



Processing of unsaturated organic acid films and aerosols by ozone

T.L. Eliason^a, S. Aloisio^{a,1}, D.J. Donaldson^b, D.J. Cziczo^c, V. Vaida^{a,*}

^a *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA*

^b *Department of Chemistry, University of Toronto, Toronto, Canada*

^c *NOAA Aeronomy Laboratory, Boulder and CIRES, University of Colorado, CO, USA*

Received 30 September 2002; received in revised form 6 February 2003; accepted 13 February 2003

Abstract

For any organic-containing aerosol, the species present at the particle's surface are extremely susceptible to oxidation by atmospheric oxidants, such as OH, halogen atoms, ozone and nitrogen trioxide. In this work, thin films and pure organic aerosols were investigated as proxies for these surface organic compounds. The mechanisms of processing by ozone of unsaturated carboxylic acids, specifically 2-octenoic acid and 10-undecenoic acid, in a thin film are compared to that on pure aerosols. The organic acids utilized were chosen to investigate the effect of substitution on the ozonolysis mechanism. The gas-phase and condensed-phase products were probed via a combination of infrared spectroscopy and mass spectrometry. A significant change was measured in the chemical composition of both the thin films and the aerosols following ozonolysis, and some of the products formed have been identified. Consequences of this chemical processing of aerosols to atmospheric chemistry, climate and transport will be discussed.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Ozone-alkene reaction; Mechanism; Atmospheric chemistry; Organic aerosol; Surface film

1. Introduction

Recent field measurements have shown that a significant mass fraction of atmospheric aerosols consists of organic compounds (Matsumoto et al., 1997; Middlebrook et al., 1998; Murphy et al., 1998a,b; Novakov et al., 1997a,b; Novakov and Penner, 1993; Rogge et al., 1993). Some of these are pure organic aerosols, which may be formed by primary particle emissions or by the partitioning of organic gases to existing aerosols. Organic compounds often constitute a component of mixed aerosols, which might also contain water, mineral oxides and inorganic salts. Mass spectrometry has identified alkanes, alkenes, fatty acids, alcohols and aromatics in aerosol samples (Finlayson-

Pitts and Pitts, 2000; Rogge et al., 1993; Seinfeld and Pandis, 1998). Many of these organic molecules have, in general, a low solubility in water, and some are known to be amphiphilic. In mixed aerosols, the result is an insoluble hydrophobic layer coating the outside of an aqueous, mineral or salt core (Ellison et al., 1999; Vaida et al., 2000). Organic compounds have been shown to retard evaporation and condensation of water from flat surfaces and aerosols (Barnes, 1986; Feingold and Chuang, 2002; Garrett, 1971; McNamee et al., 1998; Otani and Wang, 1984; Xiong et al., 1998). Recent studies focus on the potential effect of surface films on cloud formation. An inverted micelle model (Ellison et al., 1999), suggested by electron microscopy experiments (Husar and Shu, 1975; Tervahattu et al., 2002a), has been confirmed by recent field measurements. Chemical processing of this surface organic layer will modify the chemical composition of the aerosol (Bertram et al., 2001; Cruz and Pandis, 1998; Ellison et al., 1999; Feingold and Chuang, 2002; Moise and

*Corresponding author. Fax: +1-303-492-5894.

E-mail address: vaida@spot.colorado.edu (V. Vaida).

¹Current address: Department of Chemistry, California State University Channel Island, Camarillo, CA 93010.

Rudich, 2000, 2002; Morris et al., 2002; Rudich et al., 2000; Smith et al., 2002; Thomas et al., 2001; Vaida et al., 2000). Recent results suggest that the optical and chemical properties could be affected by chemical processing.

For any organic aerosol, the species present at the particle surface are extremely susceptible to oxidation by atmospheric oxidants, such as OH, halogen atoms, ozone, and nitrogen trioxide (Bertram et al., 2001; Moise and Rudich, 2001, 2002; Morris et al., 2002; Smith et al., 2002). Such oxidative processing may release volatile organic compounds, altering the surface and bulk compositions and size of the aerosol. The size dependence of aerosol ozone processing kinetics and uptake have recently been investigated and shown to have significant consequences to atmospheric radiative transfer (Morris et al., 2002). Oxidation of the hydrophobic organic molecules at the surface of an aerosol has the potential to alter the hygroscopic character of the particle by generating hydrophilic sites, consequently affecting the cloud condensation nucleating (CCN) ability of the particle (Mircea et al., 2002; Prenni et al., 2001; Yu, 2000). Recent work of Demou et al. (2002) has demonstrated that water will condense on a film of organic acid at a lower relative humidity and to a greater extent than it does on a film of alcohol or alkane compounds. Mircea et al. (2002) have also calculated that the supersaturation necessary to activate a particle containing soluble organic compounds is lower than for a pure water aerosol. Finally, the volatile products have the potential to participate in further atmospheric oxidation reactions, giving rise to a net production of HO_x and affecting the balance of atmospheric oxidants (Jaegle et al., 2001).

Recent experiments have focused on the reactivity of surface molecules (Bertram et al., 2001; Moise and Rudich, 2002; Morris et al., 2002; Smith et al., 2002; Wadia et al., 2000) with atmospheric oxidants, adding to the previous body of literature investigating these reaction mechanisms in the gas (Atkinson et al., 1995; Criegee, 1975; Grosjean and Grosjean, 1998; Paulson et al., 1999) and condensed (de Gouw and Lovejoy, 1998; Giamalva et al., 1986; Heath, 1978) phases. Ozone is fairly unreactive towards saturated organic molecules, but acts as a strong oxidant in reactions at unsaturated sites. In this context, processing by ozone of unsaturated sites on model systems for organic aerosols have been performed (Bertram et al., 2001; Moise and Rudich, 2002; Morris et al., 2002; Smith et al., 2002; Wadia et al., 2000) to characterize the oxidation reaction rates and mechanisms. Mechanisms and oxidation reaction rates are being characterized and measured. Elegant experiments have recently been performed to study the processing of surface organic molecules with very reactive atmospheric radicals such as OH, (Bertram et al., 2001) Cl and Br (Moise and Rudich, 2001).

In this paper, we report measurements of ozone oxidation of thin films and aerosols, which are composed of unsaturated organic acids. In this work, we compare the mechanisms for ozonolysis on a thin film to that on aerosols. By performing this experiment using aerosol particles, we have the potential to greatly increase the surface area available for processing over that available to the experiments using organic films and monolayers. We ran two sets of experiments on 2-octenoic acid and 10-undecenoic acid to investigate the effect of substitution on the ozonolysis mechanism. We probed both the gas-phase products as well as the products remaining in the condensed-phase. We have measured a significant change in the chemical composition of both the thin films and the aerosol following ozonolysis, and identified some of the products formed, using FTIR spectroscopy and GC–MS analysis.

2. Experimental methods

2.1. Aerosol flow tube

The experimental setup for the flow tube spectroscopic experiments is shown in Fig. 1. An aerosol sample was generated by flowing filtered N₂ at 3000 sccm through a bubbler containing the liquid organic sample of interest, then directed via a mixing chamber to the atmospheric pressure flow tube. A bypass valve allowed the carrier gas flow to be directed to or diverted away from the bubbler. The bubbler was immersed in an isothermal bath, held between 50°C and 80°C depending on the experiment. This heating was used to create a warm region immediately above the bubbler, and a cool region beyond, ensuring super-saturation and further aiding aerosol formation. In the mixing chamber, a second 500 sccm flow of either O₂ or a mixture of <0.5% O₃ in O₂ was permitted to mix with the aerosol sample prior to entering the cell. The flow reactor/detection cell was a 70 cm long by 7 cm diameter Pyrex cylinder, with o-ring joints at either end for mounting the silver chloride windows. For the given flow conditions, particle exposure time to ozone in the mixing region and flow cell was ~60 s. After passing through the detection cell, the aerosols flowed through a trap containing methanol where the soluble compounds were collected and analyzed using a GC–MS instrument.

Particles were sized using a CLIMET 208A particle analyzer and total particle number densities were obtained using a TSI 3022A CPC counter. The particle diameters were well described by log-normal distributions, with $R = 4.0 \pm 1.0 \mu\text{m}$ and $\sigma = 2.5 \pm 0.5 \mu\text{m}$. The particle distributions used in this work overlap with the coarse-particle mode aerosols that dominate the volume of particles found in the troposphere and represent a more atmospherically relevant surface than those in bulk studies.

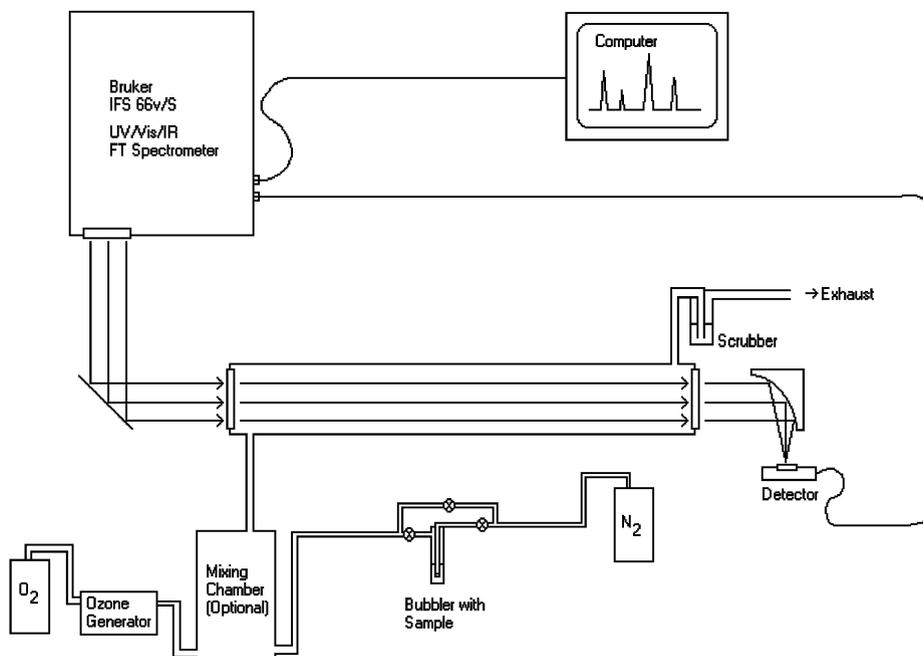


Fig. 1. Schematic of the atmospheric pressure flow reactor with FTIR detection.

2.2. Thin film chamber

The experimental setup used to study the reaction of ozone with a thin organic film consists of a stainless steel chamber, with gas inlets and outlets on one face. The thin films were created by mixing solutions of varying concentrations of the organic compound of interest with hexane and spreading in a Teflon trough, with a surface area of approximately 423 cm². The hexane was allowed to evaporate prior to turning the ozone generator on. Gas-phase products from the reaction were observed spectroscopically with the light from the Bruker IFS passing latitudinally along the cell, a pathlength of 24 cm, through CaF₂ windows, which limited the spectral range for these experiments to approximately 950–8000 cm⁻¹. A 1000 sccm flow of filtered N₂ and a 300 sccm flow of either O₂ or a mixture of <0.5% O₃ in O₂ were flowed through the chamber. A trap containing methanol was placed on the exit line from the chamber to collect any soluble products for subsequent analysis by GC–MS. Products remaining in the trough were collected into methanol after ozonolysis and also run on the GC–MS.

2.3. Materials

The present work used samples of 2-octenoic acid (85%) and 10-undecenoic acid (98%). All compounds were purchased commercially from Aldrich and used without further purification. The dominant impurity in

the 2-octenoic acid was identified via GC–MS as 4-octenoic acid.

A mixture of <0.5% O₃ in O₂ was generated by flowing pure oxygen through an electrostatic ozone generator (Sorbus ESG 001.2). The concentration of ozone was determined by comparing the band strength of the $\nu_1 + \nu_3$ band, centered at approximately 2112 cm⁻¹ to the HITRAN database of known cross sections. Gas flows of O₂ and N₂, used as a carrier gas, were controlled using needle valves and measured with mass flow meters (Gilmont Instruments).

2.4. FTIR spectroscopic setup

Spectroscopic measurements were made using a Bruker IFS 66v/S Fourier transform spectrometer. A silicon carbide globar source was used, with a KBr beamsplitter and a DLATGS detector, providing a spectral range of approximately 500–8000 cm⁻¹. The FTS instrument was used in external mode, with the modulated light beam directed into the cell. Light passed through the cell to a parabolic mirror, which focused it onto the detector.

The experimental procedure consisted of measuring the spectrum of the cell contents before and during the addition of ozone to the mixture. For each spectrum, a total of 100 scans were co-added at a resolution of 4 cm⁻¹ with an approximate sample time of 65 s. Scans with no organic compounds in the chamber were taken

regularly to ensure that there was minimal condensation on the windows of the cell.

2.5. GC–MS analysis

All collected samples from these experiments were analyzed using a commercial GC–MS instrument (Hewlett-Packard 5890) equipped with an HP-5 cross-linked 5% phenyl methyl silicone GC column. The samples were treated by heating the solutions in the presence of hydrochloric acid to 60°C for 15 min. This procedure derivatized any carboxylic acid compound to their methyl esters and aldehyde compounds to an acetal (Drozd, 1981), resulting in more effective recovery and separation on the GC column. The derivatized products were then extracted into hexane and introduced into the GC–MS. The GC column was fixed at 60°C for two minutes and then ramped at 6°C per minute to 250°C. Mass spectra of the compounds separated in the GC were compared to standard libraries (Database, 1992) to identify the species present in the flow tube effluent.

3. Results

3.1. 2-octenoic acid thin film

Fig. 2 shows spectra of a thin film of 2-octenoic acid with the ozone generator off (a) and on (b), respectively.

We are observing the infrared spectra of gas-phase molecules above the film, therefore, the only peaks seen in any of our experiments prior to the ozone generator being turned on, Fig. 2(a), include water (centered at 1600 cm^{-1}), carbon dioxide (centered at 2349 cm^{-1}) and hexane (C–H stretch at 2900 cm^{-1} and C–H bends at 1385 and 1467 cm^{-1}). We can monitor, control, and quantify the concentration of these gas-phase species. In the experiment presented in Fig. 2, the concentration of water vapor was extremely low. The absence of a peak at 1660 cm^{-1} , corresponding to a C=C stretch, confirms that the 2-octenoic acid is in the surface layer and not the gas-phase.

Fig. 2(b) displays the infrared spectrum obtained when the ozone generator was turned on and the organic film was exposed to a mixture of <0.5% O_3 in O_2 . There are significant changes in this spectrum, indicating that the film is being processed and gas-phase products are being released. The most remarkable peaks are those centered at 1105 and 1776 cm^{-1} . Both of these peaks correspond well with a reference spectrum taken of formic acid. Formic acid is expected as a product of this reaction as the Criegee intermediate decomposes. As the reaction proceeds, the carbon dioxide peak centered at 2349 cm^{-1} intensifies, indicating that the reaction is producing CO_2 , also a product from the decomposition of the Criegee intermediate.

After processing, the condensed-phase products were analyzed using the GC–MS procedure. We were able to identify hexanal, hexanoic acid, and butanoic acid.

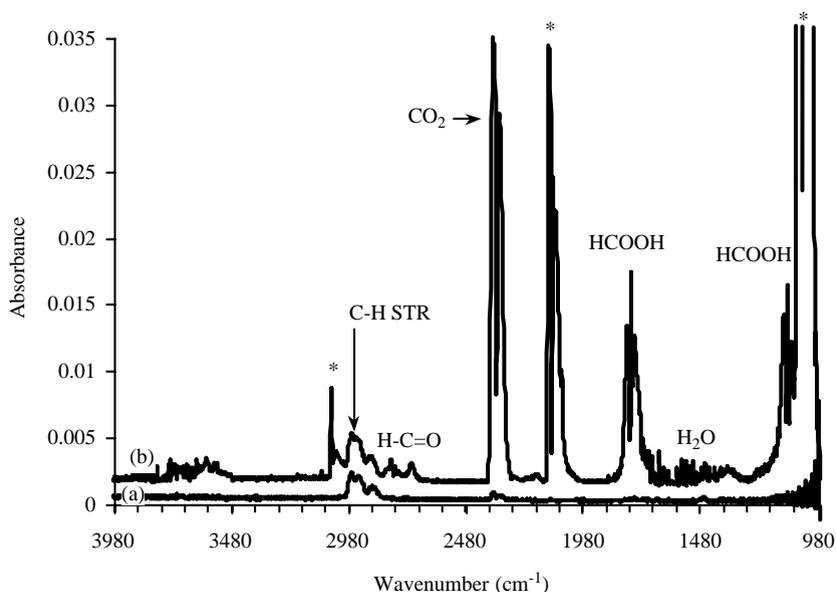


Fig. 2. Infrared spectrum of gas-phase above an unprocessed (a) and a processed (b), offset for clarity, film of 2-octenoic acid, approximately 3000 molecules thick. The bands labeled with * are ozone absorptions. Note the new features at 1745 and 2843 cm^{-1} and the increased intensity of the CO_2 peak.

These compounds, as well as formic acid and carbon dioxide seen in the gas-phase, can all be rationalized as having been formed via ozonolysis of the parent acid compounds, following known mechanisms as shown in Fig. 3. The first step of such reactions produces Criegee intermediates, which may undergo decomposition or

further reactions. This mechanism for the oxidation of 2-octenoic acid is outlined in Fig. 3 and includes pathways to products that are seen in our experiment. The butanoic acid seen by GC–MS would have formed via a similar mechanism by reaction with the 4-octenoic acid impurity.

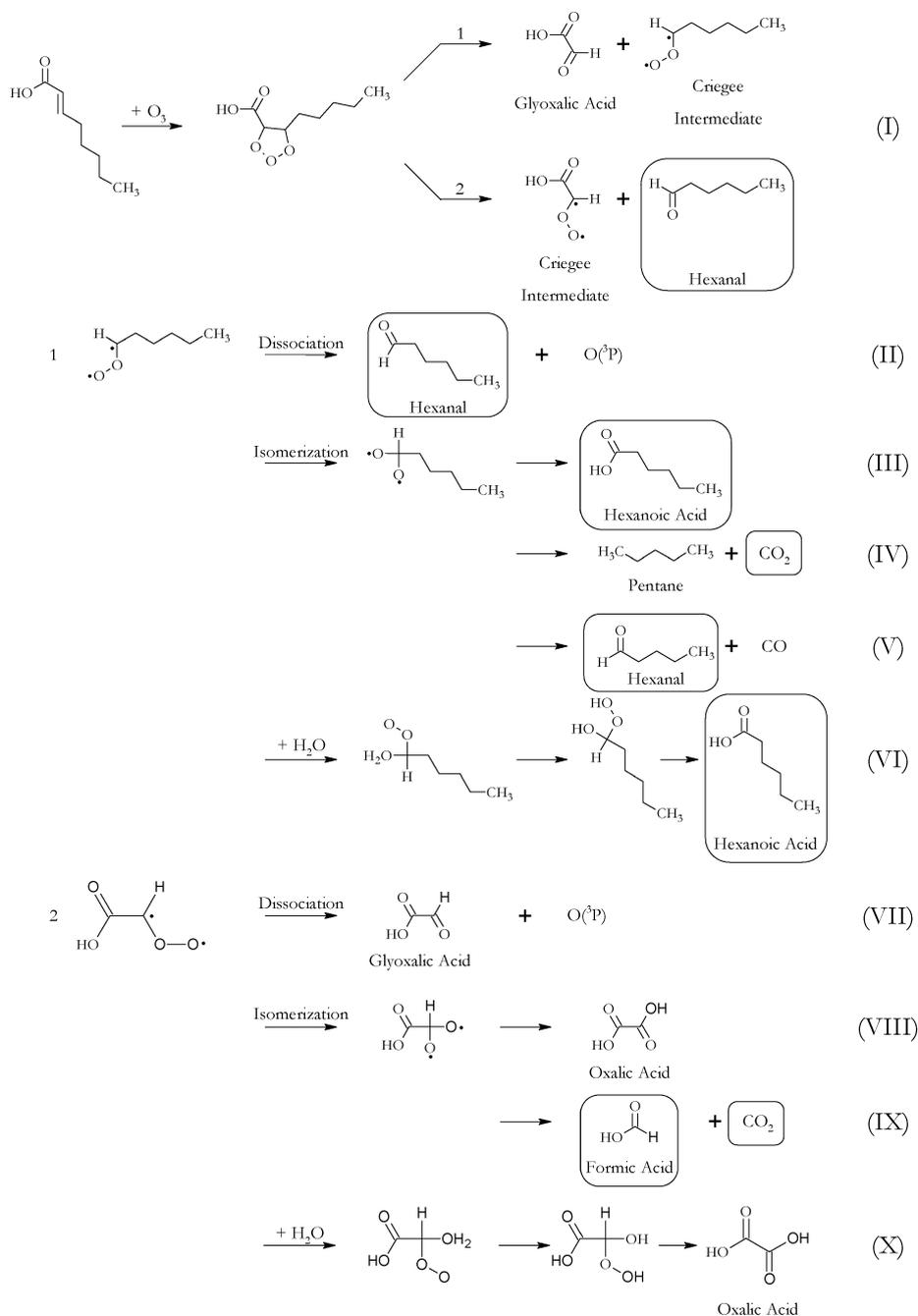


Fig. 3. Reaction mechanism for the oxidation of 2-octenoic acid by reaction with ozone (Bailey, 1978; Criegee, 1975; Wadia et al., 2000). Products in boxes are those seen in our experiments.

3.2. 2-octenoic acid aerosol

Figs. 4(a) and (b) show spectra of 2-octenoic acid aerosols with the ozone generator off and on, respectively. In both figures, there is a characteristic increase in extinction with increasing wavenumber due to light scattering by the particles. The broad liquid phase features of 2-octenoic acid between about 2500 and 3100 cm^{-1} , corresponding to C–H and O–H stretches, are apparent in Fig. 4(a). These features have maxima at 2956, 2929, 2872, and 2858 cm^{-1} that match up with library spectra of the acid. Also clear in the unprocessed sample are the C=O stretch, at 1697 cm^{-1} , and the C=C stretch at 1649 cm^{-1} . The C–H and O–H bends are observed as weak features between 1200 and 1480 cm^{-1} . These have maxima at 1462, 1421, 1306,

1284, and 1230 cm^{-1} ; which also match up well with the library spectrum (Pouchert, 1985) of 2-octenoic acid.

Fig. 4(b) displays the infrared spectrum obtained when the ozone generator was turned on and the organic aerosols were exposed to the mixture of <0.5% O_3 in O_2 . There are dramatic differences between this spectrum and that shown in Fig. 4(a), most notably in the O–H and C=O stretching regions. A broad peak centered around 3396 cm^{-1} is apparent; the broad features seen between about 2500 and 3100 cm^{-1} in the unprocessed spectrum are greatly reduced in intensity. Both the C=O and C=C stretches at 1697 and 1649 cm^{-1} are completely absent in the spectrum measured with ozone present; these are replaced by a new C=O stretch feature, with a maximum at

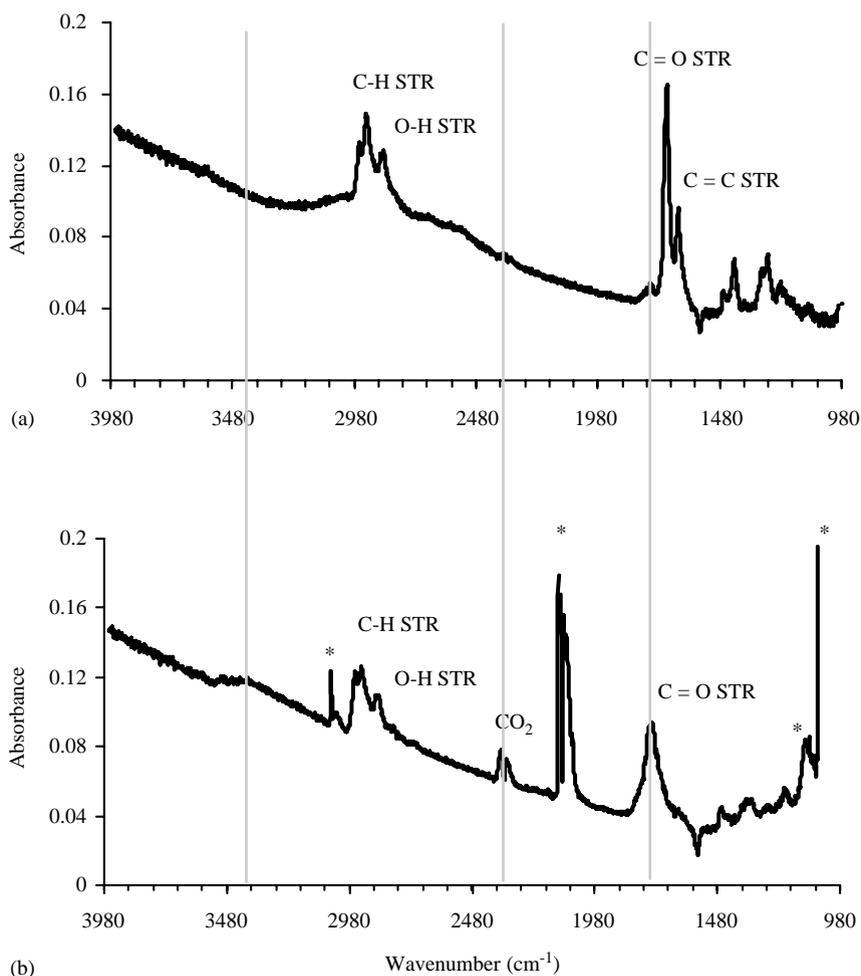


Fig. 4. (a) Infrared spectrum of unprocessed 2-octenoic acid aerosols. The rising baseline with higher wavenumber is due to scattering by the $4.0 \pm 1.0 \mu\text{m}$ diameter particles. The spectrum is similar to that of 2-octenoic acid in the liquid-phase. (b) Infrared spectrum of processed 2-octenoic acid aerosols. The bands labeled with * are ozone absorptions. Note the intense new features near 1759 cm^{-1} and the appearance of CO_2 absorption at 2349 cm^{-1} .

1745 cm^{-1} . The features in Fig. 4(a) lying between 1150 and 1400 cm^{-1} are not observed in the spectrum shown in Fig. 4(b), being replaced by three broad, weakly absorbing peaks at 1468 , 1362 , and 1207 cm^{-1} . The appearance of a new feature at 2349 cm^{-1} indicates that gas-phase carbon dioxide was also formed when ozone was present.

The condensed-phase products collected from the flow cell were then analyzed by GC-MS. The products identified include butanoic acid, hexanoic acid, and hexanal. These products are consistent with the reaction mechanism outlined in Fig. 3 as well as the products identified in the thin film studies.

3.3. 10-undecenoic acid thin film

In an attempt to probe the effect of substitution on the reaction pathways of the Criegee intermediate, we repeated the experiment using 10-undecenoic acid. This molecule has a terminal $\text{C}=\text{C}$ double bond, and is therefore expected to produce formaldehyde as a primary product of ozonolysis. The spectra of a thin film of 10-undecenoic acid before (a) and after (b) being processed by ozone are shown in Fig. 5. Qualitatively, the same general trend is seen as in the 2-octenoic acid thin film experiment. Prior to processing, there is no evidence of any gas-phase compounds except water, carbon dioxide and hexane in the gas phase. After the ozone generator is turned on, Fig. 5(b) shows an increase in the carbon dioxide peaks and a new

peaks at 1745 and 2843 cm^{-1} . As predicted, these new peaks correspond well to a reference spectrum of formaldehyde.

GC-MS analysis of the condensed-phase products after ozonolysis showed nonanoic acid, decanedioic acid, and 10-oxododecanoic acid. These compounds as well as formaldehyde and carbon dioxide can be rationalized from the reaction mechanism for the ozonolysis of 10-undecenoic acid, shown in Fig. 6.

3.4. 10-undecenoic acid aerosol

Fig. 7(a) and (b) show the spectra of 10-undecenoic acid aerosols before and after reaction with ozone, respectively. Qualitatively, the same changes to the spectrum are observed upon exposure to ozone as are seen in the octenoic acid case, with new features appearing in the $\text{O}-\text{H}$ and $\text{C}=\text{O}$ stretch regions. In the unprocessed sample the $\text{C}=\text{O}$ stretch is observed at 1707 cm^{-1} , while the $\text{C}=\text{C}$ stretch is at 1652 cm^{-1} . When the aerosols are processed with ozone, the latter peak ($\text{C}=\text{C}$) is no longer seen, and the $\text{C}=\text{O}$ region displays some structure between 1790 cm^{-1} and about 1720 cm^{-1} , superimposed upon a broader, featureless band. This feature is consistent with the $\text{C}=\text{O}$ stretch vibration of a gas-phase species, superimposed on that of some liquid-phase compound. The gas-phase species may be formaldehyde, which has a strong gas-phase absorption peak at 1746 cm^{-1} . Formaldehyde also has strong absorption peaks at 2843 and 2783 cm^{-1} .

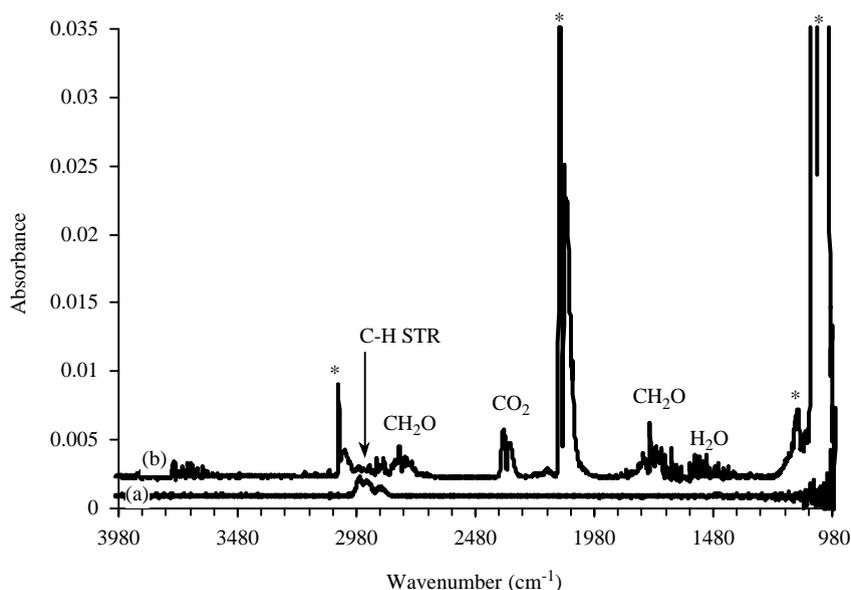


Fig. 5. Infrared spectrum of gas-phase above an unprocessed (a) and a processed (b), offset for clarity, film of 10-undecenoic acid, approximately 100 molecules thick. The bands labeled with * are ozone absorptions. Note the new features at 1745 and 2843 cm^{-1} and the increased intensity of the CO_2 peak.

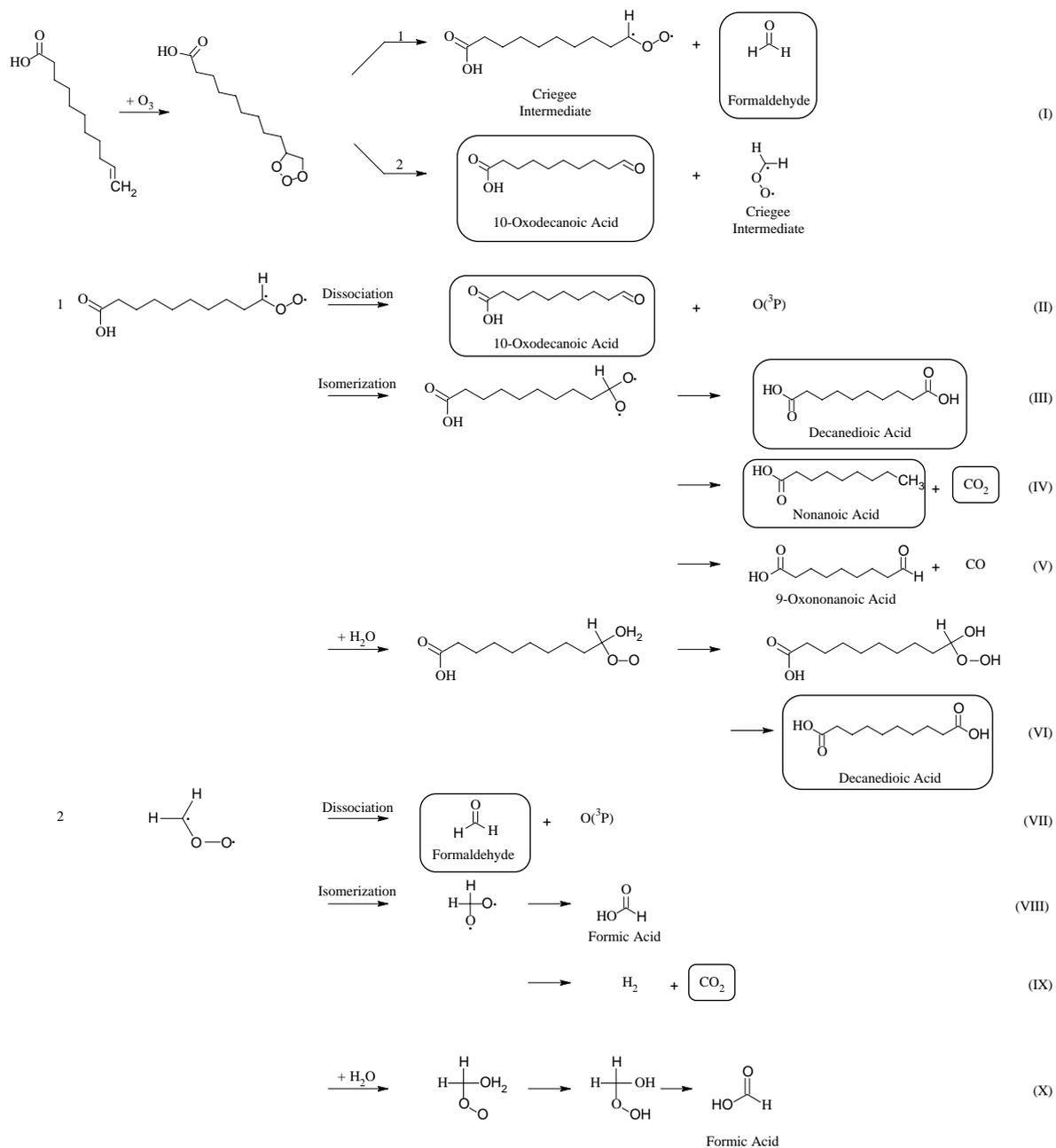


Fig. 6. Reaction mechanism for the oxidation of 10-undecenoic acid by reaction with ozone (Bailey, 1978; Criegee, 1975; Wadia et al., 2000). Products in boxes are those seen in our experiments.

We do observe a new feature near 2783 cm^{-1} , but at 2843 cm^{-1} , there is significant overlap with other features present in the spectrum to not allow a quantitative assignment.

After ozonolysis, the collected aerosols were analyzed by GC-MS. However, no products or parent compounds were detected in any of our trials.

4. Discussion

All of the organic acid films and aerosols discussed above exhibit similar chemistry upon ozonolysis at unsaturated carbon sites. Processing with ozone results in a complete disappearance of parent compound observed in the infrared spectrum of the organic

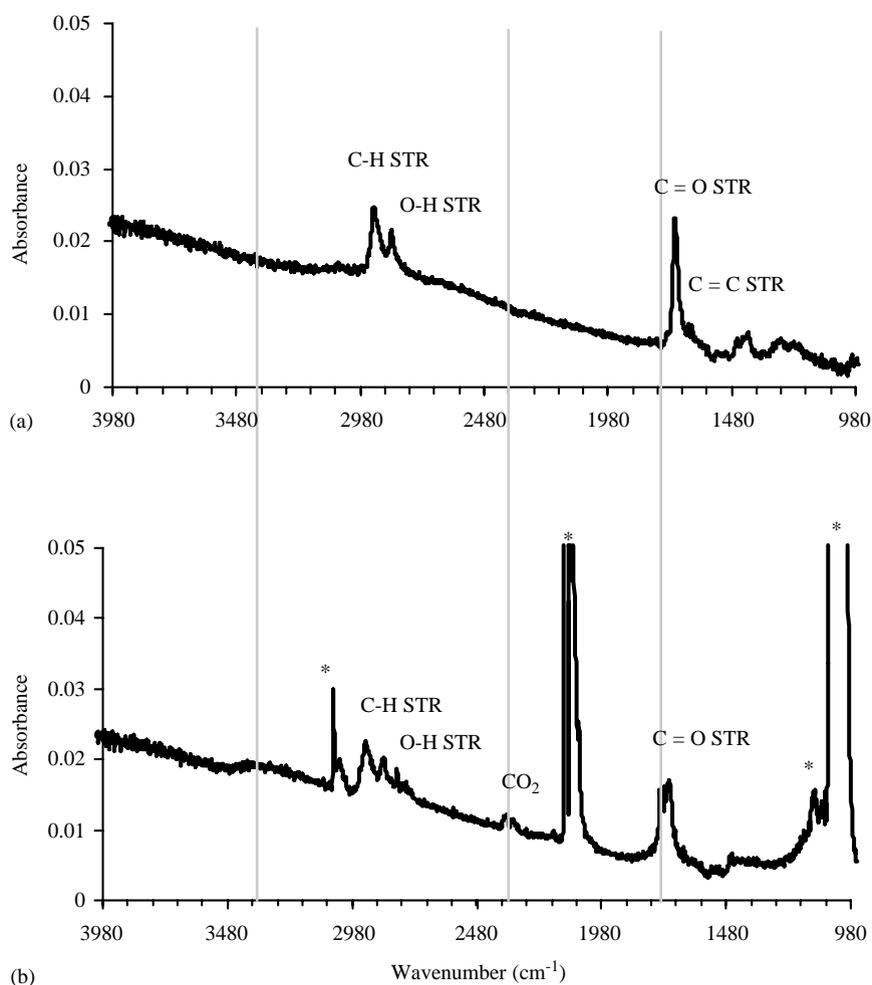


Fig. 7. (a) Infrared spectrum of unprocessed 10-undecenoic acid aerosols. The rising baseline with higher wavenumber is due to scattering by the $4.0 \pm 1.0 \mu\text{m}$ diameter particles. (b) Infrared spectrum of processed 10-undecenoic acid aerosols. The bands labeled with a * are ozone absorptions. Note the large changes in the C=O stretching region, the C–H and O–H stretching regions and the appearance of CO₂ in this figure as compared to Fig. 7(a).

aerosols and in post-reaction mass spectral analysis. The thin film and aerosol studies give similar chemical results. However, as anticipated, the infrared spectra of the aerosols ride on a Mie scattering background governed by the approximately $4 \mu\text{m}$ size of the aerosols generated.

The reaction between 2- and 4-octenoic acids and ozone produces shorter chain carboxylic acids, including hexanoic acid and butanoic acid, and an aldehyde, hexanal, consistent with ozone attack at the unsaturated site and subsequent reaction of both potential Criegee intermediates formed in this primary step (see Fig. 3).

Consistent with ozone attack at the double bond, and the greater stabilization of the more substituted Criegee intermediate, the primary gas-phase products seen in the reaction of 10-undecenoic acid are formaldehyde and carbon dioxide (see Fig. 6). Both Criegee intermediates

then undergo subsequent reactions, leading to the less volatile products seen in the gas chromatogram, including nonanoic acid, decanedioic acid, and 10-oxodecanoic acid.

These results suggest that atmospheric aerosols may indeed be subject to facile oxidative processing by ozone. In the present experiment, processing of unsaturated acids by ozone leads to the appearance of oxidized, hydrophilic, and more volatile product compounds. These results are consistent with recent studies published in the literature of the ozonolysis reactions with unsaturated sites on a surface (Bertram et al., 2001; Moise and Rudich, 2002; Morris et al., 2002; Smith et al., 2002; Wadia et al., 2000). Elegant studies by Wadia et al. (2000) studied the ozonolysis reaction at the air–water interface and found that there is an enhanced kinetic effect in this environment compared to the gas-phase.

The kinetic studies of Morris et al. (2002) and Smith et al. (2002) analyzed the ozone reaction on aerosols of oleic acid and concluded that the reaction would alter the size of the aerosol particles and also be dependent on the diffusivity of oleic acid to the surface of the aerosol.

The presence of water could significantly affect the distribution of products resulting from ozonolysis of alkenes. It has been shown (Glasius et al., 2000; Neeb et al., 1997) that the decomposition of the Criegee intermediate to a carboxylic acid is a minor pathway without the help of water (Steps III and VIII on Figs. 3 and 6). In these studies, we have attempted to minimize the water vapor, but a trace cannot be avoided since we are working under ambient conditions. Further experiments need to be run to determine if the hydroperoxy compound (Steps VI and X in Fig. 6) is stable and therefore remains intact until we inject it onto the GC–MS column where these compounds are known to readily degrade, or if this decomposition to the carboxylic acid is accomplished in situ. For the 10-undecenoic acid experiments, we see evidence of the diacid (Steps III, VI, VIII and X in Fig. 6) which would result from in situ reactions as well as the oxoacid which is the degradation product resulting from reaction in the GC column. However, we have also run these experiments with the presence of water vapor and we see no differences in the chemical mechanisms, suggesting that at atmospheric conditions, hydrolysis of the Criegee intermediate occurs even at low relative humidity.

5. Atmospheric implications and conclusions

Processing of organics by gas-phase radicals in the atmosphere will be dominated by hydroxyl radical chemistry. The hydroxyl radical has a high rate for hydrogen abstraction from even the most stable, saturated alkanes (Bertram et al., 2001). It reacts with alkenes by a mechanism involving the addition of OH to the C=C double bond. Organic compounds found on aerosols, especially marine aerosols, contain a significant number of unsaturated sites (Gershey, 1983; Hoffman and Duce, 1976; Lion and Leckie, 1981; Tseng et al., 1992). For example, recent field measurements found oleic acid to constitute surface films on a significant fraction of marine aerosols (Rogge et al., 1991; Tervahattu et al., 2002a, b). In addition, urban aerosols have been found to contain organic compounds with carbon chains as long as 34 carbons and varying degrees of unsaturation (Finlayson-Pitts and Pitts, 2000; George et al., 1999; Seinfeld and Pandis, 1998).

We anticipate that given the strong diurnal cycle of OH, processing of organic aerosols by ozone will be important at nighttime and, depending on the relative abundances of ozone and OH, during the day in some locations. In polluted urban sites exemplified by Los

Angeles, OH could be $4\text{--}6 \times 10^6$ molecules/cm³ while ozone has been measured at about $8\text{--}12 \times 10^9$ molecules/cm³ (George et al., 1999). In a clean site such as Tasmania, OH concentrations were measured in the vicinity of $2\text{--}4 \times 10^6$ molecules/cm³ and ozone's concentration is 2×10^9 (Frost et al., 1999; Suhre et al., 1998). In the past year, rates of OH processing of saturated sites on organic molecules have been made available and are very fast. The reactivity of unsaturated sites at a surface to OH has yet to be measured. Even allowing for much faster reactions for OH addition to C=C double bonds, processing by ozone will contribute significantly to the oxidation of organics in the atmosphere.

Several recent experiments have measured the reactive uptake probability (γ) of ozone by oleic acid to be on the order of 10^{-3} (Moise and Rudich, 2002; Morris et al., 2002). The reaction probability of OH at an unsaturated site in an organic film is not available to our knowledge. However, in an elegant set of recent experiments, the reaction probability for saturated organic surfaces with OH were measured to be greater than 0.1 (Bertram et al., 2001). With an almost collisional reaction rate, there should be no preference of the OH reaction at the unsaturated site. Consequently, processing by OH may still allow everything but a terminal double bond to have a significant atmospheric lifetime; for example, atmospheric measurements imply that oleic acid molecules have a lifetime on the order of days (Rogge et al., 1991). Processing with OH is at least two orders of magnitude more efficient than processing by ozone. However, various tropospheric scenarios show that the concentration of OH is three orders of magnitude less than that of ozone. This comparison suggests that processing by ozone could be competitive during the day as well as the nighttime.

Chemical processing is expected to have several consequences on the atmospheric radiative transfer. Our studies and other recent experiments show that oxidation of organic films, which could be proxies for the surface of aerosols, will alter the CCN abilities of aerosol particles since the more highly oxidized surface should act as a more effective site for water condensation (Demou et al., 2002; Mircea et al., 2002; Prenni et al., 2001; Rudich et al., 2000). We observed the formation of butanoic and hexanoic acids on processing of 2- and 4-octenoic acids, which could either remain at the surface or be released into the gas-phase. For the longer-chain, 10-undecenoic acid, we observed the formation of compounds with two terminal oxygenated functional groups, including 10-decanedioic acid, thereby exposing a carboxylic acid group to the atmosphere. Chromophores capable of hydrogen bonding have been shown to be more effective at nucleating water than the homogeneous nucleation of water (Aloisio et al., 2002; Cruz and Pandis, 1997; Mmereki and Donaldson, 2002). Our studies have also shown that processing of the

aerosol surface results in the formation of volatile product species such as formaldehyde and formic acid; thereby diminishing the size of the aerosol particle. Therefore, the manner in which aerosol size distributions are altered as a consequence of processing will depend sensitively on the local relative humidity.

Chemical processing will have consequences to atmospheric chemistry as these reactions can give rise to HO_x by the gas-phase oxidation of volatile product compounds (Jaegle et al., 2001). Local oxidation and ozone chemistry could thus be altered by the addition of this excess HO_x. Since aerosol particles are subject to long range vertical transport, their processing in the upper troposphere could be responsible for the appearance of partially oxidized compounds there, and ultimately could play a role in explaining the discrepancies between modeled and observed ozone levels.

Acknowledgements

This work was funded by the National Science Foundation and an innovative research grant from CIRES (University of Colorado). SA thanks the Camille and Henry Dreyfus Foundation for financial support. DJD acknowledges ongoing financial support from NSERC, and thanks CIRES for the award of a Visiting Fellowship. We thank Professor GB Ellison for discussion of the chemical processes involved.

References

- Aloisio, S., Hintze, P.E., Vaida, V., 2002. The hydration of formic acid. *Journal of Physical Chemistry A* 106 (2), 363–370.
- Atkinson, R., Tuazon, E.C., Aschmann, S.M., 1995. Products of the gas-phase reactions of *o*-3 with alkenes. *Environmental Science and Technology* 29 (7), 1860–1866.
- Bailey, P.S., 1978. *Ozonation in Organic Chemistry*, Vol. I. Academic Press, New York.
- Barnes, G.T., 1986. The effects of monolayers on the evaporation of liquids. *Advances in Colloid and Interface Science* 25 (2), 89–200.
- Bertram, A.K., Ivanov, A.V., Hunter, M., Molina, L.T., Molina, M.J., 2001. The reaction probability of oh on organic surfaces of tropospheric interest. *Journal of Physical Chemistry A* 105 (41), 9415–9421.
- Criegee, R., 1975. Mechanism of ozonolysis. *Angewandte Chemie (International Edition in English)* 14 (11), 745–752.
- Cruz, C.N., Pandis, S.N., 1997. A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei. *Atmospheric Environment* 31 (15), 2205–2214.
- Cruz, C.N., Pandis, S.N., 1998. The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol. *Journal of Geophysical Research-Atmospheres* 103 (D11), 13111–13123.
- Database, N.E.N.M.S., 1992. Standard reference database 1, Gaithersburg.
- de Gouw, J.A., Lovejoy, E.R., 1998. Reactive uptake of ozone by liquid organic compounds. *Geophysical Research Letters* 25 (6), 931–934.
- Demou, E., Visram, H., Makar, P., Donaldson, D.J., 2002, in press.
- Droz, J., 1981. Chemical derivatization in gas chromatography. *Journal of Chromatography Library*, 19.
- Ellison, G.B., Tuck, A.F., Vaida, V., 1999. Atmospheric processing of organic aerosols. *Journal of Geophysical Research-Atmospheres* 104 (D9), 11633–11641.
- Feingold, G., Chuang, P.Y., 2002. Analysis of the influence of film-forming compounds on droplet growth: implications for cloud microphysical processes and climate. *Journal of the Atmospheric Sciences* 59 (12), 2006–2018.
- Finlayson-Pitts, B.J., Pitts, J.J.N., 2000. *Chemistry of the Upper and Lower Atmosphere*. Academic Press, San Diego.
- Frost, G.J., Trainer, M., Mauldin, R.L., Eisele, F.L., Prevot, A.S.H., Flocke, S.J., Madronich, S., Kok, G., Schillawski, R.D., Baumgardner, D., Bradshaw, J., 1999. Photochemical modeling of oh levels during the first aerosol characterization experiment (ace 1). *Journal of Geophysical Research-Atmospheres* 104 (D13), 16041–16052.
- Garrett, W.D., 1971. Retardation of water drop evaporation with monomolecular surface films. *Journal of the Atmospheric Sciences* 28 (5), 816–819.
- George, L.A., Hard, T.M., O'Brien, R.J., 1999. Measurement of free radicals oh and ho₂ in Los Angeles smog. *Journal of Geophysical Research-Atmospheres* 104 (D9), 11643–11655.
- Gershey, R.M., 1983. Characterization of seawater organic-matter carried by bubble-generated aerosols. *Limnology and Oceanography* 28 (2), 309–319.
- Giamalva, D.H., Church, D.F., Pryor, W.A., 1986. Kinetics of ozonation 4. Reactions of ozone with alpha-tocopherol and oleate and linoleate esters in carbon-tetrachloride and in aqueous micellar solvents. *Journal of the American Chemical Society* 108 (21), 6646–66651.
- Glasiu, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N.R., Hjorth, J., Kotzias, D., Larsen, B.R., 2000. Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone. *Environmental Science and Technology* 34 (6), 1001–1010.
- Grosjean, E., Grosjean, D., 1998. Rate constants for the gas-phase reaction of ozone with unsaturated oxygenates. *International Journal of Chemical Kinetics* 30 (1), 21–29.
- Heath, R.L., 1978. Reaction stoichiometry between ozone and unsaturated fatty-acids in an aqueous environment. *Chemistry and Physics of Lipids* 22 (1), 25–37.
- Hoffman, E.J., Duce, R.A., 1976. Factors influencing organic-carbon content of marine aerosols - laboratory study. *Journal of Geophysical Research-Oceans and Atmospheres* 81 (21), 3667–3670.
- Husar, R.B., Shu, W.R., 1975. Thermal analyses of Los-Angeles smog aerosol. *Journal of Applied Meteorology* 14 (8), 1558–1565.
- Jaegle, L., Jacob, D.J., Brune, W.H., Wennberg, P.O., 2001. Chemistry of hox radicals in the upper troposphere. *Atmospheric Environment* 35 (3), 469–489.

- Lion, L.W., Leckie, J.O., 1981. The biogeochemistry of the air–sea interface. *Annual Review of Earth and Planetary Sciences* 9, 449–486.
- Matsumoto, K., Tanaka, H., Nagao, I., Ishizaka, Y., 1997. Contribution of particulate sulfate and organic carbon to cloud condensation nuclei in the marine atmosphere. *Geophysical Research Letters* 24 (6), 655–658.
- McNamee, C.E., Barnes, G.T., Gentle, I.R., Peng, J.B., Steitz, R., Probert, R., 1998. The evaporation resistance of mixed monolayers of octadecanol and cholesterol. *Journal of Colloid and Interface Science* 207 (2), 258–263.
- Middlebrook, A.M., Murphy, D.M., Thomson, D.S., 1998. Observations of organic material in individual marine particles at cape grim during the first aerosol characterization experiment (ace 1). *Journal of Geophysical Research-Atmospheres* 103 (D13), 16475–16483.
- Mircea, M., Facchini, M.C., Decesari, S., Fuzzi, S., Charlson, R.J., 2002. The influence of the organic aerosol component on ccn supersaturation spectra for different aerosol types. *Tellus Series B-Chemical and Physical Meteorology* 54 (1), 74–81.
- Mmerekki, B.T., Donaldson, D.J., 2002. Ab-initio and density functional theory study of complexes between the methyl amines and water. *Journal of Physical Chemistry A* 106, 3185–3190.
- Moise, T., Rudich, Y., 2000. Reactive uptake of ozone by proxies for organic aerosols: surface versus bulk processes. *Journal of Geophysical Research-Atmospheres* 105 (D11), 14667–14676.
- Moise, T., Rudich, Y., 2001. Uptake of cl and br by organic surfaces - a perspective on organic aerosols processing by tropospheric oxidants. *Geophysical Research Letters* 28 (21), 4083–4086.
- Moise, T., Rudich, Y., 2002. Reactive uptake of ozone by aerosol-associated unsaturated fatty acids: kinetics, mechanism, and products. *Journal of Physical Chemistry A* 106 (27), 6469–6476.
- Morris, J.W., Davidovits, P., Jayne, J.T., Jimenez, J.L., Shi, Q., Kolb, C.E., Worsnop, D.R., Barney, W.S., Cass, G., 2002. Kinetics of submicron oleic acid aerosols with ozone; a novel aerosol mass spectrometric technique. *Geographical Research Letters* 29 (9), article no. 1357.
- Murphy, D.M., Thomson, D.S., Mahoney, T.M.J., 1998a. In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 km. *Science* 282 (5394), 1664–1669.
- Murphy, D.M., Thomson, D.S., Middlebrook, A.M., Schein, M.E., 1998b. In situ single-particle characterization at cape grim. *Journal of Geophysical Research-Atmospheres* 103 (D13), 16485–16491.
- Neeb, P., Sauer, F., Horie, O., Moortgat, G.K., 1997. Formation of hydroxymethyl hydroperoxide and formic acid in alkene ozonolysis in the presence of water vapour. *Atmospheric Environment* 31 (10), 1417–1423.
- Novakov, T., Corrigan, C.E., Penner, J.E., Chuang, C.C., Rosario, O., Bracero, O.L.M., 1997a. Organic aerosols in the Caribbean trade winds: a natural source? *Journal of Geophysical Research-Atmospheres* 102 (D17), 21307–21313.
- Novakov, T., Hegg, D.A., Hobbs, P.V., 1997b. Airborne measurements of carbonaceous aerosols on the east coast of the United States. *Journal of Geophysical Research-Atmospheres* 102 (D25), 30023–30030.
- Novakov, T., Penner, J.E., 1993. Large contribution of organic aerosols to cloud-condensation- nuclei concentrations. *Nature* 365 (6449), 823–826.
- Otani, Y., Wang, C.S., 1984. Growth and deposition of saline droplets covered with a monolayer of surfactant. *Aerosol Science and Technology* 3 (2), 155–166.
- Paulson, S.E., Chung, M.Y., Hasson, A.S., 1999. Oh radical formation from the gas-phase reaction of ozone with terminal alkenes and the relationship between structure and mechanism. *Journal of Physical Chemistry A* 103 (41), 8125–8138.
- Pouchert, C.J. (Ed.), 1985. *The Aldrich Library of FT-IR Spectra*, Vol. I. Aldrich Chemical Company, Milwaukee.
- Prenni, A.J., DeMott, P.J., Kreidenweis, S.M., Sherman, D.E., Russell, L.M., Ming, Y., 2001. The effects of low molecular weight dicarboxylic acids on cloud formation. *Journal of Physical Chemistry A* 105 (50), 11240–11248.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simonelt, B.R.T., 1991. Sources of fine organic aerosol. I. Charbroilers and meat cooking operations. *Environmental Science and Technology* 25 (6), 1112–11125.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simoneit, B.R.T., 1993. Quantification of urban organic aerosols at a molecular-level - identification, abundance and seasonal-variation. *Atmospheric Environment Part A-General Topics* 27 (8), 1309–1330.
- Rudich, Y., Benjamin, I., Naaman, R., Thomas, E., Trakhtenberg, S., Ussyshkin, R., 2000. Wetting of hydrophobic organic surfaces and its implications to organic aerosols in the atmosphere. *Journal of Physical Chemistry A* 104 (22), 5238–5245.
- Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric Chemistry and Physics*. Wiley-Interscience, New York.
- Smith, G.D., Woods III, E., DeForest, C.L., Baer, T., Miller, R.E., 2002. Reactive uptake of ozone by oleic acid aerosol particles: application of single-particle mass spectrometry to heterogeneous reaction kinetics. *Journal of Physical Chemistry A* 106(35), 8085–8095.
- Suhre, K., Mari, C., Bates, T.S., Johnson, J.E., Rosset, R., Wang, Q., Bandy, A.R., Blake, D.R., Businger, S., Eisele, F.L., Huebert, B.J., Kok, G.L., Mauldin, R.L., Prevot, A.S.H., Schillawski, R.D., Tanner, D.J., Thornton, D.C., 1998. Physico-chemical modeling of the first aerosol characterization experiment (ace 1) Lagrangian b-1. A moving column approach. *Journal of Geophysical Research-Atmospheres* 103 (D13), 16433–16455.
- Tervahattu, H., Hartonen, K., Kerminen, V.M., Kupiainen, K., Aarnio, P., Koskentalo, T., Tuck, A.F., Vaida, V., 2002a. New evidence of an organic layer on marine aerosols. *Journal of Geophysical Research-Atmospheres* 107 (D7), 10 1029/2000JD000282.
- Tervahattu, H., Juhanoja, J., Kupiainen, K., 2002b. Identification of an organic coating on marine aerosol particles by tof-sims. *Journal of Geophysical Research-Atmospheres* 107 (D16), 10 1029/2001JD001403.
- Thomas, E.R., Frost, G.J., Rudich, Y., 2001. Reactive uptake of ozone by proxies for organic aerosols: surface-bound and gas-phase products. *Journal of Geophysical Research-Atmospheres* 106 (D3), 3045–3056.

- Tseng, R.S., Viechnicki, J.T., Skop, R.A., Brown, J.W., 1992. Sea-to-air transfer of surface-active organic-compounds by bursting bubbles. *Journal of Geophysical Research-Oceans* 97 (C4), 5201–5206.
- Vaida, V., Tuck, A.F., Ellison, G.B., 2000. Optical and chemical properties of atmospheric organic aerosols. *Physics and Chemistry of the Earth Part C-Solar-Terrestrial and Planetary Science* 25 (3), 195–198.
- Wadia, Y., Tobias, D.J., Stafford, R., Finlayson-Pitts, B.J., 2000. Real-time monitoring of the kinetics and gas-phase products of the reaction of ozone with an unsaturated phospholipid at the air–water interface. *Langmuir* 16 (24), 9321–9330.
- Xiong, J.Q., Zhong, M.H., Fang, C.P., Chen, L.C., Lippmann, M., 1998. Influence of organic films on the hygroscopicity of ultrafine sulfuric acid aerosol. *Environmental Science and Technology* 32 (22), 3536–3541.
- Yu, S.C., 2000. Role of organic acids (formic, acetic, pyruvic and oxalic) in the formation of cloud condensation nuclei (ccn): a review. *Atmospheric Research* 53 (4), 185–217.