Characterization of Polar Compounds and Oligomers in Secondary Organic Aerosol Using Liquid Chromatography Coupled to Mass Spectrometry

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A generic method has been developed for the analysis of polar compounds and oligomers in secondary organic aerosol (SOA) formed during atmospheric simulation chamber experiments. The technique has been successfully applied to SOA formed in a variety of systems, ranging from ozonolysis of biogenic volatile organic compounds to aromatic photooxidation. An example application of the method is described for the SOA produced from the reaction of ozone with *cis*-3-hexenyl acetate, an important biogenic precursor. A range of solvents were tested as extraction media, and water was found to yield the highest recovery. Extracts were analyzed using reversed-phase liquid chromatography coupled to ion trap mass spectrometry. In order to determine correct molecular weight assignments and increase sensitivity for less polar species, a series of low-concentration mobile-phase additives were used (NaCl, LiBr, NH₄OH). Lithium bromide produced better fragmentation patterns, with more structural information than in the other cases with no reduction in sensitivity. The main reaction products identified in the particle-phase were 3-acetoxypropanal, 3-acetoxypropanoic acid, and 3-acetoxypropane peroxoic acid and a series of dimers and trimers up to 500 Da. Structural identification of oligomers indicates the presence of linear polyesters possibly formed via esterfication reactions or decomposition of peroxyhemiacetals.

Atmospheric aerosols have recently received much attention due to their effect on Earth's climate and human health.¹ The environmental impact of atmospheric aerosols depends strongly on the chemical composition, and in particular on the inorganic, black carbon and organic carbon fractions. A significant amount of the organic fraction is attributed to secondary organic aerosol (SOA) formed as a result of gas-particle transfer of species during the oxidation of volatile organic compounds (VOCs) in the

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atmosphere. The major precursors of SOA formation are biogenic compounds such as terpenes and anthropogenic compounds such as aromatic hydrocarbons.² Since global emissions of biogenic VOCs are ~10 times larger than anthropogenic emissions,³ the SOA produced from biogenic VOCs is expected to make the largest contribution to the atmospheric aerosol burden.

Recent evidence from atmospheric simulation chamber studies has shown that the oxidation of gas-phase organic species may lead ultimately to the formation of macromolecules (oligomers and polymers up to 1000 Da) in aerosols.⁴ Oligomer formation is now proposed as being a key mechanism by which VOCs are incorporated into the particle phase. The sheer complexity of organic compounds found in atmospheric aerosol is the main practical barrier to relating condensed-phase organic species to their parent gas-phase precursors, and a full structural evaluation would require the use of a range of complementary techniques. In order to simplify this complexity, controlled simulation chamber experiments focusing on a single hydrocarbon allow direct links between primary emitted organics and their conversion to SOA to be investigated. A range of on-line and off-line techniques have been used to investigate the polar and oligomeric content of SOA formed during chamber experiments. On-line techniques such as aerosol mass spectrometry, photoelectron resonance capture ionization aerosol mass spectrometry, and thermal desorption particle beam mass spectrometry provide real-time bulk properties of SOA but give limited structural information.⁵⁻⁸ Off-line techniques, where samples are collected onto a substrate and analyzed by gas or liquid chromatography or mass spectrometry, provide

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detailed chemical speciation but at the expense of time resolution. Gas chromatography is not particularly suited to the most polar fraction of SOA, i.e., the water-soluble organic carbon, and may cause thermal decomposition of oligomers, although some limitations can be reduced using derivatization.⁹ Liquid chromatography (LC) is becoming increasingly popular for the analysis of polar compounds in aerosol and is routinely used for the analysis of carboxylic acids. Tolocka et al.¹⁰ applied LC combined with matrixassisted laser desorption/ionization (MALDI), electrospray ionization (ESI), and chemical ionization (CI) mass spectrometry for the analysis of oligomers in SOA. CI was found to cause decomposition of the parent oligomer, but MALDI and ESI provided similar oligomer distributions. Gao et al.¹¹ used LC coupled to an ion trap mass spectrometer (LC-ITMS) to identify oligomers up to 1600 Da in SOA formed during cyclohexene ozonolysis and estimated that they accounted for $\sim 10\%$ of the total mass fraction. Fragmentation patterns for structural analysis were performed in negative ionization mode, but a wider range of species could be detected in positive ionization mode as [M + Na]⁺ adducts. Hamilton et al.¹² also investigated the formation of oligomers in the cyclohexene system using LC-ITMS. The major components of the SOA were dicarboxylic acids, which were detected in both positive and negative modes. Higher sensitivity was achieved for the $[M + Na]^+$ adducts formed in the positive mode, but due to poor fragmentation in the ion trap, these data could not be used for structural analysis.

As oligomers grow larger, there may be some species with low ionization potentials, which are unlikely to be identified in positive mode electrospray ionization unless they form adducts. The formation of adducts with metal ions, such as sodium and potassium, can reduce sensitivity and can cause problems when interpreting mass spectra as the operator is unsure of the correct molecular weight, for example, due to uncertainty whether the highest mass is due to the $[M + H]^+$ or $[M + Na]^+$ ion. In the analysis of polymers, such as polyesters and polyethers, cationisation agents, such as alkali buffers, can be added to the mobile phase to increase the abundance of one specific ion $[M + Cat]^+$, which can lead to increased sensitivity.^{13,14} In the case of polyglycols, the molecular ions can be difficult to fragment in collisioninduced dissociation tandem MS, but lithium adducts readily undergo fragmentation yielding structurally informative product ion spectra.^{15,16} This technique has recently been applied to the analysis of airborne isocyantes as dibutylamine derivatives, result-

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ing in complete domination of the $[M + Li]^+$ adducts but did not improve detection limits.¹⁷

This paper presents the development of a LC-MS technique for the analysis of polar compounds and oligomers in secondary organic aerosols. The extraction of oligomers and polar species in a range of solvents was tested to ensure maximum efficiency. Total mass distributions were obtained by directly introducing extracts into the MS using a syringe pump. The influence of a series of cationization agents in the mobile phase was investigated in order to maximize sensitivity and improve identification. The technique has been successfully applied to SOA formed in 10 systems, ranging from biogenic VOC ozonolysis to aromatic photooxidation. The structural analysis of the SOA formed during the ozonolysis of cis-3-hexenyl acetate in a simulation chamber experiment is presented as an example. cis-3-Hexenyl acetate, also known as leaf acetate, is a volatile compound emitted by green foliage. Kirstine et al.¹⁸ analyzed the head space of grass clippings (primarily Lolium perenee) shortly after it had been cut and found that 40% of the grass emissions were cis-3-hexenyl acetate, with the other related C₆ oxygenated VOCs (hexenols and hexenals) contributing 29%. The cutting or grazing of pastures induces the production a range of hexenyl-type compounds, which act as antibiotics at the site of the wound to prevent fungal growth and bacterial infection.

EXPERIMENTAL SECTION

LC-MS/MS. LC-MS/MS analysis was performed using a HCT Plus ion trap mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany) equipped with an Eclipse ODS-C₁₈ column with 5- μ m particle size (Agilent, 4.6 mm \times 150 mm). Samples (60 μ L) were injected via an autosampler (Agilent 1100 series), and a binary gradient elution was performed using (A) 0.2 μ g mL⁻¹ cationization agent (NaCl, LiBr, NH₄OH) and 0.1% formic acid in HPLC-MS grade water (100 to 40% over 40 min, hold for 10 min, return to starting conditions) and (B) HPLC grade methanol, at a flow rate of 0.6 mL min⁻¹. ESI was carried out at 300 °C, with a nebulizer pressure of 70 psi and nitrogen dry gas flow rate of 12 L min⁻¹. The mass spectrometer was used in positive ion mode, scanning from 50 to 600 Da. The automated MS² function from the Esquire software (Bruker Daltonics GmbH) was used to fragment ions, where the two most abundant ions at each scan were subjected to CID. After five consecutive scans, a mass was rejected from auto-MS² for 1 min before being reactivated to allow minor components to be analyzed.

Simulation Chamber Experiments. Experiments were carried out at the European Photoreactor (EUPHORE), which consists of two large atmospheric simulation chambers located on the roof of a building in Valencia, Spain. Technical information concerning the installation and its use for VOC oxidation experiments has been previously reported in the literature.^{19–21} The

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Table 1. Initial Conditions and Aerosol Yields for cis-3-Hexenyl Acetate SOA Experiment in EUPHORE

	EUPHORE 05/05/06
initial <i>cis</i> —3-hexenyl acetate concn	1614 ppbV (1.915 g)
ozone concn SOA vield ^a	1600 ppbV added over 60 min 24%
maximum SOA concn ^a aerosol mass on filter	$903 \ \mu g/m^3$ 0.5926 mg
	0

^a Assuming a SOA density of 1.0 g cm⁻³.

chambers are hemispheres made of fluorinated ethylenepropylene film, with a volume of $\sim 200 \text{ m}^3$, and are surrounded by a retractable steel housing. The chamber is operated at ambient temperature and approximately atmospheric pressure using dry purified air, while two large fans ensure homogeneous mixing of the chamber contents. The ozonolysis of cis-3-hexenyl acetate was performed using starting concentrations of ~ 1.6 ppmV. No radical scavenger or seed aerosol was used, and the relative humidity was $\sim 6\%$. The average temperature during the experiment was 19 °C. The decay of the hydrocarbon was monitored by FT-IR spectroscopy, and the formation and evolution of SOA was measured using a scanning mobility particle sizer (TSI 3022A condensation particle counter and TSI 3081 differential mobility analyzer). Samples of SOA were collected when the particle concentration in the chamber had reached a maximum, ~4 h after the start of the reaction. Samples were collected on 47-mmdiameter quartz-fiber filters using a high-volume sample pump operating at 12 L min⁻¹ for 1 h. Filters were prefired at 500 °C for 12 h prior to sample collection and were stored in foil below 4 °C until analysis. Experimental details including the SOA yield and total mass of aerosol collected are shown in Table 1.

Filter Extraction. The filter was divided into four pieces, and each piece was then placed into a vial with 5 mL of a high-purity solvent (water, methanol, tetrahydrofuran, acetonitrile) purchased from Fisher Chemicals. The sample vial was wrapped in foil to avoid any possible degradation and left for 2 h. This was sonicated for 1 h and the extraction filtered using a 0.45-mm PVDF syringe filter (Whatman). Extracts were evaporated to dryness using a V10 vacuum solvent evaporator (Biotage) at 30 °C, and the residue was redissolved in 1 mL of a 50:50 solution of HPLC-MS grade water and methanol.

RESULTS

Extraction. The aerosol mass yield (*Y*) from the simulation of ozonolysis of *cis*-hexenyl acetate presented here was 24%, assuming spheric particles with an effective density of 1.0 g cm⁻³. The extracts of the SOA formed were analyzed by LC–MS in positive ion mode, and the base peak chromatograms (BPC) are shown in Figure 1. The optimum extraction solvent was determined by picking five peaks, spread across the entire chromatogram, and comparing the average peak areas of three replicate analyses for each of the solvents used. For the first peak, with a retention time of ~14 min, the $[M + H]^+ = 133$ Da and the $[M + Na]^+ = 155$ Da signals were detected and both areas were determined. Since the concentrations are unknown, extraction recoveries could not be used. Peak areas were corrected for the



Figure 1. Comparison of LC-MS chromatograms of the SOA produced from the ozonlysis of *cis*-3-hexenyl acetate obtained using a range of solvents for extraction. (A) water. (B) methanol. (C) acetonitrile. (D) tetrahydrofuran.

Table	2. Relativ	e Extractio	on Efficier	ncies	(REE)	and
Repro	ducibility	(RSD) of S	OA Comp	onents	s ^a	

	water		methanol		acetonitrile		tetrahydrofuran	
peak	REE	RSD (%)	REE	RSD (%)	REE	RSD (%)	REE	RSD (%)
133	1.86	9.6	1.27	4.4	0.48	4.7	0.39	11.9
155	1.26	5.4	1.33	2.9	0.58	3.7	0.83	14.8
199	0.87	1.0	1.10	6.3	1.03	5.5	n.d.	n.d.
271	0.90	4.0	1.21	2.7	1.11	3.0	0.79	7.6
297	1.04	3.5	1.00	4.1	1.00	0.5	0.95	5.9
308	1.38	10.9	0.80	1.9	1.20	3.1	0.62	7.8
mean	1.22	5.75	1.12	3.71	0.90	3.40	0.60	9.60
^a Peaks used correspond to those marked in Figure 1.								

relative mass of each quarter of filter paper, and the average was taken. Good precision was obtained with relative standard deviations in peak areas below 8% in most cases. For each peak, a mean response of the four extraction solvents was calculated and the relative extraction efficiency (REE) determined using the expression; REE = A_s/A_m , where A_s is the average area for a specific solvent and A_m is the average area of all solvents. Therefore, a REE value above 1 indicates a better than average extraction and below 1 indicates a poorer extraction. The REE and RSD values for each extraction solvent are shown in Table 2. Tetrahydrofuran was discounted due to high levels of impurities (see Figure 1d).



Figure 2. Averaged mass spectra of the water-soluble extract of SOA produced from the ozonolysis of *cis*-3-hexenyl acetate. The four spectra show the effect of a series of cationization agents. (A) uncatalyzed extract. (B) NaCl. (C) LiBr. (D) NH₄OH.

Both methanol and water provided good extraction of oligomers and polar compounds with good run-to-run reproducibility. Water was chosen for further extractions due to lower levels of impurities. The use of the vacuum solvent evaporator significantly reduced sample preparation time compared with conventional rotary evaporation, with 5-mL water extracts evaporated to dryness in 6 min at near-ambient temperatures.

Molecular Weight Distribution. To determine the mass distribution of SOA components, the water extract was directly injected into the ESI source of the ion trap MS using a syringe pump. This allows a direct and quick characterization of the molecular weight range of organic species in the sample as shown in Figure 2. It is clear that the SOA from *cis*-3-hexenyl acetate is dominated by species below 350 Da, but the mass spectrum does extend to 500 Da, indicating the presence of oligomers. The peaks at 328 and 330 Da are due to an artifact from the simulation chamber (also present in blank filter samples) and should be ignored. During previous analysis of SOA formed during cyclohexene ozonolysis,¹² it was found that fragmentation patterns obtained without preseparation were generally from a mixture of species with the same nominal mass and could not be used to determine structures.

The positive ionization mass spectrum is complex, and peaks may correspond to the protonated molecular ion $[M + H]^+$ or an adduct, likely $[M + Na]^+$. Often both peaks appear in the same spectrum 22 Da apart, making the presence of the adduct obvious, but there is no evidence of this in the SOA extract. To determine the correct molecular weight assignments, 100- μ L aliquots of the

extract were mixed with 100 μ L of a 2 μ g mL⁻¹ solution of cationisation agent (LiBr, NaCl, NH4OH) in high-purity water and injected using the syringe pump. The large excess of cationization reagent results in the exclusive formation of $[M + Cat]^+$, shifting the position of peaks in the mass spectra as seen in Figure 2, except for NH₄OH, which had no effect. Comparison of the spectra for the uncatalyzed extract and the NaCl extract indicates that only sodium adducts are present in the original extract, even without the addition of extra sodium, perhaps as a result of the highly oxidized nature of SOA. This is confirmed by the [M + Li⁺ spectrum, where peaks are shifted down by 16 Da with respect to the corresponding $[M + Na]^+$ peaks, reflecting the difference in cation mass ($Li^+ = 7$ Da, $Na^+ = 23$ Da). Using this technique, the correct molecular weights can be assigned to the dominant peaks in the spectra. For example, the three large peaks below 200 Da ($[M + Na]^+ = 139, 155, and 171 Da and <math>[M + Li]^+$ = 123, 139, 155 Da) correspond to the neutral species with molecular mass 116, 132, and 148 Da. Peak intensities are similar in all four spectra, indicating that, for the highly oxidized species found in SOA, cationisation agents can be used without any detrimental effect on sensitivity.

Negative ionization could only be used for the uncatalyzed extract and the NH₄OH solution due to the complete domination of adducts of Cl⁻ and Br⁻ in the other extracts. Negative ionization was significantly less sensitive and the mass spectrum was dominated by impurities in the methanol. This suggests that the SOA formed in the ozonlysis of *cis*-3-hexenyl acetate does not contain a significant acidic fraction, unlike the previous study of



Figure 3. LC-MS chromatograms (BPC) of water-soluble SOA components using a series of cationization agents ($0.2 \mu g m L^{-1}$) in the aqueous 0.1% formic acid mobile phase. (A) uncatalyzed. (B) NaCl. (C) LiBr. (D) NH₄OH.

cyclohexene SOA, which was dominated by dicarboxylic acids and their heterogeneous reaction products.¹²

Chromatography and Structural Analysis. In order to obtain daughter ion spectra for each individual compound, LC separation was required. The chromatograms were similar for each of the mobile phases used as shown in Figure 3, with a small reduction in chromatographic efficiency and shift in retention time observed when using the NaCl and LiBr solutions. Sensitivity was slightly reduced for oligomers, but enhanced signals were seen for the most polar species with all three cationization agents. The NH₄OH mobile phase again provided no improvement over the uncatalyzed solution and is not considered further.

One of the major problems experienced in positive ionization of highly oxidized species is the dominance of the $[M + Na]^+$ adduct as shown in the direct injection of the uncatalyzed extract above. In many cases, these adducts do not generate product spectra when fragmented in the ion trap, due to complete degradation. An example from the *cis*-3-hexenyl acetate extract is shown in Figure 4 for $[132 + Na]^+ = 155$ Da, one of the major small polar molecules. The sodium adduct is completely destroyed and yields no fragments, only a noisy spectrum with no distinct peaks. However, replacing the Na⁺ with Li⁺ completely reverses this situation and yields highly informative product ion spectra as shown in Figure 4 for the same species $[132 + Li]^+$. In addition, when fragmenting $[M + Li]^+$, a heavier peak is often seen 18 Da higher, indicating the formation of a water adduct, i.e., [M + Li $+ H_2O]^+$ as shown in Figure 4 (*m*/*z* 157 Da).

A complete elucidation of the SOA composition is beyond the scope of this paper. However, as seen in the averaged mass spectrum in Figure 2, the SOA is dominated by a small number of compounds and the structural elucidation of these species has been performed. The three most abundant small reaction products in the *cis*-3-hexenyl acetate SOA were identified from their Li⁺ adducts using LC–MS as 3-acetoxypropanal (116 Da), 3-acetoxypropanoic acid (132 Da. See Figure 4 for MS² spectra.), and 3-acetoxypropane peroxoic acid (148 Da) and are shown in Table 3. These three species are among the gas-phase reaction products expected from the ozonolysis of *cis*-3-hexenyl acetate^{22–23} and are therefore present in the particle phase as a result of condensation. The remaining, higher molecular weight, reaction products detected in the SOA samples are likely due to reaction of the first-generation products in the particle-phase.

Six of the most abundant heterogeneous reaction products were identified, and possible structures are given in Table 3. The oligomers identified contain ester and ether linkages, and all contain the 3-acetoxypropanoic acid (APA) unit as indicated by the common loss of 132 Da during fragmentation. The smallest oligomer, 2-hydroxyethyl-3-acetoxypropanoate M = 176 Da, is an ester and appears to be a building block for larger oligomers. It may be formed through an esterfication reaction of APA with 1,2ethanediol or from the decomposition of a peroxyhemiacetal²⁴ (formed from reaction of 2-hydroperoxyethanol and 3-acetoxypropanal). The oligomers, M = 232 Da and M = 248 Da, are both based on this building block and are structurally similar differing only by one oxygen atom, reflecting the incorporation of either 3-hydroxylpropanal or 3-hydroxypropanoic acid formed from the Criegee intermediate of the alkyl end of cis-3-hexenyl acetate.²²⁻²³ The larger oligomers, M = 274, 290, and 348 Da, appear to be formed from a mixture of monomers from both ends of the cis-

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Figure 4. Product ion spectra (MS²) for 3-acetoxypropanoic acid. Upper: uncatalyzed extract, compound present as $[M + Na]^+ = 155$ Da and produces no useful fragmentation pattern. Lower: LiBr-catalyzed extract, compound present as $[M + Li]^+ = 139$ Da and produces a well-defined fragmentation pattern showing losses of 42 (CH₂CO), 60 (CH₃COOH), and 72 (CH₂CHCOOH) Da. A water adduct is also present $[M + Li + H_2O]^+ = 157$ Da.

3-hexenyl acetate molecule. There are a number of molecules that would produce the fragmentation patterns obtained, but the proposed structures are those most likely based on known reaction mechanisms, although the formation mechanisms are far from being understood. Structural analysis of larger oligomers (M = 464 and 498 Da) indicates the presence of at least three ester linkages, suggesting the formation of linear polyesters within the SOA produced in this reaction.

The vapor pressures of 3-acetoxypropanal, 3-acetoxypropanoic acid, and 3-acetoxypropane peroxoic acid were estimated using the expanded Clausius–Clapeyron equation method in Jenkin et al.,²⁵ and the mean was 1.41×10^{-4} Torr, indicating these are semivolatile species. Therefore, these species would be expected

to be partitioned between the gas and condensed phases. In addition, if the APA undergoes reactive uptake, where it reacts irreversibly in the aerosol phase, this will allow more APA to partition from the gas phase. There is the possibility that these small molecules are fragments of oligomer molecules that break down during sample preparation. However, this has been minimized by carrying out the workup at ambient temperatures. The sample preparation method has also been tested on a standard mixture containing a range of commercially available esters, acids, and alcohols and no degradation of the analytes was observed.

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Table 3. Polar Compounds and Oligomers Identified in *cis*-3-Hexenyl Acetate Ozonolysis SOA Using LC-MS with Li⁺ Cationisation

Name	Structure	MWt	$[M+Na]^+$	$[M+Li]^+$
3-oxo-propyl acetate		116	139	123
3-acetoxy- propanoic acid	O OH	132	155	139
3-acetoxypropane peroxoic acid		148	171	155
2-hydroxyethyl 3- acetoxypropanoate		176	199	183
2-(3-oxo propyl)ethyl 3- acetoxy propanoate		232	255	239
2-(2-(3-acetoxy propanoyloxy)etho xy) propanoic acid	ОН ССТАНИИ СТАНИИ С	248	271	255
5-acetoxy-3- oxopentyl-3- acetoxypropanoate	Lo Co Co Co	274	297	281
Ethane-1,2-diyl bis(3- acetoxypropanoate)		290	313	297
3-(2-(3-acetoxy propoxy)ethoxy)-3- oxopropyl-3- acetoxy propanoate	$\left \overset{\circ}{\longrightarrow} \overset{\circ}{\to} \overset$	348	369	355

Fifteen additional oligomer structures were investigated, and all contained the APA monomer unit indicating that only a limited number of key chemical fragments are needed to describe much of the composition. This is consistent with our previous study of cyclohexene—ozone SOA where many of the oligomers contained a common unit, adipic acid. If the formation of oligomers can be explained using a limited subset of key intermediates, the incorporation of heterogeneous reactions into detailed SOA models, such as MCM-SOA,^{25–26} will be simplified and may ultimately lead to reduced mechanisms for transport and climate models. The data presented here are a first look at the composition of SOA from this biogenic VOC, and further studies are required at more atmospherically relevant conditions.

CONCLUSIONS

The addition of LiBr as a cationization agent in the LC–MS analysis has significantly increased the amount of structural information that could be obtained on polar compounds and oligomers in SOA. The use of cationization agents improved the reliability of molecular weight assignments also. Only a small

subset of agents were tested, and other ions, such as Ag^+ or Co^{2+} , may provide further enhancements such as increased sensitivity. Understanding the chemical composition of SOA, in particular heterogeneous reaction products, is a key mechanism for understanding their formation. The method presented has provided information on both early-generation reaction products, which have partitioned to the particle phase, and oligomers, including linear polyesters, which may have formed on the surface or in the bulk of the aerosol particle.

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