N_2O_5 from the atmosphere (Dentener and Crutzen, 1993). Therefore, uptake coefficients below 0.1 are more likely to be the case on mineral dust aerosol. To date, there have been few reports in the literature of laboratory measurements of the heterogeneous uptake of N_2O_5 on mineral dust (Seisel et al., 2005; Karagulian et al., 2006). Seisel et al.

measured the heterogeneous uptake kinetics of N_2O_5 on a powdered Saharan dust sample in a Knudsen cell reactor. An initial uptake coefficient of $(8.0 \pm 0.3) \times 10^{-2}$ was reported under dry conditions. Because Saharan sand is a complex mixture of particles of varying mineralogy with different chemical and physical properties, it is difficult to know much about the relative importance of the different components from this study. In another very recent Knudsen cell study, a few mineral dust components (kaolinite and calcite) were investigated and it was determined that their reactivity was different (Karagulian et al., 2006). Since the reactivity of mineral dust aerosol will depend on its chemical composition (Krueger et al., 2004), reactivity will also correlate with the source region (Claquin et al., 1999). Therefore, to get a better idea about N_2O_5 loss mechanisms, its reactivity towards a wider range of mineral dust components should be measured.

In the current study, the uptake and hydrolysis of N_2O_5 are investigated on several different components of mineral dust aerosol including carbonate, clay and oxide minerals. The heterogeneous reaction kinetics are measured in an environmental aerosol chamber. The kinetic data for the mineral dust components are compared to that measured for NaCl, a major component of sea salt aerosol. Apparent uptake coefficients determined for mineral dust aerosol are all found to be higher than those measured for NaCl.

2. Experimental methods

2.1. Environmental aerosol reaction chamber and aerosol generation

Experiments were performed in an environmental aerosol reaction chamber at $T = 290 \text{ K}$. The schematic of environmental chamber is shown in Fig. 1. The environmental aerosol reaction chamber is 151 L in volume with a surface to volume ratio of 10.7 m^{-1} . The reaction chamber is FEP-Teflon coated to minimize wall reactions. The chamber is provided with large openings at the top and bottom, and with eight side arms to access the chamber interior. All flanges are made from aluminum, with interior sides Teflon coated, and all connections to the chamber are made with non-reactive surfaces like glass or Teflon-coated materials. Other ports connect the chamber to a mechanical pump, a sample preparation line and capacitance manometers to measure the pressure.

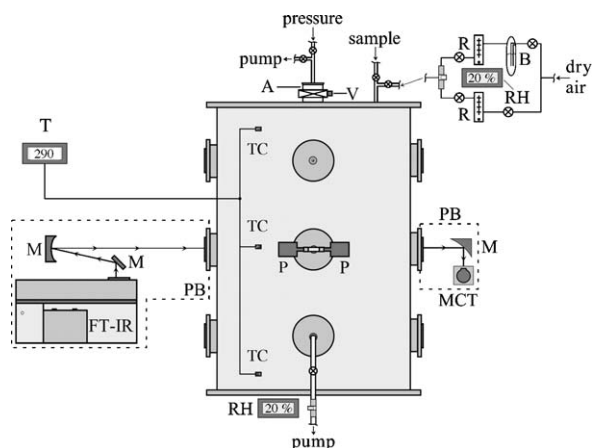


Fig. 1. A schematic diagram of the atmospheric chamber and associated instrumentation showing the sample cartridge (A), antechamber valve (V), water bubbler (B), flow meters (R), relative humidity sensors (RH), FT-IR spectrometer (FT-IR), mirrors for external IR beam (M), mid-band HgCdTe IR detector (MCT), purge boxes for external beam path (PB), thermocouples (TC), temperature read out (T), and pressure transducers (P).

An aerosol is generated in the chamber by pressurizing a sample cartridge that contains the powder under investigation to 100 psi. A pulsed solenoid valve between the sample cartridge and reaction chamber is activated and the aerosol is rapidly introduced into the chamber. The dust enters the chamber through a nozzle and impactor plate assembly, which ensures deagglomeration of the sample. Prior to introduction into the chamber, the powder sample is held under vacuum for approximately 3 h to remove residual water.

2.2. N_2O_5 synthesis

N_2O_5 is formed *in situ* by adding NO_2 (Specialty Gases of America, 99.5 + %) to the environmental chamber which contained a mixture of ozone and oxygen. Ozone is made by flowing UPC grade oxygen (air products) through an electric discharge ozone generator (OREC-5). The synthesized N_2O_5 initially contains less than 9% HNO_3 .

2.3. Calibration of gas-phase concentrations

The concentrations of the different gases in the environmental aerosol reaction chamber are quantified by *in situ* FT-IR spectroscopy (*vide infra*) using a Beer–Lambert law analysis. The absorption cross section for N_2O_5 at 1246.6 cm^{-1} has been

measured to be $8.56 \times 10^{-19}\text{ cm}^2\text{ mole}^{-1}$ (Wangberg et al., 1997). Because of overlapping absorptions with HNO_3 and NO_2 at this frequency, we used the 1246.6 cm^{-1} to calibrate the N_2O_5 absorption cross section at 742.5 cm^{-1} which was then used to quantify N_2O_5 concentrations. Previously, HNO_3 was calibrated in the environmental chamber using the absorption at 1331 cm^{-1} (Preszler Prince, 2004; Preszler Prince et al., 2002). The water absorption band at 3853 cm^{-1} was used to quantify the relative humidity inside of the chamber.

2.4. Sources for the components of mineral dust and sea salt aerosol

The specific surfaces investigated include hematite ($\alpha\text{-Fe}_2\text{O}_3$, Aldrich, 99 + %), kaolinite (Alfa Aesar, 99 + %), calcite (Alfa Aesar, 99.95 + %), montmorillonite (Alfa Aesar, 99.5%) and quartz (Strem Chemicals, 99.9%). In addition, NaCl (Fischer Scientific, 99.5%), the major component of sea salt, was also investigated in this work. The results for the mineral dust components were then compared to the more well-studied NaCl aerosol.

BET surface areas were determined for all of the powdered samples using an automated multipoint BET analysis (Quantochrome Nova 1200). The BET specific surface areas of these samples were determined to be $2.8\text{ m}^2\text{ g}^{-1}$ for hematite, $6.4\text{ m}^2\text{ g}^{-1}$ for kaolinite, $1.4\text{ m}^2\text{ g}^{-1}$ for calcite, $1.8\text{ m}^2\text{ g}^{-1}$ for montmorillonite, $1.6\text{ m}^2\text{ g}^{-1}$ for quartz and $2.5\text{ m}^2\text{ g}^{-1}$ for NaCl. In this study, the BET surface area of the aerosol introduced into the environmental chamber was kept constant at a value of ca. 0.25 m^2 .

2.5. Experimental protocol

In a typical experiment, the chamber is evacuated to a base pressure of $<10\text{ mTorr}$. Ozone, along with residual oxygen, is introduced into the chamber followed by NO_2 . The chamber is filled with air from a purge gas generator to a total pressure of 760 Torr. Using the gas directly from the purge generator yielded the driest conditions that can be obtained, $<1\%$ RH. Ultimately a Beer–Lambert law infrared calibration was used to determine the exact water vapor concentration inside the chamber. The component of aerosol under investigation was then introduced into the chamber as described in more detail above. Once the aerosol is introduced into the chamber, N_2O_5 decay is monitored via

FT-IR spectroscopy using a Mattson Infinity 60 AR spectrometer. The IR beam is coupled through the chamber in a single-pass configuration using a series of gold-coated mirrors and then focused with an off-axis parabolic mirror onto an external liquid-nitrogen cooled, MCT detector. Spectra were collected at regular time intervals over the course of the entire experiment. Analysis of the collected spectra yielded gas-phase concentrations of reactants and products as a function of time. Separate experiments were conducted without the presence of aerosol in order to quantify the loss of N_2O_5 due to wall reactions under various RH conditions. These kinetic data were then further analyzed as described in the next section.

3. Results and discussion

3.1. FTIR spectra, kinetic analysis and calculated apparent uptake coefficients

Fig. 2 shows some typical time-course spectra. In particular, Fig. 2 shows the FT-IR spectra for N_2O_5 uptake on montmorillonite at $<1\%$ RH collected as a function of reaction time. Even under these dry conditions, water absorption bands are present in the FT-IR spectra. However for the spectra shown in Fig. 2, the water bands have been subtracted so that the absorptions of N_2O_5 and HNO_3 could be more easily observed and quantified. From the

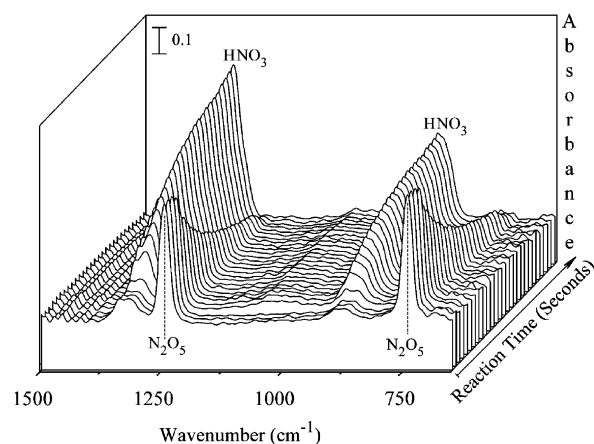


Fig. 2. FT-IR spectra as a function of time for N_2O_5 uptake on montmorillonite, a clay component of mineral dust aerosol, $<1\%$ RH. The mineral dust is introduced after the third FT-IR spectrum in the plot. The hydrolysis reaction occurs readily even at this very low RH. Spectra are recorded every 5 s with each spectrum representing an average of 16 scans at an instrument resolution of 8 cm^{-1} .

spectra, it can be seen that initially strong N_2O_5 absorptions at 743 and 1247 cm^{-1} decrease in intensity as the hydrolysis reaction takes place and the nitric acid product bands appear at 887 and 1331 cm^{-1} . The conversion of N_2O_5 to HNO_3 occurs readily even at very low RH less than 1% . Smaller absorption features appear to be constant due to overlapping absorptions of the product HNO_3 and reactant N_2O_5 .

Concentration versus time plots are shown for N_2O_5 and HNO_3 in Fig. 3 for a number of experiments on several different mineral dust aerosol including oxides (quartz and hematite), clays (kaolinite and montmorillonite) and carbonate (calcite). Data for reaction with NaCl are also included. The aerosol is introduced into the reaction chamber at time, $t = 0$, and growth or decay of the gas-phase concentration corresponds to the hydrolysis reaction. The decay curves for N_2O_5 are plotted in Fig. 3a and, the growth curves for HNO_3 are plotted in Fig. 3b. The ratio of HNO_3 produced to N_2O_5 reacted is approximately two in all cases in agreement with the expected stoichiometry of the hydrolysis reaction.

The decay of N_2O_5 prior to the introduction of aerosol amounts to less than 5% over a period of 5 min. However, all of the remaining N_2O_5 is reacted away in approximately 1 min in the presence of kaolinite at $<1\%$ RH. For the other mineral dust, the reaction is slower than that found for kaolinite but all the mineral dust samples react more quickly than NaCl. In addition, assuming a surface site density of $5 \times 10^{14}\text{ mole cm}^{-2}$, the reaction appears to be catalytic with respect to N_2O_5 uptake and hydrolysis as the turnover number (the ratio of the number of molecules reacted divided by the number of surface sites) is over 200 for the minerals investigated, indicating that the reaction is catalytic on mineral surfaces.

In order to quantify differences in reaction rates, the N_2O_5 decay curves were fit to a single exponential function. These first-order fits to the data can be used to calculate an apparent uptake coefficient. In general, the adsorption of a gas phase reactant onto a particle surface can be described by the following simple kinetic mechanism



where R is the concentration of the gaseous reactant, S is the concentration of the available surface sites in the reaction volume, and P represents both adsorbed and gas phase products.

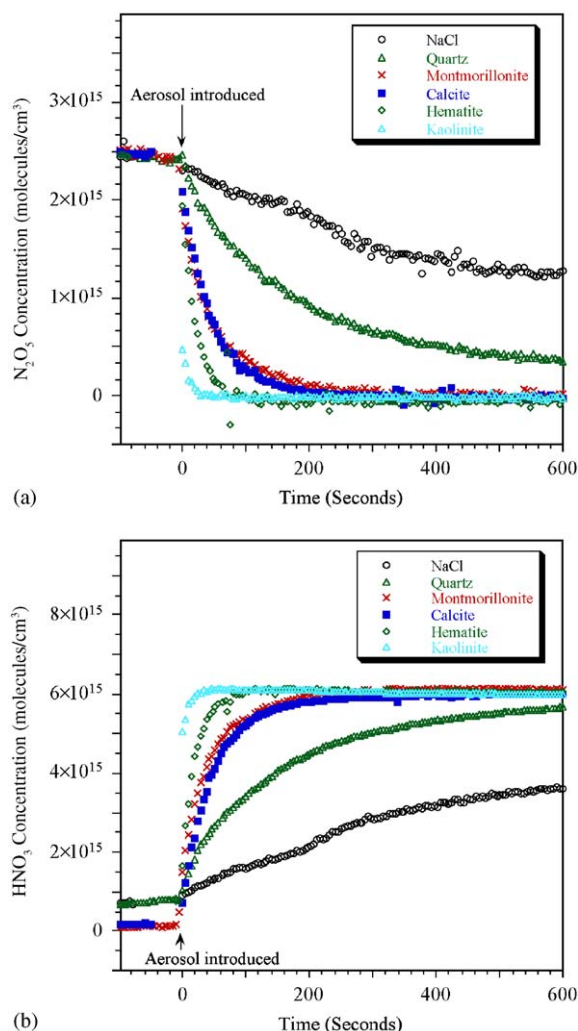


Fig. 3. (a) Decay curves for N_2O_5 uptake and hydrolysis on several components of mineral dust aerosol including carbonate (calcite), oxide (hematite and quartz) and clay (kaolinite and montmorillonite) minerals compared to NaCl, the major component of sea salt aerosol, for the same total surface area in the environmental aerosol chamber (see Table 1 for details). The data decay curves show that N_2O_5 uptake is much faster on the components of mineral dust aerosol compared to NaCl. The data in Fig. 3 are shown for the lowest relative humidity investigated, <1% RH, (b) HNO_3 growth curves are plotted for the different components of mineral dust aerosol and NaCl. These data show the prompt formation of HNO_3 as N_2O_5 undergoes hydrolysis on the surface of the aerosol under these experimental conditions.

For reaction (R4), a pseudo first-order rate constant can be determined from

$$k = \gamma(c/4)S_{\text{BET}}[C_{\text{mass}}], \quad (\text{E1})$$

where c is the mean speed of the gas phase species (ms^{-1}), C_{mass} is the mass concentration of the

sample (g m^{-3}), S_{BET} is the specific surface area of the aerosol ($\text{m}^2 \text{g}^{-1}$) determined by BET analysis and γ is the apparent heterogeneous uptake coefficient.

A fit of the data to a first-order decay yields a characteristic decay time constant, τ , where

$$k = 1/\tau. \quad (\text{E2})$$

Thus, the apparent uptake coefficient can be written in terms of τ according to

$$\gamma = 4/(cS_{\text{BET}}\tau[C_{\text{mass}}]). \quad (\text{E3})$$

The fitted decay time was corrected for wall loss by assuming parallel first-order processes. The correction was approximately 6% for the NaCl data and much less for the other dust components. The reported errors in the uptake have been propagated from the various experimental uncertainties. Repeat experiments for certain samples verified that the calculated value of γ was within the reported error.

The calculated decay constants and apparent uptake coefficients are given in Table 1 as well as the ratio of the uptake coefficient of mineral dust aerosol to that of NaCl. It can be seen from the data that mineral dusts are all more reactive than NaCl under dry conditions. For example, for kaolinite the reactivity is greater than that of NaCl by a factor of fifty. Furthermore, the different components of mineral dusts show differences in their reactivity with quartz being the least reactive. The fact that the different components of dust have different reactivities confirm previous studies that have shown the importance of particle mineralogy on mineral dust aerosol reactivity (Usher et al., 2003; Michel et al., 2003; Krueger et al., 2004; Sullivan et al., 2006). Most notable is that quartz has been shown to be less reactive than other oxides with respect to heterogeneous uptake of other trace atmospheric gases including O_3 (Michel et al., 2003), SO_2 (Usher et al., 2002) and HNO_3 (Underwood et al., 2001). The fact that quartz has lower reactivity than other oxides and clay minerals may be related to the lack of reactive Lewis acid sites (e.g., Al^{3+} , Fe^{3+} sites) on quartz surfaces. Carbonate minerals such as calcite are very reactive toward the nitric acid product and this may play a role in the chemistry of N_2O_5 . However, it should be noted that there is very little known about the role of the underlying substrate in the heterogeneous hydrolysis of N_2O_5 as, to our knowledge, there have

Table 1

Analysis of N₂O₅ decay curves to obtain first order decay constants, τ , and apparent uptake coefficients, γ_{app}

Mineral dust and sea salt components and experimental conditions	Total BET surface area (cm ²)	τ (min) ^a	γ_{app}	
<i>Dry conditions (<1% RH)</i>				$\gamma_{\text{Dust}}/\gamma_{\text{NaCl}}$
NaCl	2500	9.2 ± 0.2	$(1.8 \pm 0.2) \times 10^{-5}$	1
Quartz (SiO ₂)	2500	3.8 ± 0.1	$(4.4 \pm 0.4) \times 10^{-5}$	2
Montmorillonite	2520	0.90 ± 0.01	$(1.8 \pm 0.2) \times 10^{-4}$	10
Calcite (CaCO ₃)	2660	0.80 ± 0.01	$(1.9 \pm 0.2) \times 10^{-4}$	11
Hematite (α -Fe ₂ O ₃)	2500	0.40 ± 0.01	$(4.0 \pm 0.4) \times 10^{-4}$	22
Kaolinite	2600	0.10 ± 0.01	$(9.8 \pm 0.1) \times 10^{-4}$	54
<i>Relative humidity dependence</i>				$\gamma_{\text{RH}}/\gamma_{\text{Dry}}$
NaCl (<1% RH)	2500	9.2 ± 0.2	$(1.8 \pm 0.2) \times 10^{-5}$	1
NaCl 9% RH	2500	7.8 ± 0.2	$(2.1 \pm 0.3) \times 10^{-5}$	1.2
NaCl 18% RH	2500	6.8 ± 0.2	$(2.5 \pm 0.4) \times 10^{-5}$	1.4
NaCl 38% RH	2500	5.4 ± 0.1	$(3.1 \pm 0.3) \times 10^{-5}$	1.7
<i>Relative humidity dependence</i>				$\gamma_{\text{RH}}/\gamma_{\text{Dry}}$
Quartz (<1% RH)	2500	3.8 ± 0.1	$(4.4 \pm 0.4) \times 10^{-5}$	1
Quartz 11% RH	2500	1.8 ± 0.1	$(9.3 \pm 0.1) \times 10^{-5}$	2.1
Quartz 19% RH	2500	1.4 ± 0.1	$(1.2 \pm 0.2) \times 10^{-4}$	2.7
Quartz 43% RH	2500	0.9 ± 0.1	$(1.8 \pm 0.4) \times 10^{-4}$	4.0

^aFirst-order decay lifetime fit of the data.

been no spectroscopic studies on the interaction of N₂O₅ on solid particles.

3.2. Measured decay rates and apparent uptake coefficients as a function of RH

Decay and growth curves for N₂O₅ reaction with NaCl at different RH values are shown in Fig. 4a. Decay of N₂O₅ prior to NaCl aerosol introduction due to wall reactions is found to increase as the relative humidity increases. Still, less than 15% of the N₂O₅ decays prior to aerosol introduction. Although from an atmospheric relevance perspective higher relative humidity studies are very desirable to perform, N₂O₅ hydrolysis on the walls of the reactor become too significant to be feasible for higher RH experiments.

Decay curves were again fit to a single exponential decay as described previously and an apparent uptake coefficient was extracted. The results, given in Table 1, have also been corrected for wall loss and constitute, at most, a correction of approximately 12% in the case of the higher RH data. The ratio of the apparent uptake coefficient at higher RH to that measured under dry conditions ($\gamma_{\text{RH}}/\gamma_{\text{dry}}$) is tabulated in Table 1 and shows that the uptake increases by a factor of approximately two

at the highest relative humidity studied (38% RH). This RH is below the deliquescence point for NaCl aerosol. The reaction of NaCl with N₂O₅ is also known to form other reaction products including ClNO₂ and HCl, from reaction of the product HNO₃ with NaCl (Hoffman et al., 2003). These products were also seen in the FT-IR spectrum but in low yield under the conditions of this study.

Because most of the mineral dust samples exhibited fast decay kinetics, the relative humidity dependence was investigated only on quartz which exhibited the slowest hydrolysis rate. The data for quartz are shown in Fig. 4b and the kinetic parameters derived from the experimental data are tabulated in Table 1. The values have been corrected for wall loss, although the difference is only about 2% due to the relatively fast uptake on quartz. It can be seen that similar to NaCl, there is an increase in the rate of reaction with increasing RH. For quartz, a factor of four increase is determined at the highest relative humidity of 43%. Analysis of the measured rise times of HNO₃ production (not shown) indicate that as the RH increases the HNO₃ gas-phase product formation is delayed suggesting that HNO₃ desorption is slowed in the presence of adsorbed water on the particle surface.

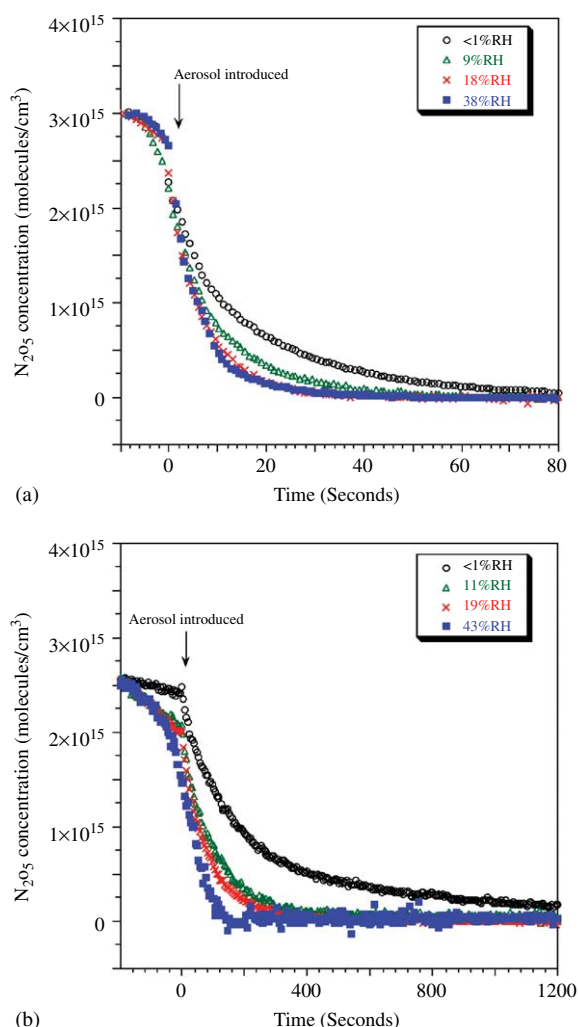


Fig. 4. (a) Decay of N_2O_5 on quartz, SiO_2 , as a $f(RH)$, (b) Decay of N_2O_5 on NaCl as a $f(RH)$. Note the different time scales of the time-axes.

3.3. Atmospheric implications

N_2O_5 hydrolysis on various components of sea salt has been well studied and N_2O_5 is known to readily hydrolyze on NaCl. In a study by Hoffman et al. (2003), an initial uptake coefficient of 2.9×10^{-3} under dry conditions was measured. In our experiments done at higher pressures, an overall apparent uptake coefficient is determined and is lower than that measured by Hoffman et al. (2003). Assuming the apparent uptake values that are measured here are linearly related to an initial uptake, we can scale our apparent uptake coefficients to the NaCl value reported by Hoffman et al. (2003). With this assumption, an initial uptake

coefficient ranging from 0.007 to 0.15 can be inferred for mineral dust aerosol under dry conditions. For the least reactive dust, the rate is found to increase by a factor of four at 40% RH. Thus, the value of an initial uptake coefficient for mineral dust aerosol under relevant atmospheric conditions would be between 0.03 and 0.15 with the relevant value of the uptake would need to take into account the variable reactivity of the mineral dust aerosol with kaolinite, a clay component, and hematite, an oxide component, being the most reactive.

4. Conclusions

The uptake of N_2O_5 on the components of mineral dust aerosol was investigated and found to be catalytic and highly dependent on the mineralogy of the dust with kaolinite and hematite being the most reactive, exhibiting hydrolysis rates twenty to fifty times larger than NaCl below its deliquescence point. Based on several considerations and assumptions, an initial uptake coefficient of 0.03–0.15 is recommended for atmospheric chemistry models that include heterogeneous hydrolysis of N_2O_5 on mineral dust aerosol, with the lower value appropriate for dust sources with high quartz content.

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References

- Bauer, S.E., Balkanski, Y., Schulz, M., Hauglustaine, D.A., Dentener, F., 2004. Global modeling of heterogeneous chemistry on mineral aerosol surfaces: Influence on tropospheric ozone chemistry and comparison to observations. *Journal of Geophysical Research Atmospheres* 109, D02304, doi:10.1029/2003JD003868.
- Claquin, T., Schulz, M., Balkanski, Y.J., 1999. Modeling the mineralogy of atmospheric dust sources. *Journal of Geophysical Research Atmospheres* 104, 22243–22256.
- Dentener, F.J., Crutzen, P.J., 1993. Reaction of N_2O_5 on tropospheric aerosols—Impact on the global distributions of NO_x , O_3 , and OH. *Journal of Geophysical Research Atmospheres* 98, 7149–7163.

- Dentener, F.J., Carmichael, G.R., Zhang, Y., Lelieveld, J., Crutzen, P.J., 1996. Role of mineral aerosol as a reactive surface in the global troposphere. *Journal of Geophysical Research Atmospheres* 101, 22869–22889.
- Evans, M.J., Jacob, D.J., 2005. Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH. *Geophysical Research Letters* 32, L09813, doi:10.1029/2005GL022469.
- Geyer, A., Stutz, J., 2004. Vertical profiles of NO_3 , N_2O_5 , O_3 , and NO_x in the nocturnal boundary layer: 2. Model studies on the altitude dependence of composition and chemistry. *Journal of Geophysical Research Atmospheres* 109, D12307, doi:10.1029/2003JD004211.
- Hoffman, R.C., Gebel, M.E., Fox, B.S., Finlayson-Pitts, B.J., 2003. Knudsen cell studies of the reactions of N_2O_5 and ClONO_2 with NaCl: Development and application of a model for estimating available surface areas and corrected uptake coefficients. *Physical Chemistry and Chemical Physics* 5, 1780–1789.
- Johnson, E.R., Grassian, V.H., 2005. Environmental catalysis in earth's atmosphere: heterogeneous reactions on mineral dust aerosol. In: Grassian, V.H. (Ed.), *Environmental Catalysis*. Taylor & Francis Group, London, pp. 129–156.
- Karagulian, F., Santschi, C., Rossi, M.J., 2006. The heterogeneous chemical kinetics of N_2O_5 on CaCO_3 and other atmospheric mineral dust surrogates. *Atmospheric Chemistry and Physics* 6, 1373–1388.
- Krueger, B.J., Grassian, V.H., Laskin, A., Cowin, J., 2004. Heterogeneous chemistry of individual mineral dust particles from different dust source regions: The importance of particle mineralogy. *Atmospheric Environment* 38, 6253–6261.
- Martin, R.V., Jacob, D.J., Yantosca, R.M., Chin, M., Ginoux, P., 2003. Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols. *Journal of Geophysical Research Atmospheres* 108 (D3), 4097, doi:10.1029/2002JD002622.
- Mentel, T.F., Sohn, M., Wahner, A., 1999. Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols. *Physical Chemistry and Chemical Physics* 1, 5451–5457.
- Michel, A.E., Usher, C.R., Grassian, V.H., 2003. Reactive uptake of ozone on mineral oxides and mineral dusts. *Atmospheric Environment* 37, 3201–3211.
- Preszler Prince, A.M., 2004. Investigations into the heterogeneous atmospheric interactions of isolated metal oxide, carbonate and soot aerosol, Ph.D. dissertation, University of Iowa, Iowa City, 217.
- Preszler Prince, A.P., Wade, J.L., Grassian, V.H., Kleiber, P.D., Young, M.A., 2002. Heterogeneous reactions of soot aerosols with nitrogen dioxide and nitric acid: Atmospheric chamber and Knudsen cell studies. *Atmospheric Environment* 36, 5729–5740.
- Seisel, S., Böresen, C., Vogt, R., Zellner, R., 2005. Kinetics and mechanism of the uptake of N_2O_5 on mineral dust at 298 K. *Atmospheric Chemistry and Physics* 5, 3423–3432.
- Sullivan, R.C., Guazzotti, S.A., Sodeman, D.A., Prather, K.A., 2006. Direct observation of the atmospheric processing of Asian mineral dust. *Atmospheric Chemistry and Physics* 6, 4109–4170 Discuss.
- Tie, X.X., Emmons, L., Horowitz, L., Brasseur, G., Ridley, B., Atlas, E., Stround, C., Hess, P., Klonecki, A., Madronich, S., Talbot, R., Dibb, J., 2003. Effect of sulfate aerosol on tropospheric NO_x and ozone budgets: Model simulations and TOPSE evidence. *Journal of Geophysical Research Atmospheres* 108 (D4), 8364, doi:10.1029/2001JD001508.
- Underwood, G.M., Li, P., Al-Abadleh, H., Grassian, V.H., 2001. A Knudsen cell study of the heterogeneous reactivity of nitric acid on oxide and mineral dust particles. *Journal of Physical Chemistry A* 105, 6609–6620.
- Usher, C.R., Al-Hosney, H., Carlos-Cuellar, S., Grassian, V.H., 2002. Heterogeneous uptake and oxidation of SO_2 on mineral dust. *Journal of Geophysical Research Atmospheres* 107 (D23), 4713, doi:10.1029/2002JD002051.
- Usher, C.R., Michel, A.E., Grassian, V.H., 2003. Reactions on mineral dust. *Chemical Reviews* 103, 4883–4939.
- Wahner, A., Mentel, T.F., Sohn, M., 1998. Gas-phase reaction of N_2O_5 with water vapor: Importance of heterogeneous hydrolysis of N_2O_5 and surface desorption of HNO_3 in a large teflon chamber. *Geophysical Research Letters* 25, 2169–2172.
- Wangberg, I., Etzkorn, T., Barnes, I., Platt, U., Becker, K.H., 1997. Absolute determination of the temperature behavior of the $\text{NO}_2 + \text{NO}_3 + (\text{M}) \leftrightarrow \text{N}_2\text{O}_5 + (\text{M})$ equilibrium. *Journal of Physics and Chemistry A* 101, 9694–9698.
- Zhang, Y., Carmichael, G.R., 1999. The role of mineral aerosol in tropospheric chemistry in East Asia—a model study. *Journal of Applied Meteorology* 38, 353–366.