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Potentially important nighttime heterogeneous chemistry: NO_3 with aldehydes and N_2O_5 with alcohols

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We report the first measurements of the reactive uptake of NO_3 with condensed-phase aldehydes. Specifically, we studied NO₃ uptake on solid tridecanal and the uptake on liquid binary mixtures containing tridecanal and saturated organic molecules (diethyl sebacate, dioctyl sebacate, and squalane) which we call matrix molecules. Uptake on the solid was shown to be efficient, where $\gamma = (1.6 \pm 0.8) \times 10^{-2}$. For liquid binary mixtures the reactivity of aldehyde depended on the matrix molecule. Assuming a bulk reaction, $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^\circ,\text{aldehyde}}}$ varied by a factor of 2.6, and assuming a surface reaction $H_{\text{matrix}}^{S} K_{\text{matrix}}^{S} k_{2^{\circ},\text{aldehyde}}^{S}$ varied by a factor of 2.9, where $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^{\circ},\text{aldehyde}}}$ and $H_{\text{matrix}}^{\text{S}}K_{2^{\circ},\text{aldehyde}}^{\text{S}}$ are constants extracted from the data using the resistor model. By assuming either a bulk or surface reaction, the atmospheric lifetimes for aldehydes were estimated to range from 1.9-7.5 h. We also carried out detailed studies of N_2O_5 uptake kinetics on alcohols. We show that uptake coefficients of N2O5 for five different organics at 293 K varied by more than 2 orders of magnitude, ranging from 3×10^{-4} to 1.8×10^{-2} . We show that the uptake coefficients correlate with $\sqrt{D_{alcohol}(OH \text{ concentration})}$ but more work is needed with other alcohols to completely understand the dependence. Using this kinetic data we show that the atmospheric lifetime of alcohols with respect to N_2O_5 heterogeneous chemistry can vary from 0.6–130 h, depending on the physical and chemical properties of the organic liquid.

1. Introduction

Liquid and solid aerosol particles are abundant in the troposphere and field measurements have shown a broad variety of particulate material, both organic and inorganic. The organic fraction can comprise 10–90% of the total aerosol mass in the troposphere.^{1–3} This organic material can be in the form of pure organic particles, or alternatively the organic material can be mixed with inorganic material.^{4–7}

The composition of condensed-phase organic material is very diverse, with hundreds to thousands of different organic compounds identified.^{8–11} Some of the component classes in the organic fraction include alkanes,^{12,13} alcohols,^{12,14,15} alkanoic and alkenoic acids,^{12,15,16} dicarboxylic acids,^{17–20} polycyclic aromatic hydrocarbons (PAHs),^{21–23} and aldehydes.^{24,25}

Organic particles or mixed organic–inorganic particles, whilst in the atmosphere, experience reactions with gas-phase species that may lead to the modification of the particle or coating composition. These heterogeneous reactions can have a number of effects. For example, they may lead to toxic or carcinogenic compounds.^{8,26} These reactions may be a loss pathway of organic compounds in the atmosphere.^{26–31} Under certain conditions, these reactions may be an important sink for

organic compounds (VOCs) in the atmosphere.^{28,37,38} Heterogeneous reactions may also 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.³⁹
 Recently heterogeneous reactions between organic particles and OH, ^{27,28,33,40} O₃,^{41–47} and Cl^{29,48,49} have received significant attention. In addition, some studies have focused on

and OH, 21,28,33,40 O₃, $^{41-47}$ and Cl^{29,48,49} have received significant attention. In addition, some studies have focused on heterogeneous reactions between organic particles and NO₃ $^{32,50-56}$ and N₂O₅, $^{52,57-60}$ important nighttime species. NO₃ is formed by the gas-phase reaction of NO₂ with ozone.⁶¹ Concentrations of this radical range from <10 pptV to 430 pptV.⁶²⁻⁶⁷ N₂O₅ is present in equilibrium with gas-phase NO₂ and NO₃ and can reach concentrations of up to approximately 15 ppbV.⁶⁸

gas-phase species.³² Also, these reactions can lead to volatilisation

of organic particulate matter^{33–36} and are a source of volatile

Recently, we investigated the reactive uptake of N_2O_5 on a range of organic substrates including oleic acid, diethyl sebacate, glycerol, and linoleic acid.⁵² That study showed that the reactive uptake coefficient of N_2O_5 on liquid glycerol is relatively large with a value of $(3.2-8.5) \times 10^{-4}$, suggesting that N_2O_5 heterogeneous reactions with alcohols may be atmospherically relevant. However, the N_2O_5 -alcohol uptake results from Gross *et al.*⁵²

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only examined one alcohol compound, glycerol, thus additional studies with other alcohols are also needed to determine the generality of the results. We have also recently explored the reactive uptake of NO₃ on a range of organic substrates with diverse functionalities.^{51–54,57} One reaction class that has not been studied, however, are those reactions of NO₃ with condensed phase aldehydes. This reaction is known to be fast in the gas-phase and so the expectation is that it will also be fast in the condensed phase.

We have determined in this investigation the kinetics for N₂O₅ reactions with alcohols and NO₃ reactions with aldehydes. This information is then used to assess the lifetime of alcohols and aldehydes in the condensed phase in the atmosphere. For the N_2O_5 reactions we studied the uptake on five different liquid alcohols at 263-303 K. For the NO₃ reaction we studied the kinetics with the C_{13} aldehyde tridecanal. The uptake of NO_3 on the solid C_{13} aldehyde was determined at (263 ± 1) K. For the pure aldehyde we were limited to this temperature since the vapour pressure of the aldehyde was high. To explore the reactions of NO₃ with aldehydes in the liquid state we studied several binary mixtures of tridecanal with diethyl sebacate (DES), dioctyl sebacate (DOS), and squalane. DES, DOS, and squalane react slowly with NO₃ and will be referred to as matrix compounds within this paper. By using binary mixtures where the concentration of the aldehyde is less than approximately 5.5% w/w, the overall partial pressure of the aldehyde in the gas phase was reduced (which is a practical requirement for these flow tube studies). The study of binary mixtures also has the added advantage in that we could assess the importance of the matrix molecules on the NO₃-aldehyde kinetics.

2. Experimental

2.1 Rotating-wall flow tube and chemical ionisation mass spectrometer (CIMS)

Uptake experiments were conducted in a cylindrical, rotating-wall flow tube reactor coupled to a CIMS. The setup and procedure of the experiments are similar to several recent studies.^{54,57,69} The flow tube was composed of borosilicate glass. The inside wall of a Pyrex tube (12 cm length, 1.77 cm I.D.) provided a surface for a thin coating of the studied liquid or solid.

Total pressures in the flow cell during experiments were 2–4 Torr whereas flow velocities ranged from 480–600 cm s⁻¹. Fast flow rates of the carrier gas were chosen to reduce the extent of corrections for axial diffusion. The carrier gas through the cell was a mixture of O_2 (~10–15%) in He. NO₃ or N₂O₅ was added through a movable injector whereby the reactive distance, and thus the reaction time, could be quickly changed. The injector position was moved in one centimetre increments every 40–60 s during an experiment to expose an increasing surface area of the organic coating to NO₃ or N₂O₅.

For liquid experiments, approximately 0.5-1 mL of liquid was distributed onto the inner wall of the rotating glass cylinder (at a rotation rate of ~10 rotations min⁻¹). This produced a uniform film approximately 0.5 mm thick. For solid experiments, a liquid was distributed onto the inner wall glass cylinder and then the temperature was decreased to

below the freezing point while the inner wall of the glass cylinder was continuously rotated.

2.2 Procedures for NO₃ and N₂O₅ uptake experiments

N₂O₅ was generated by reacting NO₂ with an excess amount of O₃ in a flow system as described by Schott and Davidson⁷⁰ and Cosman *et al.*⁷¹ Pure O₂ was passed through an ultraviolet light source (Model 600 Ozone Generator, Jelight, Irvine, CA) to generate the O₃ necessary for N₂O₅ production.^{70,71} N₂O₅ was trapped and stored as solid white crystals at 197 K. N₂O₅ was detected as NO₃⁻ in the mass spectrometer after chemical ionisation by I⁻, generated by passing a trace amount of CH₃I in N₂ through a ²¹⁰Po source (model Po-2031, NRD). The average N₂O₅ concentration inside the flow tube was estimated at $(3.6-8.5) \times 10^{11}$ molecules cm⁻³ based on the rate constant for the gas-phase N₂O₅ + I⁻ reaction.⁷² The uncertainty of the N₂O₅ concentration was approximately 40% based on the uncertainty of the ion molecule reaction rate constant.

NO3 radicals were obtained by thermal conversion of gaseous N₂O₅ to NO₃ and NO₂ at 430 K in a Teflon coated glass oven before entering the movable injector. Approximately 20% of the NO₃ thermally dissociates in the Teflon coated glass oven based on well-known gas-phase reaction rates and modelling studies using the Acuchem chemical kinetics simulation program. NO₃ was also detected as NO₃⁻ in the mass spectrometer after chemical ionisation by I^{-.53} NO₃ concentrations were estimated at $(3.5-16) \times 10^{10}$ molecules cm⁻³ through the assumption that all N_2O_5 is converted to NO_3 and NO_2 . Quantitative conversion of N2O5 to NO3 and NO2 in the oven was confirmed by adding high levels of NO to the exit of the flow tube. This conversion by NO also served as a convenient way to quantify the background signal in the NO₃ experiments. NO was added in excess which completely titrated NO₃ 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 5% of the total signal. Since the residence time for NO_3/N_2O_5 inside the flow tube is very short $(\sim 50 \text{ ms})$, no biases are expected due to equilibrium processes between the two species (*i.e.*, the time for NO₃ and N_2O_5 to approach equilibrium is on the order of 1 min).

2.3 Determination of reactive uptake coefficients (γ)

From the collected CIMS traces, plots were generated for the natural logarithm of the depletion of the NO₃ or N₂O₅ signal as a function of reaction time. The slopes of the linear fits were used to determine the observed first-order loss rate coefficients, $k_{\rm obs}$. Corrections for both radial and axial diffusion were applied to all $k_{\rm obs}$ values using the formulations described by Brown⁷³ and Howard,⁷⁴ respectively. Reactive uptake coefficients (denoted by γ) were calculated from the corrected rate constants, $k_{\rm corr}$, using a procedure described by Knopf *et al.*⁷⁵ Diffusion coefficients used within these calculations were taken from Rudich *et al.*⁷⁶ and Knopf *et al.*⁶⁹

The two main sources of uncertainty for the uptake coefficient measurements were the gas-phase diffusion coefficients of NO₃ and N₂O₅ and the measurement of k_{obs} . We calculated the error from gas phase diffusion by assuming a 20% uncertainty of these diffusion coefficients. This uncertainty determined for the NO₃ uptake experiments is based on the those reported by Rudich *et al.*,⁷⁷ where the uncertainties of the gas-phase diffusion coefficients for NO₃ in helium is ~8% and that for NO₃ in O₂ is ~20%. In our study, the carrier gas is a mixture of He and O₂. We used the larger uncertainty (20%) as the uncertainty for the NO₃ gas phase diffusion coefficient in the He-O₂ mixture. The uncertainty for N₂O₅ uptake experiments is also assumed to be 20% (see Knopf *et al.*⁶⁹ and references therein). For the uncertainty of k_{obs} , we used the standard deviation (1 σ) of the measurements. Reported errors include both uncertainties.

2.4 Chemicals and gases

Tridecanal, ($\geq 95\%$), squalane (99%), diethyl sebacate (98%), bis(2-ethylhexyl) sebacate (or dioctyl sebacate) ($\geq 97.0\%$), poly(ethylene glycol) (PEG-300 and PEG-400), (+)-diethyl-L-tartrate (>99%), and 1,2,6-trihydroxyhexane (96%) were obtained from Sigma-Aldrich. All chemicals were used as delivered. NO₂ (99.5%) was acquired from Matheson while N₂ (99.999%), O₂ (99.993%), and He (99.999%) gases were procured from Praxair. Fig. 1 provides molecular structures for all organic compounds studied.



Fig. 1 Molecular structures for all studied organic compounds. The *n* value in poly(ethylene glycol) (PEG) depends on the molecular weight (*e.g.*, PEG-300 represents PEG with an average MW of 300 g mol⁻¹).

3. Results and discussion

3.1 Kinetics of the NO₃ reaction with solid tridecanal and liquid binary mixtures of tridecanal and matrix molecules

For the uptake of NO₃ on pure solid tridecanal at (263 ± 1) K, seven reactive uptake coefficients were measured. The mean ν value was determined as $(1.6 \pm 0.8) \times 10^{-2}$, where the uncertainty represents the 95% confidence interval. Table 1 provides a comparison of our measured uptake coefficients with those uptake coefficients of NO3 measured on other single component solid surfaces. Table 1 illustrates that indeed the reaction of NO3 with aldehydes is an efficient heterogeneous reaction compared with other heterogeneous substrates. For the classes of organics studied, the following trend is observed: PAHs > alkenoic acids > aldehydes > alcohols > alkanoates. Assuming that the alkenoic acid reaction is due to the carboncarbon double bond, this trend is roughly consistent with that of measured gas-phase rate constants of NO₃ reactions at 298 K: 10^{-10} - 10^{-13} for PAHs and alkenes, 10^{-14} - 10^{-15} for aldehydes, 10^{-15} - 10^{-16} alcohols, and 10^{-16} - 10^{-18} for alkanoates (all in units of cm^3 molecule⁻¹ s⁻¹).⁷⁸

Fig. 2 provides results for the uptake coefficient of NO₃ on binary liquid mixtures containing the aldehyde. The uptake coefficients with 0 wt% tridecanal represent the reactions of NO₃ with pure matrix molecules (DES, DOS, and squalane). For all the matrix compounds studied, the addition of small amounts of tridecanal (<6 wt%) increased γ . Also, the increase depends on the type of matrix. For example, at approximately 4.5 wt% tridecanal, the reactive uptake coefficient in DES increased by a factor of 3 but in squalane the γ value only increased by a factor of 1.4.

To check whether the uptake is a reversible or irreversible, at the end of every experiment the injector was moved 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. This irreversibility in uptake also applies to all the N_2O_5 experiments in section 3.3.

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

To analyse the uptake results presented in Fig. 2, the resistor model of gas-substrate interactions was used.⁷⁹ 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 the binary liquid mixtures (see Appendix):

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

where γ_{mixture} is the reactive uptake coefficient of NO₃ in the two-component mixture, γ_{matrix} is the reactive uptake coefficient of NO₃ with the pure matrix molecules, H_{matrix} is the Henry's law solubility constant of NO₃ in the matrix (mol L⁻¹ atm⁻¹), *R* is the gas constant (L atm mol⁻¹ K⁻¹), T is the temperature (K), D_{matrix} is the diffusion coefficient for NO₃ in pure matrix molecules (cm² s⁻¹), $k_{2^\circ,\text{aldehyde}}$ is the bulk second-order rate

Table 1 Comparison of reactive uptake coefficients for heterogeneous reactions involving solid organic substrates and NO₃ radicals^a

Class	Chemical	Т, К	Reactive uptake coefficient (γ)
Polycyclic Aromatic Hydrocarbons	Benz[a]anthracene	273–297	$1.0-66 \times 10^{-2b}$
	Pyrene	273-297	$> 8.0 \times 10^{-2b,c}$
	Fluoranthene	273-297	$> 2.0 \times 10^{-2b}$
Alkenoic Acid	Conjugated linoleic Acid	263	$(8.0 \pm 3.0) \times 10^{-2d}$
	Oleic Acid	268-283	$(5.3 \pm 1.1) \times 10^{-2d}$
Aldehyde	Tridecanal	263	$(1.6 \pm 0.8) \times 10^{-2e}$
Alcohol	Glycerol	268-293	$(0.8-1.7) \times 10^{-3d}$
Alkanoate	Diethyl sebacate (DES)	263–272	$(2.3-4.1) \times 10^{-4d}$

^{*a*} Only γ results from this laboratory group have been included and they have been ordered by decreasing γ values. The only other report of γ values for NO₃ uptake on pure organics is found in Moise *et al.*³² and our results are generally similar to their γ values except in the case of alkanoic acids (this is discussed in further detail in Gross *et al.*⁵²). ^{*b*} Taken from Gross and Bertram.^{57 *c*} Taken from Mak *et al.*^{54 *d*} Taken from Gross *et al.*^{52 *e*} This study.

2.0 1.8 Tridecanal in DES Tridecanal in DOS 16 Tridecanal in Squalane 1.4 Reactive Uptake Coefficent (γ), 10⁻² 1.2 1.0 0.8 0.6 ð 0.4 0.2 3.0 4.0 5.0 6.0 1.0 2.0 Wt% Tridecanal

constant for NO₃ reaction with the aldehyde (mol L⁻¹ s⁻¹), c_{NO_3} is the mean molecular velocity of NO₃ (cm s⁻¹), and $M_{aldehyde}$ is the molarity of the aldehyde in each matrix (mol L⁻¹). According to eqn (1), a plot of $\gamma_{mixture}^2 - \gamma_{matrix}^2$ against $M_{aldehyde}$ 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 the binary liquid mixtures (see Appendix):

$$\gamma_{\text{mixture}} - \gamma_{\text{matrix}} = \frac{4H_{\text{matrix}}^{\text{S}} RTK_{\text{matrix}}^{\text{S}} k_{2^{\circ},\text{aldehyde}}^{\text{S}}}{c_{\text{NO}_3}} M_{\text{aldehyde}},$$
(2)

Fig. 2 Measured uptake coefficients of the NO₃ reaction with tridecanal in DES, DOS, and squalane matrices at 275 K.

where $H_{\text{matrix}}^{\text{S}}$ is the surface analogue for the Henry's law equilibrium for the bulk, $K_{\text{matrix}}^{\text{S}}$ is an equilibrium constant linking the surface concentration to the bulk concentration



Fig. 3 Plots of $\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2$ (panels a–c) and $\gamma_{\text{mixture}} - \gamma_{\text{matrix}}$ (panels d–f) as a function of M_{aldehyde} . Panels a and d correspond to the reaction of NO₃ + tridecanal in DES, panels b and e correspond to the reaction of NO₃ + tridecanal in DOS, panels c and f correspond to the reaction of NO₃ + tridecanal in squalane.

of the organic liquid, $k_{2^{\circ},aldehyde}^{S}$ is the second-order rate constant for NO₃ reaction with the reactant at the surface, and $M_{aldehyde}$ is the molarity of aldehyde in each matrix.

If the reaction occurs at the surface and the assumptions outlined above are valid, then a plot of $\gamma_{mixture} - \gamma_{matrix}$ against $M_{\rm aldehyde}$ is expected to yield a straight line. In Fig. 3, panels a-c, we have plotted $\gamma_{\text{mixture}}^2 - \gamma_{\text{matrix}}^2$ against M_{aldehyde} and in panels d–f, we have plotted $\gamma_{\text{mixture}} - \gamma_{\text{matrix}}$ against M_{aldehyde} . To evaluate the goodness-of-fit for the two different models (bulk and surface) we calculated the R^2 values, the results of which are included in Fig. 3. Based on the R^2 values, kinetics for DOS and squalane mixtures are explained well by both the bulk and surface model. For DES, the kinetic data fit better to the surface model than the bulk model. Conservatively, below we use results from both models when estimating the lifetime of aldehydes in the atmosphere as well as making conclusions about the effect of the matrix on the NO₃-aldehyde organic reactions. As it happens similar conclusions are reached regardless of the model used for the interpretation of the results.

Table 2 summarises values of $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^\circ,\text{aldehyde}}}$ and $H_{\text{matrix}}^{S} K_{\text{matrix}}^{S} k_{2^{\circ}, \text{aldehyde}}^{S}$ that were extracted from the kinetic measurements of NO3 with tridecanal in the different matrices. It is interesting to note that the trend in $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^{\circ},\text{aldehyde}}}$ is in the order of DES > DOS > squalane. This trend is the same as that of D_{matrix} . The diffusion coefficients can be estimated using the Stokes-Einstein equation $D_{\text{matrix}} = k_b T (6\pi\eta r)^{-1}$, where k_b is the Boltzmann constant, T is the temperature, η is the viscosity of pure matrix molecules, and r is the radius of the diffusing species (i.e., NO₃ radicals). The D_{matrix} values for DES, DOS, and squalane were calculated as 1.8×10^{-6} , 4.3×10^{-7} , and 3.0×10^{-7} cm² s⁻¹, respectively, at 293 K. As mentioned above $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^{\circ},\text{aldehyde}}}$ and $H_{\text{matrix}}^{\text{S}}K_{2^{\circ},\text{aldehyde}}^{\text{S}}$ values are directly proportional to the slopes in Fig. 3. Hence the trends in $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^{\circ},\text{aldehyde}}}$ and $H_{\text{matrix}}^{S}K_{2^{\circ},\text{aldehyde}}^{S}$ values are the same as the trends in the slopes in Fig. 3.

3.3 Reactive uptake of N₂O₅ with alcohols

Our previous study⁵² showed that the reactive uptake coefficients of N₂O₅ on liquid glycerol ranged from $(3.2-8.5) \times 10^{-4}$ between 268–303 K and thus the heterogeneous reaction between N₂O₅ and alcohols may be potentially important in the atmosphere. In this study, we investigated the heterogeneous N₂O₅ reaction with four other organic reactants which all contain hydroxyl groups. Fig. 4 provides the measured uptake coefficients for the N₂O₅ reaction as well as the glycerol results for comparison. The N₂O₅ reactive uptake coefficient on PEG-300 was the largest, $(1.5-1.9) \times 10^{-2}$, while the smallest was on 1,2,6-trihydroxyhexane which was $(0.8-1.5) \times 10^{-4}$. The overall trend in the reactive uptake coefficients was PEG-300 > PEG-400 > glycerol > (+)-diethyl-L-tartrate > 1,2,6-trihydroxyhexane.

For PEG-400, above 278 K the film was liquid and below this temperature the film was solid. A sharp decrease in the γ value for the experiment below the freezing point of PEG-400 suggests that the net liquid-phase reaction may be a combination of both a surface reaction and a bulk reaction, since the freezing process is expected to greatly decrease the importance of any bulk reactions in our experiments. Alternatively, the reactive uptake for both the liquid- and solid-phase experiments might only be due to surface reactions, where the liquid surface is much more favourable for uptake and reactivity.

3.4 Trend of N₂O₅ reactivity

The uptake coefficients of N_2O_5 for single-component experiments varied by more than 2 orders of magnitude, which was surprisingly large. To try to rationalise these findings, we again used the resistor model of gas-liquid interactions.

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), the reactive uptake coefficient for a single-component alcohol can be explained with the following equation:

$$y = \frac{4RTH_{\text{alcohol}}\sqrt{D_{\text{alcohol}}k_{1^\circ,\text{alcohol}}}}{c_{N_2O_5}},$$
 (3)

where γ is the reactive uptake coefficient of N₂O₅ with the reactant, H_{alcohol} is the Henry's law solubility constant of N₂O₅ in the alcohol, R is the gas constant, T is the temperature, D_{alcohol} is the diffusion coefficient for N₂O₅ in the alcohol, $k_{1^\circ,alcohol}$ is the bulk first-order rate constant for reaction between N_2O_5 and the alcohol, and $c_{N_2O_5}$ is the mean molecular velocity of N₂O₅. According to eqn (3) the reactive uptake coefficient should be proportional to $H_{\text{alcohol}}\sqrt{D_{\text{alcohol}}k_{1^{\circ},\text{alcohol}}}$. Here we assume that the reaction rate constant $k_{1^\circ,alcohol}$ is proportional to the concentration of hydroxyl functional groups in the liquid that could potentially react with N₂O₅. To represent the concentration of hydroxyl groups in the liquid we use "OH concentration," or [-OH], with units of -OH groups L^{-1} of the organic component. Table 3 summarises the viscosity (η) , diffusion coefficient ($D_{alcohol}$), OH concentration, the product of Dalcohol and OH concentration, and the corresponding uptake coefficients at 293 K for reactions of N2O5 with alcohols.

Table 2 Calculated values for $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^\circ,\text{aldehyde}}}$ and $H_{\text{matrix}}^{\text{S}}K_{2^\circ,\text{aldehyde}}^{\text{S}}$ for the reactions of NO₃ with tridecanal in different matrices at 275 K

Matrix:	$H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^{\circ},\text{aldehyde}}},$ cm M ^{0.5} atm ⁻¹ s ^{-1a}	$H_{\text{matrix}}^{\text{S}} K_{\text{matrix}}^{\text{S}} k_{2^{\circ}, \text{aldehyde}}^{\text{S}},$ L cm ⁻² atm ⁻¹ s ^{-1a}
DES	9.44 ± 2.47	14.43 ± 0.42
DOS	6.93 ± 2.29	12.43 ± 1.04
Squalane	3.65 ± 0.50	4.91 ± 0.64
^{<i>a</i>} Error estimates obtained from	1σ standard deviations of each corresponding slope in Fig. 3.	



Fig. 4 Measured reactive uptake coefficients for reactions of N_2O_5 with liquid and solid polyalcohols as a function of temperature. Solid lines are meant to guide one's eye and they do not represent fits to the data. Dashed lines are used to show phase changes for the organics. The uptake coefficients for glycerol were obtained from Gross *et al.*⁵²

According to eqn (3), if we assume all the alcohols have similar H_{alcohol} values, the reactive uptake coefficient γ should be proportional to $\sqrt{D_{\text{alcohol}}k_{1^\circ,\text{alcohol}}}$. Then plotting values of γ against $\sqrt{D_{\text{alcohol}} \times [-OH]}$ is expected to yield a straight line fit to the data.

In contrast to a bulk reaction, if the reaction occurs 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), the reactive uptake coefficient can be explained with the following equation:

$$\gamma = \frac{4RTH_{\text{alcohol}}^{S}K_{\text{alcohol}}^{S}k_{1^{\circ},\text{alcohol}}^{S}}{c_{N_{2}O_{5}}},$$
(4)

where $H_{alcohol}^{S}$ is the surface Henry's law constant, analogous to a Henry's law equilibrium for the bulk condensed phase,

 K_{alcohol}^{S} is an equilibrium constant linking the surface concentration to the bulk concentration of the organic liquid, and $k_{1^{\circ},\text{alcohol}}^{S}$ is the first-order rate constant for the N₂O₅ reaction with alcohol at the surface. At a fixed temperature (*i.e.*, at 293 K), eqn (4) shows that the reactive uptake coefficient is proportional to $H_{\text{alcohol}}^{S}K_{\text{alcohol}}^{S}k_{1^{\circ},\text{alcohol}}^{S}$. We assumed that all the reactants here have similar $H_{\text{alcohol}}^{S}K_{\text{alcohol}}^{S}$ values and also that $k_{1^{\circ},\text{alcohol}}^{S}$ was proportional to the "OH concentration." Then, for a surface reaction, plotting values of γ against [–OH] is expected to yield a straight-line fit to the data.

In Fig. 5, we plot the reactive uptake coefficient as a functions of $(D_{\text{alcohol}} \times [-\text{OH}])^{0.5}$ (Panel a) and [-OH] (Panel b). Panel b shows that the surface model with the assumptions listed above cannot explain the data ($R^2 = 0.336$). In contrast, Panel a shows that the reactive uptake coefficient is correlated well with $(D_{\text{alcohol}} \times [-\text{OH}])^{0.5} (R^2 = 0.792)$. However the bulk model does not completely capture the trend in the data. This could be because the bulk model is not appropriate for some or all the alcohols studied and/or the assumptions discussed above (such as a single Henry's law solubility for all the alcohols) are not appropriate. Regarding the former, it is interesting to note that for both glycerol and 1,2,6-trihydroxyhexane, the self-diffusion coefficient is on the order of 10^{-10} cm² s⁻¹. This is in the range where calculations suggest that the transport of the condensed phase reactant can start to limit the overall uptake coefficient.⁸⁰ This process is not included in the bulk model discussed above and may be, in part, why the bulk model does not accurately represent all the data.

For the purpose of comparison, we have also plotted the reactive uptake coefficient as functions of solely the diffusion coefficient of N₂O₅ in the alcohol and the square root of $D_{\rm alcohol}$ (graphs not shown). In these cases the R^2 values for plots against $D_{\rm alcohol}$ and $D_{\rm alcohol}^{0.5}$ were 0.732 and 0.763, respectively. Because those values are lower than the 0.792 R^2 value presented in Table 3, it is demonstrated that the inclusion of OH concentration [–OH] leads to a better description of the observed trends in reactive uptake.

We conclude that γ does correlate with $(D_{\text{alcohol}} \times [-\text{OH}])^{0.5}$ but more work is needed with other alcohols to completely understand the dependence. It is likely that properties such as the Henry's low solubility of the different alcohols, steric effects on the OH reaction rate constant, and transport of the alcohol within the matrix need to be considered.

Table 3 Information pertaining to the discussion of the trend of N2O5 uptake coefficients

Compound	η, cP	$D_{alcohol}, cm^2 s^{-1a}$	OH concentration, (mol –OH) L^{-1}	$\begin{array}{l} D_{alcohol} \times \mbox{[-OH]}, \\ cm^2 \mbox{ mol } L^{-1} \mbox{ s}^{-1} \end{array}$	γ at 293 K
PEG-300	70	8.0×10^{-8}	7.5	5.8×10^{-7}	1.80×10^{-2}
PEG-400	90	6.0×10^{-8}	5.6	3.4×10^{-7}	9.20×10^{-3}
Glycerol	1500	3.6×10^{-9}	40.7	1.5×10^{-7}	6.45×10^{-3}
(+)-Diethyl-L-Tartrate	N/A	N/A	11.7	N/A	5.17×10^{-4}
1,2,6-Trihydroxyhexane	2630	2.0×10^{-9}	24.8	5.0×10^{-8}	3×10^{-4} b

^{*a*} The diffusion coefficient of a species in a liquid is related to the viscosity through the Stokes–Einstein equation $D = k_b T (6\pi\eta r)^{-1}$, where *D* is the diffusion coefficient, k_b is the Boltzmann constant, *T* is the temperature, η is the viscosity of the liquid, and *r* is the radius of the diffusing species. Here we have calculated the diffusion coefficient of N₂O₅ in the alcohols based on their viscosity at 293 K. The radius of the N₂O₅ particles was estimated as twice of the radius for O₃. The radius of O₃ was obtained based on a recent modelling study.^{45 b} This value was estimated from the γ value of 1,2,6-trihydroxyhexane at 278 K according to the general trend of uptake coefficients at different temperatures.



Fig. 5 Plots of the reactive uptake coefficient as a function of $(D_{\text{alcohol}} \times [-\text{OH}])^{0.5}$ for the bulk assumption (panel a), and as a function of [-OH] for the surface assumption (panel b). In both assumptions, the fit line is forced through 0.

In the next section, we use both the surface model and the bulk model to obtain an order of magnitude estimate of the atmospheric lifetime of the alcohols. The conclusions regarding the lifetime do not depend strongly on the model used.

4. Atmospheric implications

4.1 Lifetime of aldehyde due to NO₃ oxidation

Next we use the kinetic parameters measured above for the mixtures, to estimate the lifetime of an aldehyde in the troposphere. If the reaction occurs in the bulk then the following equation⁸¹⁻⁸³ can be used together with parameters shown in Table 2 to estimate the lifetime:

$$\sqrt{[\text{aldehyde}]} = \sqrt{[\text{aldehyde}]_0} - \frac{3P_{\text{NO}_3}H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^\circ,\text{aldehyde}}}}{2r_{\text{particle}}}t,$$
(5)

where [aldehyde] is the concentration of an aldehyde at time t, [aldehyde]₀ is the initial concentration of the aldehyde in the particle, P_{NO_3} is the NO₃ partial pressure in the atmosphere, t is the time that the particle was exposed to NO₃, and $r_{particle}$ is the radius of the particle in the atmosphere.

If the reaction occurs at the surface then the following equation together with parameters in Table 2 can be used to estimate the lifetime of an aldehyde in the atmosphere:

$$\ln\left(\frac{[\text{aldehyde}]}{[\text{aldehyde}]_0}\right) = -\frac{3P_{\text{NO}_3}H_{\text{matrix}}^S K_{\text{alcohol}}^S k_{2^\circ,\text{aldehyde}}^S}{r_{\text{particle}}}t.$$
 (6)

Table 4 shows the estimated lifetime of an aldehyde calculated using kinetic parameters determined with aldehyde in different matrices at 275 K and using an NO₃ volume mixing ratio of 25 pptV (24 h average) which is representative of moderately polluted levels.⁸⁴ Several conclusions can be drawn from the data available in Table 4. A comparison of the calculated bulk and surface cases reveals that the lifetimes differ by only a factor of 2. This is a reasonably small effect upon consideration of the uncertainties that arise when extrapolating laboratory data to the atmosphere (*e.g.*, particle composition). When making the comparison between the different matrices studied, the lifetimes differ by a factor of 2–3. This is also reasonably small. Finally,

regardless of the matrix or the assumption of liquid *vs.* bulk dominance, all calculated lifetimes are short (*i.e.*, all <8 h). One can thus conclude that the lifetime of aldehydes similar to tridecanal is likely short in the atmosphere if the NO₃ concentrations are >25 pptV, the particle matrix is in the liquid state, and the diffusion coefficient of the aldehyde in the matrix is greater than 10^{-10} to 10^{-15} cm² s⁻¹.^{80,85} At smaller diffusion coefficients the reactive uptake can be limited by the diffusion of the aldehyde in the particle. As a result, different equations other than eqn (5) and (6) would be used to calculate the lifetime of the particle.^{80,83,85}

4.2 Lifetime of alcohols due to N₂O₅ oxidation

Here we assume the reaction of N₂O₅ with alcohols should follow either a bulk mechanism or a surface mechanism. Equations analogous to eqn (1), (2), (5), and (6) were used to calculate $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^{\circ},\text{aldehyde}}}$ values, $H_{\text{matrix}}^{S}K_{2^{\circ},\text{aldehyde}}^{S}$ values, and atmospheric lifetimes for alcohols. Table 5 summarises the calculated $H_{\text{matrix}}\sqrt{D_{\text{matrix}}k_{2^{\circ},\text{aldehyde}}}$ and $H_{\text{matrix}}^{S}K_{2^{\circ},\text{aldehyde}}^{S}k_{2^{\circ},\text{aldehyde}}$ values and the estimated atmospheric lifetimes of different pure alcohol particles due to N₂O₅ oxidation. An N₂O₅ concentration of 1 ppbV was used in these calculations, roughly corresponding to moderately polluted levels.⁸⁴

Several conclusions can be drawn from Table 5. First, comparing the calculations assuming bulk with the calculations assuming surface, the lifetimes only differ by a factor of 1.3 which is a small effect. Second, the lifetime of alcohols with respect to N₂O₅ can be very short, consistent with initial work based on glycerol.⁵² Third, the lifetime of alcohols with respect to N₂O₅ can also be long, depending on the physical and chemical properties of the organic liquid. As a result, one should be careful when applying the uptake results of one molecule to a whole class of compounds. Details such as steric effects, Henry's law solubilities, and transport of the reactant in the liquid all need to be considered. With this in mind, one should also be cautious when applying our tridecanal results liberally to all aldehydes. Studies with other aldehydes are also needed, as well as studies in other matrices such as solids or glasses.86

The N_2O_5 studies with alcohols give some indications that diffusion of the condensed phase reactant could be important. Limitations of the overall uptake by diffusion of the condensed phase species is an important area for future research, especially

Table 4 Estimates of the atmospheric lifetimes of Aldehyde-containing organics aerosol particles, $\tau_{aldehyde}$, using parameters determined from uptake experiments with tridecanal in different matrices (DES, DOS, and squalane)

	$ au_{ m aldehyde},{ m h}^a$		
System used for determining kinetic parameters	Assuming a bulk mechanism	Assuming a surface mechanism	
Tridecanal in DES	1.90	2.56	
Tridecanal in DOS	1.98	2.96	
Tridecanal in squalane	3.60	7.54	

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

Table 5 Estimated $H_{\text{alcohol}}\sqrt{D_{N_2O_5}k_{2^\circ,\text{alcohol}}}$ and $H^{\text{S}}_{\text{alcohol}}K^{\text{S}}K^{\text{S}}_{2^\circ,\text{alcohol}}$ values and the oxidation lifetimes (τ)^{*a*} of pure polyalcohol particles exposed to N₂O₅ radicals

Compound	$H_{\rm alcohol} \sqrt{D_{\rm N_2O_5} k_{2^\circ, \rm alcohol}},$ cm M ^{0.5} atm ⁻¹ s ⁻¹	τ, h^b	$H_{\text{alcohol}}^{\text{S}} K^{\text{S}} k_{2^{\circ},\text{alcohol}}^{\text{S}}$, L cm ⁻² atm ⁻¹ s ⁻¹	τ, h^c
PEG-300	2.18	0.65	1.13	0.82
PEG-400	1.29	0.95	0.75	1.24
Glycerol	0.41	6.50	0.11	8.34
(+)-Diethyl-L-	0.05	35.2	0.02	44.1
Tartrate				
1,2,6-	0.02	104.7	0.007	130.4
Trihydroxyhexane				

^{*a*} Calculations of atmospheric lifetimes were performed under the assumptions of pure alcohol particles with a diameter of 200 nm. ^{*b*} Lifetime estimates where reactions dominated by the bulk mechanism are assumed. ^{*c*} Lifetime estimates where reactions dominated by the surface mechanism are assumed.

considering that recent work suggests that organic particles in the atmosphere can often be in a glass state, where the self diffusion coefficient of the condensed phase is small.⁸⁶

4.3 Possible condensed-phase reaction products from N_2O_5 and NO_3 oxidation

We can speculate on the products of the reactions discussed above based on previous gas-phase or condensed phase chemistry. For N_2O_5 , reactions with condensed phase saturated alcohols are known to produce organonitrates.⁸⁷ The mechanism has been suggested to occur *via* a six-membered ring, leading to an organic nitrate and HNO₃.⁸⁸ For NO₃, reactions with gas-phase saturated aldehydes are known to produce peroxyacyl nitrates and aldehydes smaller than the starting material.⁸⁹ We hypothesise that similar chemistry may occur in the condensed phase. However, additional studies are needed to verify such chemistry.

Appendix

Derivation of eqn (1)

According to the resistor model, if the reaction occurs in the bulk, and if NO₃ can react with both tridecanal 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:^{76,79,90}

γ_{mixture}

$$=\frac{4H_{\text{mixture}}RT\sqrt{D_{\text{mixture}}(k_{2^{\circ},\text{matrix}}M_{\text{matrix}}+k_{2^{\circ},\text{aldehyde}}M_{\text{aldehyde}})}}{c_{\text{NO}_{3}}},$$
(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, $k_{2^\circ,\text{matrix}}$ 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 (tridecanal) was always very small (wt% <6%) in the mixture. As 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_{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:

$$\gamma_{\text{mixture}}^{2} = \frac{(4H_{\text{matrix}}RT)^{2}D_{\text{matrix}}}{c_{\text{NO}_{3}}^{2}}k_{2^{\circ},\text{matrix}}M_{\text{matrix}}$$
$$+\frac{(4H_{\text{matrix}}RT)^{2}D_{\text{matrix}}}{c_{\text{NO}_{3}}^{2}}k_{2^{\circ},\text{aldehyde}}M_{\text{aldehyde}}.$$
(A2)

For our study $\gamma_{\text{mixture}}^2$ varies at least by a factor of 1.4, 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 . After making this assumption and substitution we obtain the following:

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

Eqn (A3) is equivalent to eqn (1) in the main text. A similar equation to that of eqn (A1) was used in the literature to describe the uptake coefficient of NO_3 on an aqueous solution that had two parallel bulk reactions: a reaction with water and a reaction with ions.^{76,90}

Derivation of eqn (2)

According to the resistor model, if NO₃ can react with both tridecanal 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:^{79,83,91}

$$\gamma_{\text{mixture}} = \frac{4RTH_{\text{mixture}}^{S}K_{\text{mixture}}^{S}K_{2^{\circ},\text{matrix}}^{S}M_{\text{matrix}}}{c_{\text{NO}_{3}}} + \frac{4RTH_{\text{mixture}}^{S}K_{\text{mixture}}^{S}K_{2^{\circ},\text{aldehyde}}^{S}M_{\text{aldehyde}}}{c_{\text{NO}_{3}}}.$$
(A4)

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

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$$\gamma_{\text{mixture}} = \frac{4RTH_{\text{matrix}}^{S} K_{\text{matrix}}^{S} K_{2^{\circ},\text{matrix}}^{S} M_{\text{matrix}}}{c_{\text{NO}_{3}}} + \frac{4RTH_{\text{matrix}}^{S} K_{2^{\circ},\text{aldehyde}}^{S} M_{\text{aldehyde}}}{c_{\text{NO}_{3}}}.$$
(A5)

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

$$\gamma_{\text{mixture}} - \gamma_{\text{matrix}} = \frac{4RTH_{\text{matrix}}^{\text{S}} K_{\text{matrix}}^{\text{S}} k_{2^{\circ},\text{aldehyde}}^{\text{S}}}{c_{\text{NO}_{3}}} M_{\text{aldehyde}}.$$
(A6)

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

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