Reactive uptake of NO$_3$ by liquid and frozen organics

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[1] The reactive uptake of the NO$_3$ radical by liquid and frozen organics was studied in a rotating wall flow tube coupled to a White cell. The organic liquids used included alkanes, alkenes, an alcohol, and carboxylic acids with conjugated and nonconjugated unsaturated bonds. The reactive uptake coefficients, γ, of NO$_3$ on n-hexadecane, 1-octadecene, 1-hexadecene, *cis + trans* 7-tetradecene, n-octanoic acid, 2,2,4,4,6,8,8 heptamethyl nonane, 1-octanol, *cis*, *trans* 9,11 and 10,12 octadecadienoic acid, *cis*-9, *cis*-12 octadecadienoic acid were determined. The reactive uptake coefficients measured with the organic liquids varied from 1.4×10^{-3} to 1.5×10^{-2}. The uptake coefficients of NO$_3$ by n-hexadecane and n-octanoic acid decreased by a factor of $\sim$5 upon freezing. This behavior is explained by reaction occurring in the bulk of the organic liquid as well as on the surface. For the rest of the compounds the change in values of γ upon freezing of the liquids was within the experimental uncertainty. This is attributed to predominant uptake of NO$_3$ by the top few molecular surface layers of the organic substrate and continuous replenishment of the surface layer by evaporation and/or mobility of the surface. These conclusions are corroborated by estimation of the diffuso-reactive length and solubility constant of NO$_3$ in these liquids. The reactivity of NO$_3$ with the organic surfaces is shown to correlate well with the known gas-phase chemistry of NO$_3$. The effect on the atmospheric chemistry of the NO$_3$ radical due to its interaction with organic aerosols is studied using an atmospheric box model applying realistic atmospheric scenarios. The inclusion of NO$_3$ uptake on organic aerosol can decrease the NO$_3$ lifetime by 10% or more. *INDEX TERMS*: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801), 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties, 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); *KEYWORDS*: nitrate radical, organic aerosols, aerosol processing

1. Introduction

[2] Aerosols play major roles in several central environmental issues. They influence the chemistry of the atmosphere via heterogeneous reactions, the climate via radiative forcing and modification of cloud properties [*Andreae and Crutzen*, 1997; *Baker*, 1997; *Ravishankara*, 1997], as well as the health and well-being of people via inhalation of small size particles [*Kaiser*, 2000a, 2000b]. An important development in atmospheric chemistry is the recent recognition that organic material in atmospheric aerosols is abundant in many regions of the troposphere, sometimes overwhelming the inorganic material [*Middlebrook et al.*, 1998; *Murphy et al.*, 1998]. Organic matter significantly affects the physical and chemical properties of aerosols including their total mass, hygroscopic properties, acidity, deposition rate, and radiative properties [*Andrews and Larson*, 1993; *Daumer et al.*, 1992; *Novakov and Penner*, 1993; *Saxena et al.*, 1995]. These properties can be further changed by interactions of gas-phase radicals and oxidants such as OH, halogens, NO$_3$, and ozone with the organic matter in aerosols.

[3] It has been proposed that surface reactions on organic aerosols may be a net sink for gas-phase species such as ozone [*de Gouw and Lovejoy*, 1998; *Ravishankara and Longfellow*, 1999] and HO$_2$ radicals [*Saylor*, 1997]. Recently, we determined the reactive uptake coefficients and identified the reaction products of the interaction of ozone with organic liquids and surfaces serving as proxies for organic aerosols [*Moise and Rudich*, 2000; *Thomas et al.*, 2001]. It was shown that the reactive uptake does not affect tropospheric ozone concentrations, as the total aerosol surface area is small. However, the release of photolabile compounds can affect atmospheric chemistry in specific locations [*Thomas et al.*, 2001]. In addition, as a result of the surface reactions, the organic surface becomes more polar. This can increase the ability of the aerosols to absorb water, which is an important aspect of their influence in the atmosphere [*Cruz and Pandis*, 1998; *Novakov and Penner*, 1993; *Rosenfeld*, 2000].

[4] It is clear therefore that reliable atmospheric modeling must include heterogeneous and multiphase chemistry, yet many of these important processes are still not well characterized [*Andreae and Crutzen*, 1997; *Finlayson-Pitts and Pitts*, 1997; *Jacobson et al.*, 2000; *Molina et al.*, 1996; *Ravishankara*, 1997; *Ravishankara and Longfellow*, 1999]. Specifically, many parameters required for modeling the chemistry and physics of organic aerosols, such as reactive uptake and mass accommodation coefficients, are still unknown. Previous studies regarding organic aerosols have (1) investigated the effects of organic coatings on mass transfer of water and other species into inorganic cores [*Andrews and Larson*, 1993; *Cruz et al.*, 2000; *Cruz and Pandis*, 1998; *Daumer et al.*, 1992], (2) probed the effect of chemical aging on the coagulation and activation of carbonaceous aerosols [*Corrigan and Novakov*, 1999; *Kotzick and Niessner*, 1999; *Kotzick et al.*, 1997], and (3) quantified the reactive uptake of various gas phase compounds (O$_3$, NO$_2$, HNO$_3$, and SO$_2$) by black soot and amorphous carbon, simulating elemental carbon aerosols [*Longfellow et al.*, 1999; *Rogaski et al.*, 1997; *Schurath and Naumann*,

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1998]. The laboratory kinetic studies that have evaluated reactive uptake by organic aerosols rather than by elemental carbon are limited [*de Gouw and Lovejoy*, 1998; *Hanson*, 1995; *Moise and Rudich*, 2000].

[5] The exact nature of organic aerosols is complex and not well known. Organics can be found both as solid matter [*Seinfeld and Pandis*, 1997] and as viscous fluids [*Jang et al.*, 1997], as coatings upon an inorganic core or internally mixed with inorganic compounds [*Ellison et al.*, 1999; *Facchini et al.*, 1999; *Gill and Graedel*, 1983; *Law and Diamond*, 1998; *Seidl*, 2000]. The composition of the organic material is also diverse, encompassing hundreds of compounds [*Rogge et al.*, 1993]. Another complexity arises due to the hydrophobicity of the organic aerosols, which varies with time as a result of reactions and uptake processes. Owing to this enormous heterogeneity, it is impossible to experimentally explore all atmospheric systems and conditions. Therefore it is important to obtain fundamental understanding of the nature of gas-surface chemistry and to develop tools and concepts that will enable prediction of the behavior of organic aerosols over a wide range of chemical and physical conditions [*Andreae and Crutzen*, 1997; *Jacobson et al.*, 2000].

[6] In this study we determined the reactive uptake coefficients of the nitrate radical, an important nighttime oxidant [*Wayne et al.*, 1991], with organic liquids serving as proxies for organic aerosols. These proxies are relevant since the adsorption of semivolatile organics by aerosols can lead to the formation of particles coated by an organic liquid-like layer [*Finizio et al.*, 1997; *Harner and Bidleman*, 1998; *Harner and Mackay*, 1995; *Pankow*, 1998]. To obtain fundamental information on the reactive uptake of the NO$_3$ radical, liquids possessing different functional groups and structures have been chosen. By comparing the reactive uptake of NO$_3$ by liquids and frozen liquids, information is obtained on whether the reaction occurs on the surface or in the bulk liquid. Finally, a box model with real atmospheric scenarios is used to assess the possible effect of the reactive uptake of NO$_3$ on atmospheric chemistry.

2. Experiment

[7] The experiments employed a rotating wall flow tube (inner diameter equal to 1.77 cm) coupled to a White cell. A stable diode laser system was used for the detection of NO$_3$. The liquid uptake experiments were performed with a rotating wetted wall reactor [*de Gouw and Lovejoy*, 1998; *Hanson and Lovejoy*, 1996; *Longfellow et al.*, 1998; *Lovejoy et al.*, 1995; *Moise and Rudich*, 2000]. The White cell has been described previously [*Imamura et al.*, 1997; *Rudich et al.*, 1996a, 1996b, 1996c]. The diode laser was operated by a highly stabilized current source. Wavelength tuning was achieved by adjusting the temperature and current of the laser diode. The laser intensity beam entering the White cell was recently improved by inserting an acousto-optic (AO) modulator in the system. The laser beam was focused into a fiber optic, and on its exit, was split into 70/30% using a near-normal incidence beam splitter. The photocurrent detected from the 30% reflected beam was subtracted from a stable offset current to provide an error signal. This error signal was integrated and fed to the AO modulator driver, providing an intensity control servo loop with a bandwidth of 100 kHz. The laser output after the modulator was adjusted to 80 to 90% of the maximum laser intensity by adjusting the stable offset current. NO$_3$ was detected by use of its absorption at 661.8 nm and measured as the ratio of the signal that traversed the White cell to the signal from the 30% reflected beam that did not go through the White cell. The stability of the signal was 5 × 10^{-4} which is equivalent to a detection limit for the system of 2 × 10^{10} cm^{-3} (1σ). As a test, the White cell's photodetector was moved to detect the beam entering the cell; the intensity fluctuations were an order of magnitude smaller than the intensity noise of the beam traversing an empty cell. This indicated that the signal

detection was limited by multiple beam interference fringe effects (etalons) originating within the White cell.

[8] NO$_3$ was generated by the thermal decomposition of N$_2$O$_5$ in an oven (operated at 75° to 90°C) connected to the movable injector. N$_2$O$_5$ was synthesized by reacting NO$_2$ with O$_3$. NO$_2$ was prepared by reaction of NO with O$_2$. The O$_2$ and NO gas flows were passed through cooled molecular sieves and silica gel traps (both maintained at 195 K), respectively, to remove trace amounts of water. The entire gas handling system and the N$_2$O$_5$ bubbler were extensively flushed with ozone before trapping the N$_2$O$_5$ gas in a cooled bubbler, also maintained at 195 K. The bubbler was well passivated with N$_2$O$_5$ flow to avoid any accumulation of HNO$_3$ formed by reaction of N$_2$O$_5$ with H$_2$O. The product N$_2$O$_5$ was a white flaky powder that showed no contamination of HNO$_3$ crystals. The N$_2$O$_5$ reservoir was kept at a temperature of −55°C. The absolute NO$_3$ concentration was determined by its complete titration with NO. Typical NO$_3$ concentrations employed in these experiments were 5 × 10^{11} to 5 × 10^{12} cm^{-3}.

[9] The pressure in the flow tube was measured with capacitance manometers. Ultrahigh-purity helium was used as a carrier gas, and the flow rates were determined using calibrated mass flowmeters. The experiments were conducted in the temperature range 230 to 290 K. Where possible, the uptake of NO$_3$ by organic compounds was measured on both liquid and frozen surfaces. The liquids were deposited on the bottom of the rotating tube and allowed to freeze slowly while rotating. Typical flow velocities and pressures were between 500 and 2000 cm s^{-1} and between 1 and 10 torr, respectively. Under these conditions, laminar flow was established in the flow tube within approximately 1 cm downstream from the gas inlet. It was verified that the temperature along the flow tube was constant by inserting a shielded thermocouple through the movable injector.

[10] Only compounds with melting points lower than 298 K were used to avoid condensation on the walls of the White cell and transfer tubing. This restricted the uptake to a well-defined region in the thermostated flow tube. The reactive uptake of NO$_3$ by the following organic liquids was studied: n-hexadecane (>99%), 1-octadecene (97%). 1-hexadecene (99%), *cis + trans* 7-tetradecene (99.8%), n-octanoic acid (>99.5%), 2,2,4,4,6,8,8 heptamethyl nonane (98%), 1-octanol (99%), a mixture of *cis* and *trans* 9,11 and 10,12 octadecadienoic acid (conjugated linoleic acid, >99%), cis-9, cis-12 octadecadienoic acid (non-conjugated linoleic acid, >99%). All compounds were purchased from Sigma-Aldrich Ltd. and used as obtained without further purification.

[11] The uptake on bare glass and water ice was also measured. The rate constant for the gas-phase reaction of NO$_3$ with 1-butene was measured as a validation of the experimental apparatus and the data acquisition system.

[12] The reactive uptake coefficients of NO$_3$ were calculated from the measured first-order loss rate coefficients of NO$_3$ from the gas-phase, k_w, due to its loss on the organic-coated reactor wall. The loss of NO$_3$ from the gas phase is described by

$$[NO_3]_{z_2} = [NO_3]_{z_1} \exp(-k_w z/c), \qquad (1)$$

where $[NO_3]_{z_1}$ and $[NO_3]_{z_2}$ are the NO$_3$ concentrations at injector positions z_1 and z_2, with $z = z_2 − z_1$, and c is the gas flow velocity. A plot of ln[NO$_3$] versus relative injector position z yields a straight line with a slope of $−k_w/c$. The coefficient k_w was corrected for the radial concentration gradient generated by the uptake of NO$_3$ into the liquid, using the method developed by *Brown* [1978]. A correction to k_w due to axial diffusion [*Howard*, 1979] was for most cases <1% and hence has been ignored. The gas-phase diffusion coefficients of NO$_3$ in He and H$_2$O were taken from *Rudich et al.* [1996b].

[13] The reactive uptake coefficient, γ, was calculated from the corrected first-order rate coefficient, k, from the relation for a cylindrical reactor [Howard, 1979]

$$\gamma = 2\,r\,k/\omega, \tag{2}$$

where ω is the average molecular speed of NO$_3$ and r is the flow tube radius. The coefficient k_w was measured several times for each liquid, while pressure, temperature, and flow velocities were varied. The relationship between γ and reactive loss in the aqueous phase is given by

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\gamma_r}, \tag{3}$$

where α is the mass accommodation coefficient and γr is the reactive uptake coefficient. Under the assumption that $\alpha \gg \gamma_r$, the measured uptake coefficient is the reactive uptake coefficient, i.e., $\gamma = \gamma_r$ [Hanson et al., 1994].

3. Results

3.1. Validation of the Experimental Apparatus

[14] To test the system's performance, the gas-phase rate coefficient for the reaction

(R1)   NO$_3$ + 1$-$butene $\rightarrow$ products
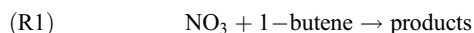
was measured at 295 K, yielding a value of $k_1 = (1.06 \pm 0.16) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The recommended value of k_1 at 295 K is $(1.17 \pm 0.35) \times 10^{-14}$ [Atkinson, 1994].

[15] In addition, the reactive uptake of NO$_3$ on water ice was also measured. The experiment was conducted at 233 K to minimize vaporization of the water molecules. Visual inspection showed smooth, evenly spread ice. The loss of NO$_3$ was very small, and only an upper limit of $\gamma \leq 2 \times 10^{-4}$ was determined. This result is consistent with the measurement of Fenter and Rossi

[1997], who determined an upper limit of $\gamma \leq 1 \times 10^{-3}$ on vapor-deposited ice at temperatures between 170 and 200 K.

[16] The recombination of NO$_3$ with NO$_2$ within the reactor tube can cause a gas-phase loss of NO$_3$ that would lead to overestimation of γ. The recombination rate can be calculated for the NO$_3$ concentration, pressure, and temperature conditions of each experiment. In all our experiments the calculated loss due to recombination was much smaller than the measured NO$_3$ loss on the organic substrate, and was therefore not considered.

[17] Finally, we monitored the effect of changing the speed of rotation of the internal tube on the loss rate of NO$_3$ on both the bare glass and the organic liquids, to verify that uptake was not augmented at higher rotation speeds. No dependence of the uptake coefficient was observed when changing the speed of rotation between 3 and 10 rpm. This suggested that there was no significant rippling effect on the surface of the liquid film and the turbulence in the gas flow near the surface.

3.2. Uptake on Organic Liquids

[18] First-order loss rates, k_w, of NO$_3$ due to reactive uptake by liquid heptamethyl nonane and conjugated and nonconjugated linoleic acid are shown in Figure 1. Uptake coefficients were measured with liquids and the frozen organics. The measurements with the frozen liquids were carried out close to the freezing point to ensure that the rate coefficient and the vapor pressure do not change substantially. For some of the compounds the uptake coefficient was dependent on the flow velocity. For 1-octanol and heptamethyl nonane, γ increased by a factor of 2 at the higher velocities, both in the liquid and frozen states. For 7-tetradecene the increase was by an order of magnitude in the liquid phase and by a factor of 2 in the frozen state. The physical properties of these compounds, such as viscosity, surface tension, and density, and the estimated evaporative flux at the various velocities, could not suggest an explanation for the dependence observed for these compounds specifically. Hence we attribute this dependence to the fact that the higher velocities may have caused enhanced uptake due to formation of ripples in the liquid and eddies in the gas flow
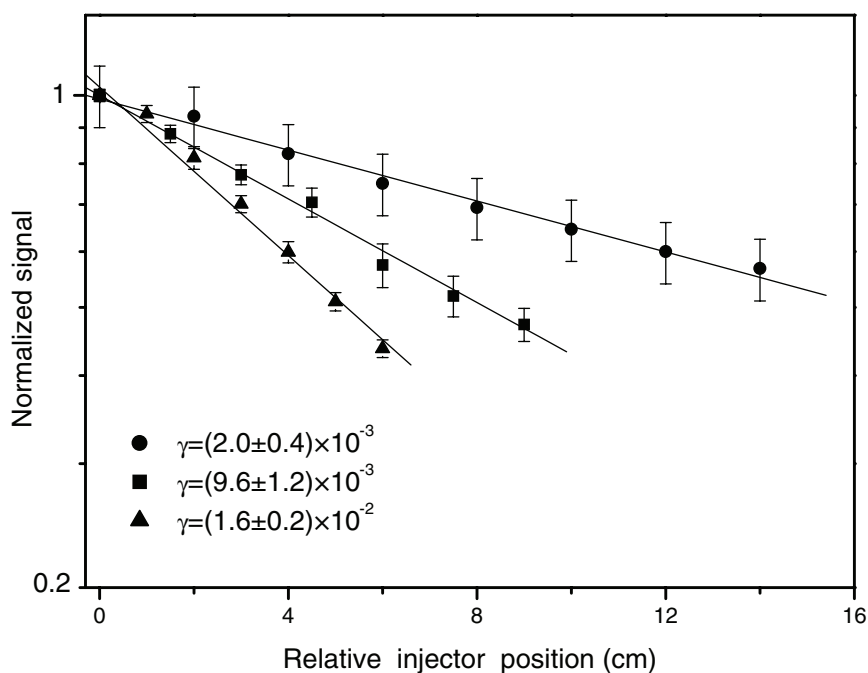
Figure 1. First-order loss of NO$_3$ by organic liquids: heptamethyl nonane (circles), nonconjugated linoleic acid (squares), and conjugated linoleic acid (triangles).

Table 1. Summary of All the Uptake Coefficients Measured in This Study on Liquid and Frozen Organics[a]

Proxy	T, K	γ_{liquid} ($\times 10^3$)	T, K	γ_{solid} ($\times 10^3$)
Ice			233	<0.1
n-hexadecane	293	2.6 ± 0.8	283–289	0.38 ± 0.10
n-octanoic acid	290	2.1 ± 0.3	287	0.44 ± 0.08
1-octadecene	293	1.6 ± 0.3	283	1.4 ± 0.1
1-hexadecene	277	2.3 ± 0.9	254–274	1.8 ± 0.3
Heptamethyl nonane	253	2.1 ± 0.8	234	2.6 ± 0.9
1-octanol	258	7.1 ± 1.6	248	4.1 ± 1.0
7-tetradecene	246	5.8 ± 2.0	238	5.2 ± 2.0
Conjugated linoleic acid	273	7.9 ± 1.2	253 – 263	7.8 ± 1.4
Nonconjugated linoleic acid	288	15.0 ± 2.0	248 – 263	11 ± 3.0

[a] The values are averaged from the measurements in the lower velocity range of the experiments (see text). The stated error is the standard deviation of the averaged results (1σ).

close to the nonsmooth frozen surface. A summary of the uptake coefficients measured at the lower flow velocities and at temperatures close to the phase change is shown in Table 1. The stated error is the standard deviation (1σ) of the averaged results.

[19] To ensure that the gas-phase reaction of NO_3 with organics was negligible in these experiments, long-chain organic compounds with low vapor pressure were chosen. The first- order gas-phase loss rates k_g^I of NO_3 due to reactions with alkanes and alkenes that evaporate from the organic liquid were estimated. One of the difficulties in estimating k_g^I is the lack of rate coefficient data and vapor pressure data, which was therefore estimated with the Clausius-Clapeyron equation. Assuming the vapor pressure of tetradecene to be $\leq 10^{-4}$ torr at 243 K and a rate coefficient as high as 1×10^{-12} cm^3 molecule^{-1} s^{-1}, a first-order loss rate of ≤ 5 s^{-1} is calculated. In contrast, the measured first-order loss rate of NO_3 on tetradecene surfaces was between 50 and 280 s^{-1}. For alkanes, carboxylic acids, and octanol the calculated gas-phase loss rate was even lower due to either the lower vapor pressures of these compounds or lower gas-phase rate coefficients. Therefore γ was calculated assuming that the dominant loss process of NO_3 in these experiments is its loss on the walls of the flow tube and that gas-phase loss is negligible.

[20] In addition, we attempted to measure the loss of NO_3 on some polyaromatic hydrocarbons (PAH). However, owing to the sublimation of these high melting point compounds and their subsequent adsorption and condensation on the White cell walls and mirrors, it was not possible to determine the reactive uptake coefficients of NO_3 for the polyaromatics.

4. Discussion

[21] The reactive uptake of NO_3 by various organic compounds was measured in this study. The chosen organic compounds possess a broad spectrum of functional groups. Although these compounds do not represent species that are necessarily present in atmospheric particulate matter, the different functional groups are common in aerosols, and their span enables a general characterization of the NO_3 chemistry with the condensed organic phase.

[22] The measured uptake may be due to physical solubility or reversible adsorption (nonreactive processes) or due to chemical reactions, either on the surface of the liquids or in the bulk. To check for the first and second scenarios, both of which would indicate a reversible uptake, the injector was pulled upstream of the organic-coated (liquid or frozen) region such that the entire organic layer was exposed to NO_3 and an uptake was observed. When the injector was swiftly returned downstream of the flow tube (just past the organic layer), no release of NO_3 was observed, indicating permanent loss of NO_3 by the organic liquid, typical of reactive processes. Another possibility for NO_3 loss is decomposition of NO_3 on the surface or recombination with NO_2 on the surface.

However, the surfaces of alkanes and alkenes are not likely to be different except for the chemical reactivity. Therefore the differences observed in the reactivity of NO_3 on different surfaces cannot be due to its decomposition or its recombination with NO_2 on the surface.

[23] The loss of NO_3 on the frozen liquids was constant, with no surface poisoning or depletion of reactive sites observed even after long exposure times. This is in contrast to uptake of ozone by solids, such as organic monolayers and carbon soot aerosol, for which γ decreases as the surface is processed [*Kamm et al.*, 1999; *Moise and Rudich*, 2000]. The constant NO_3 uptake suggests the existence of some mechanism that replenishes the frozen liquid surface. One possibility for such a mechanism is the continual vaporization of the organic compound from the condensed surface due to pumping. The evaporative flux from the surface can be estimated from the vapor pressure, the flows, and the pressure in each experiment. This rate can then be compared to the reactive collision rate to see whether a fresh surface can be exposed at a rate greater than its rate of depletion through reaction. If this were the case, the uptake coefficient would remain unchanged. For most of the compounds in this study, this is a feasible explanation. However, the low vapor pressures and hence small evaporative fluxes of 1-octadecene and the unsaturated carboxylic acids are such that the surface and hence reactive sites are not renewed on a timescale greater than that for depletion. We would thus expect a decrease in the NO_3 uptake at any given position over time. As this is not observed, it is assumed that although the surface is frozen, there is enough mobility of the organic layer or penetration of NO_3 beyond the surface to support the observed constant uptake. In Figure 2 the reactive uptake coefficient of NO_3 on conjugated octadecadienoic acid versus temperature is plotted. On cooling from 273 to 253 K, changing from the liquid phase to the frozen state, γ decreased slowly from 8×10^{-3} to 6×10^{-3}, whereas at 243 K, γ decreased to below 1×10^{-3}. Below 243 K the uptake was even smaller. It is possible that at ~250 K the mobility of the surface diminishes greatly and once all the surface molecules have reacted, the surface is no longer reactive toward the incoming NO_3. The loss of NO_3 on two compounds, n-hexadecane and n-octanoic acid, showed a large (factor of ~5) decrease in γ between the liquid and frozen states (see Table 1). The experiments with the liquid and frozen states were conducted over a small temperature range, ensuring that the rate coefficients and the evaporation from the surface do not change substantially upon freezing. The decrease of γ upon freezing suggests that the reactive uptake by n-hexadecane and n-octanoic acid is composed of both surface reactivity and diffusion followed by reaction in the bulk. Upon freezing, there is a sudden decrease in the diffusion coefficient into the bulk, causing the bulk channel to shut off and the uptake to decrease, because the uptake by the frozen liquid is restricted to reactions on the surface. This behavior can be explained in terms of the resistor model, in which the reactive channel has parallel surface reactivity and bulk reactivity resistances [*Hanson*, 1997; *Hu et al.*, 1995; *Kolb et al.*,
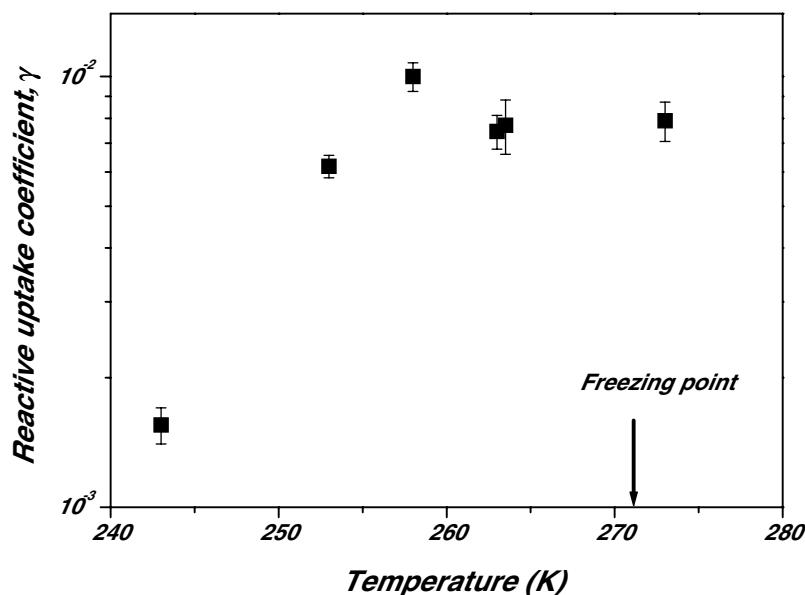
Figure 2. The temperature dependence of γ for linoleic acid. Freezing occurs at 272 K.

1995]. Contribution of diffusion and reaction in the liquid was also observed for ozone reactions with liquids of terminal alkenes [*Moise and Rudich*, 2000]. For all other compounds used in this study, the change in reactivity between the liquid and the frozen states is very small, indicating that the dominant loss occurs directly on the surface.

[24] Estimation of the solubility constant and the diffuso-reactive length of NO₃ in the liquid organic compounds support these conclusions. There are no available data on the solubility of NO₃ in organic liquids. However, the uptake measurements can be used to estimate $H\sqrt{(D_\ell k_\ell^I)}$ as well as the solubility of NO₃ in the organic liquid from

$$\gamma = \frac{4RT}{\omega} H\sqrt{D_\ell k_\ell^I},\qquad(4)$$

where D_ℓ (cm² s⁻¹) is the diffusion coefficient of NO₃ in the organic liquid and k_ℓ^I (s⁻¹) is the first-order loss rate of NO₃ in the liquid. On the basis of the diffusion coefficients of different inorganic compounds in n-hexane and other solvents [*Lide*, 1998] we have chosen an average value of $D_\ell = 2 \times 10^{-5}$ cm² s⁻¹ for the diffusion coefficient of NO₃ in organic liquids. The rate coefficient for NO₃ in liquid was estimated based on its gas-phase rate coefficients. For example, assuming a gas-phase rate coefficient for an alkane of 1×10^{-16} cm³ molecule⁻¹ s⁻¹, a liquid-phase rate coefficient of $k_\ell = 6 \times 10^4 M^{-1}$ s⁻¹ is obtained. Using the measured γ of 2×10^{-3} for n-hexadecane at 292 K, we obtain $H\sqrt{(D_\ell k_\ell^I)} = 0.84\ M$ cm atm⁻¹ s⁻¹ and $H \approx 0.8\ M$ atm⁻¹ (the activity of a pure organic liquid is taken to be 1). This solubility is of the same order of magnitude as the solubility determined for NO₃ in water ($0.6 \pm 0.3\ M$ atm⁻¹ [*Rudich et al.*, 1996c]).

[25] The reactivity in the bulk could be the result of this limited solubility, and thus NO₃ could react to a depth equal to the diffuso-reactive length ℓ in the liquid. This length is defined as [*Hanson et al.*, 1994]

$$\ell = \sqrt{\frac{D_\ell}{k_\ell^I}}.\qquad(5)$$

[26] The diffuso-reactive length can be estimated by assuming the same values as for the calculation of the solubility constant. For

hexadecane a value of $\ell \approx 1 \times 10^{-5}$ cm was obtained, which is much deeper than the first couple of surface layers. For long alkenes, assuming a gas-phase rate coefficient of 1×10^{-13} cm³ molecule⁻¹ s⁻¹, one obtains that in the liquid phase the first-order loss rate for octadecene would be $k_\ell^I = 6 \times 10^8 M^{-1}$ s⁻¹, yielding $\ell \approx 6 \times 10^{-7}$ cm. This length is on the order of a few molecular layers. This is consistent with the reaction occurring very close to the surface of the organic layer, rather than in the bulk. The two compounds for which bulk reactivity is dominant have lower gas-phase rate constants, approximately 10^{-16} cm³ molecule⁻¹ s⁻¹ for n-hexadecane and approximately 10^{-17} cm³ molecule⁻¹ s⁻¹ for n-octanoic acid. These values are based on the measured rate constants for similar compounds [*Atkinson*, 1994]. All other compounds in this study have a faster gas-phase reaction rate constant, $>10^{-14}$ cm³ molecule⁻¹ s⁻¹, and exhibit mostly a surface reaction. The trend in the condensed phase reactivity thus qualitatively correlates with the gas phase reactivity for the majority of the compounds studied here.

[27] The measured uptake coefficients vary with the chemical structure and the number of reactive functional groups. The values of γ can be best appraised by comparing the reactive uptake coefficient values for the frozen surfaces where there is no contribution from reaction in the bulk. The reactivity trend of the long chain molecules in this study is shown in Figure 3. The least reactive are the n-alkane and the octanoic acid. The reactivity increases with the addition of more reactive functional groups, such as a double bond [*Atkinson*, 1994]. Since the carboxylic acid is not in itself a reactive group, the measured uptake on the linoleic acid is attributed to the double bonds. As the liquid changes from 1-alkene to an alkene with two double bonds, the reactivity increases. Within the uncertainty associated with high γ, the uptake coefficient of a molecule with two conjugated double bonds is similar to that of a molecule with two nonconjugated double bonds (see Table 1). It is also seen that the branched alkane (heptamethyl nonane) is more reactive than the n-alkane, and the substituted alkene (7-tetradecene) is more reactive than the terminal alkenes. This trend is consistent with the known gas phase reactivity of NO₃ (alkane < branched alkane, alkane < alkene, terminal alkene < substituted alkene, alkene < diene). Despite its higher concentration relative to the 18-carbon compounds, 1-octanol shows higher uptake than could be expected based on its gas-phase chemistry. An alcohol is expected to be more reactive than an alkane, as the α-hydrogen atom to the OH group is more labile [*Chew et al.*, 1998], thus
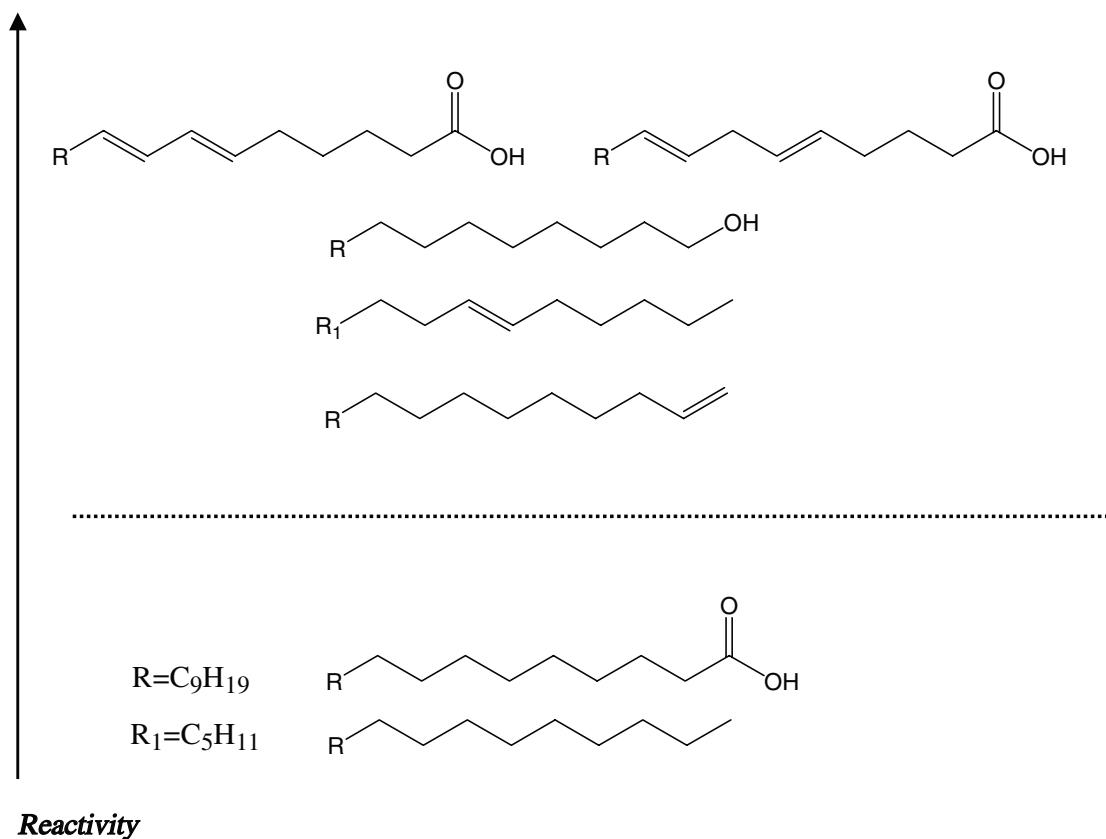
Reactivity

Figure 3. The trend of NO$_3$ reactivity toward frozen organic liquids in this study.

facilitating the hydrogen abstraction (e.g., for butane, k_g(298 K) = 6.6×10^{-17} cm^3 molecule^{-1} s^{-1} and for n-butanol, k_g(298 K) $\leq 2.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} [*Chew et al.*, 1998; *Rudich et al.*, 1996a]). However, in the gas-phase the NO$_3$ addition rate to the unsaturated bond is greater than the rate for the abstraction pathway (e.g., for 1 butene, k_g(298 K) = 1.2×10^{-14} cm^3 [*Atkinson*, 1994]). We do not have an explanation for the deviation of octanol from the similarity to the gas-phase trend shown for the rest of the compounds in this study. The observed reactivity trend of NO$_3$ in the liquid phase and in the gas phase can assist in our understanding and prediction of the NO$_3$ reactivity with additional organic liquids.

[28] The role of organic aerosols in atmospheric chemical interactions is still poorly understood. Kinetic parameters needed to quantify their reaction with gas-phase species include reactive uptake coefficients, solubility, and bulk-phase rate coefficients. The present study is part of a series of studies regarding the

reactivity of atmospheric radicals and oxidants with proxies for organic aerosols. In this study, we examined the uptake of the NO$_3$ radical with pure organic liquids, serving as proxies for both pure liquid and solid organic aerosols. Recent measurements in the atmosphere have shown that the atmospheric aerosol is usually very complex, containing both organic and inorganic matter. Our intent in future work is to conduct uptake studies on mixed liquids in addition to pure compounds, and to include subsequent identification and quantification of the reaction products.

5. Atmospheric Implications: Box Model Calculations

[29] A detailed gas-phase box model modified to include reactive uptake of gas-phase species by organic aerosols [*Thomas*

Table 2. Modeled Nighttime Reactions of NO$_3^t$ Besides NO$_3$ Uptake by Organic Aerosols[a]

Reaction No.	Reaction	Reference for Rate Data
(R3)	NO$_2$ + O$_3$ → NO$_3$ + O$_2$	*DeMore et al.* [1997]
(R4a)	NO$_3$ + NO$_2$ + M → N$_2$O$_5$ + M	*DeMore et al.* [1997]
(R4b)	N$_2$O$_5$ + M → NO$_3$ + NO$_2$ + M	*DeMore et al.* [1997]
(R5)	N$_2$O$_5$ + H$_2$O → 2HNO$_3$	*DeMore et al.* [1997]
(R6)	NO$_3$ + TVOC[b] → HNO$_3$ + products	*Atkinson* [1994]
(R7)	N$_2$O$_5$ + aqueous aerosol → HNO$_3$ + products	*DeMore et al.* [1997]
(R8)	NO$_3$ + aqueous aerosol → products	*DeMore et al.* [1997]

[a] While the daytime NO$_3^t$ chemistry, including photolysis reactions, was included in the model mechanism, it is shown here for simplicity. Daytime NO$_3^t$ concentrations were extremely small due to rapid photolysis by visible light, so we focus here only on NO$_3^t$ chemistry at night when [NO$_3^t$] was much higher.

[b] TVOC was composed of (1) anthropogenic volatile organic compounds (VOC's), including ethylene, propylene, and higher alkenes, aromatics, and alkanes of seven carbons or larger; and (2) biogenic VOC's, including α-pinene and isoprene. TVOC did not include dimethyl sulfide (DMS). This work examines the maximum effects of organic aerosol uptake of NO$_3$, and the presence of DMS would decrease the impacts of aerosol uptake.

Table 3. Relevant Input Data, Modeled [NO$_3^t$] and Lifetime Without NO$_3$ Uptake by Organic Aerosols (Reaction (R2)), Percent Changes Including Reaction (R2), and Percent Contribution of Individual Sinks to the Total NO$_3^t(g)$ Loss Rate for Selected Model Runs

| Scenario	Marine		Rural Unforested[a]	
	$\gamma = 3 \times 10^{-3}$	$\gamma = 1 \times 10^{-2}$	$\gamma = 3 \times 10^{-3}$	$\gamma = 1 \times 10^{-2}$
Input parameters				
Temperature, °C	25	25	25	25
[O$_3$], ppbv	40	40	40	40
[NO$_x$], pptv	41	41	440	440
Surface area,[b] cm^2 cm^{-3}	1.9×10^{-7}	1.9×10^{-7}	1.9×10^{-6}	1.9×10^{-6}
Concentrations and lifetime[c]				
[NO$_3$], pptv	29	29	30	30
[N$_2$O$_5$], pptv	0.8	0.8	9	9
Δ[NO$_3^t$] including reaction (R2), %	−7	−20	−10	−26
τ, min[d]	720	720	47	47
$\delta\tau$ including reaction (R2),[d] %	−17	−41	−10	−26
Contribution to $L(NO_3^t)$,[c] %				
N$_2$O$_5$ + H$_2$O(g) (R5)	75	53	45	36
NO$_3$ + TVOC(g) (R6)	1	1	9	8
N$_2$O$_5$ + aqueous aerosol (R7)	6	4	36	29
NO$_3$ + aqueous aerosol (R8)	1	1	1	1
NO$_3$ + organic aerosol (R2)	17	41	9	26

[a] Same as rural forested scenario without biogenic VOCs.
[b] The particle number distributions used in these scenarios are based on the observed marine organic aerosol size distribution of *Novakov and Penner* [1993]. These data were used without modification for the marine scenario, while the number per cubic centimeter in each size bin was increased by a factor of 10 in the rural unforested scenario. The total surface areas from these distributions agree with typical observations for these locations [*Whitby and Sverdrup*, 1980].
[c] At last time step before sunrise in the last steady state diurnal cycle of each model run (see text).
[d] Here τ is equal to the lifetime of NO$_3^t$ as defined by equation (6).

et al., 2001] was used to investigate the atmospheric implications of the measured NO$_3$ reactions with organic surfaces. The reactive uptake of NO$_3$ by organic aerosols was modeled as

(R2)   NO$_3(g)$ + RS → products,
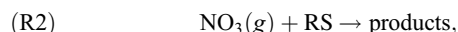
with RS representing an organic aerosol reactive site, in this case either an alkane or alkene compound. Reaction (R2) was treated simply as an additional loss process for gas-phase NO$_3$ because the explicit products of this reaction have not yet been characterized. The processing of aerosols by NO$_3$ to produce new compounds may have significant atmospheric impacts, which are not discussed here. The uptake rate was described by the Fuchs-Sutugin expression [*Fuchs and Sutugin*, 1970] and was a function of the average diameter of the aerosols in each size bin, the reactive uptake coefficient γ, and the NO$_3(g)$ diffusion coefficient and average molecular speed. The model could also properly account for the effect of reaction (R2) on the time-dependent amount of RS [*Thomas et al.*, 2001]. However, in order to assess the maximum possible effect that organic aerosols might have on [NO$_3(g)$], our modeling studies kept [RS] fixed and assumed complete coverage of the aerosol surface by RS.

[30] A summary of other chemical reactions involving NO$_3$ included in the model is given in Table 2. We used $\gamma = 3 \times 10^{-3}$ for reaction (R2) in the base runs, and as a sensitivity test we increased γ to 1×10^{-2}. Input organic aerosol size
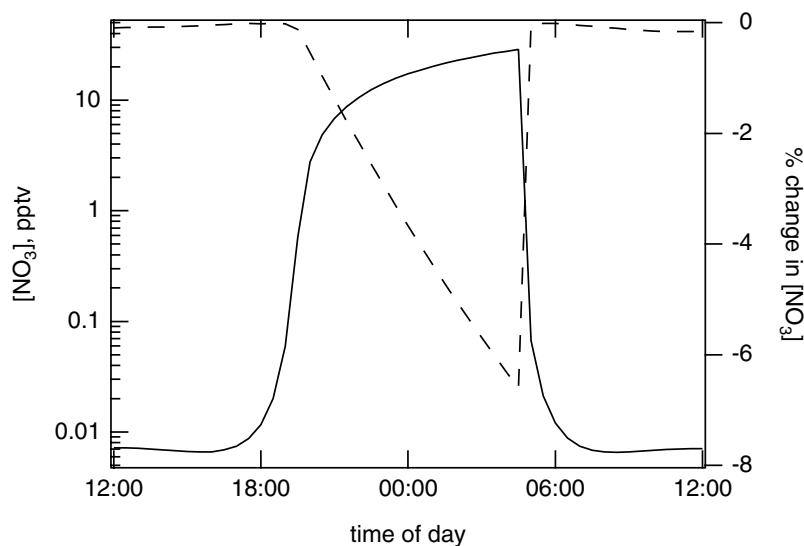
Figure 4. Time dependence of [NO$_3$] in the marine scenario without reaction (R2) (solid line) and the percent change in [NO$_3$] when reaction (R2) is included with $\gamma = 3 \times 10^{-3}$ (dotted line). In this case, NO$_3$ accounts for greater than 97% of [NO$_3^t$] at all times.

distributions were based on the observations of *Novakov and Penner* [1993] (see notes to Table 3). We used $\gamma = 0.05$ for N$_2$O$_5$ and $\gamma = 2 \times 10^{-4}$ for NO$_3$ [*DeMore et al.*, 1997] in the aqueous aerosol uptake reactions (R7) and (R8). The surface area available for reactions (R7) and (R8) was assumed to be equal to that of the organic aerosols in reaction (R2). Because of the rapid equilibration between NO$_3$ and N$_2$O$_5$ (reaction (R4)), we consider here the effects of NO$_3$ uptake on the group NO$_3^t$ = NO$_3$ + N$_2$O$_5$. The concentrations of O$_3$, NO$_x$ (= NO + NO$_2$), CO, hydrocarbons, and long-lived oxygenated volatile organic compounds (VOCs) such as ketones and methanol were held fixed in the calculations. The levels of all other gas-phase species in the model (NO$_3$, N$_2$O$_5$, NO$_3^t$, OH, HO$_2$, RO$_2$, HNO$_3$, organic nitrates, peroxides, and aldehydes) were simultaneously calculated at each time step. Though NO$_x$ was held constant, NO and NO$_2$ were repartitioned at every time step, and NO$_x$ = NO$_2$ at night. The model was run through complete diurnal cycles until a reproducible cycle in all time-varying concentrations was reached.

[31] A number of atmospheric scenarios were examined using input data from various field missions (see *Thomas et al.* [2001] for a detailed list of the data sources), including boundary layer cases representative of summertime midlatitude marine, summertime midlatitude rural forested and unforested, summertime midlatitude urban, and springtime polar locations, and a case representing the summertime midlatitude marine free troposphere. While not exhaustive, these scenarios covered a range of conditions including a large variation in [NO$_x$], [VOCs], and aerosol surface area. Significant impacts from reaction (R2) were observed only for the summertime marine and rural unforested boundary layer scenarios, which are discussed in more detail here (see Table 3 for a summary of input parameters). For each scenario, two calculations were carried out, one without reaction (R2) and one including reaction (R2) but otherwise identical to the first calculation. A typical pair of calculations is demonstrated in Figure 4, which shows [NO$_3$] modeled without reaction (R2) and the percent change in [NO$_3$] when reaction (R2) was included.

[32] Table 3 shows the calculated NO$_3$ and N$_2$O$_5$ mixing ratios and lifetime of NO$_3^t$, τ, in runs without reaction (R2) and the decreases in these quantities when reaction (R2) was included. We define NO$_3^t$ lifetime,

$$\tau = 1/L, \tag{6}$$

based on the rate of change of [NO$_3^t$] at each model time step,

$$d[\text{NO}_3^t]/dt = P - L[\text{NO}_3^t], \tag{7}$$

where P is the total NO$_3^t$ production rate (molecule cm^{-3} s^{-1}) and L is the total NO$_3^t$ loss frequency (s^{-1}). The model output in Table 3 is given at a point just before sunrise. In scenarios where NO$_3^t$ did not reach a nighttime steady state, such as the marine case shown in Figure 4, this was the point at which [NO$_3^t$] reached a nighttime maximum. In other scenarios such as the rural and urban cases, [NO$_3^t$] was in steady state throughout the entire night.

[33] The change in modeled [NO$_3^t$] when reaction (R2) was included was rather small in all cases that were examined. The scenarios summarized in Table 3 showed the largest impacts from reaction (R2), with [NO$_3^t$] decreases on the order of 10% for $\gamma = 3 \times 10^{-3}$. The percent changes in τ were generally the same as those in [NO$_3^t$]. The relatively small impact of reaction (R2) stems from its small contribution (less than 10% in most cases) to the total NO$_3^t$ sink (Table 3). One exception was the marine case, where the fractional contribution from reaction (R2) was larger than in the other scenarios and the fractional decrease in τ (17%) upon inclusion of reaction (R2) was substantially greater than the decrease in [NO$_3^t$] (about 7%). In the marine case, NO$_3^t$ did not

reach steady state at night, and the NO$_3^t$ loss frequency L was so small that even large increases in L were not sufficient to comparably affect [NO$_3^t$] before sunrise, when a daytime steady state was established. Increasing γ to 1×10^{-2} caused [NO$_3^t$] to decrease up to 26% and decreased τ by as much as 40% (Table 3). However, an uptake coefficient as large as 1×10^{-2} for actual atmospheric organic aerosols seems unlikely based on the laboratory work discussed here.

[34] These calculations suggest that in much of the troposphere the effect of reaction (R2) on gas-phase NO$_3^t$ will be small, and thus its impact on other gas-phase species is expected to be even smaller. This conclusion seems particularly valid considering that these calculations represent an upper limit because they ignore the removal of aerosol organic reactive sites by reaction (R2). However, the importance of reaction (R2) should be reexamined in a particular location if more complete aerosol data exist, and if these data indicate that the levels of organic aerosols are larger than those assumed here.

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