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PAPER

Reactive uptake kinetics of NO₃ on multicomponent and multiphase organic mixtures containing unsaturated and saturated organics

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We investigated the reactive uptake of NO₃ (an important night-time oxidant in the atmosphere) on binary mixtures containing an unsaturated organic (methyl oleate) and saturated molecules (diethyl sebacate, dioctyl sebacate, and squalane) which we call matrix molecules. These studies were carried out to better understand the reactivity of unsaturated organics in multicomponent and multiphase atmospheric particles. For liquid binary mixtures the reactivity of methyl oleate depended on the matrix molecule. Assuming a bulk reaction, $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{\text{oleate}}}$ varied by a factor of 2.7, and assuming a surface reaction $H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S$ varied by a factor of 3.6, where $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{\text{oleate}}}$ and $H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S$ are constants extracted from the data using the resistor model. For solid–liquid mixtures, the reactive uptake coefficient depended on exposure time: the uptake decreased by a factor of 10 after exposure to NO₃ for approximately 90 min. By assuming either a bulk or surface reaction, the atmospheric lifetime of methyl oleate in different matrices was estimated for moderately polluted atmospheric conditions. For all liquid mixtures, the lifetime was in the order of a few minutes (with an upper limit of 35 min). These lifetimes can be used as lower limits to the lifetimes in semi-solid mixtures. Our studies emphasize that the lifetime of unsaturated organics (similar to methyl oleate) is likely short if the particle matrix is in a liquid state.

1. Introduction

Organic material contributes about 20–90% to the total fine aerosol mass in the troposphere.^{1,2} This organic material can be in the form of pure organic particles or alternatively the organic can be internally mixed with inorganic material.^{3,4} Adding to the complexity, the organic material can consist of thousands of different organic compounds with a range of functional groups.^{5,6} Organic and mixed organic–inorganic particles can also be solids, liquids, liquid–liquid mixtures, liquid–solid mixtures or glasses.^{7–16}

While in the atmosphere these organic and mixed organic–inorganic particles can undergo reactions with gas-phase species such as OH,^{17–20} O₃,^{21–25} NO₃,^{26–33} and Cl.^{34–36} These heterogeneous reactions can be important for several reasons.^{18,37–39} As an example, heterogeneous reactions have implications for source apportionment. Specific organic species often serve as molecular markers for probing sources of organic particles. If heterogeneous reactions change the concentrations of the selected molecular markers they can lead to errors when calculating source strengths.⁴⁰

Despite the potential importance of organic heterogeneous chemistry in the atmosphere and the fact that organic particles

in the atmosphere are complex, there have been relatively few heterogeneous chemistry studies using multicomponent or multiphase organic mixtures. Recent studies using multicomponent and multiphase organics have mainly involved O₃, OH and Cl chemistry. See for example ref. 9, 21, 24, 29, 34, 35, 41–59.

Recently we studied the reactive uptake coefficient of NO₃ on single-component organics and concluded that the NO₃–alkene reaction could potentially be an important loss process of particle-phase unsaturated organic compounds in the atmosphere and in laboratory secondary organic aerosol studies.²⁷ However, these conclusions were based on measurements with single-component substrates. The NO₃ kinetics may be different in multicomponent and multiphase mixtures based on past studies using multicomponent and multiphase mixtures with O₃, OH and Cl. See for example ref. 9, 18, 23, 24, 29, 35, 41–44, 46, 47, 52, 54, 57, 58 and 60.

In the following we investigate NO₃ reactive uptake on multicomponent and multiphase mixtures containing an unsaturated organic. For the unsaturated organic we used methyl oleate (see Fig. 1). Based on previous work we expect that the reaction between NO₃ and the carbon–carbon double bond is efficient and the ester functional group does not play a significant role in the chemistry or kinetics.²⁷ Other molecules used in this study were diethyl sebacate (DES), dioctyl sebacate (DOS) and squalane. These molecules cover a range of viscosities,

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Fig. 1 Molecular structures of the organic compounds used in this study.

molecular weights and functional groups (See Fig. 1 and Table 1). Also these molecules have low vapor pressures (which is a prerequisite for the flow tube studies). Here we refer to these saturated organics as matrix molecules.

At a temperature of 278 K we studied the following binary mixtures: methyl oleate–DES, methyl oleate–DOS and methyl oleate–squalane. At this temperature the mixtures were all liquid. This allowed us to probe multicomponent liquid mixtures and assess the effect of the matrix molecules on the NO_3 uptake kinetics. At 268 K we studied binary mixtures of methyl oleate–DES. At this temperature the binary system was a solid–liquid mixture. This allowed us to probe the effect of particle phase on the NO_3 chemistry. In all experiments the concentration of methyl oleate in the binary mixtures were always kept less than 4 wt% methyl oleate. At these concentrations physical properties of the binary mixtures, such as solubility and molecular diffusion, will be controlled mainly by the matrix molecules.

In this paper we present the reactive uptake coefficient measurements for these multicomponent and multiphase mixtures. The reactive uptake coefficient (γ) is defined as the fraction of collisions with a surface that leads to reactive loss. The results are analyzed using the resistor model, and the results from this analysis are then used to assess the effect of the matrix molecules on the NO_3 uptake kinetics and the lifetime of unsaturated organics in the atmosphere.

2. Experimental

2.1 Experimental setup

Experiments were conducted in a cylindrical, rotating-wall flow tube reactor coupled to a chemical ionization mass spectrometer (CIMS). The setup and procedure are similar to several recent studies.⁹ A rotating Pyrex tube (~ 12 cm length, 1.77 cm inner diameter) fitted snugly inside the flow tube reactor. The inside wall of the glass tube provided a surface for a thin coating of the studied organic material. NO_3 entered the flow tube through a movable injector. By varying the distance between the injector tip and the exit of the flow tube, loss of NO_3 can be determined as a function of reaction distance and thus reaction time.

NO_3 radicals were obtained by thermal conversion of gaseous N_2O_5 to NO_3 and NO_2 at 430 K in a Teflon coated glass oven before entering the movable injector. N_2O_5 was generated by reacting NO_2 with an excess amount of O_3 in a flow system as described by Schott and Davidson⁶¹ and Cosman *et al.*⁶² N_2O_5 was trapped and stored as solid white crystals at 197 K.

After thermal conversion of N_2O_5 to NO_3 and NO_2 , the recombination of NO_3 and NO_2 was negligible due to the short residence time of the gases in the flow tube reactor (typically 20–100 ms), NO_3 was detected as NO_3^- in the mass spectrometer after chemical ionization by I^- which was generated by passing a trace amount of CH_3I in N_2 through a ^{210}Po source (model Po-2031, NRD).

Total pressures in the flow cell during experiments were typically 2.6–3.2 Torr whereas flow velocities ranged from 380–600 cm s^{-1} . The carrier gas through the cell was a mixture of O_2 (~ 10 –15%) in He. NO_3 concentrations for all experiments were estimated as $(3.5\text{--}16) \times 10^{10}$ molecules cm^{-3} by assuming that all N_2O_5 is converted to NO_3 and NO_2 and approximately 20% of the NO_3 thermally dissociates in the Teflon coated glass oven based on well-known gas-phase reaction rates and modeling studies using the Acuchem chemical kinetics simulation program.⁶³ Quantitative conversion of N_2O_5 to NO_3 and NO_2 in the oven was confirmed by adding high levels of NO to the exit of the flow tube. This conversion reaction with NO also served as a convenient way to quantify the background signal in the NO_3 experiments. NO was added in excess which completely titrated NO_3 to NO_2 . Any remaining signal at mass 62 after titration by NO was assigned to the background. The background signal was typically less than 10% of the total signal. The uncertainty of the NO_3 concentration, based on the uncertainty of the rate constant for the gas-phase $\text{N}_2\text{O}_5 + \text{I}^-$ reaction, is 40%.⁶⁴

Table 1 Properties of the organic compounds used in this study

Compound	Molecular Formula	Molecular weight (g mol^{-1})	Viscosity at 293–298 K (mPa s)	Diffusion Coefficient ^a at 293 K ($\text{cm}^2 \text{s}^{-1}$)
Methyl oleate	$\text{C}_{19}\text{H}_{36}\text{O}_2$	296.49	N/A	N/A
DES	$\text{C}_{14}\text{H}_{26}\text{O}_4$	258.36	5.88 ⁷⁸	1.8×10^{-6}
DOS	$\text{C}_{26}\text{H}_{50}\text{O}_4$	426.67	25 ^b	4.3×10^{-7}
Squalane	$\text{C}_{30}\text{H}_{62}$	422.81	36.0 ⁷⁹	3.0×10^{-7}

^a The diffusion coefficient is calculated by the Stokes–Einstein equation²⁷ and by assuming the radius of the diffusing species (NO_3) was the same as O_3 as done in a recent paper.⁸⁰ ^b Taken from www.kicgroup.com/dos.htm.

Fig. 2 Plot of the natural logarithm of the NO_3 signal vs. reaction time from several experiments. The substrates used in these studies were liquid DES and two liquid binary mixtures of methyl oleate and DES (0.57 and 1.72 wt% methyl oleate).

Observed first-order loss rate coefficients, k_{obs} , were calculated from the depletion of the oxidant signal with increasing reaction time. Typical plots of the natural logarithm of the NO_3 signal as a function of time are shown in Fig. 2. The slopes of the linear fits were used to determine k_{obs} , which was in turn corrected for concentration gradients that formed close to the flow-tube wall by using the procedure described by Brown.⁶⁵ Uptake coefficients (γ) were calculated from the corrected rate constants, k_{corr} , using a standard procedure.⁹ Diffusion coefficients of NO_3 used in these calculations were taken from Rudich *et al.*⁶⁶

The two main sources of uncertainty for the uptake coefficient measurements were the gas phase NO_3 diffusion coefficient and the measurement of k_{obs} . We calculated the error from gas phase diffusion by assuming a 20% uncertainty for the NO_3 diffusion coefficient.⁶⁷ The uncertainty for the gas phase diffusion coefficient of NO_3 in Helium is about 8%, and for NO_3 in O_2 is about 20%. In our study, the carrier gas is a mixture of He and O_2 . To be conservative we used the larger uncertainty (20%) as the uncertainty of NO_3 in the He– O_2 mixture. For the uncertainty of k_{obs} , we used the standard deviation (1σ) of the measurements. Reported errors include both the uncertainty from the diffusion coefficient and uncertainty from measuring k_{obs} . The vapor pressure of pure methyl oleate is 4×10^{-5} Torr at 25 °C, and in the mixtures it should be decreased by more than an order of magnitude assuming Raoult's Law behaviour. At these low vapor pressures, the loss due to gas-phase reactions between methyl oleate and NO_3 should be less than 0.1% of the observed loss of NO_3 .

For reactive uptake studies on liquids, approximately 0.5 to 0.8 ml of the liquid was added to the inner wall of a rotating glass cylinder. A rotation rate of ~ 10 rotations min^{-1} was used for all experiments to ensure an even coating of the liquid on the inside of the glass tube.

For reactive uptake studies on solid–liquid mixtures, a smooth solid–liquid film was prepared following the procedure outlined by Knopf *et al.*⁹ First a liquid mixture of methyl oleate in DES (1.4 wt% methyl oleate) was prepared. This

liquid mixture was added to a glass tube at room temperature and rotated. Next, the glass tube was rapidly immersed into liquid N_2 . Subsequently, the tube was taken out of the liquid N_2 and located inside the flow tube reactor at (268 ± 1) K. There was no apparent change in the phase after the reactions.

2.2 Measurements of the temperature-composition phase diagram for mixtures of methyl oleate in DES

The temperature-composition phase diagram for methyl oleate–DES mixtures is not known. We determined this phase diagram by means of differential scanning calorimetry (DSC). The phase diagram was necessary to determine properties of the solid phase (*e.g.* pure solid DES or a solid solution containing methyl oleate and DES) that formed in the experiments mentioned above as well as determine mass partitioning between solid and liquid phases.

Determination of the phase diagram consisted of the following steps: 40 μL of liquid mixture (methyl oleate and DES) were added to a sample pan. The temperature of the sample was decreased to -50 °C, and then increased to 30 °C at a rate of 5 °C min^{-1} . The phase diagram was constructed from the melting peaks in the thermogram.⁶⁸

2.3 Chemicals

Diethyl sebacate (98%) and squalane (99%) were obtained from Sigma-Aldrich; Methyl oleate ($\geq 99\%$) and dioctyl sebacate ($\geq 97\%$) were purchased from Fluka; NO_2 was purchased from Matheson. N_2 (99.999%), O_2 (99.993%), and He (99.999%) were purchased from Praxair. O_3 was produced by photolysis of O_2 .

3. Results

3.1 Reactive uptake coefficients of NO_3 on single component organics

The resistor model is used to analyze the reactive uptake data for binary mixtures. Ideally, for this analysis the NO_3 reactive uptake coefficients on the pure matrix molecules are available. Table 2 provides the uptake coefficients for NO_3 on the pure matrix molecules, as well as the uptake on pure methyl oleate for comparison.

The uptake result for methyl oleate is in good agreement with measurements of other unsaturated organics (oleic acid, linoleic acid and conjugated linoleic acid).²⁷ Also, the uptake coefficient of NO_3 on methyl oleate is about 2–3 orders of magnitude higher than those of NO_3 on saturated organics (DES, DOS and squalane). This trend is roughly consistent with the trend observed in the gas phase.⁶⁹ The uptake

Table 2 Measured uptake coefficients of NO_3 on single-component organic compounds

Compound	<i>T</i> (K)	Phase	γ
DES	278	Liquid	$(4.4 \pm 0.4) \times 10^{-3}$
DES	272	Solid	$(3.6 \pm 0.5) \times 10^{-4a}$
DOS	278	Liquid	$(3.9 \pm 0.3) \times 10^{-3}$
Squalane	278	Liquid	$(5.2 \pm 0.4) \times 10^{-3}$
Methyl oleate	278	Liquid	$(1.4 + 8.6/-0.5) \times 10^{-1}$

^a This uptake coefficient was obtained from our previous work.²⁷

coefficient of NO_3 with solid DES is about 90% lower than the corresponding liquid-phase data.

3.2 Reactive uptake coefficients of NO_3 on binary liquid mixtures containing methyl oleate

Fig. 3 shows the measured uptake coefficients of NO_3 on different binary mixtures as a function of the methyl oleate concentration. For all matrices studied the addition of small amounts of methyl oleate (less than 4 wt%) significantly increases the reactive uptake coefficient. Also, the magnitude of increase depends of the type of matrix. For example at approximately 2.3 wt% methyl oleate the reactive uptake coefficient in DES increased by a factor of 20 compared to the pure case, but in squalane the reactive uptake coefficient only increased by a factor of 4.

To check whether the uptake is reversible or irreversible, at the end of every experiment we moved the injector to a position where the coated organic mixture was no longer exposed to the NO_3 flow. The absence of any release of NO_3 indicated that the uptake was irreversible.

3.3 Analysis of the reactive uptake coefficient data using the resistor model

To analyze the liquid uptake results presented in Fig. 3, we used the resistor model for gas-substrate interactions.⁷⁰ If the reaction occurs in the bulk and the reactive uptake coefficient is not limited by the mass accommodation coefficient (*i.e.*, $\alpha \gg \gamma$, where α is the mass accommodation coefficient) then the following equation applies for our binary liquid mixtures (see Appendix).

$$\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2 = \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}} k_{\text{oleate}}}{c_{\text{NO}_3}^2} M_{\text{oleate}} \quad (1)$$

Fig. 3 Measured uptake coefficients of NO_3 on binary liquid mixtures containing methyl oleate. Some of the error bars for methyl oleate in DES exceed maximum γ -values shown in this figure. Typically, when the γ value is greater than 0.05 such as the last three data points for the methyl oleate–DES mixtures, the gas-phase diffusion of NO_3 to the reactive surface greatly influences the measured γ values. In this case, a small uncertainty in the diffusion coefficient will result in a large uncertainty in the measured γ value. All experiments were carried out at (278 ± 1) K.

where γ_{mixture} is the reactive uptake coefficient of NO_3 in the two component mixture, γ_{matrix} is the reactive uptake coefficient of NO_3 with the pure matrix molecules, H_{matrix} is the Henry's law solubility constant of NO_3 in the matrix, R is the gas constant, T is the temperature, D_{matrix} is the diffusion coefficient for NO_3 in the matrix, k_{oleate} is the bulk second-order rate constant for the NO_3 reaction with methyl oleate, c_{NO_3} is the mean molecular velocity of NO_3 , and M_{oleate} is the molarity of the methyl oleate in each matrix. According to eqn (1), a plot of $(\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2)$ vs. M_{oleate} is expected to yield a straight line.

In contrast to eqn (1), if the reaction occurs on the surface and assuming the reactive uptake coefficient is not limited by the adsorption coefficient, the following equation applies for our binary liquid mixtures (see Appendix).

$$\gamma_{\text{mixture}} - \gamma_{\text{matrix}} = \frac{4H_{\text{matrix}}^S RT K_{\text{matrix}}^S k_{\text{oleate}}^S}{c_{\text{NO}_3}} M_{\text{oleate}} \quad (2)$$

where γ_{mixture} is the reactive uptake coefficient of NO_3 with the binary mixture, γ_{matrix} is the reactive uptake coefficient of NO_3 with the corresponding pure matrix, H_{matrix}^S is the surface Henry's law equilibrium analogous to a Henry's law equilibrium for bulk condensed phase, K_{matrix}^S is an equilibrium constant linking the surface concentration to the bulk concentration of the organic liquid, k_{oleate}^S is the second-order rate constant for the NO_3 reaction with methyl oleate at the surface, and M_{oleate} is the molarity of methyl oleate in each matrix. If the reaction occurs at the surface and the assumptions outlined above are valid, then a plot of $(\gamma_{\text{mixture}} - \gamma_{\text{matrix}})$ vs. M_{oleate} is expected to yield a straight line.

In Fig. 4 panels a–c, we have plotted $(\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2)$ vs. M_{oleate} and panels d–f, we have plotted $(\gamma_{\text{mixture}} - \gamma_{\text{matrix}})$ vs. M_{oleate} . Fig. 4 shows that the data can be fit reasonably well by assuming either a bulk reaction or a surface reaction. To evaluate the goodness-of-fit for the two different models (bulk and surface), we calculated χ^2 values. Smaller χ^2 values represents a better fit to the data. The results from these calculations are included in Fig. 4. Based on the χ^2 values, kinetics for DOS and squalane mixtures is explained well by both the bulk and surface model. For DES, the kinetic data fit better to the surface model than the bulk model, although even the bulk model does a reasonable job of describing the trend in the reactive uptake data.

Table 3 shows values of $H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{oleate}}}$ and $H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S$ determined from the slopes of the lines shown in Fig. 4. If the reaction occurs in the bulk, then the $H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{oleate}}}$ values vary by a factor of 2.7. If the reaction occurs on the surface, then the $H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S$ values vary by a factor of 3.6. This shows that the matrix has an effect on the kinetics as expected. It is also interesting to compare the trends observed for the different matrices. For example, the trend in $H_{\text{matrix}} \sqrt{D_{\text{matrix}} k_{\text{oleate}}}$ is DES > DOS > squalane. This trend is the same as the trend in the diffusion coefficients (D_{matrix}) of the matrices (see Table 1).

Fig. 4 Plot ($\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2$) (panel a, b, c) and ($\gamma_{\text{mixture}} - \gamma_{\text{matrix}}$) (panel d, e, f) as a function of M_{oleate} . Panel a and d correspond to the reaction of NO_3 with a methyl oleate–DES mixture, panel b and e correspond to the reaction of NO_3 with methyl oleate–DOS mixtures, panel c and f correspond to the reaction of NO_3 with methyl oleate–squalane mixtures.

Table 3 $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{\text{oleate}}}$ and $H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S$ values determined from the slopes of the lines in Fig. 4. The reported uncertainties are based on the standard deviation (1σ) of the slopes in Fig. 4

Matrix molecule	$H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{\text{oleate}}} (\text{cm M}^{1/2} \text{atm}^{-1} \text{s}^{-1})$	$H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S (\text{L cm}^{-2} \text{atm}^{-1} \text{s}^{-1})$
DES	69.4 ± 5.8	281.3 ± 11.8
DOS	35.4 ± 2.4	120.9 ± 4.2
Squalane	26.1 ± 1.5	78.0 ± 2.7

3.4 Temperature-composition phase diagram for methyl oleate–DES mixtures

Shown in Fig. 5 are results from the differential calorimetry measurements. According to the phase diagram, methyl oleate and DES are miscible in the liquid state but immiscible in the solid state. The eutectic temperature for the binary system was determined to be $(250.7 \pm 0.5) \text{ K}$.

3.5 Reactive uptake coefficient measurements of NO_3 on solid–liquid mixtures containing methyl oleate and DES

The solid triangle in Fig. 5 shows the temperature and composition at which we studied the reactive uptake coefficient of partially solid mixtures of methyl oleate and DES. According to the phase diagram, the mixture consists of solid DES in equilibrium with a binary liquid mixture of approximately 45 wt% methyl oleate in DES.

Contrary to measurements with liquids, the measured reactive uptake coefficients for these mixtures decrease with time. This is illustrated in Fig. 6. After approximately 90 min the reactive uptake coefficient on the solid–liquid mixture decreased by a factor of 10. In contrast the reactive uptake coefficient of NO_3 on a liquid methyl oleate–DES mixture with the same weight percent methyl oleate did not decrease with

time as expected. Fig. 6 illustrates that the phase of the mixture can significantly influence the kinetics, consistent with previous measurements using O_3 , Cl and OH as the oxidants. See for example ref. 9, 18, 29, 35, 41–44, 47, 52, 54 and 60.

In our studies the liquid–solid mixture is likely to have a surface that is partially solid DES and partially a liquid mixture of methyl oleate and DES. As the carbon–carbon double bonds in the exposed liquid regions are oxidized, the uptake is expected to decrease, consistent with observations. During the 90 min exposure approximately 4×10^{16} molecules of NO_3 were lost to the surface. Assuming that one molecule of NO_3 reacts with one molecule of methyl oleate and that one monolayer of methyl oleate corresponds to roughly 6×10^{14} molecules cm^{-2} , then during the 90 min exposure approximately 10 monolayers of methyl oleate is oxidized. This is consistent with only the top few monolayers of the material being available for reaction when the material is in the semi-solid state.

4. Atmospheric implications

4.1 Lifetime of unsaturated organics in liquid organic particles

Next we use the kinetic parameters for the liquids, to estimate the lifetime of condensed-phase unsaturated organics in the

Fig. 5 Temperature-composition phase diagram for the methyl oleate-DES system. S and L indicate solid and liquid phases, respectively. MO represents methyl oleate. The symbols ■ and ▼ represent the melting temperatures of DES and methyl oleate, respectively, in the binary mixtures. The symbol ● represents the measured eutectic temperature of the mixture. Each point represents the average of two runs. The symbol ▲ represents the conditions at which the uptake kinetics was investigated. The line and curves were added to guide the eye.

Fig. 6 Measured uptake coefficient (γ) of NO_3 on mixtures of methyl oleate with DES (composition = 1.37 wt% methyl oleate). Experiments were carried out by continuously exposing the surface to NO_3 , and periodically measuring the NO_3 uptake coefficients. The open symbols represent experiments carried out at 278 K and correspond to a liquid, whereas the solid symbols represent experiments carried out at 268 K and correspond to a solid-liquid mixture.

Table 4 Estimated atmospheric lifetimes of unsaturated organics, $\tau_{\text{unsaturated}}$, using parameters determined from studies with methyl oleate in different matrices (DES, DOS and squalane)

System used for determining kinetic parameters	$\tau_{\text{unsaturated}}$ (min) ^a	
	Assuming bulk reaction	Assuming surface reaction
Liquid mixture of methyl oleate in DES	13.0	8.0
Liquid mixture of methyl oleate in DOS	25.7	18.4
Liquid mixture of methyl oleate in squalane	34.8	28.5

^a When calculating the atmospheric lifetime it was assumed that the mole fraction of the unsaturated organic in the particle was 0.1 and the particle diameter was 200 nm.

atmosphere. If the reaction occurs in the bulk then the following equation can be used together with parameters shown in Table 3 to estimate the atmospheric lifetime.^{71–73}

$$\sqrt{[\text{UnsaturatedOrganic}]_t} = \sqrt{[\text{UnsaturatedOrganic}]_0} - \frac{3P_{\text{NO}_3}H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{\text{oleate}}}}{2r_{\text{particle}}}t \quad (3)$$

where P_{NO_3} is the NO_3 partial pressure in the atmosphere, r_{particle} is the radius of the particle in the atmosphere, $[\text{UnsaturatedOrganic}]_0$ is the initial concentration of the unsaturated organic in the particle and $[\text{UnsaturatedOrganic}]_t$ is the concentration of an unsaturated organic after reaction time t .

If the reaction occurs at the surface then the following equation together with parameters in Table 3 can be used to estimate the lifetime of an unsaturated organic in the atmosphere.⁷¹

$$\ln \frac{[\text{UnsaturatedOrganic}]_t}{[\text{UnsaturatedOrganic}]_0} = - \frac{3P_{\text{NO}_3}H_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S}{r_{\text{particle}}}t \quad (4)$$

Shown in Table 4 are the calculated lifetimes of unsaturated organics using eqn (3) and (4) and the parameters listed in Table 3, and assuming a radius of 100 nm, and a NO_3 concentration of 25 ppt NO_3 (24 h average). The NO_3 concentration corresponds to roughly moderately polluted levels.⁷⁴

Several conclusions can be drawn from Table 4. First, comparing the calculations assuming bulk with the calculations assuming surface, the lifetimes only differ by a factor of 1.5. Second, the lifetimes differ by only factor of 3 when comparing different liquid matrices. Third, regardless of the liquid matrix, or the assumption of surface *vs.* bulk, the lifetimes are short (all less than 35 min) for liquids. Hence we can conclude that the lifetime of unsaturated organics (similar to methyl oleate) are likely short in the atmosphere if the particle matrix is in a liquid state and NO_3 concentrations are approximately 25 ppt. These lifetimes are comparable to the lifetimes reported for O_3 with oleic acid^{9,40} (a molecule similar to methyl oleate) but are considerably shorter than the lifetimes for OH with oleic acid.⁴⁰

Significant amounts of oleic acid, an unsaturated compound similar to methyl oleate, have been observed in the atmosphere.

This suggests that particles containing oleic acid in the atmosphere are most likely not liquids, rather solids, semi-solids or glasses, based on our NO₃ kinetics. A similar conclusion has been made by others based on measured reaction rates between O₃ and liquid oleic acid in the laboratory.

4.2 Lifetime of unsaturated organics in semi-solid organic matrices

The lifetime of unsaturated organics in semi-solid organic matrices is difficult to estimate from our measurements. Until further measurements are available, the results for the liquid mixtures can be used as a lower limit to the lifetime of unsaturated organics in semi-solid organic matrices based on Fig. 6.

Appendix

1. Derivation of eqn (1)

According to the resistor model, if the reaction occurs in the bulk, and if NO₃ can react with both methyl oleate and the matrix molecules, and if the reactive uptake coefficient is not limited by the mass accommodation coefficient (*i.e.*, $\alpha \gg \gamma$, where α is the mass accommodation coefficient) then the following equation applies for our binary liquid mixtures:^{70,75,76}

$$\gamma_{\text{mixture}} = \frac{4H_{\text{mixture}}RT\sqrt{D_{\text{mixture}}(k_{\text{matrix}}M_{\text{matrix}} + k_{\text{oleate}}M_{\text{oleate}})}}{c_{\text{NO}_3}} \quad (\text{A1})$$

where H_{mixture} corresponds to the Henry's law solubility constant of NO₃ in the mixture, D_{mixture} corresponds to the diffusion coefficient for NO₃ in the mixture, k_{matrix} is the second-order rate constant for the NO₃ reaction with matrix molecules, and M_{matrix} is the molarity of the matrix molecules in the mixture.

In this study, the amount of the reactant (methyl oleate) is always small (wt% < 4%) in the mixture. As a result the Henry's law solubility constant and the diffusion coefficient of NO₃ in the mixture is approximately the same as the Henry's law solubility constant and the diffusion coefficient of NO₃ in pure matrix molecules (*i.e.* $H_{\text{mixture}} \approx H_{\text{matrix}}$ and $D_{\text{mixture}} \approx D_{\text{matrix}}$ where H_{matrix} is the Henry's law solubility constant of NO₃ in the pure liquid of matrix molecules, and D_{matrix} is the diffusion coefficient of NO₃ in the pure liquid of matrix molecules). Substituting these approximations into eqn (A1) results in the following equation.

$$\gamma_{\text{mixture}}^2 = \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}} k_{\text{matrix}} M_{\text{matrix}}}{c_{\text{NO}_3}^2} + \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}} k_{\text{oleate}} M_{\text{oleate}}}{c_{\text{NO}_3}^2} \quad (\text{A2})$$

For our study, $\gamma_{\text{mixture}}^2$ varies at least by a factor of 5, but M_{matrix} only varies by 3%. Hence we assume that the first term in eqn (A2) is constant and equal to γ^2 for a pure liquid of matrix molecules. We refer to this as γ_{matrix}^2 which can be

calculated from the γ value in Table 1. After making this assumption and substitution we have the following:

$$\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2 = \frac{(4H_{\text{matrix}}RT)^2 D_{\text{matrix}} k_{\text{oleate}}}{c_{\text{NO}_3}^2} M_{\text{oleate}} \quad (\text{A3})$$

Eqn (A3) is equivalent to eqn (1) above. A similar equation to eqn (A3) was used to describe the uptake coefficient of NO₃ on an aqueous solution that had two parallel bulk reactions: a reaction with water and a reaction with ions.^{75,76}

2. Derivation of eqn (2)

According to the resistor model, if NO₃ can react with both methyl oleate and the matrix molecules at the surface and the reactive uptake coefficient is not limited by the adsorption coefficient (*i.e.*, $S \gg \gamma$, where S is the adsorption coefficient) then the following equation applies for our binary liquid mixtures.^{70,71,77}

$$\gamma_{\text{mixture}} = \frac{4RTH_{\text{mixture}}^S K_{\text{mixture}}^S k_{\text{matrix}}^S M_{\text{matrix}}}{c_{\text{NO}_3}} + \frac{4RTH_{\text{mixture}}^S K_{\text{mixture}}^S k_{\text{oleate}}^S M_{\text{oleate}}}{c_{\text{NO}_3}} \quad (\text{A4})$$

Employing approximations similar to the ones used to derive eqn (A2) above, we derive eqn (A5) below.

$$\gamma_{\text{mixture}} = \frac{4RTH_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{matrix}}^S M_{\text{matrix}}}{c_{\text{NO}_3}} + \frac{4RTH_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S M_{\text{oleate}}}{c_{\text{NO}_3}} \quad (\text{A5})$$

Employing approximations similar to the ones used to derive eqn (A3) above, we derive eqn (A6):

$$\gamma_{\text{mixture}} - \gamma_{\text{matrix}} = \frac{4RTH_{\text{matrix}}^S K_{\text{matrix}}^S k_{\text{oleate}}^S M_{\text{oleate}}}{c_{\text{NO}_3}} \quad (\text{A6})$$

Eqn (A6) is equivalent to eqn (2) in the main text.

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