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Reaction of Oleic Acid Particles with NO_3 Radicals: Products, Mechanism, and Implications for Radical-Initiated Organic Aerosol Oxidation

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The heterogeneous reaction of liquid oleic acid aerosol particles with NO_3 radicals in the presence of NO_2, N_2O_5, and O_2 was investigated in an environmental chamber using a combination of on-line and off-line mass spectrometric techniques. The results indicate that the major reaction products, which are all carboxylic acids, consist of hydroxy nitrates, carbonyl nitrates, dinitrates, hydroxydinitrates, and possibly more highly nitrated products. The key intermediate in the reaction is the nitrooxyalkylperoxy radical, which is formed by the addition of NO_3 to the carbon−carbon double bond and subsequent addition of O_2. The nitrooxyalkylperoxy radicals undergo self-reactions to form hydroxy nitrates and carbonyl nitrates, and may also react with NO_2 to form nitrooxy peroxynitrates. The latter compounds are unstable and decompose to carbonyl nitrates and dinitrates. It is noteworthy that in this reaction nitrooxyalkoxy radicals appear not to be formed, as indicated by the absence of the expected products of decomposition or isomerization of these species. This is different from gas-phase alkene−NO_3 reactions, in which a large fraction of the products are formed through these pathways. The results may indicate that, for liquid organic aerosol particles in low NO_x environments, the major products of the radical-initiated oxidation (including by OH radicals) of unsaturated and saturated organic compounds will be substituted forms of the parent compound rather than smaller decomposition products. These compounds will remain in the particle and can potentially enhance particle hygroscopicity and the ability of particles to act as cloud condensation nuclei.

Introduction

Atmospheric fine (diameter <2.5 μm) particles are a complex mixture of inorganic and organic material. Whereas the inorganic fraction is predominantly sulfates, nitrates, and metals, the organic fraction is composed of hundreds to thousands of organic compounds.[1,2] The organic particulate matter is either emitted directly to the atmosphere (primary organic aerosol, POA), mainly from combustion sources or it is formed in situ by condensation of low-volatility products of the oxidation of volatile organic compounds (secondary organic aerosol, SOA).[3] POA and SOA can be transformed in the atmosphere by heterogeneous reactions with OH and NO_3 radicals and O_3, the same oxidants that are responsible for the formation of SOA.[4] This oxidative processing, or "aging", of organic particles is important because it can enhance hygroscopic properties and thereby increase the ability of particles to scatter light and to act as cloud condensation nuclei (CCN),[5] both of which can impact global climate.[6]

The extent to which SOA and processed POA contribute to the oxygenated component of organic aerosol is not yet known, but it is an issue of considerable interest and the object of past and present field, laboratory, and modeling activities. For the past 20 or more years, most laboratory research has focused on SOA formation,[6] but more recently, increasing attention has been given to POA oxidation.[4] The most well-studied heterogeneous reaction has been that of O_3 with unsaturated compounds, especially oleic acid, in the form of organic films,[7−10] deposited particles,[11] and aerosols.[12−19] Experiments have included measurements of gas- and particle-phase products, kinetics, hygroscopicity, and CCN behavior. The result has been an impressive, though still incomplete, understanding of these reactions and their effects on organic aerosol physicochemical properties. There have been far fewer studies on the heterogeneous oxidation of organic compounds by OH and NO_3 radicals. The kinetics of the reaction of organic films with OH radicals have been investigated,[20−22] and in one case products were analyzed and a mechanism proposed.[22] The kinetics of the reaction of organic films with NO_3 radicals has also been investigated,[23] as have the products and mechanism of the reaction of deposited oleic acid particles with NO_3 radicals.[11] This past emphasis on heterogeneous alkene−O_3 chemistry will undoubtedly change, because most POA consists of saturated compounds[3] whose major atmospheric reaction is with OH radicals.[4]

Recently, we have begun studies on the radical-initiated heterogeneous reactions of organic compounds. Rather than immediately focus on OH radicals, however, our approach has been to first investigate the reactions of NO_3 radicals with oleic acid particles. This allows us to initially avoid some experimental challenges and to simplify the chemistry since the reaction is primarily localized to the region of the carbon−carbon double bond. The result should be a more limited set of products than would be the case for a reaction with OH radicals, which can attack almost anywhere on the parent compound as well as on the reaction products. Since the gas-phase chemistries of NO_3 and OH radical oxidation are similar in many respects, with both involving alkyl, alkoxy, and alkylperoxy radicals,[24,25]

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the results are still expected to provide valuable insight into the general mechanisms of radical-initiated heterogeneous reactions. This is less the case for O_3 reactions, whose products depend to a large extent on the fate of Criegee intermediates[26,27] that are not formed in OH or NO_3 radical reactions. This choice of systems also has the advantage of allowing us to use results from our recent studies of SOA formation from linear alkene−NO_3 reactions[28] and the reaction of O_3 with oleic acid particles[19] to aid in interpreting the data. The study employs a combination of mass spectrometric (and other) methods to obtain detailed information on reaction products, which is used to develop a mechanism that includes both surface and liquid-phase chemistry.

Experimental Section

Materials. Oleic acid (99%), 3-decanone (98%), 2-ethylhexyl nitrate (97%), and nonanoic acid (96%) were obtained from Sigma-Aldrich Co., and 2-decanol (96%) was obtained from ChemSampCo. All chemicals were used without further purification.

Environmental Chamber Technique. Oleic acid [$CH_3(CH_2)_7$-$CH{=}CH(CH_2)_7C(O)OH$] particles were reacted with NO_3 radicals in the presence of NO_2 and N_2O_5 at room temperature (∼25 °C) and pressure (∼97 kPa) in a ∼6600 L PTFE film chamber filled with dry, clean air (RH ∼0.5% and hydrocarbons <5 ppbv) from a pure air generator (Aadco). Particles were created by flushing hot oleic acid vapor into the chamber using clean air. As the vapor cooled, particles formed by homogeneous nucleation and condensation. Particle mass concentrations were typically ∼500 $\mu g\ m^{-3}$ (equivalent to ∼40 ppbv) and the peak in the size distribution was ∼0.2 μm. Nitrate radicals were generated from N_2O_5, which thermally decomposes in the gas phase to establish equilibrium with NO_2 and NO_3 radicals. The N_2O_5 was synthesized according to the procedure of Atkinson et al.[29] and kept on a glass vacuum rack in liquid nitrogen until it was used. A glass bulb containing an amount of N_2O_5 equivalent to a chamber concentration of ∼5 ppmv was then flushed into the chamber using clean air. On the basis of previous studies, <20% was lost to the walls of the vacuum rack, glass bulb, and chamber. With an N_2O_5 concentration of ∼5 ppmv, which is far in excess of the oleic acid concentration, the initial equilibrium concentrations of NO_3 and NO_2 are ∼80 ppbv (calculated using an equilibrium constant of 2.9×10^{-11} $cm^3\ molecule^{-1}$ [2]). A fan was turned on to mix the chamber air while adding reactants. Reactions began immediately upon adding N_2O_5.

Particle Analysis. A thermal desorption particle beam mass spectrometer (TDPBMS) was used to analyze particle composition in real-time[30] and by temperature-programmed thermal desorption.[31] Aerosol is sampled from the chamber into the TDPBMS through an aerodynamic lens,[32,33] and the resulting particle beam impacts in a V-shaped notch in the tip of a copper vaporizer rod coated with a nonstick polymer. Vapor molecules are ionized by 70 eV electrons and analyzed in a quadrupole mass spectrometer. For real-time analysis the rod was resistively heated to ∼165 °C, while for TPTD analysis particles were collected on the rod at −30 °C for ∼15 min and then heated to ∼150 °C at 2 °C min^{-1}. Compounds desorb according to their vapor pressures, allowing separation of components for mass spectral analysis. The mass spectrum was scanned from 10 to 500 Da. Aerosol volume concentrations were calculated from particle size distributions measured using an SMPS.[34,35] In one of these experiments, ∼10 ppmv of NO was flushed into the chamber after the oleic acid was completely reacted (∼5 min). The NO rapidly converts NO_3 radicals to NO_2,[2] thereby instantly terminating NO_3 and N_2O_5 reactions.

Two additional experiments were performed with >2500 $\mu g\ m^{-3}$ of pure oleic acid particles and ∼5 and ∼1 ppmv added N_2O_5, respectively, after which the particles in ∼0.8 m^3 of air were collected on a filter for off-line analyses. In the first case, two filter samples were collected and analyzed immediately for the total concentration of organic aerosol peroxides using an iodometric-spectrophotometric procedure we have employed previously for SOA.[36] In the second case, the filtered material was extracted in ethyl acetate, dried in a stream of N_2, and redissolved in acetonitrile. This sample was then analyzed using an Agilent 1100 Series HPLC coupled to a UV diode array detector and a Waters Micromass Ultima Global QTOF high-resolution mass spectrometer with electrospray ionization (HPLC/ESI-MS). The HPLC contained a 150 × 0.5 mm Zorbax 5 μm SB−C18 column that operated at room temperature. The HPLC method employed gradient elution using two solvent mixtures: (A) 0.1% (by volume) formic acid in water and (B) 0.1% formic acid in acetonitrile, with the contribution of B to the mobile phase increasing from an initial value of 2% to a final value of 85% in 90 min. The flow rate was 6 $\mu L\ min^{-1}$, and the sample injection volume was 2 μL. During the analysis, a UV chromatogram was obtained at 210 nm and major peaks were analyzed by ESI-MS. The mass spectrum was scanned from 100 to 1000 Da. As will be shown below, the major reaction products are expected to contain carbonyl, hydroxyl, carboxyl, and nitrooxy groups. To determine which functional group(s) were detected at 210 nm, the molar absorptivities of 3-decanone [$CH_3CH_2C(O)(CH_2)_6CH_3$], 2-decanol [$CH_3CH(OH)$-$(CH_2)_7CH_3$], nonanoic acid [$CH_3(CH_2)_7C(O)OH$], 2-ethylhexyl nitrate [$CH_3(CH_2)_3CH(CH_2CH_3)CH_2ONO_2$], and oleic acid in acetonitrile were measured at this wavelength using a Cary 2200 UV/vis spectrophotometer. The values were approximately 3, 3, 50, 4000, and 200, respectively, indicating that the chromatographic peaks were due to nitrates.

Results and Discussion

General Reaction Mechanism. On the basis of measurements of reactive uptake of NO_3 radicals by liquid and frozen alkene films, Moise et al.[23] concluded that the reaction occurs within the top few molecular surface layers. Because of the transitional nature of the interfacial region, the mechanism could have properties of both gas- and liquid-phase reactions, which, although similar in many respects, have significant differences. Here, we begin by presenting a general reaction mechanism based on current state of knowledge of the gas-phase chemistry and then discuss features of the liquid-phase reaction that are relevant to this investigation.

From previous studies of the volatile[37−42] and SOA[28] products of gas-phase reactions of linear alkenes with NO_3 radicals in the presence of NO_2, N_2O_5, and O_2 it would be expected that the reaction with oleic acid in air can potentially form products **1**−**7** by the mechanism shown in Figure 1. Since the mechanism is not affected by functional groups on R_1 and R_2, for simplicity we call these alkyl groups even though one is a carboxyl. The reaction is initiated by addition of NO_3 to the carbon−carbon double bond, with the reactions with NO_2 and N_2O_5 being too slow to be important for the $[NO_3]/[NO_2]$ and $[NO_3]/[N_2O_5]$ ratios present in these experiments.[24,43,44] The resulting nitrooxyalkyl radical then reacts solely with O_2 to form a nitrooxyalkylperoxy radical. Other species would need to be present at concentrations greater than ∼100 ppmv and react at the gas kinetic limit to compete with O_2 at ∼2×10^5 ppmv.[24]

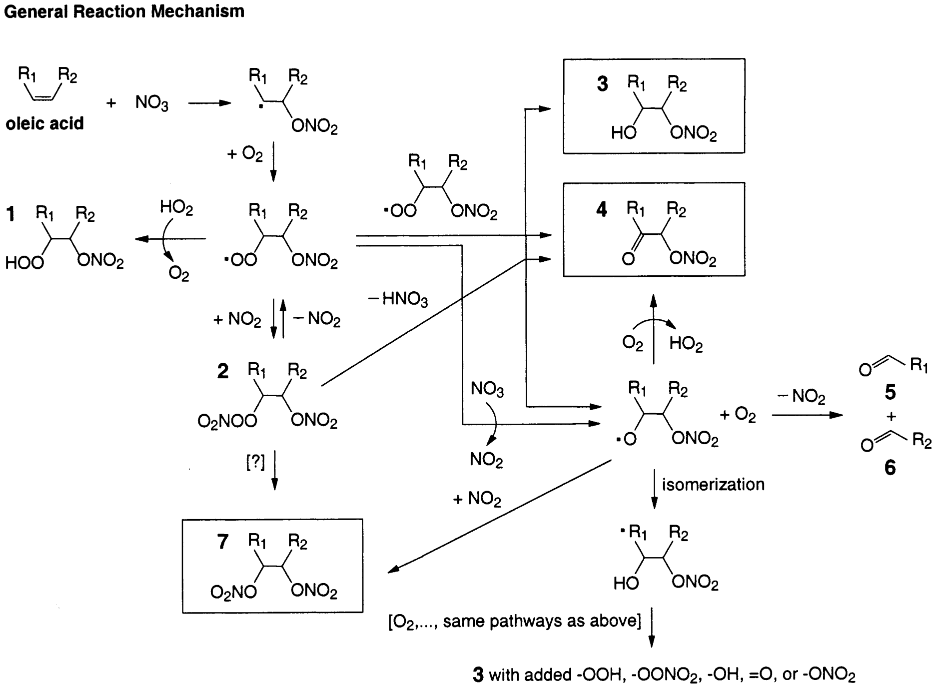


Figure 1. Proposed mechanism for forming first generation products from the reaction of NO_3 radicals with oleic acid [$R_1 = CH_3(CH_2)_7$ and $R_2 = HO(O)C(CH_2)_7$ or vice versa]. The identified products are in boxes.

The nitrooxyalkylperoxy radical can react with HO_2 to form a hydroperoxy nitrate [**1**] or with NO_2 to form a nitrooxy peroxynitrate [**2**], which is thermally unstable (the time constant for the reverse reaction is ~1 s at 25 °C[45]) and therefore acts as a temporary reservoir for the nitrooxyalkylperoxy radical. The nitrooxyalkylperoxy radical can undergo a self-reaction to form a hydroxy nitrate [**3**] and carbonyl nitrate [**4**] or a nitrooxyalkoxy radical that can also be formed by reaction with a NO_3 radical. The branching ratios for formation of the carbonyl and alcohol pair from the gas-phase self-reactions of alkylperoxy radicals are typically ~0.3−0.8 (and therefore ~0.7−0.2 for formation of alkoxy radicals) at room temperature.[24] The nitrooxyalkoxy radical can react with O_2 to form a carbonyl nitrate [**4**] plus HO_2, decompose to aldehydes [**5**, **6**] (in this case nonanal [$CH_3(CH_2)_7CHO$] and 9-oxononanoic acid [$OHC(CH_2)_7C(O)OH$]), or react with NO_2 to form a dinitrate [**7**]. Because of the strong propensity for β-substituted alkoxy radicals to decompose,[46] the aldehydes would almost certainly be present if nitrooxyalkoxy radicals formed. The nitrooxyalkoxy radical can also isomerize through a 1,5-H atom shift to a nitrooxyhydroxyalkyl radical and then react according to the nitrooxyalkyl radical mechanism. Although OH radicals are apparently produced in these reactions, the concentrations are much too low to compete with the rapid alkene−NO_3 reactions under these conditions and therefore do not impact the chemistry.[47]

Much less is known about the products and mechanism of the reactions of alkenes with NO_3 radicals in the presence of NO_2 and N_2O_5 in the liquid phase, and we are aware of only one study performed in the presence of O_2. This was carried out on deposited, millimeter-size liquid oleic acid particles.[11] Infrared analysis indicated the presence of compounds containing carbonyl, carboxyl, nitro, nitrooxy, and possibly nitroperoxy groups, while GCMS and HPLC/ESI-MS analysis indicated an absence of carbonyl decomposition products [**5**, **6**] and provided evidence for oligomers. One study of the reaction of stilbene [$C_6H_5CH{=}CHC_6H_5$] identified nitronitrates and mixtures of nitroalkenes and suggested the reaction mechanism may involve addition of either NO_3^- or N_2O_5 to the double bond, but these experiments were performed in the absence of O_2.[48]

A number of studies have investigated the products and mechanism of the liquid-phase reaction of alkenes with NO_2 in the presence of N_2O_4 and O_2, and these are also relevant to this discussion.[49−51] These experiments were usually carried out by bubbling the gases through an alkene solution, which may produce reaction conditions similar to those employed here. The major products were a hydroxy nitrite, carbonyl nitrite, and nitrooxy nitrite, analogous to the hydroxy nitrate [**3**], carbonyl nitrate [**4**], and dinitrate [**7**] shown in Figure 1. The formation of these products can be explained by the mechanism shown in Figure 1, except that the reaction is initiated by addition of NO_2 rather than a NO_3 radical to the double bond, thereby forming a nitroalkyl radical rather than a nitrooxyalkyl radical. As with all liquid-phase reactions carried out in air at atmospheric pressure,[52] the nitroalkyl radicals are expected to react exclusively with O_2 to form nitroalkylperoxy radicals. When secondary alkylperoxy radicals (this is also the type formed from the reaction of oleic acid with NO_3 radicals) such as these undergo a self-reaction in the liquid phase they apparently produce only a carbonyl and alcohol pair[52] via a tetroxide intermediate, in accordance with the Russell mechanism.[53] Unlike the gas-phase reaction, few alkoxy radicals appear to be formed at room temperature. The reason for this difference has not been determined. In the NO_2-initiated reaction, the nitrooxy nitrite and some fraction of the carbonyl nitrite were apparently formed by decomposition of a nitro peroxynitrate (analogous to the nitrooxy peroxynitrate [**2**] decomposing to the carbonyl nitrate [**4**] and dinitrate [**7**]), which was highly unstable above ~0 °C.[51] The carbonyl nitrite was apparently formed by loss of HNO_3, while the mechanism by which the nitrooxy nitrite was formed is not known.

According to studies of polymer formation from the radical-initiated oxidation of styrene [$C_6H_5CH{=}CH_2$] in the presence of O_2,[54] there are a number of other reactions that could occur in the liquid phase but not in the gas phase. The most important to consider are abstraction of an H atom (for alkylperoxy radicals these must come from resonance-weakened bonds such as allylic C−H bonds in unsaturated compounds[52]) and addition to the oleic acid double bond by alkylperoxy radicals. These reactions will form hydroperoxides and peroxide polymers, respectively. Peroxide polymerization also opens new channels for the formation of alkoxy radicals, which can react by H atom abstraction to form alcohols and add to the oleic acid double bond, thereby adding ether linkages within the peroxide polymers. The latter can then depolymerize to form carbonyls by decomposition reactions similar to those shown in Figure 1 for other alkoxy radicals. Because our results indicate that peroxides were not formed in these reactions, and that nonperoxide polymers were not formed by addition of species to the oleic acid double bond, these reactions are not included in the figure.

To summarize, the mechanism shown in Figure 1 includes a number of possible reaction pathways that have been identified in previous studies of gas- and liquid-phase reactions. The chemistries of the gas and liquid phases have many common features, but also differences. There are also reactions that can occur under some circumstances that are not included in the mechanism, since our results indicate they are not significant in these experiments. The mechanism shown in Figure 1 is meant to provide a convenient framework for discussing our results and identifying which of the possible reaction pathways are important for the heterogeneous reaction of NO_3 radicals with oleic acid in the presence of NO_2, N_2O_5, and O_2. After presenting and discussing our results, the mechanism will be further simplified.

Mass Spectral Analysis of Reaction Products. The major challenge in using TDPBMS mass spectra to identify reaction products is that standards are only available for the aldehyde products [**5**, **6**] shown in Figure 1. The approach taken here was to use mass spectra of compounds with related structures, well-known electron impact ionization fragmentation pathways,[55] and TPTD profiles to determine which of the potential products appear to be present. Important information was also obtained from HPLC/ESI-MS analysis.

TDPBMS Analysis. Real-time TDPBMS mass spectra of oleic acid aerosol particles before and after reaction with NO_3 radicals are shown in Figure 2A,B. The oleic acid mass spectrum has distinctive high-mass peaks at *m*/*z* 282 and 264 from the molecular ion and the fragment formed by loss of H_2O, respectively, as well as many lower mass peaks. After 35 min of reaction the oleic acid is gone, as indicated by the disappearance of all peaks above *m*/*z* 173. The largest, most distinctive high-mass product peaks are those at *m*/*z* 125, 141, 155, and 171. It is also noteworthy that a large peak appears at *m*/*z* 46. This is due to NO_2^+ and is indicative of organic nitrates. Figure 2C shows the time-dependent signal of selected mass fragments from oleic acid and reaction products. The sharp decrease in *m*/*z* 264 after adding N_2O_5 shows that oleic acid reacts completely within ∼1−2 min. There is a corresponding sharp increase in *m*/*z* 155 (*m*/*z* 125, 141, and 171 behave similarly) followed by a slow decrease, probably due to wall loss and possibly further reaction. The *m*/*z* 46 ion behaves differently, in that it increases more slowly than the other product ions and appears to reach a plateau after ∼10 min. As a result, the intensity of *m*/*z* 46 increases with time relative to *m*/*z* 125, 141, 155, and 171.

Results of TPTD analysis of the reaction of oleic acid with NO_3 radicals are shown in Figure 3. This technique separates compounds according to volatility, and so provides additional information on composition. Desorption profiles for selected *m*/*z* values and total ion signal (*m*/*z* 40−200) of the reacted aerosol are shown in Figure 3A. Because the total signal is approximately proportional to the organic mass,[56] this profile represents the distribution of organic mass with respect to volatility. The desorption profiles exhibit maxima at approximately 87, 120, and 135 °C, representing single compounds or groups of compounds with similar volatilities. Also labeled in the figure are the approximate temperatures at which 9-oxononanoic acid (28 °C), a potential product, and unreacted oleic acid (40 °C) would be expected to desorb.

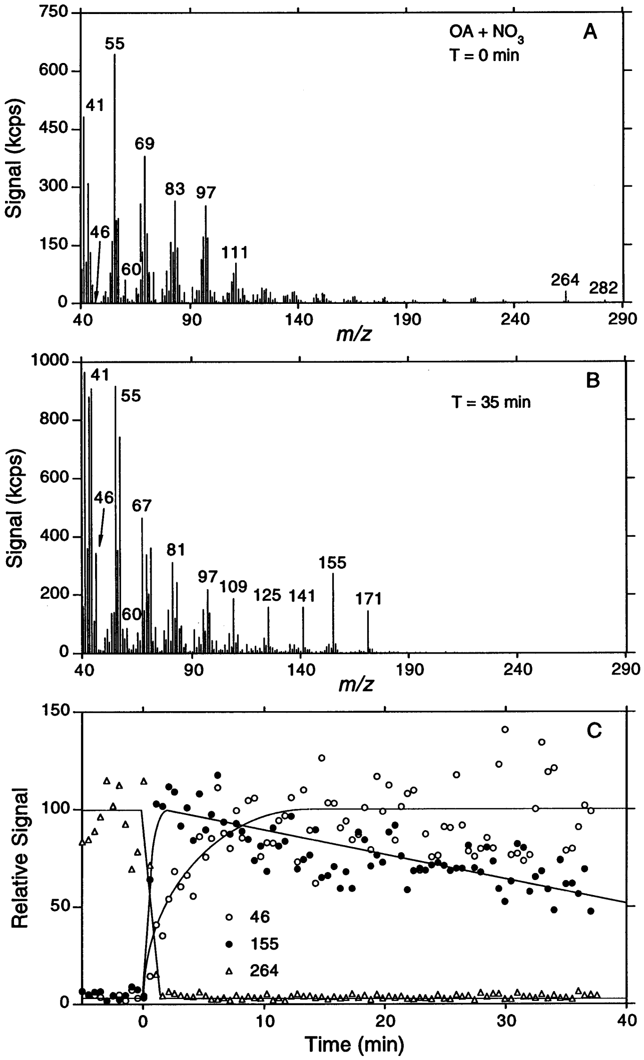


Figure 2. Time-dependent TDPBMS (A, B) mass spectra and (C) normalized single ion signal for the reaction of oleic acid particles with NO_3 radicals.

We begin the TPTD data analysis by considering the two possible aldehyde products, nonanal and 9-oxononanoic acid [**5**, **6**]. The mass spectra of these compounds have characteristic ion fragments that can be used to evaluate their abundance among the reaction products. The mass spectra and fragmentation pathways are shown in Figures 1S and 3S (Supporting Information), respectively. For nonanal, the ions are *m*/*z* 124 and 114 from loss of H_2O and $CH_2{=}CH_2$, and for 9-oxononanoic acid they are *m*/*z* 154, 144, and 136 from loss of H_2O, $CH_2{=}CH_2$, and $2H_2O$. As shown in the mass spectra of the oleic acid reaction products (Figures 2 and 3), these peaks are all very small, indicating the compounds are not present in significant amounts. One explanation for the absence of nonanal

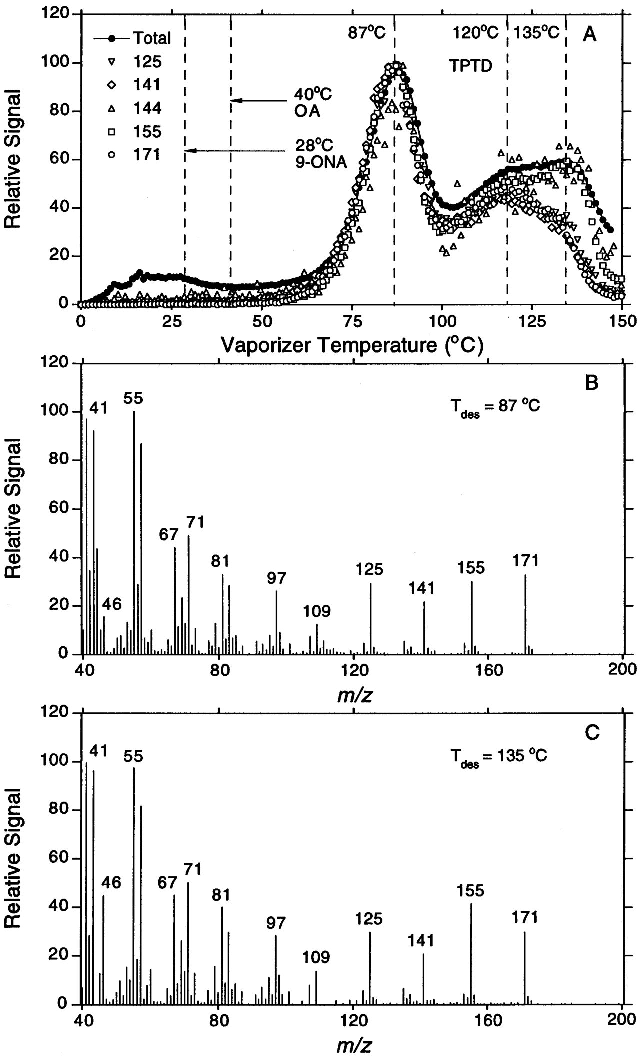


Figure 3. TPTD (A) desorption profiles and mass spectra obtained at (B) 87 °C and (C) 135 °C for the reaction of oleic acid particles with NO_3 radicals. OA and 9-ONA refer to oleic acid and 9-oxononanoic acid.

could be that it is too volatile to remain in the aerosol on the time scale of these experiments. For example, a number of studies of the reaction of oleic acid with O_3, for which nonanal is a major product, have shown that it can rapidly evaporate from films and particles.[7,8,14] This does not explain the absence of 9-oxononanoic acid, however, which is a major particle-phase product of the O_3 reaction.[12,16−19] In our previous study of the reactions of O_3 with oleic acid particles and with gas-phase 9-decenoic acid [$HO(O)C(CH_2)_7CH{=}CH_2$], which forms SOA, 9-oxononanoic acid was identified in the particle phase.[19] For the 9-decenoic acid reaction, the desorption profile had a maximum at ~28 °C and the corresponding mass spectrum matched that of the 9-oxononanoic standard. In the oleic acid reaction, 9-oxononanoic acid could not be completely isolated from the complex mixture of products, but its presence was indicated by overlapping *m*/*z* 136, 144, and 154 profiles that exhibited a distinct shoulder near 28 °C. Conversely, the signal from *m*/*z* 144 (*m*/*z* 136 and 154 behave similarly) shown in Figure 3A is essentially zero below ~50 °C. On the basis of the small intensity of the characteristic 9-oxononanoic ions in the product mass spectra, and the desorption profiles, we conclude that this compound is not formed in the reaction. Since nonanal is an expected coproduct of the decomposition reaction that would produce 9-oxononanoic acid (Figure 1), we conclude that nonanal also is not formed. This conclusion is supported by the observation that the aerosol volume measured with the SMPS increased by ~8% after reaction of oleic acid with NO_3 radicals (presumably due to the replacement of H atoms by functional groups containing N and/or O atoms), indicating no obvious loss of mass by volatilization.

Mass spectra obtained at the 87 and 135 °C desorption maxima are shown in Figures 3B,C. The spectra are similar, except that the relative intensity of *m*/*z* 46 is larger at the higher desorption temperature (i.e., lower compound volatility). The tendency for the *m*/*z* 46 signal to increase with desorption temperature and with time of reaction (Figure 2C), relative to the *m*/*z* 125, 141, 155, and 171 signals suggests that there is a relation between compound volatility and time of formation. One possibility is that the products created later in the reaction, after the oleic acid is gone, are lower volatility compounds formed by adding nitrooxy groups to first generation products. This could happen in two ways. One is by reaction of nitrogen oxides with hydroxyl groups on first generation products, such as the hydroxy nitrate [**3**]. For example, it has been proposed that the reaction

$$R_1CH(OH)R_2 + N_2O_5 \rightarrow R_1CH(ONO_2)R_2 + HNO_3 \quad (1)$$

occurs in the condensed-phase synthesis of nitrates from the reaction of alcohols with N_2O_5,[57] and also by a slow gas-phase reaction (with undetermined contributions from heterogeneous wall reactions).[58] One proposed mechanism involves the formation of an energetically favored six-membered ring with a N atom and O atom from N_2O_5 bound to the O atom and H atom in the OH group.[58] Another possible reaction is H atom abstraction by a NO_3 radical, which has been shown to occur on saturated organic films at rates that are similar or slightly slower than NO_3 radical addition to alkene films.[23] This reaction would generate a substituted alkyl radical that could be converted to a nitrooxy or hydroxyl group by pathways shown in Figure 1 for other alkyl radicals. The hydroxyl group could then react according to reaction 1. To test this hypothesis, in one experiment NO was added to the chamber soon after the oleic acid reacted (~5 min), but before significant amounts of higher generation products could form. The NO reacts rapidly with NO_3 radicals (forming two NO_2 molecules),[2] thereby instantly terminating NO_3 and N_2O_5 reactions. From this time onward, the *m*/*z* 46, 125, 141, 155, and 171 signals all exhibited similar slow decays such that the ratio of the intensity of *m*/*z* 46 to the other ions remained approximately constant, rather than increasing as in the other experiment. In addition, TPTD analysis of the products of the reaction yielded very different desorption profiles, as shown in Figure 4. Instead of three peaks, only a peak at 87 °C was present. The mass spectrum is similar to that observed without added NO (the *m*/*z* 155 peak is probably higher because of slight differences in the relative proportions of the products). This result supports the hypothesis that the peaks at 120 and 135 °C are due to more highly nitrated, higher generation products. The result also indicates that any polymers formed in the absence of NO cannot be formed by the addition of nitrooxyalkylperoxy or nitrooxyalkoxy radicals to the oleic acid double bond. Otherwise, adding NO after the oleic acid has been reacted would not so effectively eliminate the formation of the low-volatility material that might contain a polymeric component.

The results discussed thus far suggest that the compounds associated with the 87 °C desorption maximum are some combination of first generation products, which subsequently add nitrooxy groups to form higher generation products that

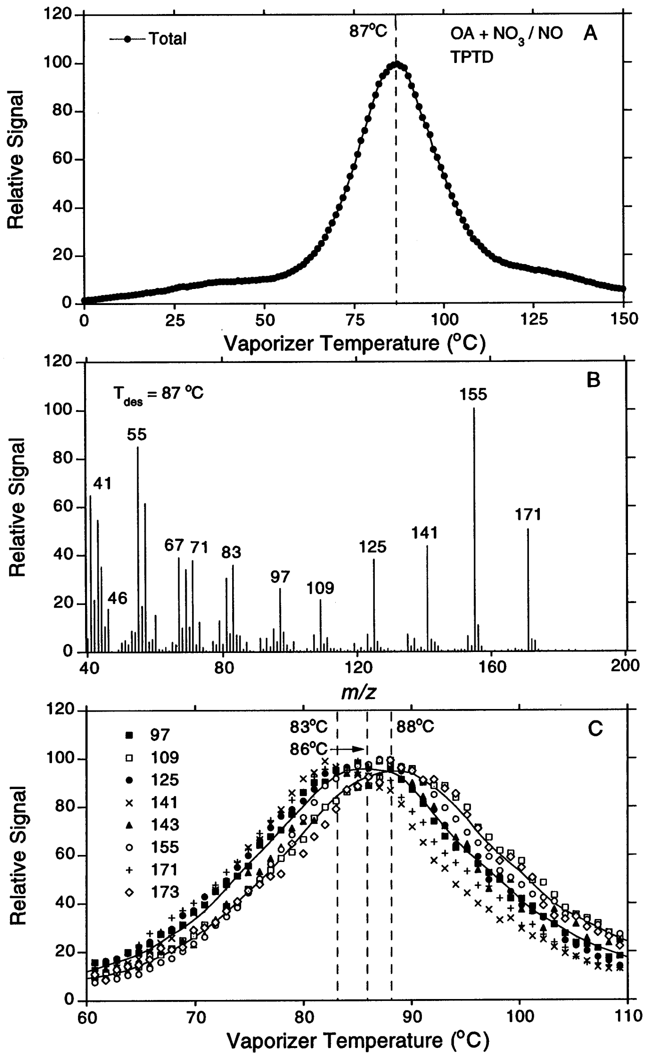


Figure 4. TPTD (A, C) desorption profiles and (B) mass spectrum obtained at 87 °C for the reaction of oleic acid particles with NO_3 radicals, followed by the addition of NO.

desorb at approximately 120 and 135 °C. Additional information on the identity of the first generation products can be obtained by comparing TPTD profiles of characteristic *m*/*z* values with predictions based on expected fragmentation pathways. Because of the simpler desorption profiles obtained when NO was added, these data are shown in Figure 4. Although no authentic mass spectral standards are available, reasonable predictions regarding fragmentation patterns can be made based on established fragmentation mechanisms[55] and mass spectra of related compounds. The mass spectra chosen for this purpose are 5,6-dihydroxydecane, 1-hydroxy-2-nitroxytetradecane, and 2-oxoadipic acid, which are shown along with proposed fragmentation pathways in Figures 2S and 3S (Supporting Information). One important generalization that can be made from these spectra is that electron impact ionization of a molecule containing two adjacent functional groups always leads to scission of the C−C bond between the functional groups. When scission occurs between hydroxyl, carbonyl, and nitrooxy groups, the fragmentation pathways can also involve loss H_2O and $CH_2{=}CH_2$, CO, and NO_2 and H (by transfer to a radical fragment), respectively. From the mass spectrum of 9-oxononanoic acid, it is also seen that carboxylic acids lose H_2O.

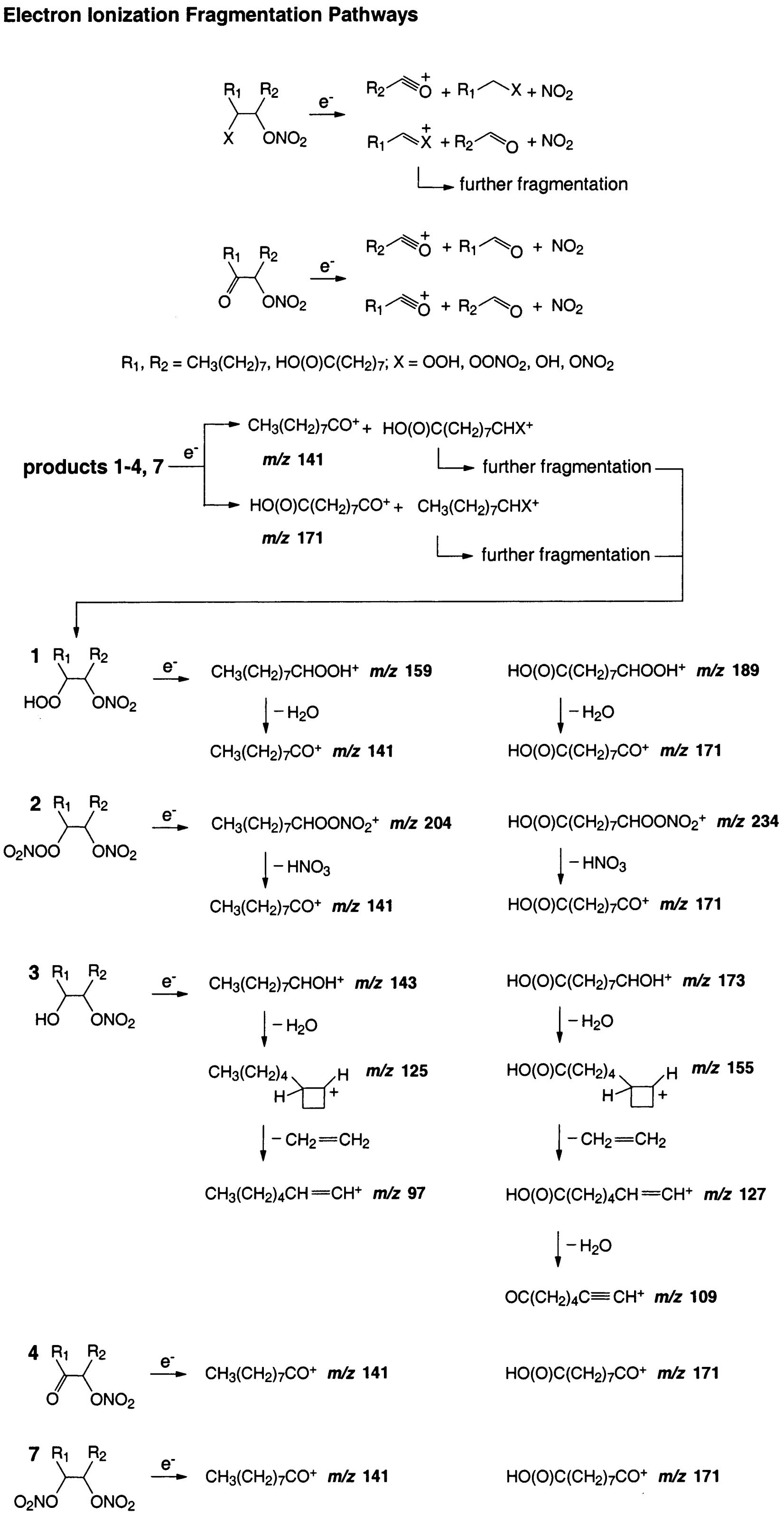
On the basis of these fragmentation pathways, we can explain the presence of large peaks in the reaction product mass spectra at *m*/*z* 97, 109, 125, 141, 155, and 171, as well as minor peaks at *m*/*z* 143 and 173, and the absence of peaks above *m*/*z* 173. The proposed pathways are shown in Figure 5. Those proposed for the nitrooxy hydroperoxide [**1**] and nitrooxy peroxynitrate [**2**] are only meant to demonstrate ways that these compounds could generate observed ions, since no appropriate standards are available. Desorption profiles plotted in Figure 4C show that ions expected to be generated from the same molecule, including *m*/*z* 97, 125, and 143; 109, 155, and 173; and 141 and 171; have overlapping profiles.

The first important conclusion that can be made from this analysis is that one of the first generation products is the hydroxy nitrate [**3**]. This is the only potential product that is likely to generate peaks at *m*/*z* 97, 125, and 143, and at *m*/*z* 109, 155, and 173. The slight differences in the maxima in the desorption profiles of these two sets of ions (86 and 88 °C, respectively) suggests that the isomers have different volatilities. If the hydroxy nitrate [**3**] is formed, the reaction mechanism (Figure 1) indicates that the carbonyl nitrate [**4**] is also formed. This compound could contribute to *m*/*z* 141 and 171, although the hydroxy nitrate [**3**] and dinitrate [**7**] could also contribute. We can rule out the presence of significant amounts of the nitrooxy hydroperoxide [**1**], since the measured concentration of organic peroxides was below the detection limit of our method (~ 1 μmole m^{-3}), which corresponds to a maximum peroxide contribution of $\sim$5−10% to the aerosol mass. Alkyl hydroperoxides such as the nitrooxy hydroperoxide [**1**] should be sufficiently stable to survive the few hours of the experiment and sample collection prior to analysis.[36] This may not be true for the nitrooxy peroxynitrate [**2**], however, which is much less stable.[51] It is possible that this compound forms and then decomposes in the chamber or on the filter by pathways shown in Figure 1. It is also unlikely that the dinitrate [**7**] contributes to the 87 °C peak. In previous studies,[28,59] we observed that the presence of a nitrooxy group increases the desorption temperature significantly more than a hydroxyl or carbonyl group, which had similar effects on volatility. This trend is more consistent with the hydroxy nitrate [**3**] and carbonyl nitrate [**4**] desorbing at 87 °C and dinitrates desorbing at higher temperatures.

HPLC/ESI-MS Analysis. Additional support for our assignment of aerosol products was obtained from filter samples analyzed by HPLC/ESI-MS. Compounds were separated by HPLC, a UV chromatogram was obtained at 210 nm, and the major peaks were analyzed by ESI-MS (including MS/MS). The chromatogram is shown in Figure 6, and the 6 major peaks analyzed by ESI-MS (positive ions) are labeled in the order in which they are discussed. As shown in the Experimental Section, absorption at 210 nm is apparently due overwhelmingly to the nitrooxy group, indicating that the chromatographic analysis was especially selective toward nitrates. This should not significantly bias the analysis, since TDPBMS analysis indicates that all the products are nitrates.

Figure 7A shows the mass spectrum obtained for peak 1. In ESI-MS analysis, positive ions usually correspond to protonated molecules, dimers, or fragments formed by the loss of simple molecules such as H_2O. The compound associated with peak 1 has ions at *m*/*z* 360 and 719, which most likely are due to the protonated monomer and dimer of a molecule with molecular weight 359. We therefore assign peak 1 to the carbonyl nitrate [**4**].

The mass spectrum obtained for peak 2 is shown in Figure 7B. The ions at *m*/*z* 362 and 723 are most likely due to the protonated monomer and dimer of a molecule with molecular



Electron Ionization Fragmentation Pathways

Figure 5. Proposed electron impact ionization fragmentation pathways for potential products of the reaction of oleic acid particles with NO_3 radicals.

weight 361. We therefore assign peak 2 to the hydroxy nitrate [**3**]. The *m*/*z* 297 ion is associated with an unidentified coeluting compound. This can be seen from the MS/MS spectrum shown in Figure 7C, since no *m*/*z* 297 ion is formed when the *m*/*z* 362 ion (or *m*/*z* 723, which gives the same MS/MS spectrum) fragments. The ions generated at *m*/*z* 299, 281, 263, and 245 can be explained by loss of one HNO_3 molecule and zero, one, two, or three H_2O molecules. This is consistent with the presence of one nitrooxy, one hydroxy, and one carboxyl group, which can generate losses of one HNO_3, one H_2O, and one or two H_2O molecules, respectively.

The mass spectrum obtained for peak 3 is shown in Figure 8A. The ions at *m*/*z* 407 and 813 are most likely due to the protonated monomer and dimer of a molecule with molecular

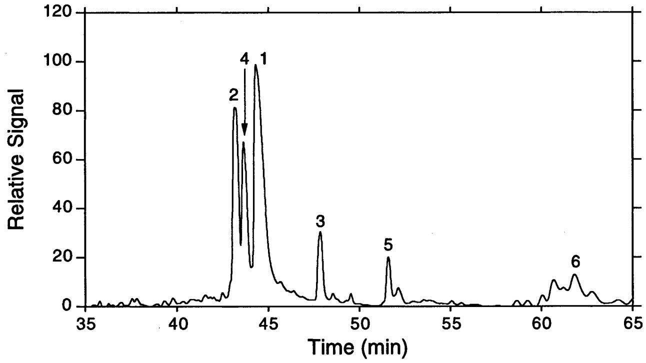


Figure 6. HPLC−UV chromatogram of the products of the reaction of oleic acid particles with NO_3 radicals.

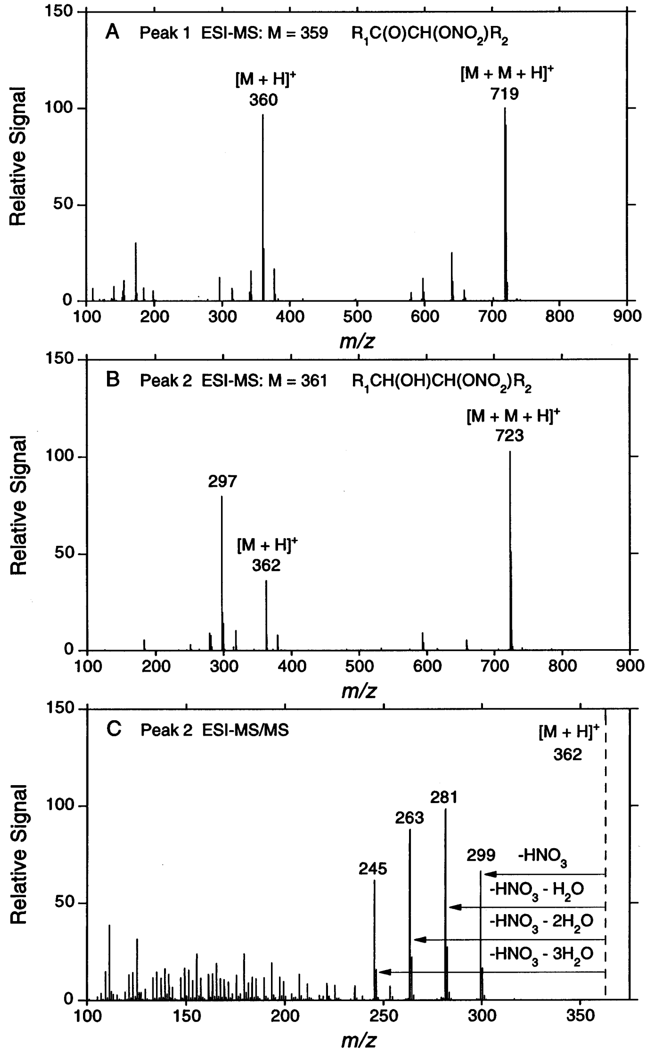


Figure 7. Electrospray ionization mass spectra (ESI-MS and ESI MS/MS) of the products of the reaction of oleic acid particles with NO_3 radicals. Peaks 1 and 2 are from the HPLC−UV chromatogram in Figure 6. *M* is the molecular weight of the proposed product.

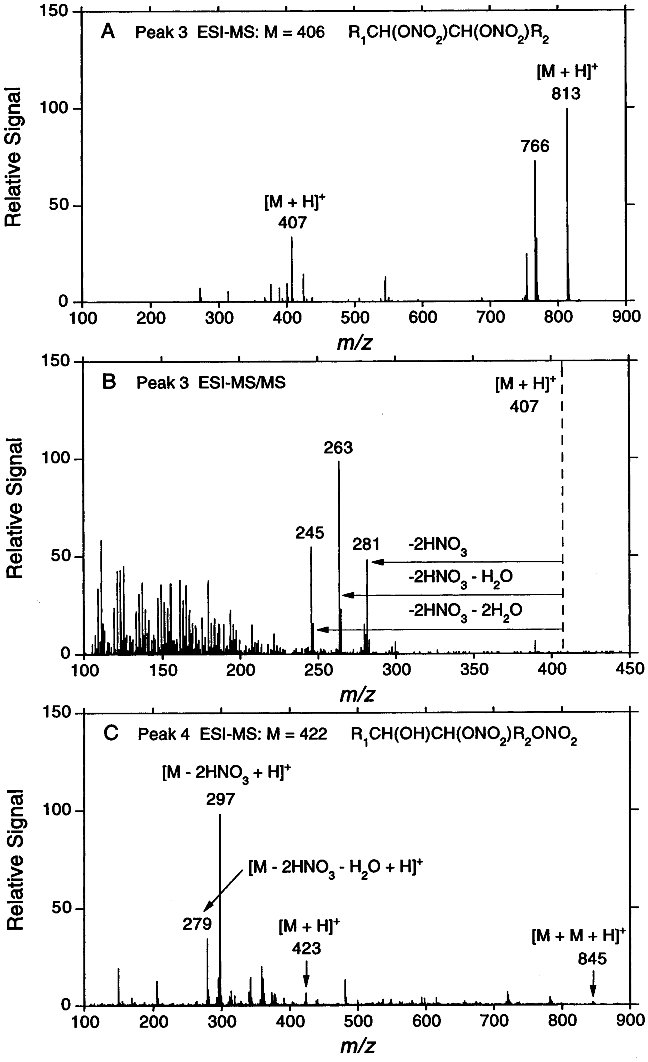


Figure 8. Electrospray ionization mass spectra (ESI-MS and ESI MS/MS) of the products of the reaction of oleic acid particles with NO_3 radicals. Peaks 3 and 4 are from the HPLC−UV chromatogram in Figure 6. *M* is the molecular weight of the proposed product.

weight 406. We therefore assign peak 3 to the dinitrate [**7**]. The *m*/*z* 766 ion is associated with an unidentified coeluting compound, since it does not appear in the MS/MS spectrum of *m*/*z* 813 (the same as that shown in Figure 8B for *m*/*z* 407). The ions generated at *m*/*z* 281, 263, and 245 can be explained by loss of two HNO_3 molecules and zero, one, or two H_2O molecules. This is consistent with the presence of two nitrooxy groups and one carboxyl group, which can generate losses of two HNO_3 and one or two H_2O molecules, respectively.

The mass spectrum obtained for peak 4 is shown in Figure 8C. The ions at *m*/*z* 423 and 845 are most likely are due to the protonated monomer and dimer of a molecule with molecular weight 422. We therefore assign peak 4 to a hydroxy dinitrate, possibly formed by the reaction of N_2O_5 with a dihydroxy nitrate as in reaction 1. The ions generated at *m*/*z* 297 and 279 can be explained by loss of two HNO_3 molecules and zero or one H_2O molecules. This is consistent with the presence of two nitrooxy groups and one hydroxyl group, which can generate losses of 2 HNO_3 and one H_2O molecules, respectively. Unlike the other products no further loss of either one or two H_2O molecules from the carboxyl group is observed. Although the nitrooxy peroxynitrate [**2**] also has a molecular weight of 422, this compound is probably not present since no peroxide was detected in the particles and it is apparently unstable at room temperature.[51]

The mass spectra of peaks 5 and 6 are not shown. The mass spectrum of peak 5 contained ions indicative of oleic acid as well as other ions up to *m*/*z* 798, while peak 6 showed only high-mass ions between *m*/*z* 338 and 972. The amount of oleic acid could not be estimated, since the chromatographic peak has contributions from other compounds and ESI-MS is not quantitative. Also, the TDPBMS was not available at this time. The most likely reasons why oleic acid was present in this experiment and not those shown in Figures 2−4 is that the conditions were somewhat different. In this experiment, much more oleic acid was added to the chamber to maximize the concentrations of products for HPLC/ESI-MS analysis. The mass concentration could not be quantified, however, because the additional oleic acid caused the particle size distribution to extend well beyond the limit of the SMPS (∼0.8 μm). On the basis of the observed distribution, the concentration was probably ∼4−5 mg m^{-3} (∼0.4 ppmv) or more, compared to ∼0.5 mg m^{-3} for the other experiments. Furthermore, in this experiment the concentration of N_2O_5 was reduced from ∼5 to ∼1 ppmv to limit the extent of reaction during sample collection. Considering the uncertainty in the oleic acid mass concentration and in the N_2O_5 concentration (due to wall losses), it may be that oleic acid remained because it was present in excess of N_2O_5. It is also possible that for these larger oleic acid particles some oleic acid was inaccessible to NO_3 because of reduced diffusion through reaction products. Regardless of the reason, the presence of oleic acid does not affect the interpretation of our results.

The high-mass ions observed in peaks 5 and 6 may be indicative of oligomeric species. If this is true, then additional studies are needed to determine the mechanism by which they form. According to studies of polymer formation from the radical-initiated oxidation of styrene in the presence of O_2,[54] the most likely reactions would involve addition of nitrooxyalkylperoxy and/or nitrooxyalkoxy radicals to the oleic acid double bond. As discussed above, however, the results of our peroxide analyses and our experiment in which NO was added to the chamber after the oleic acid was reacted indicates that neither of these two reactions is important here. It is worth noting that radical-initiated styrene polymerization in the presence of O_2 is carried out at oxidation rates that are orders of magnitude slower than those occurring here,[54] thereby dramatically enhancing the rates of reactions of alkylperoxy radicals with the styrene double bond relative to self-reactions.

Neither nonanal nor 9-oxononanoic acid was detected by HPLC/ESI-MS, but this is not an appropriate method for these compounds because they are not nitrates and so do not absorb strongly enough at 210 nm to appear in the chromatogram. Their absence from TDPBMS analyses shows, however, that they were not formed to any significant extent in these reactions.

Some of these results are similar to those reported by Hung et al.,[11] who used HPLC/ESI-MS, GCMS, and infrared spectroscopy to analyze the products of the reaction of NO_3 radicals with deposited, millimeter-sized oleic acid droplets. They also did not detect nonanal or 9-oxononanoic acid, which they should have if they were present, and found evidence for oligomers in their mass spectra. They did not, however, definitively identify any of the nitrate products observed here. A time series of infrared spectra indicated the formation of first and higher generation products containing carbonyl, carboxyl, nitro, nitrooxy, and possibly nitroperoxy groups, with strong evidence for a carbonyl nitrate but not a hydroxy nitrate.

Time Constant Analysis and Simplified Reaction Mechanism. We can now present a simplified reaction mechanism that is consistent with our results. Before doing so, however, we present a simple time constant analysis of some of the processes and reactions occurring in the system. The analysis supports the proposed mechanism and also allows the inclusion of useful additional details.

Time Constant Analysis. The initial product formed when a NO_3 radical adds to the double bond is a nitrooxyalkyl radical, which immediately reacts with O_2 to form a nitrooxyalkylperoxy radical ($RO_2^\bullet$).[52] We begin this analysis by showing that these $RO_2^\bullet$ radicals probably diffuse throughout the particle before reacting. This could be important if surface chemistry differs significantly from bulk chemistry. The rate of formation of $RO_2^\bullet$ radicals, $R_{RO_2^\bullet}$, is equal to the rate of reaction of oleic acid, R_{OA}. From Figure 2, an oleic acid particle reacts completely in a time $t \sim 90$ s. For a particle with density $\rho = 0.9$ g cm^{-3} and molecular weight $M = 282$ g mol^{-1}, this corresponds to

$$R_{RO_2^\bullet} = R_{OA} = \rho N_A/Mt = 2 \times 10^{19}\ \text{molecules cm}^{-3}\ \text{s}^{-1} \quad (2)$$

where N_A is Avogadro's number. If the rate of loss of $RO_2^\bullet$ radicals is primarily by the self-reaction, then at steady state

$$R_{RO_2^\bullet} = k_{RO_2^\bullet - RO_2^\bullet}[RO_2^\bullet]^2 \quad (3)$$

Solving for $[RO_2^\bullet]$ gives

$$[RO_2^\bullet] = (R_{RO_2^\bullet}/k_{RO_2^\bullet - RO_2^\bullet})^{1/2} = 1.5 \times 10^{17}\ \text{molecules cm}^{-3} \quad (4)$$

where a value of $k_{RO_2^\bullet - RO_2^\bullet} = 9 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} measured for the self-reaction of $RO_2^\bullet$ radicals formed from the autoxidation of liquid methyl oleate (i.e., the methyl ester of oleic acid)[60] has been used in the calculation. Note that this value is similar to the recommended value of $\sim 5 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} for gas-phase self-reactions of secondary $RO_2^\bullet$ radicals.[24] The time constant for this second-order loss process, evaluated at the steady-state concentration, is

$$\tau_{RO_2^\bullet - RO_2^\bullet} = 1/k_{RO_2^\bullet - RO_2^\bullet}[RO_2^\bullet] \sim 7 \times 10^{-3}\ \text{s} \quad (5)$$

This calculation of $[RO_2^\bullet]$ assumes that $RO_2^\bullet$ radicals diffuse throughout the particle prior to reacting. If, however, diffusion were so slow that the self-reaction occurred in a surface layer of thickness $\delta \sim 1$ nm (approximately one molecular layer), then for a particle with diameter $d \sim 200$ nm the rate of formation of $RO_2^\bullet$ radicals in this layer, $R'_{RO_2^\bullet}$, would be

$$R'_{RO_2^\bullet} = R_{RO_2^\bullet}(\pi d^3/6)/(\pi d^2 \delta) = R_{RO_2^\bullet}(d/6\delta) = 7 \times 10^{20}\ \text{molecules cm}^{-3}\ \text{s}^{-1} \quad (6)$$

in which case $\tau_{RO_2^\bullet - RO_2^\bullet} \sim 1 \times 10^{-3}$ s.

The time constant for diffusion of a molecule with diffusion coefficient D ($\sim 2 \times 10^{-7}$ cm^2 s^{-1} for oleic acid)[61] in a particle with diameter d is[1]

$$\tau_D = d^2/4\pi^2 D \sim 5 \times 10^{-5}\ \text{s} \quad (7)$$

Since this value is much smaller than the value of $\tau_{RO_2^\bullet - RO_2^\bullet}$, the assumption that nitrooxyalkylperoxy radicals diffuse throughout the particle before reacting appears to be valid.

The time constant for the $RO_2^\bullet - NO_2$ reaction can be estimated from the equation

$$\tau_{RO_2^\bullet - NO_2} = \tau_{RO_2^\bullet - RO_2^\bullet}(k'_{RO_2^\bullet - RO_2^\bullet}[RO_2^\bullet]/k'_{RO_2^\bullet - NO_2}[NO_2]H_{NO_2}) \quad (8)$$

where the values of $\tau_{RO_2^\bullet - RO_2^\bullet}$ and $[RO_2^\bullet]$ are those calculated above, $[NO_2]$ is ∼80 ppbv (2×10^{12} molecules cm^{-3}), the rate constant ratio for the $RO_2^\bullet - RO_2^\bullet$ and $RO_2^\bullet - NO_2$ reactions is calculated from the gas-phase rate constants[24] ($k'_{\mathrm{RO_2^\bullet-RO_2^\bullet}}/k'_{\mathrm{RO_2^\bullet-NO_2}} = 5 \times 10^{-15}/9 \times 10^{-12} = 6 \times 10^{-4}$) (this should be more accurate than using the ratio $k_{\mathrm{RO_2^\bullet-RO_2^\bullet}}/k'_{\mathrm{RO_2^\bullet-NO_2}}$, which mixes liquid- and gas-phase rate constants), and the dimensionless Henry's law constant $H_{\mathrm{NO_2}}$ for dissolution of NO_2 in oleic acid is assumed to be unity, the value for CO_2 in hexadecane.[62] This gives a value of $\tau_{\mathrm{RO_2^\bullet-NO_2}} \sim 0.3$, which is ~50 times larger than $\tau_{\mathrm{RO_2^\bullet-RO_2^\bullet}}$. This suggests that the reaction between nitrooxyalkylperoxy radicals and NO_2 is only slightly competitive with the self-reaction, but considering the large uncertainties in the assumptions (i.e., $k'_{\mathrm{RO_2^\bullet-RO_2^\bullet}}/k'_{\mathrm{RO_2^\bullet-NO_2}}$ is the same for gas- and liquid-phase reactions; $H_{\mathrm{CO_2}}$ in hexadecane = $H_{\mathrm{NO_2}}$ in oleic acid) made for this calculation, we cannot rule out the possibility that the NO_2 reaction could be more competitive.

The short lifetime of $RO_2^\bullet$ radicals with respect to self-reactions also explains why hydroperoxides and peroxide polymers are unlikely to form in these experiments. Rate constants for abstraction of an allylic H atom by $RO_2^\bullet$ radicals are $\sim 2 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}, and rate constants for addition to carbon–carbon double bonds are of a similar magnitude.[52,63] Multiplying this rate constant by the concentration of pure liquid oleic acid of 1.9×10^{21} molecules cm^{-3} and taking the inverse yields a value of $\tau_{\mathrm{RO_2^\bullet-OA}} = 0.3$ s, which is ~40 times larger than $\tau_{\mathrm{RO_2^\bullet-RO_2^\bullet}}$.

Simplified Reaction Mechanism. A reaction mechanism that is consistent with the results of this study, a number of other studies, and our time constant analysis is now presented. The mechanism includes only a subset of the reactions shown in Figure 1, with no new reactions. The reader is referred to the general reaction mechanism presented above for more detailed discussions and references on specific reactions.

The reaction of oleic acid aerosol particles with NO_3 radicals in the presence of NO_2, N_2O_5, and O_2 is initiated by addition of an NO_3 radical to the carbon–carbon double bond. This occurs at the particle surface within the first few molecular layers. The resulting nitrooxyalkyl radical reacts exclusively with O_2 to form a nitrooxyalkylperoxy radical, which can diffuse throughout the particle before reacting further. Nitrooxyalkylperoxy radicals then undergo self-reactions to form hydroxy nitrates [**3**] and carbonyl nitrates [**4**], and may also react with NO_2 radicals to form nitrooxy peroxynitrates [**2**]. The latter compounds are unstable and decompose to carbonyl nitrates [**4**] and dinitrates [**7**]. None of these pathways form nitrooxyalkoxy radicals, including the reaction of nitrooxyalkylperoxy radicals with NO_3 radicals, since the latter are rapidly removed at the surface by reaction with oleic acid before they can enter the bulk. As a result, neither nonanal nor 9-oxononanoic acid [**5**, **6**] is produced. The mechanism by which hydroxydinitrates are produced probably involves H atom abstraction by NO_3 radicals from first generation products. The substituted alkyl radicals then form substituted alkylperoxy radicals that undergo self-reactions that add carbonyl and hydroxyl groups. Alcohols can further react with N_2O_5 to form more nitrated products. If oligomers are formed, the mechanism probably does not involve addition of nitrooxyalkylperoxy and/or nitrooxyalkoxy radicals to the oleic acid double bond.

Atmospheric Implications. The results of this study can be used to gain insights into the factors affecting the atmospheric aging of organic aerosol particles by either NO_3 or OH radical-initiated oxidation reactions. Reactions with NO_3 radicals occur primarily at night, while OH radical reactions occur predominantly during the day.[1,2] The key intermediates in these reactions are alkylperoxy radicals ($RO_2^\bullet$), whose fate depends on factors such as the oxidation rate, the concentrations of NO and NO_2, and the particle composition and phase (liquid or solid). As the oxidation rate increases, so does the rate of formation of $RO_2^\bullet$ radicals. Because the rate of $RO_2^\bullet$–$RO_2^\bullet$ reactions is proportional to $[RO_2^\bullet]^2$, the rates of these reactions will be enhanced with increasing oxidation rate relative to reactions of $RO_2^\bullet$ radicals with other species, which have a linear dependence on $[RO_2^\bullet]$. The products of $RO_2^\bullet$–$RO_2^\bullet$ reactions in liquid particles should be carbonyls and alcohols. Reactions of $RO_2^\bullet$ radicals by H atom abstraction from HO_2 or organic compounds, or by addition to carbon–carbon double bonds of unsaturated compounds, should form hydroperoxides and peroxide polymers, respectively. The presence of unsaturated compounds enhances not only the addition reactions, but also H atom abstraction by providing weakly bound allylic H atoms. Reactions of $RO_2^\bullet$ radicals with NO_2 should form alkylperoxy nitrates, which decompose to carbonyls and nitrates, and NO reactions should form alkyl nitrates and alkoxy radicals, with the latter decomposing to carbonyls and alkyl radicals. These reactions will be enhanced in polluted regions, where NO and NO_2 concentrations are higher.

All these reactions, with the exception of alkoxy radical decomposition, add functional groups. This helps to keep the compound in the particle phase and can increase (especially for hydroxyl groups) particle hygroscopicity [11,22] and possibly CCN activity. On the other hand, decomposition of alkoxy radicals shortens the carbon chain, leading to more volatile products that can evaporate from the particle. The effects of such reactions on particle hygroscopicity and CCN activity depend on whether the compounds being volatilized originally enhanced these properties. In addition, the reduction in particle size from volatilization will reduce CCN activity.

The volatilization process may be enhanced by the presence of a solid phase, as indicated by recent studies by Molina et al.[22] In their experiments, heterogeneous reactions of OH radicals with solid organic films initiate a series of reactions that efficiently decompose large, saturated organic molecules into smaller, more volatile species. The key feature of their proposed mechanism is that the self-reaction of $RO_2^\bullet$ radicals primarily forms alkoxy radicals, which decompose to volatile products such as aldehydes. This behavior differs dramatically from that of organic liquids, in which the $RO_2^\bullet$ radical self-reaction appears to form only a carbonyl and alcohol. One possibility, therefore, is that heterogeneous oxidation reactions occurring on solid organic surfaces more closely resemble gas-phase reactions, where typical branching ratios for forming alkoxy radicals and a carbonyl and alcohol are both ~0.5.[24]

Conclusions

The results of this study indicate that the major products of the reaction of NO_3 radicals with liquid oleic acid aerosol particles in the presence of NO_2, N_2O_5, and O_2 are hydroxy nitrates, carbonyl nitrates, dinitrates, hydroxydinitrates, and more highly nitrated compounds. It is also possible that oligomers are formed. Because the parent compound is a carboxylic acid, these products are all carboxylic acids. The formation of these products can be explained by a mechanism in which NO_3 radicals initially add to the carbon–carbon double bond, followed by O_2 addition to form nitrooxyalkylperoxy radicals. These species then undergo self-reactions to form hydroxy nitrates and carbonyl nitrates or they add NO_2 and decompose to either carbonyl nitrates or dinitrates. There also appear to be slower reactions initiated by abstraction of H atoms from saturated compounds by NO_3 radicals as well as reactions of N_2O_5 with alcohols, which form hydroxydinitrates and more highly nitrated compounds. The results are consistent with many aspects of previous studies of the gas- and liquid-phase reactions of related systems, and also with the results of a simple time constant analysis. An important implication of this study is that the products of radical-initiated oxidation reactions (including by OH radicals) of organic aerosol particles may depend significantly on particle phase. Reactions of liquid organic particles are likely to lead to the addition of carbonyl, hydroxyl, and nitrooxy groups to the particle, which may enhance hygroscopicity and CCN activity. Reactions at solid surfaces may promote volatilization of organic components by enhancing alkoxy radical formation and subsequent decomposition to more volatile compounds. The latter reactions can reduce CCN activity by reducing particle size, while effects due to composition changes will depend on the nature of the compounds being volatilized.

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Supporting Information Available: Figures showing electron ionization mass spectra of standard compounds from ref 64 (reprinted with permission of John Wiley & Sons, Inc. Copyright 1994) of nonanal, 9-oxononanoic acid, and 5,6-dihydroxydecane, TDPBMS mass spectra of 1-hydroxy-2-nitrooxytetradecane and 2-oxoadipic acid, and proposed fragmentation pathways for forming mass spectral peaks. This material is available free of charge via the Internet at http://pubs.acs.org.

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