Multiphase Reactivity of Gaseous Hydroperoxide Oligomers Produced from Isoprene Ozonolysis in the Presence of Acidified Aerosols

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Abstract

Ozonolysis of alkenes results in the formation of primary ozonides (POZs), which can subsequently decompose into carbonyl compounds and stabilized Criegee intermediates (sCIs). The sCIs generated from isoprene ozonolysis include the simplest congener, formaldehyde oxide (CH_2OO), and isomers of $\text{C}_4\text{-sCI}$. Although the bimolecular reaction with H_2O is expected to be the main fate of sCIs, it was reported that sCIs can also react with carboxylic acids and/or organic hydroperoxides leading to gas-phase oligomeric compounds. While the impact of the gas-phase composition (H_2O , sCI scavenger) on the formation of such products was recently studied, their fate remains unclear. In the present work, formation of oligomeric hydroperoxide from isoprene ozonolysis, proposed as reaction products composed of the sCI as a chain unit and formed from the insertion of sCI into a hydroperoxide or a carboxylic acid, was systematically examined in the presence of aerosol with varying compositions. The effect of hydroxyl (OH) radicals on the gas- and particle-phase compositions was investigated using diethyl ether as an OH radical scavenger. Thirty-four oligomeric compounds resulting from the insertion of sCIs into organic hydroperoxides or carboxylic acids were identified using iodide chemical ionization high-resolution mass spectrometry. Large reactive uptake onto acidified sulfate aerosol was observed for most of the characterized gaseous oligomeric species, whereas the presence of organic coatings and the lack of aerosol water significantly reduced or halted the reactive uptake of these species. These results indicate that highly oxidized molecules, such as hydroperoxides, could undergo multiphase reactions, which are significantly influenced by the chemical composition of seed aerosol. Furthermore, in addition to functionalization and accretion, decomposition and re-volatilization should be considered in the SOA formation.

1. Introduction

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the most abundant non-methane hydrocarbon emitted into the troposphere, with emissions exceeding 500 Tg yr^{-1} (Guenther et al., 2012). Atmospheric oxidation of isoprene occurs mainly by reaction with hydroxyl (OH) radical during the daytime, whereas nighttime oxidation can also occur by ozone (O_3) or nitrate (NO_3) radical. In addition, recent studies have also reported that multiphase chemistry of isoprene in wet acidic aerosols or cloud droplets could be an important source of SOA (Wang et al., 2012; Kameel et al., 2013; Szmigielski, 2016). Recent studies have shown that the OH-initiated oxidation of isoprene under low-nitric oxide (NO) conditions contributes significantly to secondary organic aerosol (SOA) formation on a global scale through multiphase chemistry of isoprene epoxydiols (IEPOX) (Surratt et al., 2010; Budisulistiorini et al., 2013; Chen et al., 2015; Hu et al., 2015; Xu et al., 2015; Rattanavaraha et al., 2016). While the reaction with ozone globally removes $\sim 10\%$ of isoprene, the contribution of isoprene ozonolysis to the SOA budget has been concluded as negligible on the basis of low SOA yields (in the range of $0.1 - 1.4 \%$) determined from high concentration smog chamber experiments in the absence of seed aerosol or with non-acidified seed aerosol (Hasson et al., 2001; Kleindienst et al. 2007; Sato et al., 2013). Jang et al. (2002) and Czoschke et al. (2003) reported that aerosol acidity enhanced SOA formation from isoprene ozonolysis, but the SOA yields remained low. We have recently reported the presence of organosulfates (OSs) and 2-methyltetrols in laboratory-generated SOA formed from isoprene ozonolysis and observed that these SOA constituents were significantly enhanced in the presence of acidic sulfate aerosols (Riva et al., 2016a). In addition, many of the laboratory-generated SOA constituents were measured for the first time in ambient aerosol samples collected from the southeastern United States, suggesting that isoprene ozonolysis could contribute to SOA formation in the atmosphere in the presence of acidic sulfate aerosol (Riva et al., 2016a).

Isoprene ozonolysis is similar to that of other unsaturated hydrocarbons. O₃ addition occurs at one of the two double bonds of isoprene to form a primary ozonide (POZ). POZs subsequently decompose to carbonyl compounds and carbonyl oxides, with a fraction of the latter collisionally deactivated, yielding stabilized Criegee intermediates (sCI) (Johnson and Marston, 2008). The sCIs generated from isoprene ozonolysis include the simplest formaldehyde oxide (CH₂OO) bi-radical and isomers of C₄-sCIs (Scheme S1). Methacrolein (MACR) and methyl vinyl ketone (MVK), which are major first-generation oxidation products from isoprene ozonolysis (Kamens et al., 1982; Sauer et al., 1999), can further react with O₃ and lead to C₃-sCIs (Scheme S1). Generally, Criegee intermediates are initially formed in the excited state and thus a fraction can isomerize to organic hydroperoxides, carboxylic acids, or fragment to smaller products (including OH radicals) in addition to formation of sCIs. In the case of isoprene ozonolysis, the sCI yields in the range of 0.56 to 0.60 have been measured (Zhang et al., 2002; Sipila et al., 2014; Newland et al., 2015; Nguyen et al., 2016). This suggests that large quantities of sCIs are generated from isoprene ozonolysis, leading to the hypothesis that sCIs formed from the ozonolysis of biogenic alkenes can add to the oxidation capacity of the atmosphere (Berndt et al., 2012; Mauldin III et al., 2012; Welz et al., 2012). Due to the relatively long lifetimes of sCIs (~ 1 s), bimolecular reactions of sCIs with atmospheric compounds, such as H₂O, SO₂, carbonyls, and organic acids, are possible (Neeb et al., 1997; Welz et al., 2012, 2014; Berndt et al., 2012, 2014a, b; Taatjes et al., 2012, 2013; Sipila et al., 2014). However, it is worth noting that H₂O vapor is expected to strongly influence the fate of sCIs in the troposphere (Newland et al., 2015; Nguyen et al., 2016).

Many studies have reported gas-phase products from isoprene ozonolysis, including carbonyls, organic hydroperoxides, and organic acids (Kamens et al., 1982; Neeb and Moortgat, 1999; Sauer et al., 1999; Huang et al., 2013; Nguyen et al., 2010; 2016). The

formation of such products was proposed to occur through the reaction of sCIs with H₂O. More recently it was proposed that the formation of oligomeric hydroperoxides identified in the gas phase and proposed as product composed of the sCI as a chain unit, proceeds through the reaction of sCIs with carboxylic acids and/or organic hydroperoxides (Nguyen et al., 2010; Sakamoto et al., 2013; Inomata et al., 2014). These studies have been performed either in the absence or with non-acidified seed particles. However, multiphase chemistry might be expected since it was recently reported that oxygenated species derived from isoprene oxidation, such as epoxides (Surratt et al., 2010; Lin et al., 2012) and organic hydroperoxides (Liu et al., 2016; Riva et al., 2016b) undergo subsequent multiphase chemical reactions leading to gas- and particle-phase products.

In this study we investigate the ozonolysis of isoprene in the presence of sulfate seed aerosols of varying acidity and composition, with a specific focus on the formation and multiphase reactions of gas-phase hydroperoxide oligomers. Because of the high yield of OH radicals from isoprene ozonolysis, experiments were conducted both in the presence and absence of an OH radical scavenger. Gas-phase products were characterized using an Aerodyne high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) equipped with iodide reagent ion chemistry. In addition, aerosol filters collected from indoor smog chamber experiments were analyzed by ultra performance liquid chromatography/electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS). Our results indicate that oligomeric products formed from the gas-phase reaction of sCIs with carboxylic acids and/or hydroperoxides undergo further acid-catalyzed reactive uptake in the presence of acidified sulfate seed aerosols. The presence of oligomeric compounds, OSs and 2-methyltetrols in the particle phase suggests that such multiphase chemical reactions lead to isoprene-derived SOA products from the ozonolysis of isoprene.

2. Experimental Section

2.1 Chamber Experiments.

Isoprene ozonolysis experiments were conducted in a 10-m³ Teflon chamber at the University of North Carolina under dark and dry conditions ($3.3 \pm 0.25\%$, RH) at 296 ± 1 K. Detailed operating procedures for this chamber facility have been previously described (Lin et al., 2012). Experiments were conducted as mentioned in our recent study (Riva et al., 2016a) and a summary of the experimental conditions is provided in Table S1. Briefly, ~ 100 ppb of isoprene (Sigma-Aldrich, 99%) was introduced into the chamber by passing a heated nitrogen (N₂) stream through a heated glass manifold. For selected experiments, ~ 35 ppm of diethyl ether was injected following the same procedure to serve as an OH radical scavenger (Sato et al., 2013). Concentrations of isoprene and diethyl ether were measured every 10 minutes with an online gas chromatography/flame ionization detector (GC-FID, Model CP-3800, Varian), which was calibrated using multiple injections of isoprene and diethyl ether. Approximately 1 hour after isoprene injection, 120–150 ppb of O₃ was introduced into the chamber using an O₃ generator (Model L21, Pacific ozone). O₃ concentration was monitored over the course of experiments using a UV photometric analyzer (Model 49P, Thermo-Environmental).

Non-acidified or acidified ammonium or magnesium sulfate seed aerosols were introduced in the chamber two hours after O₃ injection. Non-acidified seed aerosol was generated from 0.06 M magnesium sulfate (MgSO₄) or ammonium sulfate (NH₄)₂SO_{4(aq)} solutions and acidified seed aerosol from 0.06 M (MgSO₄)_(aq) or (NH₄)₂SO_{4(aq)} + 0.06 M (H₂SO₄)_(aq) solutions. Aerosol size distributions were continuously measured using a differential mobility analyzer (DMA, BMI model 2002) coupled to a mixing condensation particle counter (MCPC, BMI model 1710) in order to monitor aerosol number, surface area, and volume concentrations within the chamber. Once aerosol volume concentrations stabilized (~ 1 hour after reaction), aerosols were collected onto 47-mm diameter Teflon

filters (1.0- μm pore size, Tisch Environmental, EPA PM_{2.5} membrane) for two hours at a sampling flow rate of 25 L min⁻¹ to characterize particle-phase reaction products.

2.2 Chemical Characterization of Gas- and Particle-Phase Constituents.

Real-time measurements of gas-phase oxidation products from isoprene ozonolysis were performed with an Aerodyne high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS), equipped with iodide (I^-) reagent ion chemistry. Analyses were restricted to ions containing an iodide adduct, which guarantees detection of the parent organic compound without substantial fragmentation. Iodide-HR-ToF-CIMS has been described previously and demonstrated high sensitivity towards multifunctional oxygenated organic compounds in the gas and particle phases (Lee et al., 2014; Lopez-Hilfiker et al., 2016a,b). Typical intensities of I^- and IH_2O^- were $8.0 \times 10^{+8}$ and $2.5 \times 10^{+7}$ ion s⁻¹, respectively. Therefore, due to the small abundance of the water cluster, the impact of the water cluster in the clustering of organic compounds is expected to be negligible.

Chemical characterization of SOA constituents produced from isoprene ozonolysis was performed by UPLC/ESI-HR-QTOFMS (6520 Series, Agilent) operated in both negative and positive ion modes. Operating conditions have been described in detail elsewhere (Lin et al., 2012). Filters collected from smog chamber experiments were extracted with 22 mL of high-purity methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) by sonication for 45 min. The methanol extracts were then blown dry under a gentle N₂ (g) stream at ambient temperature. Dried extracts were reconstituted with 150 μL of a 50:50 (v/v) solvent mixture of methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) and high-purity water (Milli-Q, 18.2 M Ω). Five or 10 μL aliquots were injected onto the UPLC column (Waters ACQUITY UPLC HSS T3 column, 2.1 $\times$ 100 mm, 1.8 μm particle size) and eluted at a flow rate of 0.3 mL min⁻¹ with a solvent mixture of methanol containing 0.1% acetic acid or 0.1% ammonium

acetate (LC-MS CHROMASOLV-grade, Sigma-Aldrich) and water containing 0.1% acetic acid or 0.1% ammonium acetate (LC-MS CHROMASOLV-grade, Sigma-Aldrich) for negative and positive ion modes, respectively.

3. Results and Discussion

3.1 Chemical Characterization of Gas-Phase Reaction Products.

Chemical characterization of gas-phase reaction products generated from isoprene ozonolysis has been performed using a large variety of analytical techniques, including proton transfer reaction-mass spectrometry (PTR-MS), CIMS, and GC-FID (Kamens et al., 1982; Neeb and Moortgat, 1999; Sauer et al., 1999; Inomata et al., 2014; Nguyen et al., 2016). These studies reported the formation of volatile species, such as gas-phase hydroperoxides, carbonyls and carboxylic acids. Recent development of new reagent ion chemistries for CIMS, such as I^- or nitrate (NO_3^-), has allowed for the measurement of highly oxidized molecules (HOMs) in both gas (Ehn et al., 2014; Lee et al., 2014; Krechmer et al., 2015; Bianchi et al., 2016) and particle phases (Lopez-Hilfiker et al., 2016a,b). We further characterized the gas-phase products formed from isoprene ozonolysis by iodide-HR-ToF-CIMS, leading to the identification of more than 50 gas-phase oxidation products. Products are classified into four groups: hydroperoxides (Group 1), oligomeric hydroperoxides (Group 2), summarized in Table 1, and carboxylic acids (Group 3), oligomeric carboxylic acids (Group 4), summarized in Table S2. It should be pointed out that, as discussed by Lee et al., (2014), the formation of carboxylate anions (anions that are not complexes with I^-) as well as secondary ion chemistry are possible, leading to a complexity in the separation and/or identification of organic products by iodide-HR-ToF-CIMS. In this study, only iodide-adduct products were considered. In addition, as shown in Figure S1, no significant new particle formation (NPF) was observed in the conditions used in this study. NPF ($2000\text{-}3000\text{ particles cm}^{-3}$) was

observed only in the experiments performed without an OH radical scavenger (Figure S1a). Therefore, potential formation of observed products through chemistry in the aerosols followed by product volatilization can be ruled out (Lim and Ziemann, 2009).

Group 1 is comprised of gas-phase organic hydroperoxides, designated hydroxyalkyl hydroperoxides (HAHPs), formed by isoprene ozonolysis and reaction of the resulting sCIs with water (Kroll and Seinfeld, 2008; Huang et al., 2013). This pathway likely explains the six HAHPs reported in Table 1 (Neeb and Moortgat, 1999; Sakamoto et al., 2013; Inomata et al., 2014; Nguyen et al., 2016). Larger formation of HAHPs could be likely expected by additional gas-phase water. Organic hydroperoxides formed from the OH oxidation of isoprene, e.g. isoprene hydroxyhydroperoxides (ISOPOOH), are not included in Table 1. As discussed later in the manuscript, the addition of the radical scavenger diethyl ether leads to a significant decrease of the OH-initiated oxidation products and supports the assignment of the identified compounds as isoprene ozonolysis products.

The Group 2 is comprised of oligomeric hydroperoxides formed from the reaction of organic hydroperoxides with sCIs. The formation of such oligomers was proposed to occur through the insertion of a sCI into an organic hydroperoxide, as presented in Scheme S2 (Inomata et al., 2014). Eleven oligomeric hydroperoxides identified from isoprene ozonolysis are reported in Table 1. Among the eleven oligomers, six correspond to the insertion of the simplest C₁-sCI, formaldehyde oxide (CH₂OO), into the HAHPs in Group 1. In addition, products at *m/z* 277 (C₅H₁₀O₅I⁻) and 293 (C₅H₁₀O₆I⁻) are proposed to result from the insertion of a C₄-sCI into HMHP and HPMP, respectively. Finally, insertion of two C₁-sCIs into HPFOR, HMHP and HPMP lead to the formation of ions at *m/z* 281 (C₃H₆O₇I⁻), 283 (C₃H₈O₇I⁻) and 299 (C₃H₈O₈I⁻). No products resulting from the insertion of C₃-sCI into organic hydroperoxides were observed, suggesting that the ozonolysis of primary products (Scheme S1) was negligible under our experimental conditions.

Previous studies have reported large yields of carboxylic acids in both gas (Orzechowska and Paulson, 2002; Inomata et al., 2014) and particle phases (Nguyen et al., 2010) from isoprene ozonolysis. Ten carboxylic acids were identified in the gas-phase, including formic and pyruvic acids, and represent the third group of compounds identified in this study (Table S2). Pathways leading to the carboxylic acids reported in Table S2 have been proposed previously by Nguyen et al. (2010) to occur from the ozonolysis of isoprene through the “hydroperoxide channel” or via the ozonolysis of first generation products such as acrylic acid.

Group-4 includes oligomeric compounds that arise from the insertion of sCIs into carboxylic acids (Scheme S3), resulting in polymeric hydroperoxides (Nguyen et al., 2010; Sakamoto et al., 2013; Inomata et al., 2014). Twenty-five gaseous polymeric products were identified from isoprene ozonolysis and are reported in Table S2. Among them, eight correspond to the reaction of carboxylic acids with the CH_2OO bi-radical and nine with the $\text{C}_4\text{-sCI}$. The insertion of two sCIs was also observed for nine compounds, as reported in Table S2. Higher reactivity of $\text{C}_4\text{-sCI}$ have been observed with the carboxylic acids, in line with rate coefficients determined for the reactions of sCIs with acids and other organic compounds (Novelli et al., 2014). Rate coefficients for the reaction of sCIs with carboxylic acids were calculated to be two orders of magnitude greater ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$) than those for reaction of sCIs with other carbonyls or hydroperoxides ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$) (Novelli et al., 2014). Since the aim of this study was to investigate the formation and multiphase chemistry of isoprene-derived ozonolysis products, products generated from the OH-initiated oxidation of isoprene are not reported in Tables 1 and S2. It could be expected that products belonging to group-2 will be strongly reduced by the presence of additional gas-phase water. On the contrary, products from group-4 will likely remain formed even at larger RH, notably due to the large reactivity of sCI with carboxylic acids (Novelli et al., 2014; Welz et al., 2014).

3.2 Chemical Characterization of Particle-Phase Reaction Products.

Tables S3 and S4 summarize the isoprene-derived SOA products identified by UPLC/ESI-HR-QTOFMS operated in positive and negative ion modes, respectively. As discussed in Riva et al. (2016a), IEPOX-derived SOA products were identified in the experiments performed only in the absence of an OH radical scavenger. Concentrations of the polymeric products identified in particle phase reported here (Figure S2) along with the 2-methyltetrols and OSs reported in Riva et al. (2016a) are significantly enhanced by the presence of acidified particles (Lin et al., 2012, Riva et al., 2016a). Eighteen compounds identified in the gas-phase were also observed in the particle phase but their low abundances (i.e. signal/noise < 3) preclude quantification of these products. Direct comparison of the gas- and particle-phase concentrations was not possible due to absence of the appropriate calibration standards. Quantification of compounds observed in the positive ion mode was accomplished using 1,2-ISOPROOH and 2-methyltetrols synthesized in-house (Budisulistiorini et al., 2015; Riva et al., 2016b) as surrogate standards, resulting in large uncertainties for the estimated concentrations of the oligomers, in particular.

Particle-phase products identified in the positive and negative ion modes revealed the presence of highly oxidized molecules not identified in the gas phase (Tables S3, S4 and Figure S3). The significant concentration of particle-phase products, such as 2-methyltetrols, indicate that observed gas-phase products might undergo further multiphase reactions in the presence of sulfate seed aerosols. Formation of oligomers in particle phase has been proposed to occur via esterification, aldol condensation and/or hemiacetal reactions (Nguyen et al., 2011). In addition, recent studies have reported that gaseous HOMs (e.g., multifunctional hydroperoxides) could undergo further multiphase reactions and/or acid-catalyzed hydrolysis to yield the formation of particle-phase oligomers (Lim and Turpin, 2015; Riva et al., 2016b) and OSs (Mutzel et al., 2015; Riva et al., 2016b).

3.3 Impact of OH Scavenger on the Formation of Oligomeric Compounds.

Isoprene ozonolysis leads to OH radical formation with yields greater than 25% (Neeb and Moortgat, 1999); therefore, the OH-initiated oxidation of isoprene likely contributes to isoprene depletion. Under low-NO_x conditions, OH-initiated oxidation of isoprene produces organic peroxy radicals (RO₂) that can react with hydroperoxy radicals (HO₂) to form ISOPOOH isomers, which react further with OH radicals to give IEPOX in yields greater than 75% (St. Clair et al., 2016). ISOPOOH and IEPOX are isobars and cannot be distinguished by the CIMS used in this work. Therefore, the parent ion at m/z 245 (C₅H₁₀O₃I⁻) is assigned to ISOPOOH and/or IEPOX and was observed in the experiments performed in the absence of diethyl ether. As shown in Figure S4, during the experiments performed in the presence of OH scavenger, the signal of the ion at m/z 245 was significantly reduced, confirming that most of the OH radicals were scavenged.

Tables 1 and S2 report the gas-phase products identified in the experiments performed in the presence of the OH scavenger. Compounds with changes in peak intensities $> \pm 30\%$ in the presence and absence of OH radical scavenger were considered to be affected by the level of OH radical. In general, compounds belonging to the different groups are not significantly impacted by the presence of an OH scavenger. Similar peak intensities were observed except for compounds from Group 2 (Table 1), in which the signals of six oligomeric hydroperoxides decrease significantly in the presence of the OH scavenger (Figure 1a). The decrease of some products, such as the parent ion at m/z 235 (C₂H₄O₅I⁻), is likely correlated with the decreased concentration of HPFOR, produced from the OH-initiated oxidation of isoprene or its first-generation oxidation products. The decrease of other products, such as the parent ions at m/z 277 (C₅H₁₀O₅I⁻), 279 (C₄H₈O₆I⁻) and 293 (C₅H₁₀O₆I⁻), could be explained by the inhibition of isoprene oxidation by OH radicals (Figure 1a). Krechmer et al. (2015) reported the formation of gas-phase products with chemical compositions identical to the parent ions at

m/z 277, 279, and 293 from the OH-initiated oxidation of ISOPOOH. However, the HR-ToF-CIMS cannot distinguish between isobars that might be formed from the oxidation of isoprene by OH radical and O_3 . As evident in Figure 1b and Tables 1 and S2, the absence of OH radical could also enhance the formation of oligomeric products, such as parent ions at m/z 237 ($C_2H_6O_5I^-$) and 251 ($C_2H_4O_6I^-$). The increased abundance of these compounds might be explained by an increased depletion of isoprene by O_3 , and consequent increased formation of sCIs (formaldehyde oxide in the case of $C_2H_6O_5I^-$ and $C_2H_4O_6I^-$, Figure 1b). Finally, larger abundance of such compounds could also be due to the lack of reactivity with OH radicals.

3.4 Effect of Aerosol Composition on Gaseous Oligomeric Compounds.

The fate of HOMs (including organic hydroperoxides), and oligomeric compounds such as those identified from isoprene ozonolysis (gas-particle partitioning, photolysis, reactive uptake, etc.) has received small attention and remains unclear. In order to better characterize their potential multiphase reactivity, the effects of seed aerosol composition as well as aerosol acidity were investigated. Figure 2 presents the time series of selected oligomeric compounds belonging to Groups 2 and 4 in the presence of acidified and neutral sulfate seed particles. No significant drop of the gas-phase ion signals after the injection of non-acidified $(NH_4)_2SO_4$ seed aerosols (at ~ 350 min) was observed for compounds reported in Tables 1 and S2. It is worth noting that HOMs are expected to have low vapor pressures (Ehn et al., 2014; Li et al., 2016) and therefore to condense onto seed aerosol. However, Inomata et al. (2014) estimated that oligomeric hydroperoxides observed in the mass range of 120–160 have effective saturation concentrations of $10^3 \mu g m^{-3}$ in the volatility basis model (Donahue et al., 2012). In addition, Kurten et al. (2016) have also been reported that group-contribution methods likely under-estimate the volatility of highly oxidized compounds by ignoring intramolecular H-

bonds. Therefore, the lack of condensation suggests that observed species could be more volatile than previously expected.

Our experiments were performed at low RH and under these conditions non-acidified $(\text{NH}_4)_2\text{SO}_4$ seed aerosols are crystalline (Zelenuyk and Imre, 2005). Therefore, multiphase processes such as acid-catalyzed aqueous-phase reactions are significantly reduced or suppressed. The absence of SOA constituents derived from isoprene ozonolysis (Riva et al., 2016a) in experiments performed using non-acidified $(\text{NH}_4)_2\text{SO}_4$ seed aerosols under dry conditions confirms the lack of multiphase chemistry. However, enhanced decomposition of organic peroxides was identified in the presence of SOA and water, suggesting that water affects the condensation or reactive uptake of organic hydroperoxides (Li et al. 2016) onto seed aerosol.

Formation of oligomers and their OS derivatives was observed in the SOA generated from the reactive uptake of IEPOX in the presence of MgSO_4 seed aerosol under dry conditions (Lin et al., 2014). Non-acidified MgSO_4 aerosols do not effloresce at low-RH conditions and instead form gel-like chain structures of contact ion pairs (Chan et al., 2000). Figure 2b shows that following the injection of non-acidified MgSO_4 seed aerosols, only a slight decrease is observed in the concentration of gas-phase ions monitored at m/z 251, 281 and 293, suggesting little condensation/reactive uptake. Acidified particles significantly enhanced the reactive uptake/condensation of gas-phase products reported in Tables 1 and S2. Figure 2 shows a drop of the gas-phase ion signals immediately following the injection of either acidified MgSO_4 or $(\text{NH}_4)_2\text{SO}_4$ seed aerosols. The decrease of the concentrations of oligomeric compounds appears larger in the presence of acidified MgSO_4 (Figure 2b) than acidified $(\text{NH}_4)_2\text{SO}_4$ seed aerosol (Figure 2a). Although the effects of aerosol acidity and liquid water content on the reactive uptake of oligomeric hydroperoxides cannot be deconvoluted because water is always present in the acidified seed particles, Figure 2 suggests

that aerosol acidity promotes multiphase chemistry, as recently demonstrated for the reactive uptake of IEPOX (Gaston et al., 2014; Riedel et al., 2015). Consistent with this hypothesis and greater uptake by acidified MgSO_4 seed aerosol observed in Figure 2, Lin et al. (2014) have estimated that under low-RH conditions, acidified MgSO_4 seed aerosols are more acidic (pH 0.62) than the acidified $(\text{NH}_4)_2\text{SO}_4$ seed aerosols (pH 2.25).

An increased concentration of gas-phase ions was also observed upon injection of acidified sulfate seed particles for a different set of products in Tables 1 and S2. As shown in Figures 3a and 3b, most of the products belonging to Group 3 as well as $\text{CH}_4\text{O}_4\text{I}^-$ were enhanced in the gas phase after the injection of acidic sulfate seed particles, while the addition of non-acidified seed particles did not impact the concentrations of these products. The re-formation of these gaseous products is consistent with the acid-catalyzed decomposition of some oligomers formed by the insertion of sCIs into organic hydroperoxides or carboxylic acids and demonstrates the reactivity of such oligomeric products. It should be noted that the analytical techniques used in this study are not sensitive to volatile species such as small carbonyls (e.g. MACR or MVK) and as a consequence the importance of the re-volatilization is likely to be underestimated. Liu et al (2016) have also reported the decomposition of products of isoprene photooxidation in the presence of acidified sulfate aerosols with subsequent formation of volatile species, estimating that at least 50% of ISOPROOH taken up onto acidified aerosols react to form gas-phase species. In addition, the formation of hydrogen peroxide (H_2O_2) was reported in high yield from the decomposition of organic hydroperoxides and/or HAHPs (Huang et al., 2013; Li et al., 2016). It is worth noting that a rise of gas-phase hydrogen peroxide ion signal (IH_2O_2^-) was also observed in our experiments using only acidified seed particles, underlying the rapid decomposition of oligomeric hydroperoxides. The results presented here, combined with the existing literature, highlight the strong reactivity of hydroperoxides leading to volatile species that could undergo photooxidation

processes and might further contribute to SOA formation. Reactive uptake of hydroperoxides could also proceed through accretion reactions to yield oligomers, OSs and 2-methyltetrols that have been identified in SOA generated from isoprene ozonolysis (Riva et al., 2016a).

Reaction time profiles of the main reactive gaseous species observed in the experiments performed with and without an OH scavenger using acidified sulfate seed aerosols are presented in Figure 4. The comparison of these two sets of experiments reveals that reactive uptake of the monitored species is significantly reduced by the presence of OH radicals. As mentioned earlier and shown in Figure S4, the absence of an OH radical scavenger induces the large formation of ISOPOOH/IEPOX in the gas phase. IEPOX and ISOPOOH chemistries have been intensively examined in recent studies and it has been demonstrated that IEPOX rapidly undergoes acid-catalyzed reactive uptake (Surratt et al., 2010; Gaston et al., 2014; Riedel et al., 2015) yielding significant SOA formation, whereas ISOPOOH + OH can also yield significant amounts of SOA through non-IEPOX channels (Liu et al., 2016; Riva et al., 2016b). However, reactive uptake of gas-phase epoxides could be significantly reduced by the presence of organic coatings on pre-existing aerosols (Gaston et al., 2014; Riva et al., 2016c). Therefore, the lack of reactivity of species in the experiments performed without an OH scavenger might be explained by the large formation of IEPOX-derived SOA (Riva et al., 2016a). Hence, IEPOX chemistry could produce an organic coating and virtually halt further multiphase reactions of the oligomeric hydroperoxides. These results suggest that a potential competition exists between the multiphase reactivity of oxygenated species, and combined with a large presence of organics, might suppress any further multiphase chemistry of either gas-phase product.

4. Conclusions

Isoprene ozonolysis leads to the formation of sCIs in yields greater than 50% (Newland et al., 2015; Nguyen et al., 2016). Although the importance of the plausible bimolecular reactions of

sCIs remains unclear, formation of organic hydroperoxides, carboxylic acids and HOMs have been reported in different studies (Nguyen et al., 2010; Sakamoto et al., 2013; Inomata et al., 2014). The results presented here describe the formation of gas-phase oligomeric products through the insertion of sCIs into organic hydroperoxides and carboxylic acids and their subsequent reactive uptake onto acidified sulfate aerosols, which could lead to isoprene-derived SOA products identified in laboratory and field experiments. In addition, HAHPs, formed from the reaction of sCIs with water, could also undergo further multiphase chemistry in the presence of acidified aerosols. Our results suggest that oligomeric products and hydroperoxides decompose in the presence of acidified sulfate aerosols to release volatile organic species (e.g. formic acid or H_2O_2), which could contribute to SOA or the oxidative capacity of the atmosphere through further photochemical chemical reactions. The multiphase reactivity can be suppressed by the build-up of an organic coating or by the lack of aerosol liquid water. Further experiments on the multiphase reactivity of organic hydroperoxides and HOMs are needed to better characterize these chemical processes and to estimate their impact on SOA formation. In particular, determination of the reaction probability (γ) of epoxides and hydroperoxides onto varying aerosol compositions should be undertaken to better understand the multiphase chemistry of such reactive species. Finally, determination of the rate constants of the reaction between sCIs and acids and organic hydroperoxides should be systemically investigated to better evaluate the impact of sCI chemistry on SOA formation.

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Table 1. Accurate mass fittings of organic hydroperoxides and sCI-hydroperoxide oligomers identified from the ozonolysis of isoprene.

Measured <i>m/z</i>	Proposed Formula	DBE ^a	Name/Reaction	Reactive Uptake	Sca ^b	UPLC/ESI -QTOFMS
Group 1: Hydroperoxides						
188.897	CH ₂ O ₃ I [−]	1	HPFOR	−	−	(M + H) ⁺
190.911	CH ₄ O ₃ I [−]	0	HMHP			
204.905	CH ₂ O ₄ I [−]	1	HPFA	−		
206.910	CH ₄ O ₄ I [−]	0	HPMP	+		(M + H) [−]
228.940	C ₄ H ₆ O ₃ I [−]	2	HPMVK/HPMACR	+	−	
232.921 ^c	C ₃ H ₆ O ₄ I [−]	1	HPLA/HPHA	−	+	
Group 2: Oligomeric Hydroperoxides						
234.913	C ₂ H ₄ O ₅ I [−]	1	HPFOR + C ₁ -sCI		−	(M + H) ⁺
236.929	C ₂ H ₆ O ₅ I [−]	0	HMHP + C ₁ -sCI	+	+	
250.915	C ₂ H ₄ O ₆ I [−]	1	HPFA + C ₁ -sCI	−	+	
252.951	C ₂ H ₆ O ₆ I [−]	0	HPMP + C ₁ -sCI			(M + H) ⁺
274.948 ^c	C ₅ H ₈ O ₅ I [−]	2	HPMVK/HPMACR + C ₁ -sCI		−	
276.995	C ₅ H ₁₀ O ₅ I [−]	1	HMHP + C ₄ -sCI	−	−	
278.933 ^c	C ₄ H ₈ O ₆ I [−]	1	HPLA/HPHA + C ₁ -sCI	−	−	(M + H) ⁺
280.912	C ₃ H ₆ O ₇ I [−]	1	HPFOR + 2(C ₁ -sCI)	−	+	
282.938	C ₃ H ₈ O ₇ I [−]	0	HMHP + 2(C ₁ -sCI)			
292.959	C ₅ H ₁₀ O ₆ I [−]	1	HPMP + C ₄ -sCI	−	−	(M + H) ⁺
298.928	C ₃ H ₈ O ₈ I [−]	0	HPMP + 2(C ₁ -sCI)	−	−	

^aDBE: double bond equivalent; ^b Sca: experiments performed using an OH radical scavenger; ^c Compound could be formed from reaction of an sCI with an organic acid (Table S2); in the columns “reactive uptake” and “Sca”, (+) or (−) denotes decrease and increase of peak intensity, respectively. HPFOR: hydroperoxide formaldehyde; HMHP: hydroxymethyl hydroperoxide; HPFA: hydroxyperformic acid; HPMP: hydroperoxy methyl hydroperoxide; HPMVK/HPMACR: hydroperoxy methyl vinyl ketone/ hydroperoxy methacrolein; HPLA: hydroperoxy lactaldehyde; HPHA: hydroperoxy hydroxyacetone.

Figure 1. Time series of oligomeric products belonging to Group 2 formed by the insertion of sCIs into organic hydroperoxides (Table 1). Panels (a) and (b) show the impact of an OH radical scavenger (Sca) on the formation of the gas-phase products in the presence of non-acidified magnesium sulfate seed aerosols injected after ~ 350 min.

Figure 2. Time series of gas-phase products belonging to Group 2 formed from isoprene ozonolysis in the presence of an OH radical scavenger. **(a)** Non-acidified (NH_4) and acidified (NH_4 Ac.) ammonium sulfate and **(b)** non-acidified (Mg) and acidified (Mg Ac.) magnesium sulfate aerosols were injected after ~ 350 min (* indicates the injection of seed particles).

Figure 3. Time profiles of selected organic hydroperoxides and carboxylic acids formed by isoprene ozonolysis in the presence of an OH scavenger. Panels (a) and (b) correspond to experiments performed using non-acidified and acidified magnesium sulfate seed aerosols, respectively. Seed aerosols were injected after ~ 350 min (* indicates the injection of seed particles)).

Figure 4. Time profiles of the major reactive gaseous species in the presence of acidified sulfate seed aerosols identified generated by isoprene ozonolysis. Panels (a) and (b) correspond to the experiments performed using acidified ammonium sulfate seed particles without and with an OH radical scavenger, respectively. Panels (c) and (d) correspond to the experiments performed using acidified magnesium seed particles without and with an OH radical scavenger, respectively. Seed aerosols were injected after ~ 350 min.