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PAPER

The effect of humidity on the ozonolysis of unsaturated compounds in aerosol particles

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Atmospheric aerosol particles are important in many atmospheric processes such as: light scattering, light absorption, and cloud formation. Oxidation reactions continuously change the chemical composition of aerosol particles, especially the organic mass component, which is often the dominant fraction. These ageing processes are poorly understood but are known to significantly affect the cloud formation potential of aerosol particles. In this study we investigate the effect of humidity and ozone on the chemical composition of two model organic aerosol systems: oleic acid and arachidonic acid. These two acids are also compared to maleic acid an aerosol system we have previously studied using the same techniques. The role of relative humidity in the oxidation scheme of the three carboxylic acids is very compound specific. Relative humidity was observed to have a major influence on the oxidation scheme of maleic acid and arachidonic acid, whereas no dependence was observed for the oxidation of oleic acid. In both, maleic acid and arachidonic acid, an evaporation of volatile oxidation products could only be observed when the particle was exposed to high relative humidities. The particle phase has a strong effect on the particle processing and the effect of water on the oxidation processes. Oleic acid is liquid under all conditions at room temperature (dry or elevated humidity, pure or oxidized particle). Thus ozone can easily diffuse into the bulk of the particle irrespective of the oxidation conditions. In addition, water does not influence the oxidation reactions of oleic acid particles, which is partly explained by the structure of oxidation intermediates. The low water solubility of oleic acid and its ozonolysis products limits the effect of water. This is very different for maleic and arachidonic acid, which change their phase from liquid to solid upon oxidation or upon changes in humidity. In a solid particle the reactions of ozone and water with the organic particle are restricted to the particle surface and hence different regimes of reactivity are dictated by particle phase. The potential relevance of these three model systems to mimic ambient atmospheric processes is discussed.

Introduction

Aerosol particles significantly affect the radiative budget of the Earth by directly absorbing and scattering light and indirectly through processes such as cloud formation. All these effects depend on the chemical composition of the aerosol particles which are often very poorly understood. Organic compounds are a dominant fraction of ambient aerosols and a significant fraction, up to 10%, of the organic mass is composed of carboxylic acids.[1,2] The dominant source of these species is formation in the atmosphere through oxidation reactions. They are also directly emitted into the atmosphere. Many organic acids are highly water-soluble and thus this compound class is important for the water solubility of a particle and their ability to act as cloud condensation nuclei.

In recent years it has become evident that particle phase organic reactions play an important role in the chemical transformation of atmospheric aerosols.[3,4] The effect of these reactions on atmospherically relevant particle properties such as water uptake and cloud formation potential is largely unknown. A number of model aerosol systems have been used to elucidate these particle phase reactions in an oxidizing atmosphere. Model particle systems composed of unsaturated compounds such as oleic acid exposed to ozone have been used

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frequently as reviewed by Zahardis and Petrucci.[5] An important aspect of oleic acid oxidation is the formation of oligomers and many authors investigated the structure and possible monomeric building blocks of these oligomers.[6–9]

Ozonolysis reactions of other unsaturated carboxylic acids such as maleic acid, arachidonic acid, linoleic acid and linolenic acid have been investigated as model systems for organic aerosols, and changes in particle mass, hygroscopicity, morphology and chemical composition were observed.[10–18]

In two recent studies we investigated the effect of ozonolysis on maleic acid particles, with respect to hygroscopicity and chemical composition using a aerosol flow tube mass spectrometry apparatus and an electrodynamic balance (EDB).[10,11] Very different oxidation products were found for maleic acid when compared to oleic acid oxidation products described in the literature, and a comprehensive reaction scheme was presented to account for the observed reaction products of maleic acid. Significant differences in the oxidation scheme under dry and humid conditions were observed, which agreed well with the hygroscopic growth measurements observed in the EDB. Ozonolysis reactions performed above about 50% relative humidity (RH) resulted in much higher reaction turnover and water uptake than under low humidity conditions.

In the study presented here we compare three different organic aerosol model systems: maleic acid, oleic acid and arachidonic acid (Fig. 1a). The effect of ozone on the particle mass and the influence of water on the reaction scheme are investigated. We present a generalized reaction scheme accounting for various aspects of particle phase alkene reactivity to ozone.

Experimental

Electrodynamic balance

An electrodynamic balance (EDB) was used to levitate and measure the mass of single particles, which contain a net charge, within a synthetic air environment at 295 K. The EDB design follows the double ring electrode architecture of Davis *et al.*,[19] and a detailed description of the apparatus has been given previously.[20,21] Briefly, the changing mass of a particle can be followed by observing the electric force, which is required to balance the weight of the particle. The levitated particle is imaged with a CCD camera that is focused on the position of the balance point.

Elastic Mie scattering is used to measure the diameter of the liquid phase (spherical) particles. The technique is described in detail elsewhere.[21] Briefly, a continuous-wave 632 nm HeNe laser (Thorlabs HRP170) is directed at the levitated particle. The resulting fringe pattern of the scattered light, detected on

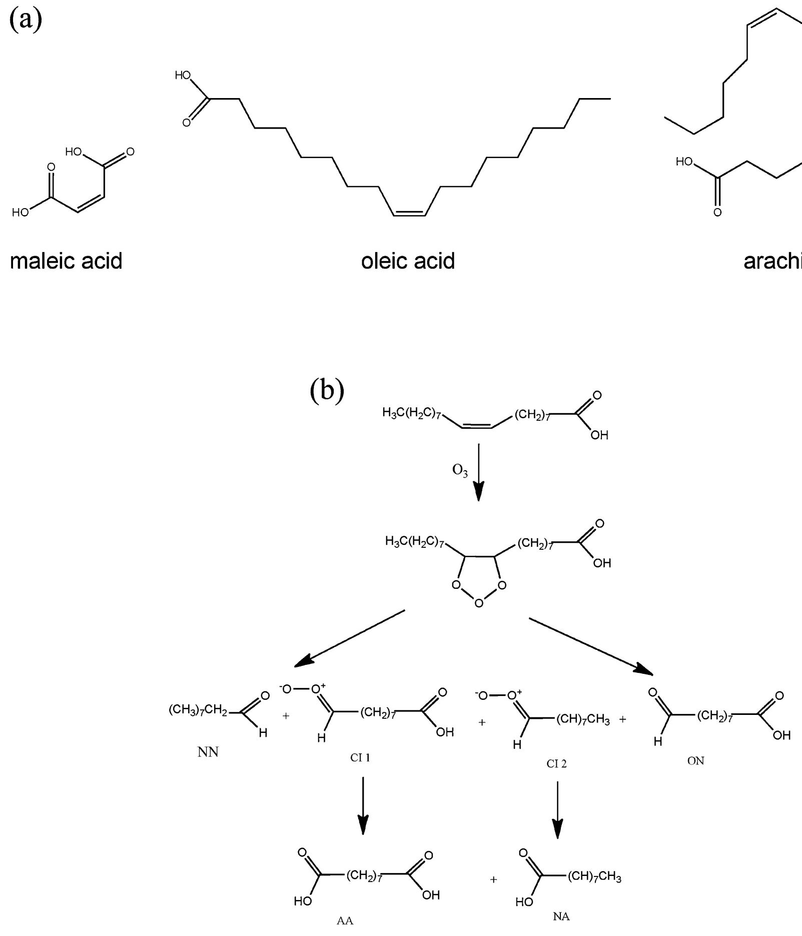

Fig. 1 Structure of maleic acid, oleic acid and arachidonic acid, the three organic aerosol model systems investigated in this study (a) and the initial steps of oleic acid oxidation (b). NN: nonanal, ON: 9-oxo-nonanoic acid, AA: azelaic acid, NA: nonanoic acid, CI1 and CI2: Criegee intermediates.

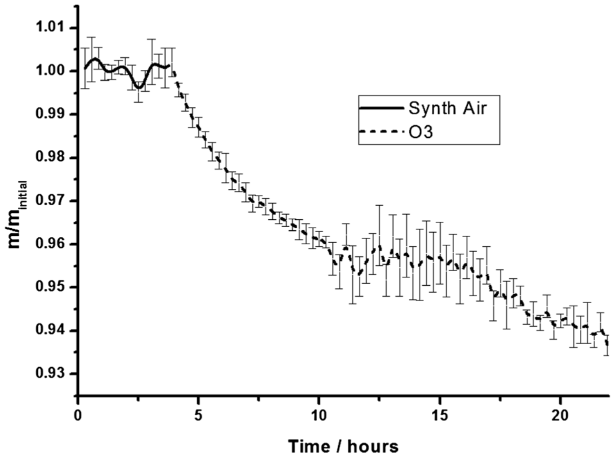

Fig. 2 The mass of an oleic acid particle in the EDB is decreasing (*i.e.*, compounds are evaporating) after addition of ozone (dashed line, ozone continuously present) while a stable mass is observed when no ozone is present (solid line).

a photodiode array (Hamamatsu H5783), is used to determine the non-absorbing particle size using a geometric optics method that approximates the Mie scattering pattern.[22]

Ozone was generated by flowing synthetic air past a 185 nm UV light source (Appleton Woods) resulting in an ozone concentration of about 2 ppm for oleic acid and 62 ppm for arachidonic acid in the EDB. The ozone concentration at the particle position within the EDB was measured before and after an experiment using a commercial ozone analyzer (Thermo Scientific 49i).

Oleic acid and arachidonic acid particles were generated from a methanol solution, and were directed into the EDB using a converted ink jet cartridge (HP, model 51612A), generating particles with a radius of about 10–20 μm. The high volatility and inertness of methanol caused the particle to rapidly evaporate leaving the desired pure substance. Repeated NMR studies, over four weeks, of the arachidonic acid and methanol solution revealed negligible difference in the composition of the solution. However, it should be noted that a previous flow tube study, with a residence time of ~20 s, by Broekhuizen *et al.* did observe a difference in the ability of oleic acid to act as cloud condensation nuclei when it had been prepared as a methanol solution.[23] In our EDB experiments the arachidonic and oleic acid particles were exposed to a constant flow of dry synthetic air for at least three hours (Fig. 2 and 3) before ozone was added to the EDB. The much longer residence times of the EDB experiments should ensure complete evaporation of the methanol.

The RH of the cell was controlled by varying the ratio of dry and water-saturated air flows that were combined and passed into the EDB chamber. Maleic acid data obtained in an earlier study are used here for comparison.[11]

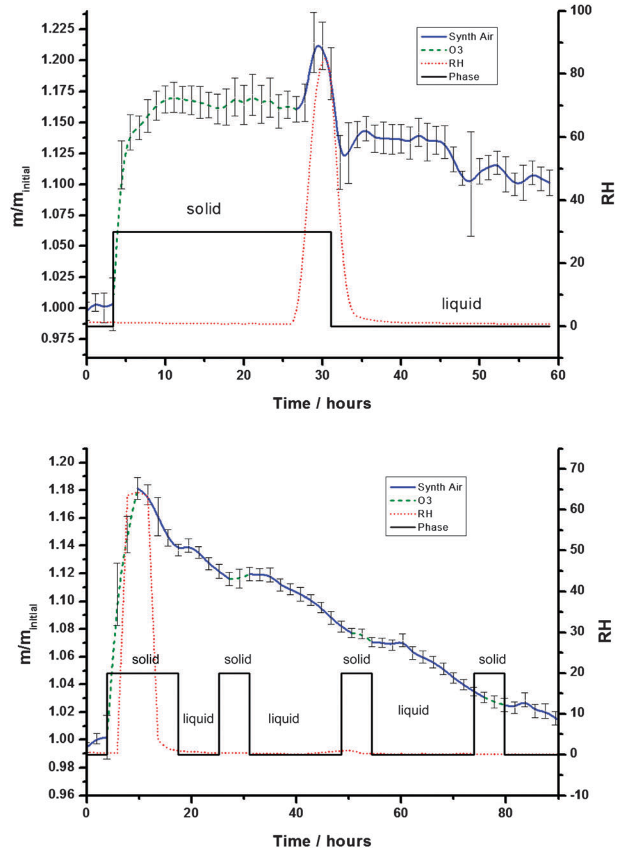

Fig. 3 (a) The mass (m) of an arachidonic acid particle measured in the EDB increases strongly after addition of ozone under dry conditions at 20 °C. Evaporation is only observed after the particle is exposed to high humidity. Pure arachidonic acid is liquid at room temperature. Upon oxidation the particle changes phase rapidly and is dissolved again upon deliquescence. (b) Phase change form liquid to solid can be induced repeatedly upon exposure to ozone. Experiment performed at 30 °C. Lines: Red line, right *y*-axis—relative humidity. Green line—particle mass with ozone present. Blue line—particle mass with no ozone present. Black line—particle phase (low position—liquid spherical phase, high position—non-liquid non spherical phase).

Mass spectrometry

The experimental set up used to generate and oxidize organic aerosol particles is similar as described previously.[10] Thus, only the main aspects are described here. Oleic acid particles were generated by heating pure oleic acid (reagent grade, 99%, Sigma-Aldrich) in a small pear-shaped flask in a silicon oil bath (oil bath T = 200 °C). Nitrogen at a flow rate of 500 ml min^{-1} was flushed through the flask. Oleic acid particles homogeneously nucleated downstream of the flask when the oleic acid vapour rapidly cooled to room temperature. Particles then passed a humidifier to adjust the relative humidity. Particle size distributions were measured using a differential mobility analyser (Hauke, model VIE-08, Gmunden, Austria). The mode of the particle number size distributions was about 80nm and total concentrations of about 1 × 10^6 particles/cm^3 were typically measured.

Ozone was generated by flowing synthetic air past a 185 nm UV light source (Appleton Woods). Ozone concentrations of 160–230 ppm were generated and were measured using an ozone analyzer (Thermo Scientific, 49i). The particle and ozone flows were combined in a stirred reaction barrel with 50 litre volume resulting in a reaction time of about 1.3 h. Experiments were performed at room temperatures (~20 °C), under dry conditions (<2% RH) and at high humidity (90% RH). After the ozonolysis reaction in the barrel, particles passed a charcoal denuder to remove ozone and gaseous organic reaction products before collection on a Teflon filter (Durapore membrane filters, hydrophilic, 0.1 mm pore size, Millipore, Watford, UK) for about 6 h. Filters were subsequently extracted in pure acetonitrile in a sonication bath for 30 min.

The signal retrieved from the mass spectrometer is dependent upon, but not directly proportional to, the concentration of the species measured. It is also dependent upon the ionization probability of the species. Calibration of the ionization probability is possible if standards can be obtained either commercially or *via* synthesis. Unfortunately, we were unable to obtain standards for many of the product species observed in this study.

Filter extracts were measured using an ultra-high resolution mass spectrometer (Orbitrap Velos, Thermo Scientific, Bremen, Germany) with direct infusion and a standard Heated Electrospray Ionisation (HESI) source. The HESI ionisation conditions were set as follows: Sample infusion flow rate 5 μL min^{-1}, HESI heater temperature 50 °C, spray voltage 2.5 kV. Mass spectra were acquired with a resolution of 100 000 at *m*/*z* 400 and a accuracy of $<$2 ppm.

Thermodynamic calculations

Particle composition calculations were performed using the Extended Aerosol inorganics Model (E-AIM, http://www.aim.env.ac.uk/aim/aim.php).[24] Within E-AIM the UNIFAC model was used to predict the activity coefficients of the aerosol components and the water activity within the particle as a whole. The UNIFAC model determines the activity coefficients by parameterizing the interaction of the different structural groups within each component.[25]

Results and discussion

Unsaturated organic acids, especially oleic acid, have been used extensively as model systems to investigate the oxidation of organic aerosol in the atmosphere with respect to hygroscopic behaviour and the formation of particle phase ozonolysis products. Oleic acid is compared in the following with maleic acid and arachidonic acid, two other unsaturated carboxylic acids (Fig. 1).

Oxidation schemes and changes in particle mass after exposure to ozone

The initial steps of oleic acid oxidation with ozone are well documented in the literature.[5,9] Four stable primary oxidation products are formed (Fig. 1b): azelaic acid (AA), 9-oxononanoic acid (ON), and nonanoic acid (NA), which all remain predominantly in the particle phase and nonanal (NN), which is found almost exclusively in the gas phase.[26] These four products are formed after an initial primary ozonide decomposes into two different reactive Criegee intermediates (CI), ON and NN.

Ozonolysis experiments of oleic acid particles performed under dry conditions ($<$2% relative humidity) in the EDB clearly show a pronounced loss of mass of oleic acid particles immediately after the addition of ozone to the EDB (Fig. 2), which can be explained by the evaporation of volatile oxidation products such as NN. In theory the mass loss data from the EDB study could be used to measure the vapour pressure of single component volatile species following the method of Ray *et al.*[27] This would assume that nonanal would be the only volatile product. However, this approach failed in this study because we have insufficient information about the mole fraction of nonanal within the oxidised aerosol particle. Fig. 4a shows mass spectra of oleic acid particles exposed to ozone in the aerosol barrel reactor. The three primary particle phase reaction products (AA, ON, NA) are clearly visible in the low *m*/*z* range of the spectrum. Due to the long reaction time and the high ozone concentrations oleic acid was completely consumed in these experiments, *i.e.*, no detectable oleic acid peak (at *m*/*z* 281) is observed.

Clearly visible are the distinct oligomer groups up to about *m*/*z* 900. Oligomer formation of oleic acid ozonolysis products has been investigated previously by a number of authors.[7,28] The oligomer formation is explained by addition reactions of a Criegee intermediates (CI) with one of the monomers (AA, ON, NA) or with CI self-reactions as schematically shown in Fig. 7 and as reviewed in detail by Zahardis and Petrucci.[5] Katrib *et al.* postulated that the CI reacts also with oleic acid with subsequent decomposition of the dimer.[28] While this dimer was not observed in our study the masses of the decomposition products are not distinguishable from the reaction product of the CI with a first generation oxidation product. Three of the most intense peaks in the dimer mass region (*m*/*z* 345, 359, 375) could be formed by either of these reactions. The high concentration of oleic acid present in

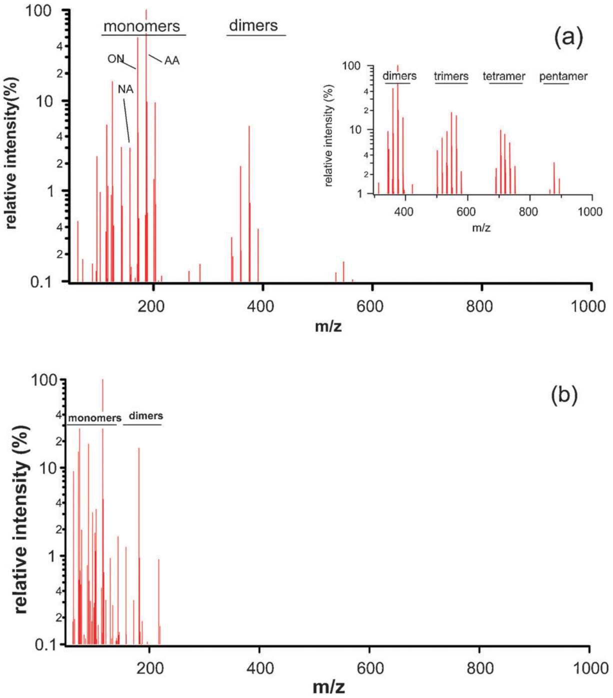

Fig. 4 (a) Mass spectrum of oxidation products of oleic acid particles exposed to ozone. Three particle phase primary oxidation products are observed (NA, ON, AA) together with a large number of oligomeric high mass peaks up to *m*/*z* 1000. The oligomer series continues up to *m*/*z* 1300 at relative intensities $<$1% (not shown here). Peaks at *m*/*z* $<$150 are likely fragments of higher mass peaks. (b) Mass spectrum of maleic acid (Gallimore *et al.*, 2011). A large number of monomeric oxidation products but no higher oligomers are observed.

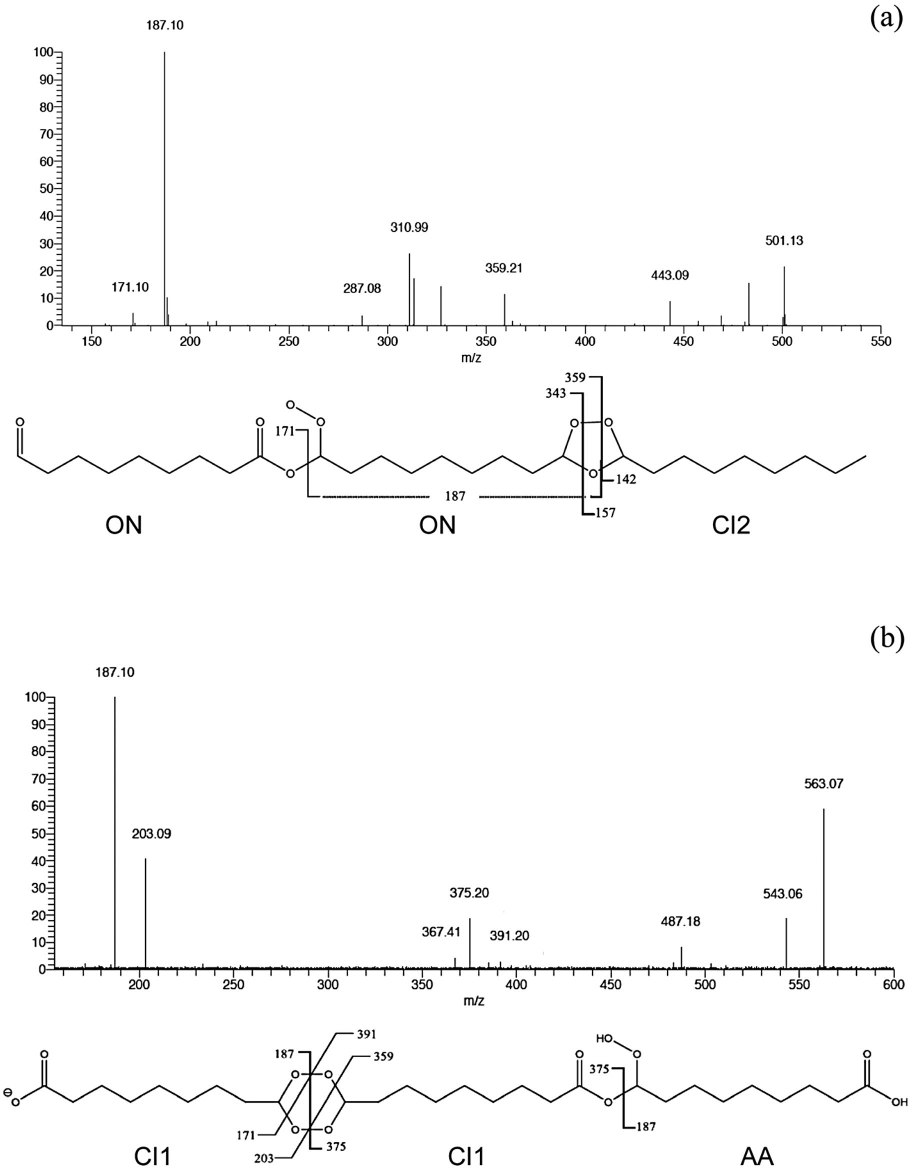

Fig. 5 Tandem mass spectra of two trimers at *m*/*z* 501 (a) and *m*/*z* 563 (b) and suggested structures.

the particles makes the reaction of CI with oleic acid a likely pathway. The propagation to higher oligomer proceeds mostly *via* CI or ON addition.[28] Fig. 5 shows two examples of tandem mass spectra of trimers supporting the proposed reaction between CI and monomeric oxidation products. The fragmentation pattern of *m*/*z* 501 (Fig. 5a) indicates that this oligomer is formed by a CI2 and two ON molecules. Mass fragments in the tandem spectrum of *m*/*z* 563 (Fig. 5b) suggest that this oligomer is composed of two CI1 and one AA molecule. Reactions of the CI with stable monomeric oxidation products form mainly diperoxides, secondary ozonides or α-acyloxyalkyl hydroperoxides and can account for almost all oligomers detected in Fig. 4a (see also Fig. 7). Experiments were performed at 2% RH and at 90% RH and no effect of humidity on the distribution of oxidation products of oleic acid was observed.

The oxidation scheme oleic acid is distinctly different from reaction products seen in the ozonolysis of maleic acid (Fig. 4b and Gallimore *et al.*[10]). The CI formed in the reaction of maleic acid with ozone has a much higher electron deficiency due to the vicinal carboxylic acid group compared to the CI of oleic acid. This strongly favours decarboxylation as the dominant reaction route of the CI rather than addition reactions. The second marked consequence of the electron deficiency of the CI formed in the maleic acid oxidation is its fast reaction with water. Thus, a variety of small reaction products are formed in the presence of water at high humidity conditions, which are not formed in the oleic acid system. Reactions influenced by humidity mainly involve decarboxylation reactions as detailed previously[10] (see also Fig. 7). The large amount of small oxidized reaction products may explain the volatility of maleic acid after oxidation at high RH conditions: In EDB experiments significant amounts of maleic acid ozonolysis products only evaporate after the particle passes through a high-humidity (deliquescent) cycle, as described in detail in our recent studies.[10,11] Under dry conditions, however, the particle is solid and only a surface layer of maleic acid is oxidized.

The expected increase in particle mass under dry conditions due to the formation of oxygenated compounds on the surface (in analogy with arachidonic acid) is not observed,[11] which might be explained by the formation of a small amount of volatile compounds such as formic acid, which balances the mass increase due to ozone uptake. Maleic acid has only one carbon-carbon double bond compared to four in arachidonic acid, which might also explain why the pronounced mass increase observed for arachidonic acid particles was not detected for maleic acid.

The only dimers observed in the maleic acid system are formed through esterification reactions of stable oxidation products such as glyoxylic acid, glyoxal and oxalic acid and their hydrates and no higher oligomers were observed (Fig. 4b). Dimers formed involving the CI are not observed in maleic acid oxidation and conversely all oligomer propagation in oleic acid involves a CI (Fig. 7).

The significant differences in reactivity between maleic acid and oleic acid might also be influenced by the reaction kinetics. Maleic acid is oxidized much slower by ozone than oleic acid because of its conjugated structure. Thus, primary oxidation products, especially the CI intermediate, are much more abundant in the oleic acid particle than in the maleic acid particle. This might contribute to the high abundance of oligomers observed in oleic acid particles.

Assuming that all double bonds in arachidonic acid are oxidized analogous to the Criegee mechanism, then the primary oxidation products are glutaric acid, 5-oxopentanoic acid, malonic acid, 3-oxopropanoic acid, hexanoic acid, and hexanal. Most of these reaction products are expected to stay predominantly in the particle phase but hexanal is likely to evaporate causing a decrease in particle volume.

The mass of arachidonic acid particles increases with exposure to ozone under dry conditions in the EDB by about 15–20% (Fig. 3), which corresponds to the addition of roughly one ozone molecule per arachidonic acid molecule. However, it is likely that due to the fast liquid to solid phase change observed upon ozone addition (see below) only an outer layer (crust) of the particle gets oxidized at low humidities and that multiple double bonds in arachidonic acid are oxidized in this surface layer.

The evaporation of maleic acid and ozone reaction products is only observed after the particle is exposed to high humidity conditions (Fig. 3a). Under dry conditions no evaporation is observed pointing to a limited reactivity of ozone where no or only small amounts of volatile oxidation products are formed as it is observed for maleic acid.

The arrangement of the multiple double bonds in arachidonic acid could lead to reaction products that are structurally similar to maleic acid—see Fig. 8 for a mechanistic interpretation: the arachidonic acid double bonds are initially non-conjugated, but the oxidation of a double bond results in products, which can undergo enolisation to form a conjugated double bond like maleic acid. The further oxidation of this conjugated products may result in a CI with similar electron deficient properties (and corresponding reactivity) as the CI formed in maleic acid oxidation and therefore to additional small, volatile and hygroscopic oxidation products. This hypothesis is strengthened by the observation of the formation of conjugated double bonds (as confirmed by Raman spectroscopy) in the ozonolysis of linolenic and linoleic acid systems both of which initially contain unconjugated multiple double bonds which are separated by a CH_2 link, *i.e.* $R–CH{=}CH–CH_2–CH{=}CH–R'$.[18] It should be noted that Lee and Chan[18] propose an auto-oxidation mechanism for the formation of conjugated double bonds as opposed to the enolisation mechanism proposed here. The mechanism proposed here (suggesting a key role of water as a reactant) may partly explain why EDB results for maleic acid and arachidonic acid are similar with respect to evaporation and water uptake.

Effect of water on particle phase and reactivity

The EDB experiments performed, in both this study and previous studies,[11] indicate that the formation of volatile oxidation products from the ozonolysis of organic aerosols is dependent on both the phase and water content of the organic aerosol. There are three main mechanisms for the influence of water content on the formation of volatiles. (1) The water content of aerosol defines the phase of aerosols which undergo well defined deliquescent and efflorescent behaviour. The presence of a non-liquid aerosol phase strongly inhibits the diffusion of ozone into the aerosol bulk and thus hinders the bulk phase oxidation that leads to volatile products. (2) If the particle is hygroscopic the particle phase water molecules can act as reactants which lead to the formation of volatile products. (3) The formation of oxidation products in the aerosol particle can lead to phase changes (*e.g.*, liquid to solid) which inhibit the formation of volatiles because of the reduced diffusion. These three mechanisms can be used to explain the observed formation, or lack thereof, of volatile species in the three model systems investigated.

Maleic acid is a crystalline solid at low RH and exposure to high RH results in the deliquescence of the solid particle. Therefore ozone can only efficiently diffuse into the bulk of the particle once it is deliquesced. Only after bulk oxidation are there enough volatile oxidation products formed to result in a measurable evaporation. Moreover, the diffusion of ozone into the particle bulk of deliquesced particles results in efficient oxidation of the bulk and can explain the increased hygroscopicity of the particle that is oxidized at high RH.

Pure arachidonic acid particles are single phase liquid at room temperature but change to a nonspherical non-liquid phase (as observed by CCD feedback camera) very quickly after exposure to ozone as determined from elastic Mie scattering pattern in the EDB experiments (see reference 21 for experimental details). After exposure to high humidity conditions the particle stays liquid even if the relative humidity decreases to $<2\%$ and evaporation sets in as described above (Fig. 3a). The non-liquid phase can be induced repeatedly for the same particle with repeated exposure to ozone as illustrated in Fig. 3b. Over *ca.* four days the particle was exposed four times to ozone at 62 ppm. The particle changes phase each time when it is exposed to ozone but becomes liquid when only pure nitrogen is flushed through the EDB. Similar phase changes were observed in the ozonolysis of linoleic acid and linolenic acid by Lee and Chan.[18] These observations can be explained by the formation of a non-liquid crust on the particle surface leading to multiple phase and non-spherical particles. The consequences on diffusivity within aerosols of crust formation and solidification are discussed by Pfrang *et al.*[29] The change in diffusivity can have a dramatic impact on half-life of reactive chemical species within aerosol particles and could potentially explain long-range transport of reactive anthropogenic compounds such as PAHs from sources to remote areas such as polar regions (*e.g.*, Sofowote *et al.*[30]).

In contrast to maleic and arachidonic acid, an increased relative humidity (up to 90%) has no effect on the phase and reactivity of oleic acid. Oleic acid particles are liquid in pure and oxidized form at room temperature, with similar hygroscopicities, and thus ozone can diffuse into the particle bulk under all conditions. In addition, oleic acid and its oxidation products are significantly hydrophobic. Thus even at high RH water is present in only small amounts in the particle bulk therefore limiting its availability as a reaction partner.

Fig. 6 indicates the predicted increase in saturated aerosol hygroscopicity after full ozonolysis of the three test molecules. The major ozonolysis products of maleic acid are glyoxylic acid, oxalic acid, formic acid and CO_2 and the detailed mechanism is given elsewhere.[10] The major non-volatile ozonolysis products of oleic acid as shown in this paper are azaleic acid, 9-oxo-nonanoic acid and nonanoic acid. The ozonolysis products of arachidonic acid have not been characterised by mass spectrometry. It is hypothesised that the full oxidation of arachidonic acid results in the ozonolysis of every double bond resulting in the formation of new carboxylic acid and aldehyde functional groups as first generation oxidation products. For this theoretical humidogram it is assumed that all the arachidonic acid reaction products are non-volatile except hexanal. The humidograms of pure oleic acid and arachidonic acid show only minor water uptake at high RH because of their large hydrocarbon chains. Maleic acid shows a clear deliquescence phase transition and significant water uptake once deliquesced. Upon oxidation the hygroscopicity of oleic acid is only weakly increased because the oxidised products still contain significant lipophilic chains. Ozonolysis of maleic acid aerosol significantly lowers the observed deliquescence point and the oxidation of arachidonic acid results in an intermediate hygroscopicity. The humidograms of all six aerosol compositions shown in Fig. 6 can be broadly rationalised by the atomic O : C ratios of the constituent molecular formulae of the species involved. The theoretical humidograms cannot be compared to the EDB data from this study and the hygroscopicity study of Vesna *et al.*[17] because the extent of the ozonolysis in the EDB data sets are not known.

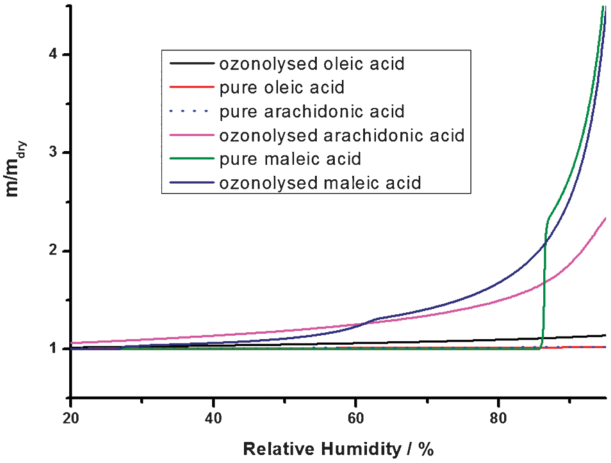

Fig. 6 Predicted hygroscopicity of the three model compounds before and after ozonolysis using the E-AIM model. It is assumed that the full ozonolysis of every alkene bond occurs.

Conclusions

Ozonolysis reaction schemes of three organic aerosol systems were investigated: oleic, maleic and arachidonic acid. Although all three compounds are unsaturated carboxylic acids they show distinct oxidation schemes upon exposure to ozone. The particle phase has a distinct effect on the oxidation of the particle and is closely related to the relative humidity the particle is exposed to. Maleic and arachidonic acid are solid or become solid upon exposure to ozone, this limits the ozone reactivity to the particle surface. Exposure to high RH results in deliquescence of the particle to the liquid phase therefore allowing diffusion of ozone into the particle bulk and an oxidative processing of the entire particle. Oxidation of oleic acid particles is less affected by water (RH) because oleic acid is liquid under all investigated conditions and therefore ozone can easily diffuse into the bulk of the particles under all RH conditions. Oxidation products of maleic acid and arachidonic acid are much more hygroscopic than oleic acid oxidation products and therefore water is present in these liquid, oxidised particles at much higher mole fractions at elevated RH than in oleic acid particles. This may partially explain the strong influence of water in oxidized maleic and arachidonic acid particle reaction schemes.

The differences in the oxidation schemes of the three carboxylic acids are mainly explained by the very different reactivity of the Criegee intermediate (CI), one of the first reaction intermediates in the oxidation scheme of all three systems (Fig. 7). In maleic acid and possibly arachidonic acid the CI is highly electron deficient, compared to oleic acid, due to the vicinal carboxyl group, which favours decarboxylation reactions of the CI and the high reactivity towards water.

Reactions of the CI of oleic acid with other primary oxidation products leads to the formation of oligomers with masses up to 1000 Da and more, with the CI and oxo-nonanoic acid as most abundant monomeric units. In contrast, the maleic acid system exhibits oxidation products are mostly monomeric (Fig. 4 and 7). Dimers (but no higher oligomers) were formed in esterification reactions from stable oxidation products. Dimers involving the CI were not observed in the maleic acid system.

In more complex and atmospherically relevant laboratory model systems such as secondary organic aerosol formed from terpenes (the most important natural precursors of organic aerosol mass in the atmosphere) ester formation are likely explaining a major fraction of the observed particle phase reactivity and especially the formation of short oligomers.[31,32] In addition, in the ambient atmosphere high-mass oligomers are rarely observed (*e.g.*, Samburova *et al.*[33]). Thus the oxidation

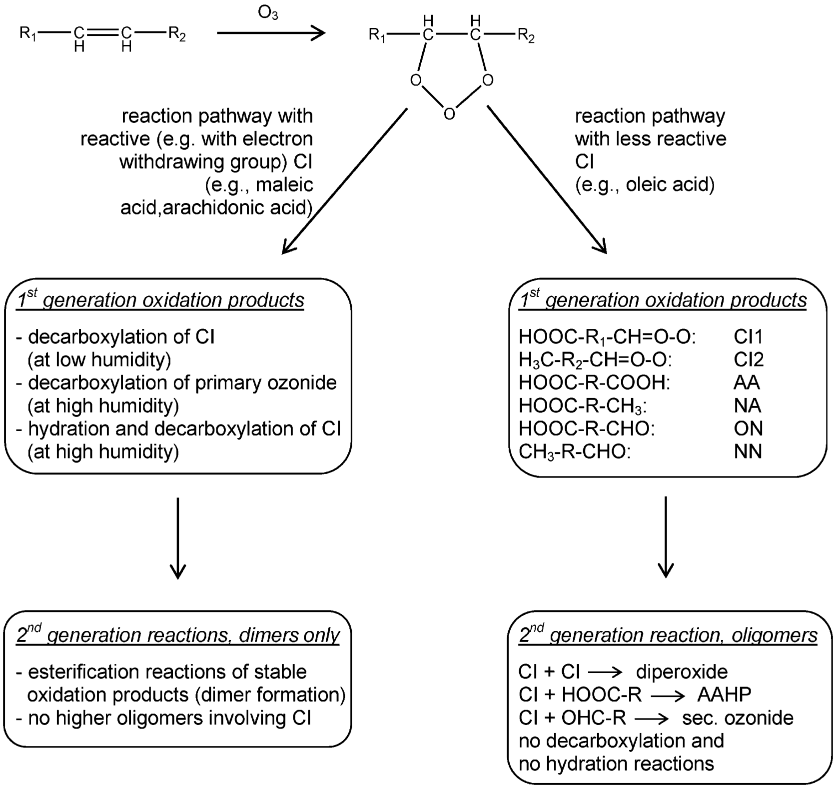

Fig. 7 Schematic oxidation scheme of unsaturated compounds with ozone emphasising the different reaction pathways due to the different reactivity of the Criegee intermediate. AAHP: α-acyloxyalkyl hydroperoxides. *sec.* ozonide: secondary ozonide.

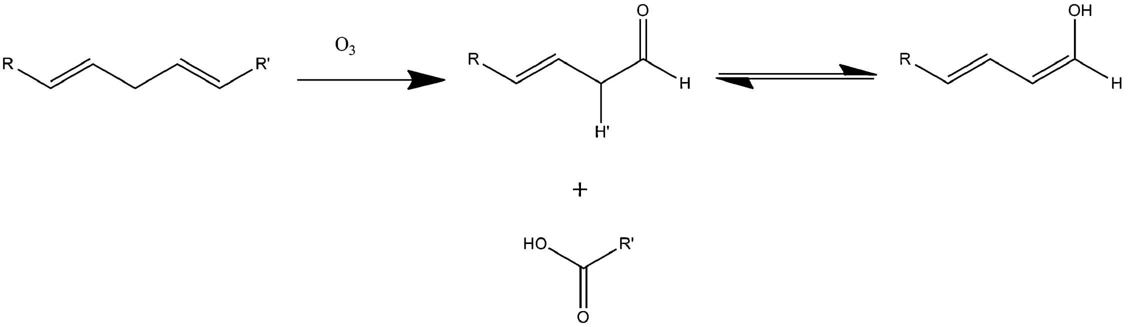

Fig. 8 Enolisation of first oxidation products of arachidonic acid lead to a conjugated polyene with similar further oxidation chemistry to maleic acid. Note H' is prone to enolisation. Enolisation of the carboxylic acid fragment is less favourable compared to the aldehyde fragment.

schemes of maleic (and possibly arachidonic acid) where only a limited degree of oligomerisation is observed might be more representative of particle phase oxidation reactions occurring in the complex mixtures of ambient particles.

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