Aqueous Phase Oligomerization of α,β -unsaturated Carbonyls and Acids Investigated using Ion Mobility Spectrometry Coupled to Mass Spectrometry (IMS-MS)

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Abstract

One of the current essential issues to unravel our ability to forecast future climate change and air quality, implies a better understanding of natural processes leading of secondary organic aerosol (SOA) formation, and in particular the formation and fate of oligomers. The difficulty in characterizing macromolecules is to discern between large oxygenated molecules from series of oligomers containing repeated small monomers of diverse structures.

In the present study, taking advantage from previously established radical vinyl oligomerization of methyl vinylketone (MVK) in the aqueous phase, where relatively simple oligomers containing up to 14 monomers were observed, we have investigated the same reactivity on several other unsaturated water soluble organic compounds (UWSOCs) and on a few mixtures of these precursor compounds. The technique used to characterize the formed oligomers was a traveling wave ion mobility spectrometry coupled to a hybrid quadrupole - time of flight mass spectrometer (IMS-MS) fitted with an electrospray source and ultra-high performance liquid chromatography (UPLC). The technique allows for an additional separation, especially for large ions, containing long carbon chains. We have shown the efficiency of the IMS-mass spectrometry technique to detect oligomers derived from MVK photooxidation in the aqueous phase. The results were then compared to other oligomers, derived from ten other individual biogenic UWSOCs. The technique allowed distinguishing

1 between different oligomers arising from different precursors. It also clearly showed that
2 compounds bearing a non-conjugated unsaturation did not provide oligomerization. Finally, it
3 was shown that the IMS-mass spectrometry technique, applied to mixtures of unsaturated
4 conjugated precursors, exhibited the ability of these precursors to co-oligomerize, i.e.
5 forming only one complex oligomer system bearing monomers of different structures. The
6 results are discussed in terms of atmospheric implications for the detection of oligomers in
7 complex chamber and/or field samples.

8 **1. Introduction**

9 Organic aerosols (OA) are well known to play a significant role in many atmospheric
10 processes resulting in an important impact on climate and human health. Secondary organic
11 aerosols (SOA) represents almost 80% of OA (Spracklen et al., 2011), and its formation and
12 growth mechanisms are not well understood. SOA formation is widely attributed to the
13 oxidation of volatile organic compounds (VOCs) in the dry gas phase, leading to the
14 formation of less volatile species that subsequently partition into the condensed phase (Claeys
15 et al., 2004; Donahue et al., 2011; Hallquist et al., 2009; Herrmann et al., 2015; Kanakidou et
16 al., 2005; Kroll and Seinfeld, 2008). However, under realistic conditions of humidity, the
17 condensed phase contains liquid water with highly variable mass concentrations as
18 theoretically predicted (Carlton and Turpin, 2013; Meng et al., 1995; Meng and Seinfeld,
19 1994; Pilinis et al., 1989) and measured (Nguyen et al., 2014; Tsai and Kuo, 2005).
20 Therefore, the polar compounds formed during the oxidation of VOCs can readily partition
21 into the aqueous phase (Blando and Turpin, 2000; Epstein et al., 2013; Ervens et al., 2011a;
22 Herrmann et al., 2015). Their subsequent chemical reactivity in this phase leads to the
23 formation of organic acids or higher molecular weight products which can remain at least in
24 part in the condensed phase when water evaporates. These aqueous processes lead to
25 additional SOA formation (aqSOA) that can be very different from those in the gas phase,
26 with likely very different physical and chemical properties (Brégonzio-Rozier et al., 2015;
27 Carlton et al., 2009; Ervens et al., 2014a; El Haddad et al., 2009; Ortiz-Montalvo et al., 2012;
28 Renard et al., 2015; Smith et al., 2014).

29 In general, α,β -unsaturated carbonyls $>C=C-C(=O)-$ and conjugated dienes $>C=C-C=C<$
30 are extremely efficient precursors for radical oligomerization (e.g. initiated by $\cdot OH$ radicals)
31 in the liquid phase (Clayden et al., 2012; Odian, 2004; Smith and March, 2007), but these
32 processes have been only scarcely studied under atmospheric conditions (Ervens et al.,
33 2014a; Ervens et al., 2014b; Kameel et al., 2013a; Liu et al., 2012; Renard et al., 2015, 2013).

1 The authors have shown that the oligomerization proceeds *via* external $\cdot\text{OH}$ -addition to a
2 C=C bond, leads to the formation of a hydroxyalkyl radical ($\text{HO-R}\cdot$) that is stabilized by the
3 resonance effect with the adjacent unsaturation (Figure S1). This $\text{HOR}\cdot$ radical has a planar
4 configuration, providing extremely low steric hindrance for further addition (Gilbert et al.,
5 1994). Thus, in competition with O_2 addition, $\text{HOR}\cdot$ radical can easily add to the C=C bond
6 of another precursor molecule, and quickly propagate the monomer units in this manner, until
7 the termination step (Figure S1). This termination step is a reaction between two radicals, by
8 coupling or by disproportionation, thus yielding a series of oligomers, each series being
9 initialized by a specific radical, depending on the initial $\cdot\text{OH}$ -attack (Kameel et al., 2013b;
10 Renard et al., 2013). Renard et al. (2013 and 2015) have studied the effects of the precursor
11 initial concentrations for methyl vinyl ketone (MVK) under initially aerated solutions, and
12 they concluded that oligomerization prevails over functionalization for precursor initial
13 concentrations of 2 mM or higher. In wet aerosol, this concentration range may be reached by
14 the sum of the unsaturated water soluble organic compounds (UWSOC) (Renard et al., 2013).
15 However, to our knowledge, the reactivity of mixtures of different atmospherically relevant
16 UWSOC has never been studied.

17 The ion mobility spectrometry (IMS) is a method to separate and characterize ions based
18 on their gas-phase transport in electric fields. For roughly 50 years, this technique has been
19 combined with mass spectrometry (MS) by inserting the IMS separation after ionization e.g.
20 by electrospray (ESI) and prior to the mass spectrometry step. This combination of an IMS
21 separation (typically occurring within milliseconds) and MS detection (typically occurring
22 within microseconds) allows an additional separation step on a MS time-frame, in addition to
23 liquid chromatography, without compromising the speed of MS detection (Lapthorn et al.,
24 2013; Shvartsburg and Smith, 2008).

25 Although the IMS-MS has been used in different scientific fields (such as structural
26 polymer chemistry, or biological analyses to fractionate complex mixtures prior to the MS
27 step), it has only recently been applied for “small molecules” such as those found in the 100-
28 500 amu (Lapthorn et al., 2013). This technique is thus very well suited to analyze
29 atmospheric oligomers, but, to our knowledge, it has not yet been used in this field.

30 The aim of this work is to investigate aqueous phase oligomerization of several
31 atmospheric UWSOC through their $\cdot\text{OH}$ -oxidation using IMS-MS. The efficiency of the
32 technique is shown on oligomers that were previously described by Renard et al., (2013), i.e.
33 derived from MVK photooxidation. The results are then compared to other oligomers,

derived from other individual biogenic UWSOCs and mixtures of these compounds. The suitability of the technique for the detection of oligomers in complex chamber and/or field samples is finally discussed.

2. Experimental

A photoreactor was used to simulate the aqueous phase $\cdot\text{OH}$ -oxidation of UWSOC. $\cdot\text{OH}$ radicals were generated from H_2O_2 photolysis. Liquid samples were collected at specific reaction times, and analyzed using ultra-performance liquid chromatography (UPLC) coupled to ion mobility spectrometry and mass spectrometry (IMS-MS). The oligomerization of the investigated UWSOCs was studied for each individual species, and in mixtures.

2.1 Oligomer precursors

Eleven atmospheric relevant UWSOCs (Table 1) were investigated, they were all purchased from Sigma-Aldrich. The initial reactant concentrations were chosen to scale in the range of those for which oligomerization was observed previously with MVK (Renard et al., 2014, 2013) or isoprene (Kameel et al., 2013a). For all experiments, the initial concentration of H_2O_2 was 200 mM. The oligomerization of each individual precursor was examined for an initial concentration of 10 mM, and the mixtures of precursors were studied starting from a total UWSOC initial concentration of 10 mM. For the solution mixtures, two control experiments were performed (in the dark; and under irradiation with no H_2O_2) and revealed no oligomer formation. The chosen precursor concentrations correspond to initial carbon mass concentrations ranging from 480 to 1200 mgC L^{-1} , depending on the compound (from C_4 to C_{10}). These concentrations are higher than the total concentrations of WSOC in cloud and fog droplets, which culminate at approximately 200-300 mgC L^{-1} (Herckes et al., 2013). However, they are much lower than the estimated WSOC concentrations in wet aerosols. Ervens et al. (2011) estimate that these concentrations scale inversely with the volume of the particles, resulting in typical concentrations of $\sim\text{M}$ in wet aerosols. Considering that UWSOC represent 2-20% of WSOC concentrations (Renard et al., 2013), the chosen 10 mM initial concentration may represent the total concentration of all UWSOCs in wet aerosol.

The eleven UWSOC investigated were chosen among a wide range of atmospheric relevant compounds, such as oxygenated isoprenoids and terpenoids, but also green leaf volatiles (GLV), Leaf-Wound Oxygenated Compounds (LWOC) and dicarboxylic acids (Table 1).

Compound	Exact mass (amu)	Class ¹	Structure ²		Maximum degree of Oligomerization ³
Methyl vinyl ketone (MVK)	70.042	Isop., LWOC	α,β -uns. carbonyl		14
Ethyl vinyl ketone (EVK)	84.058	LWOC	α,β -uns. carbonyl		14
Methacrolein (MACR)	70.042	Isop., LWOC	α,β -uns. carbonyl		12
Methacrylic acid (MA)	86.037	Isop.	α,β -uns. acid		10
Fumaric Acid	116.011	Sec.	α,β -uns. acid		7
Maleic acid	116.011	Sec.	α,β -uns. acid		5
Cis-3-Hexenal	98.073	GLV	α,γ -uns. carbonyl		2
Linalool	154.136	Terp.	non-conjugated diene		2
Cis-3-Hexen-1-ol	100.089	GLV	uns. alcohol		/
2-Methyl-3-buten-2-ol (MBO)	86.073	GLV	uns. alcohol		/
Methyl chavicol	148.088	OBVOC	phenylpropene		/

Table 1: List of the eleven studied atmospheric relevant UWSOC. ¹ the investigated compounds include oxygenated isoprenoids (isop.) and terpenoids (terp.), oxygenated biogenic VOC (OBVOC), green leaf volatiles (GLV), Leaf-Wound Oxygenated Compounds (LWOC) and secondary dicarboxylic acids (sec.). ² uns. = unsaturated ³ the maximum degree of oligomerization corresponds to the number of monomer units reached at the maximum m/z of the most intense oligomer series. Oligomerization is considered to occur for a maximum degree of oligomerization > 2.

MVK, methacrolein (MACR) and methacrylic acid (MA) are key oxidation products of isoprene, which is the most abundant emitted VOC with a global emission of 500–750 Tg yr⁻¹ (Claeys et al., 2004; Guenther et al., 2006). Linalool is a major oxygenated monoterpene (Geron and Arnts, 2010). GLV, containing 5 or 6 carbon atoms are initiated by the lipxygenase enzymes within plant cells (Jardine et al., 2012). GLV and LWOC emissions

can be elevated under different types of stresses, including severe weather, climate change, mechanical stress, insects, and pathogens (Arneth et al., 2010; Mentel et al., 2013; Richards-Henderson et al., 2014). We investigated several GLV that were observed in the atmosphere, such as cis-3-hexenal, cis-3-hexen-1-ol and 2-methyl-3-buten-2-ol (MBO) (Brilli et al., 2012; Jardine et al., 2012; Richards-Henderson et al., 2014) and LWOC, such as ethyl vinyl ketone (EVK) (Jiménez et al., 2009), MACR and MVK (Ruuskanen et al., 2011).

Methyl chavicol is a biogenic oxygenated aromatic compound (Bouvier-Brown et al., 2009a ; Bouvier-Brown et al., 2009b; Pereira et al., 2014), its atmospheric mixing ratios were reported to be strongly correlated with those of MBO.

We also studied three atmospheric unsaturated acids. In addition to methacrylic acid, we tested two isomers, fumaric and maleic acids. These dicarboxylic acids are secondary reaction products of both biogenic and anthropogenic precursors. They are highly water soluble and mostly present in particles, they may be involved with cloud condensation processes (Sempéré and Kawamura, 2003).

2.2 Photoreactor

The photoreactor set-up used was based on the one described in Renard et al. (2013). It is a 450 cm³ Pyrex thermostated photoreactor, equipped with a 1000 W xenon arc lamp (LSH 601, Oriel) and a glass filter (AM 0, ASTM 490) to reduce the lamp intensity, in particular in the infrared range (800 – 1100 nm).

All experiments were performed at 25°C. They started with irradiation of aerated UHQ water (18.2 MΩ cm, Millipore), then H₂O₂ (50 %, stabilized, Acros) was introduced, and after 10 min of H₂O₂ photolysis, the UWSOC was introduced (individually or as a mixture) at time 0. All experiments were performed in aerated UHQ water, i.e. with initial saturated O₂ concentrations.

For all experiments, the initial ratio $\frac{[H_2O_2]_0}{[UWSOC]_0} = 20$ was chosen in order to favor [•]OH reaction toward UWSOC over its reaction with H₂O₂ by more than 80 %. Under these conditions, we estimate that the [•]OH concentrations were approximately 10⁻¹⁴ - 10⁻¹³ M, in the range of the estimated values for fog droplets to wet aerosol conditions (Arakaki et al., 2013; Ervens et al., 2014b; Herrmann et al., 2015, 2010).

2.3 IMS-mass spectrometry analyses

Aliquots of the solution sampled from the photoreactor were analyzed for oligomers using an ultra-high performance liquid chromatographic system (UPLC, Waters) coupled to a

hybrid quadrupole - time of flight (Q-TOF) mass spectrometer (Synapt-G2 HDMS, Waters) fitted with an electrospray source (ESI). This instrument incorporates a traveling wave ion mobility spectrometry (TWIMS). This latter system has been widely described by (Shvartsburg and Smith, 2008). Briefly, ions are propelled into a chamber containing a buffer gas and a series of stacked ring electrodes, where a voltage pulse is passed from one to the next, creating a voltage wave in repeating sequences. The height and the speed of the travel wave constitute the main internal parameters of this ion mobility cell. Ions with different collision cross sections (CCS), (i.e., molecular shapes), travel through this ion mobility cell with different velocities, leading to their mobility-based separation (Laphorn et al., 2013) which can be quantified using the ion mobility K given by Equation 1.

$$K = \left(\frac{3q}{16N} \right) \sqrt{\left(\frac{2\pi}{\mu k_b T} \right)} \frac{1}{\Omega} \quad \text{Eq. 1}$$

Where K is the ion mobility, q is the ionic charge [C], N is the buffer gas density, μ is the reduced mass of the buffer gas and the ion [kg], k_b is the Boltzman constant [$\text{kg m}^2 \text{s}^{-2} \text{K}^{-1}$], T is the temperature [K], and Ω is the collision cross-section (CCS, [$\text{\AA}^2$]).

The drift time (DT) of each ion in the cell is inversely proportional to the ion mobility (Kim et al., 2009; Shvartsburg and Smith, 2008). This technique thus allows for an additional separation, especially for large ions, with long carbon chains. The instrument thus provides for each chromatographic peak, 3D spectra: Ion intensity - m/z – drift time.

The chromatographic separations were carried out on an UPLC column (HSS T3 C18, 2.1 $\times$ 100 mm – 1.8 μm ; Waters) at 40°C. The mobile phases consisted in (A) 0.1 % formic acid in water (Biosolve, 99 %) and (B) acetonitrile (Biosolve, ULC/MS). The gradient elution was performed at a flow rate of 600 $\mu\text{L min}^{-1}$ using 5 to 95 % of B within 7 min and held at 95 % of B for 1.5 min. Some contaminant oligomers, e.g., polyethylene glycols (PEG, (Eckers et al., 2007)), appear very often at the end of the run (mostly after 5 min), hence, the detection peak was systematically performed at retention times ranging from 0 to 4 min.

The sample injection volume was 10 μL . The optimum ESI conditions found were as follows: 0.5 kV capillary voltage, 40 V sample cone voltage, 450°C desolvation temperature, 120°C source temperature, 20 L h^{-1} cone gas flow rate and 800 L h^{-1} desolvation gas flow rate. Trap and transfer collision gas flows were set at 2.0 mL min^{-1} (0.02 mbar for Ar cell pressure). Helium cell gas flow was set at 180 mL min^{-1} , and IMS gas flow (N_2) was set at 90 mL min^{-1} and 3.0 mbar for IMS cell pressure. Travel wave height and velocity were set at 40 V and 650 m s^{-1} , respectively. Data acquisition and mass spectra treatments were provided by

the MassLynx software (v.4.1, Waters). Finally, the DriftScope software (v.2.1, Waters) was used for the treatment of m/z vs. drift-time maps, and provided 2D IMS-MS spectra. Using this software, the selected peak detection parameters were the minimum drift time peak width (0.05 ms), the drift time range (0 to 10.8 ms), the MS resolution (18000) and the minimum intensity threshold (5000 counts).

3. Results

Using the IMS-MS technique, we studied aqueous phase oligomerization by $\cdot\text{OH}$ -oxidation of each individual UWSOC listed in Table 1, starting with MVK, for which oligomerization processing was previously discussed in detail (Renard et al., 2013). The results were then compared to other oligomers, derived from the other studied individual UWSOCs. Finally, the technique was applied to different mixtures of UWSOCs. For each experiment, the solution was analyzed after 50 min of UWSOC photooxidation, roughly corresponding to the maximum of oligomer formation for each solution, as observed using UPLC-ESI-MS.

3.1 Oligomerization of individual precursors evidenced by IMS-mass spectrometry

Figure 1 shows the 3D (Intensity / Drift time / m/z) and 2D IMS-MS spectra (in the positive mode) of the oligomers derived from MVK after 50 min of aqueous phase $\cdot\text{OH}$ -oxidation. Generally, each oligomer series is characterized by a recurrent mass (corresponding to the one of the propagating monomer) and a drift time. In the present example, the oligomerization is only due to the propagation of one monomer (i.e. MVK), with a few number of different series, each one corresponding to a different radical initiator (Renard et al., 2013). The oligomers thus bear highly related structures. As a result, the 2D IMS-MS spectrum shown in Figure 1 exhibits a linear correlation between the m/z and the drift time for all these structure related oligomer series, in good agreement with the observations by Kim et al., (2009) and Fernandez-Lima et al., (2009) for very different kinds of molecules (i.e. phosphatidylcholines and crude oils respectively). Its linear regression fit, derived over four replicate experiments ($\text{drift time} = 941 (\pm 16) \times 10^{-5} m/z + 0.209 (\pm 0.040)$) characterizes the MVK-oligomer system in the positive mode. In Figure 1, the highlighted red dots label the most intense oligomer series (see the corresponding mass spectrum in Figure S2). Between two subsequent red dots, one can determine the oligomer series' characteristic mass (70.0419 amu corresponding to the molecular mass of MVK) and characteristic drift time (0.659 ms). Figure 1 also shows the double charged ions (green dots),

which exhibit a significantly lower slope than simply charged ions. In fact, according to Eq. 1, the ion mobility increases (i.e. the drift time decreases) with q . This explains why double charged ions show a shorter characteristic drift time than simply charged ions.

Figure 1: (a) 3D (Intensity / Drift time / m/z) and (b) 2D IMS-MS spectra of MVK after 50 min of photooxidation in the aqueous phase, in the positive mode. The most intense series is highlighted in red, with its characteristic MVK mass and MVK drift time. Double charged ions are highlighted in green; they are not included in the linear regression calculation.

In the negative mode, the 2D IMS-MS spectrum of the MVK-oligomers (Figure 2a) also shows a linear correlation between the drift time and m/z (Table 2), which characterizes the MVK-oligomer system in the negative mode. The same kind of observations was performed for all the other individual UWSOCs and mixtures. Thus, we further discuss and compare the results obtained under exactly the same experimental and analytical conditions using the negative mode only, as this mode scarcely shows double charged ions.

Figure 2: 2D IMS-MS spectra (in the negative mode) of different UWSOCs after 50 min of photooxidation in the aqueous phase. (a) MVK, (b) EVK, (c) MACR, (d) methacrylic acid (e) fumaric acid and (f) maleic acid (in addition to the color code, dot sizes increase with intensities).

The 2D IMS-MS spectra obtained for each UWSOC that exhibit oligomerization upon $\cdot\text{OH}$ -oxidation in the aqueous phase, are shown in Figure 2. The maximum degree of oligomerization (reported in Table 1 and Table 2) (Pearce, 1998) corresponds to the number of monomer units reached at the maximum m/z of the most intense oligomer series observed. The precursors are considered to oligomerize under our experimental conditions when the obtained maximum degree of oligomerization is higher than 2.

Table 1 clearly shows that precursor compounds bearing only one unsaturation or two non-conjugated unsaturations do not provide oligomerization (i.e. maximum degree of oligomerization < 2). Among these compounds, *cis*-3-hexenal and linalool undergo only dimerization: the former is a α,γ -unsaturated carbonyl, and the latter is a non-conjugated diene. Their dimerization can be the result of radical recombination without propagation. These results thus confirm the importance of the precursor's chemical structure on the oligomerization process, and especially the great ability of conjugated unsaturated compounds to provide oligomer formation under simulated atmospheric conditions.

Out of the eleven tested compounds, the six compounds bearing a α,β -unsaturated conjugation undergo oligomerization (Table 1). Figure 2 shows that, in the same manner as for MVK, for all these compounds, the m/z and the ion mobility are strongly correlated. However, important differences are observed from one precursor to the other on the maximum degree of oligomerization, on the number of oligomer series, or on the drift. MVK and EVK show the highest maximum degree of oligomerization (14). This result is consistent with the fact that these two compounds have very similar chemical structures, and thus they oligomerize in the same way. This is further confirmed by the fact that the linear correlations between the drift and m/z of their oligomers exhibit the same slope for both precursors, within the experimental uncertainties (Table 2).

The IMS-MS technique also evidences substantial differences between the oligomers arising from MVK and MACR (Figures 2a and 2c) although these two precursors are isomers. The lower DT- m/z slope obtained for MACR-oligomers (Table 2) indicates that they oligomerize in different ways. Compared to MVK-oligomers, MACR-oligomers also show a significantly more clustered shape of the 2D IMS-MS spectra (Figure 2), with more scattered data points, a lower correlation coefficient and a lower maximum degree of oligomerization (Table 2). These differences can be due to a more complex oligomer system (Kim et al., 2009) with MACR precursor, as discussed further hereafter.

Methacrylic acid (Figure 2d) is one of the reaction products of MACR photooxidation in the aqueous phase (Liu et al., 2009). Its oligomers exhibit statistically the same slope as those arising from MACR (Table 2). These observations can be the result of common oligomer series arising from both MACR and methacrylic acid, and thus can explain in part the more complex oligomer system observed from MACR than from MVK.

Fumaric and maleic acids are conformers (Table 1), the former one being produced from the natural photolysis of the latter one under atmospheric conditions (Fu et al., 2013). Although the IMS-MS technique is commonly used to distinguish between oligomers arising from isomers (Li et al., 2012), maleic and fumaric acids exhibit oligomers with similar trends in the 2D IMS-MS spectra (Figures 2e and 2f) and statistically the same slope (Table 2). However, the slopes obtained are significantly lower than those observed from the oligomers arising from the other precursors.

Compounds	Equation of drift time = $f(m/z)$ ($\pm$ Standard deviation)	Maximum Degree of Oligomerization
Methyl vinyl ketone (MVK)	$DT = 947 (\pm 6) \times 10^{-5} m/z + 0.051 (\pm 0.017)$	14
Ethyl vinyl ketone (EVK)	$DT = 968 (\pm 27) \times 10^{-5} m/z + 0.855 (\pm 0.040)$	14
Methacrolein (MACR)	$DT = 879 (\pm 59) \times 10^{-5} m/z + 0.217 (\pm 0.254)$	12
Methacrylic acid	$DT = 844 (\pm 15) \times 10^{-5} m/z + 0.226 (\pm 0.056)$	10
Fumaric acid	$DT = 687 (\pm 37) \times 10^{-5} m/z + 0.426 (\pm 0.167)$	7
Maleic acid	$DT = 668 (\pm 37) \times 10^{-5} m/z + 0.445 (\pm 0.151)$	5
Mixtures	Equation of drift time = $f(m/z)$ ($\pm$ Standard deviation)	Maximum degree of Oligomerization
MVK + MACR	$DT = 915 (\pm 16) \times 10^{-5} m/z + 0.098 (\pm 0.024)$	8
Fumaric + Maleic acids	$DT = 671 (\pm 12) \times 10^{-5} m/z + 0.488 (\pm 0.121)$	4
Fumaric + Maleic + methacrylic acids	$DT = 734 (\pm 13) \times 10^{-5} m/z + 0.430 (\pm 0.106)$	5 ^a
MVK + MACR + EVK + Fumaric + Maleic + methacrylic acids	$DT = 891 (\pm 15) \times 10^{-5} m/z + 0.165 (\pm 0.041)$	8 ^a

Table 2 : Linear regression of the drift time (DT) as a function of m/z ; and maximum degree of oligomerization obtained from the investigated oligomer precursors: six individual α - β unsaturated UWSOCs and four mixtures, by means of IMS-MS in the negative mode. The statistical data were derived over 1 to 4 replicate experiments. ^a for complex mixtures, the maximum degree of co-oligomerization corresponds to the maximum m/z reached by the most intense series, divided by the average molar mass of the mixture.

3.2 Co-oligomerization of precursor mixtures evidenced by IMS-mass spectrometry

In order to examine more complex mixtures, i.e. closer to atmospheric conditions, we investigate in this section IMS-MS analyses of different mixtures of the six compounds bearing a α,β -unsaturated conjugation that individually undergo oligomerization, as shown in the previous section. The aim is to observe oligomerization or co-oligomerization of mixtures containing the same initial total concentration as that used for each individual precursor (10

mM). Due to the different oligomer properties evidenced for the individual precursors, the IMS-MS is a valuable technique to examine if these precursors can undergo co-oligomerization when mixed together. Co-oligomerization is the formation of an oligomer derived from more than one species of monomer. Such co-oligomers, in which there is an irregular distribution of different monomers, mainly follows the Bernoulli Law (Oadian, 2004). In this case, co-oligomers can theoretically also be statistically characterized by the slope of the 2D IMS-MS linear regression fit formed by the detected peaks.

Figure 3 shows that this phenomenon is observed for the four different mixtures of precursors investigated. Such mixtures show extremely complex mass spectra, from which interpretation is arduous if not impossible (see for example Figure S3), whereas IMS-MS spectra exhibit a linear correlation between the m/z and the drift time which proves indubitably co-oligomerization.

Figure 3: 2D IMS-MS of four different mixtures of α - β unsaturated carbonyls and acids after 50 min of photooxidation in the aqueous phase, in the negative mode, with the equations of drift time (standard deviations are in table 2) arising from aqueous phase photooxidation of (a) MVK + MACR (5 mM each), (b) fumaric + maleic acids (5 mM each), (c) fumaric + maleic + methacrylic acids (3.33 mM each), (d) MVK + MACR + EVK + Fumaric + Maleic + methacrylic acids (1.67 mM each).

For the mixture of MVK + MACR (5 mM each), the 2D IMS-MS spectrum (Figure 3a) shows a linear regression fit with an intermediate slope value between those arising from MVK and MACR individually (Table 2).

This result confirms that we do not obtain two different oligomer systems, but rather one co-oligomerization system. The maximum degree of co-oligomerization is smaller than those arising from each individual precursors (Table 2). However, the number of series is likely higher (Figure 3a), certainly due to the enhanced complexity of the system.

For the mixture of maleic and fumaric acids (5mM each), the 2D IMS-MS spectrum (Figure 3b) shows statistically the same slope as those obtained from each individual acid (Table 2). It is thus not possible to determine if any co-oligomerization is occurring in this case.

For the mixture of maleic, fumaric and methacrylic acids (3.33 mM each) (Figure 3c), we observe one intermediate slope between the value obtained for the previous mixture (Figure 3b) and that obtained for methacrylic acid alone (Table 2). The system becomes more complex, with likely more oligomer series as denoted by the more clustered shape of the 2D IMS-MS spectra and a lower maximum degree of co-oligomerization (Table 2). Note that, in this case where co-oligomers contain various monomers of various molecular masses, the maximum degree of co-oligomerization is only an estimated value as it corresponds to the maximum m/z reached by the most intense series observed, divided by the average molecular mass of the initial mixture.

For the final mixture of the six α,β -unsaturated conjugated compounds (1,67 mM each), the 2D IMS-MS spectrum also shows a highly correlated linear plot (Figure 3d) with an intermediate slope between the six individual compounds (Table 2), with a likely more complex oligomer system, and more oligomer series.

4. Conclusions and atmospheric implications

One of the current essential issues to unravel our ability to forecast future climate change and air quality, implies a better understanding of natural processes leading to SOA formation, and in particular the formation and fate of macromolecules. The presence of macromolecules in the atmosphere has previously been monitored by ultrahigh resolution mass spectrometry techniques which have revealed the presence of organic molecules containing up to 35 carbon atoms (C_{35}) in aerosol (Kourtchev et al., 2014; LeClair et al., 2012; Mazzoleni et al., 2012; Rincón et al., 2012), in fog (Mazzoleni et al., 2010) and in rain (Mead et al., 2015, 2013). Evidence that condensed-phase reactions contribute to SOA has been obtained from

laboratory and smog chamber studies (Hallquist et al., 2009; Hall and Johnston, 2012; Herrmann et al., 2015; Zhao et al., 2012). From these studies, it seems that a substantial amount of SOA is composed of oligomers. The latter are small polymers containing less than 30 monomers. The difficulty in characterizing such molecules is to discern between large oxygenated molecules from series of oligomers containing repeated small monomers of diverse structures (Nozière et al., 2015).

In the present study, taking advantage from previously established radical vinyl oligomerization of MVK in the aqueous phase (Renard et al., 2013) where relatively simple oligomers containing up to 14 monomers were observed, we have investigated the same reactivity on several other UWSOCs and on a few mixtures of these precursor compounds. The technique used to characterize the formed oligomers was a traveling wave ion mobility spectrometry coupled to a hybrid quadrupole - time of flight mass spectrometer (IMS-MS) fitted with an electrospray source and UPLC. The technique allows for an additional separation, especially for large ions, containing long carbon chains. The technique is currently widely used in polymer chemistry, or biological analyses, it has only recently been applied for “small molecules” such as those found in the m/z 100-500 range. This technique is thus very well suited to analyze atmospheric oligomers, but, to our knowledge, it has not yet been used in this field.

We have shown in this study the efficiency of the IMS-mass spectrometry technique on oligomers derived from MVK photooxidation in the aqueous phase. The results were then compared to other oligomers, derived from ten other individual biogenic UWSOCs: methacrolein, ethyl vinylketone, methacrylic acid, fumaric and maleic acids, cis-3-hexenal, linalool, cis-3-hexen-1-ol, 2-methyl-3-buten-2-ol and methyl chavicol. The technique allowed distinguishing between different oligomers arising from different precursors. It also clearly showed that compounds bearing a non-conjugated unsaturation did not provide oligomerization. Finally, it was shown that the IMS-mass spectrometry technique, applied to mixtures of unsaturated conjugated precursors, exhibited the ability of these precursors to co-oligomerize, i.e. forming only one complex oligomer system bearing monomers of different structures.

These observations demonstrate the effectiveness of using IMS-mass spectrometry in the study of atmospheric oligomer systems. IMS-mass spectrometry has significant advantages for the analysis of very complex mixtures. It provides rapid identification of complex oligomer systems, when mass spectra are extremely difficult to interpret. In this way, the technique can be regarded as an excellent complement to the ultrahigh resolution mass

spectrometry techniques when long chain complex oligomer series are suspected to be formed, as previously demonstrated on crude oil analyses by Fernandez-Lima et al. (2009). Thus, there should be a growing interest in the use of IMS-mass spectrometry in atmospheric studies to assist in the deconvolution of complex chamber and field samples.

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Supplementary information

Figure S1: Vinylic oligomerization of an α,β -unsaturated carbonyl in the aqueous phase, initiated by $\cdot\text{OH}$ -oxidation, n is the degree of oligomerization i.e. the number of monomers (adapted from Renard et al., 2013).

Figure S2: Typical mass spectrum obtained using UPLC-ESI-MS (in the positive mode) of MVK (20mM) after 50 min of photooxidation in the aqueous phase (highlighted in red, the most intense oligomers series).

Figure S3: Typical mass spectrum obtained using UPLC-ESI-MS of a solution mixture of methyl vinylketone, methacrolein, ethyl vinylketone, methacrylic acid, fumaric and maleic acids (1.67 mM each) after 50 min of photooxidation in the aqueous phase (a) in the positive mode; (b) in the negative mode