Oligomerization Reaction of the Criegee Intermediate Leads to Secondary Organic Aerosol Formation in Ethylene Ozonolysis

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ABSTRACT: Ethylene ozonolysis was investigated in laboratory experiments using a Teflon bag reactor. A negative ion chemical ionization mass spectrometer (NI-CIMS) using SO₂Cl⁻ and Cl⁻ as reagent ions was used for product analysis. In addition to the expected gas-phase products, such as formic acid and hydroperoxymethyl formate, oligomeric hydroperoxides composed of the Criegee intermediate (CH₂OO) as a chain unit were observed. Furthermore, we observed secondary organic aerosol (SOA) formation from the ethylene ozonolysis, and the particle-phase products were also analyzed by NI-CIMS. The CH₂OO oligomers were also observed as particle-phase components, suggesting that the oligomeric hydroperoxides formed in the gas phase partition into the particle phase. By adding methanol as a stabilized Criegee intermediate scavenger, both the gas-phase oligomer formation and SOA formation were strongly suppressed. This indicates that CH₂OO plays a critical role in the formation of oligomeric hydroperoxides followed by SOA formation in ethylene ozonolysis. A new formation



mechanism for the oligomeric hydroperoxides, which includes sequential addition of CH2OO to hydroperoxides, is proposed.

INTRODUCTION

Alkene ozonolysis is an important source of free radicals and secondary organic aerosols (SOAs) in the Earth's atmosphere.¹ Although the reaction mechanism has been investigated, it is not yet understood in full detail. Most mechanistic studies of alkene ozonolysis have focused on ozonolysis of the simplest alkene, ethylene.^{2–15} Figure 1 briefly summarizes the initial steps involved in ethylene ozonolysis. First, ozone adds across the ethylene double bond to form a primary ozonide, which decomposes to formaldehyde (HCHO) and an excited Criegee



Figure 1. Brief summary of initial steps of ethylene ozonolysis.

intermediate, CH_2OO^* . While some of the CH_2OO^* subsequently decomposes to produce CO, CO_2 , H_2 , H_2O , H, and OH or isomerizes to formic acid (HCOOH), the other part is collisionally stabilized.

In ethylene ozonolysis, the stabilized Criegee intermediate (SCI), CH₂OO, has been shown to react with other products.^{2,4–8,10,11,14–16} For example, it can react with the initially produced HCHO to produce a secondary ozonide:

$$CH_2OO + \overset{O}{\underset{HCH}{\parallel}} \rightarrow \overset{H_2C}{\underset{O-O}{\vee}} \overset{O}{\underset{CH_2}{\leftarrow}} (1)$$

Additionally, the SCI may also react with H_2O and HCOOH to produce hydroxymethyl hydroperoxide (HOCH₂OOH, HMHP) and hydroperoxymethyl formate (HCOOCH₂OOH, HPMF), respectively.

$$CH_2OO + H_2O \rightarrow HO - CH_2OO - H$$
 (2)

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ CH_2OO + & HCOH \rightarrow & HCO-CH_2OO-H \end{array}$$
(3)

Neeb et al. estimated the relative rate constants for these reactions and concluded that the reaction of CH_2OO with H_2O is the dominant process under tropospheric conditions.^{5,15} While reactions with other atmospheric species such as SO_2 and NO_2 have been reported for a variety of SCIs including CH_2OO , reaction with H_2O is predicted to consume most of the SCIs

Received: August 29, 2013 Revised: November 2, 2013 Published: November 7, 2013



Figure 2. Schematic diagram of the experimental setup.

under tropospheric conditions based on indirectly estimated rate constants.¹ Recently, however, field observations suggest that SCIs may contribute to the oxidation of SO_2 and other trace gases,¹⁷ implying that SCIs including CH₂OO may be significant participants in tropospheric chemistry.

To expand our understanding of CH2OO chemistry in the troposphere, we investigated ethylene ozonolysis in laboratory experiments under dry conditions using a Teflon bag reaction enclosure. Gas-phase products were analyzed by a negative ion chemical ionization mass spectrometer (NI-CIMS) using SO_2Cl^- or Cl^- as the reagent ion. SO_2Cl^- -CIMS has the ability to ionize acidic species through a chloride ion transfer reaction because of their high chloride affinities.^{18,19} We also found that a variety of hydroperoxides can be detected using SO₂Cl⁻- and Cl⁻-CIMS. In addition, during the ethylene ozonolysis experiments, SOA formation was observed. This is intriguing because the known products of the ethylene ozonolysis are thought to be too volatile to form SOAs.²⁰ Thus, we conducted off-line NI-CIMS analyses of the particle-phase products by collecting the SOAs on a PTFE filter, which was then heated to vaporize the particle-phase components. By comparing the gas- and aerosol-phase products, we proposed a new mechanism for SOA formation from ethylene ozonolysis.

EXPERIMENTAL SECTION

Experiments were performed using a 175 cm \times 155 cm pillowshaped bag made of FEP Teflon. Figure 2 depicts the experimental setup. Synthetic air (composed of N₂ and O₂ with other contaminants below 1 ppmv, Japan Fine Products, Kawasaki, Japan) and ethylene (C₂H₄, 1% in N₂, Japan Fine Products) were introduced into the Teflon bag.

The ozonolysis reaction was initiated by introduction of ozone (O_3) , which was produced by irradiating the synthetic air with vacuum ultraviolet light at 185 nm from a low-pressure Hg lamp, into the Teflon bag containing synthetic air and ethylene. The reaction was investigated at room temperature and atmospheric pressure under dry conditions

with RH well below 1% with an initial total volume of approximately 0.85 m^3 .

Ozone and gas-phase products were monitored using a commercial ozone monitor (model 1150; Dylec Inc., Ibaraki, Japan) and a custom-built NI-CIMS, respectively. The NI-CIMS is described in the following subsection. All tubes and tube connectors used for NI-CIMS were made of Teflon because some reaction products disappeared when stainless steel tubing was used, probably due to heterogeneous reactions on the metal walls. The aerosol size distribution was measured using a scanning mobility particle sizer (SMPS, DMA model 3080, CPC model 3775; TSI Inc., Shoreview, MN, USA). To analyze the aerosol composition, nearly all the air remaining in the bag after a reaction time of 1 h was extracted using a diaphragm pump, and any particles in the extracted air were collected on a PTFE filter (ADVANTEC PF020; Tovo Roshi Kaisha, Ltd., Tokyo, Japan). This particle collection process took approximately 30 min. Then, the filter was heated at 403 K in a flow of synthetic air to vaporize components of the collected particles, and this vapor was introduced into the NI-CIMS for analysis.

Typical initial concentrations of ethylene and ozone were 2.9 and 4.5 ppmv, respectively, unless otherwise noted. Although these concentrations are several orders of magnitude higher than ambient levels, we used them due to the sensitivity limitations of our instruments. In some of the experiments, excess cyclohexane (99.8%, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was added as an OH radical scavenger,⁹ and excess methanol (99.9%, Wako Pure Chemical Industries, Ltd.) was added as an SCI scavenger.^{11,21} These scavenger compounds were used without further purification. They were injected as liquids into the Teflon bag using a syringe and allowed to vaporize prior to initiating the reaction. A typical concentration of cyclohexane was 350 ppmv. On the basis of the reported rate constant of 7.9×10^{-12} cm³ molecule⁻¹ s⁻¹ (at 1 bar air) for ethylene + OH²² and that of 7.0×10^{-12} cm³ molecule⁻¹ s⁻¹ for cyclohexane + OH,²³ approximately 99% of any product OH radicals will be scavenged by cyclohexane under the present



Figure 3. Schematic diagram of the NI-CIMS instrument.

experimental conditions. The products of cyclohexane with OH radical include cyclohexanol (c-C₆H₁₁OH), cyclohexanone (c-C₆H₁₀O), cyclohexyl hydroperoxide (c-C₆H₁₁OOH), and other products formed via ring-opening.⁹ A typical concentration of methanol was 1300 ppmv. It should be noted that in experiments with the addition of both cyclohexane and methanol, a fraction of the OH radicals was scavenged by methanol as well as cyclohexane. On the basis of the rate constant of 0.93 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ for methanol + OH,²² approximately 33% of the OH radicals will be scavenged by methanol and 67% by cyclohexane. The reaction of methanol with OH produces HCHO and HO₂ with a yield of unity.²²

Negative Ion Chemical Ionization Mass Spectrometer (NI-CIMS). In the NI-CIMS analysis, either SO_2CI^- or CI^- was used as a reagent ion. A schematic diagram of the NI-CIMS instrument is shown in Figure 3.

The SO₂Cl⁻-CIMS has been described in detail previously,¹⁹ so that only a brief description focused on relevant modifications for the present study will be given here. The reagent ion, SO₂Cl⁻, was produced through the addition of SO₂ to Cl⁻. While Cl⁻ was generated by discharge of a CH₃Cl/Ar gas mixture in previous studies, it was generated by the electron impact from a resistively heated filament onto the CH₃Cl/Ar gas mixture herein. Gas in the Teflon bag was sampled into the NI-CIMS at a flow rate of approximately 0.8 L min⁻¹ through a 0.25 mm diameter orifice. The sampled gas flow from the bag was mixed with the reagent ion flow, resulting in a chloride ion transfer reaction from the reagent SO₂Cl⁻ to a selected species, A, in the sampled air as follows:

$$A + SO_2CI^- \to ACI^- + SO_2 \tag{4}$$

Through reaction 4, species with higher chloride affinities than SO_2 are ionized effectively. Although many organic acids and hydroperoxides (ROOH) could be ionized and detected, a portion of the hydroperoxides produced from ethylene ozonolysis could not be ionized. To detect those hydroperoxides, Cl⁻ chemical ionization was also employed. The Cl⁻-CIMS is similar to the SO_2 Cl⁻-CIMS except that SO_2 is not introduced into the ion source region. Therefore, Cl⁻ ions generated from electron impact on the CH₃Cl/Ar mixture can participate in

chemical ionization directly. In Cl⁻-chemical ionization, species were ionized through a chloride attachment reaction involving a third body, M, as shown below:

$$A + Cl^{-} + M \to ACl^{-} + M \tag{5}$$

Through reaction 5, species with lower chloride affinities than SO_2 could be also ionized. Thus, Cl⁻-CIMS can detect a greater variety of species than SO_2Cl^- -CIMS. However, it is difficult to obtain quantitative information from the Cl⁻-CIMS method because the reagent Cl⁻ is largely consumed by reaction with the analyte species.

As shown in eqs 4 and 5, analyte molecules are converted to Cl⁻ adducts in both chemical ionization schemes. Because chlorine has two stable isotopes, ³⁵Cl and ³⁷Cl, at the ratio of approximately 3:1, the Cl⁻ adduct ions are expected to be detected as doublet peaks within the mass spectrum. Hereafter, we will refer to the mass-to-charge ratio (m/z) of the ions containing ³⁵Cl⁻ and will include the (m/z) of the ions containing ³⁷Cl⁻ in parentheses, for each set of doublet peaks.

RESULTS AND DISCUSSION

Analysis of Gas-Phase Products. First, the gas-phase products of ethylene ozonolysis with the addition of cyclohexane as an OH scavenger were analyzed by NI-CIMS. Figure 4a shows SO₂Cl⁻-CI mass spectra.

The orange line in this figure shows a mass spectrum obtained before the injection of ozone into the bag. The reagent ion, SO_2Cl^- , is observed at m/z 99 (101). Mass peaks at m/z 163 (165) are assigned to $(SO_2)_2Cl^-$, which was produced through a further addition of SO_2 to the reagent ion. No other peaks were observed probably because ozone, ethylene, and cyclohexane have much lower chloride affinities than SO₂ and are not efficiently ionized by SO₂Cl⁻. The blue line in Figure 4a shows a mass spectrum obtained at a reaction time of 1 h. By comparing the two mass spectra, peaks attributable to products of the ethylene ozonolysis can be identified. The peaks at m/z81 (83) are assigned to the Cl⁻ ion adduct of formic acid (FA), which has a molecular weight (MW) of 46 and is reportedly formed through isomerization of an excited Criegee intermediate, CH2OO*,²⁻⁴ and/or through decomposition of the secondary ozonide produced in eq 1.5 In similar fashion, the



Figure 4. Typical mass spectra of gas-phase products in the ethylene ozonolysis with cyclohexane obtained by SO_2CI^- -CIMS (a) and CI^- -CIMS (b) with concentrations of 2.9 ppmv C_2H_4 , 4.5 ppmv O_3 , and 350 ppmv cyclohexane. Blue line, 1 h after the initiation of the reaction; orange line, before reaction initiation. The vertical axis in panel a represents signal count rates normalized by that of $SO_2^{35}Cl$ at m/z 99. FA and HPMF denote formic acid and hydroperoxymethyl formate, respectively. OS1 denotes the oligomer series 1 (see text).

molecular weight of each analyte can be obtained by subtracting 35 (37), the mass number of chlorine, from the mass-to-charge ratio at which analyte ion signals are detected. In addition to signals attributed to formic acid, a series of mass peaks starting from m/z 127 (129) with an interval of 46 Da were observed. The strong peaks at m/z 127 (129) with MW of 92 are attributed to HCOOCH₂OOH (HPMF), which formed via the reaction between formic acid and CH₂OO (eq 3).^{5,8,10,24} The peaks at m/z 173 (175) are attributed to a compound with MW of 92 + 46, suggesting that this compound is composed of HPMF and CH₂OO. Similarly, the peaks at m/z 219 (221) are

attributed to a compound composed of HPMF and two units of CH₂OO. As discussed later, the compounds with MW of 92 + 46 n (n = 1, 2) are assigned to oligomeric hydroperoxides composed of CH₂OO as a chain unit. Hereafter, these species are denoted as OS1 (oligomer series 1). The peaks at m/z 145 (147) cannot be definitively assigned from the SO₂Cl⁻-CI mass spectrum alone, but comparison with the Cl⁻-CI mass spectrum allows their assignment, as described below.

Figure 4b shows typical Cl⁻-CI mass spectra. The orange line in the figure shows a mass spectrum obtained before ozone injection. No peaks were observed in the m/z 75–250 range. The blue line in the figure shows a mass spectrum obtained at a reaction time of 1 h under the same experimental conditions as Figure 4a. The peaks at m/z 145 (147) observed in Figure 4a are seen to disappear in Figure 4b, which indicates that the presence of SO₂ is required for their observation. Thus, we assign them as an adduct ion, SO₂Cl⁻·HCOOH. Similarly, the peaks at m/z 191 (193) are assigned to SO₂Cl⁻·HPMF. All peaks observed in the blue line mass spectrum in Figure 4b are also observed in Figure 4a, except for the peaks at m/z 151 (153) and m/z 197 (199). The peaks at m/z 151 (153) are attributed to a compound with MW of 116. The reaction between OH and cyclohexane can produce cyclohexyl hydroperoxide $(c-C_6H_{11}OOH)$ with MW of 116, and thus, we assigned this compound to $c-C_6H_{11}OOH$. Similarly, the peaks at m/z 197 (199) can be attributed to a compound composed of CH₂OO and c-C₆H₁₁OOH. These species were not observed in the SO₂Cl⁻-CIMS possibly because their chloride affinities are lower than SO₂. Using either reagent ion method, NI-CIMS could not detect formaldehyde, which is a major product of the ethylene ozonolysis.^{2-5,12,14,25} This suggests that formaldehyde has too low of a chloride affinity to be ionized, even through the chloride attachment reaction. For the same reason, other expected products such as CO2, CO, and H2 could not be detected. The observed SO₂Cl⁻- and Cl⁻-CIMS peaks are summarized in Table 1.

Then, the gas-phase products of the ethylene ozonolysis were investigated in the absence of an OH scavenger. Figure 5a shows a typical SO_2CI^- -CI mass spectrum obtained without an OH scavenger (pink line).

For comparison, we replot a mass spectrum obtained with the addition of cyclohexane as the blue line. Note that these are difference spectra and are obtained by subtracting the mass spectrum before adding O_3 from that obtained at a reaction

Table 1. Summar	y of [·]	the	Peaks	Observed	l in	the	Gas-Pha	ise Anal	lysis	by	NI-	CIMS	1	h af	ter	Initiation	of	the	Reaction
	/																		

m/z	MW^{a}	w/ cyclohexane ^b	w/o OH scavenger ^b	w/ cyclohexane and methanol ^b	attribution ^c
81(83)	46	0	0	0	FA
99(101)	64	nd	nd	\bigcirc^d	CH_3OH^d
113(115)	78	nd	0	\bigcirc^d	2-HEHP, CH ₃ OCH ₂ OOH ^d
127(129)	92	0	0	0	HPMF
145(147)	110	0	0	\bigcirc^d	FA, CH ₃ OCH ₂ OOH ^d
151(153)	116	O^d	nd	\bigcirc^d	$c-C_6H_{11}OOH^d$
159(161)	124	nd	0	nd	OS2 (n = 1)
173(175)	138	0	0	nd	OS1 $(n = 1)$
191(193)	156	0	0	nd	HPMF
197(199)	162	O^d	nd	nd	$c-C_6H_{11}OOCH_2OOH^d$
205(207)	170	nd	0	nd	OS2 (n = 2)
219(221)	184	0	0	nd	OS1 $(n = 2)$
251(253)	216	nd	0	nd	OS2 $(n = 3)$

^aObtained by subtracting 35 (37) from m/z. ^bnd: not detected. ^cOS1: m/z = 127 + 46 n. OS2: 113 + 46 n. ^dObserved in the Cl⁻-CIMS mode only.



Figure 5. Typical mass spectra of gas-phase products in the ethylene ozonolysis obtained by SO₂Cl⁻-CIMS (a) and Cl⁻-CIMS (b) 1 h after the initiation of the reaction. The pink lines in both panels show the spectra without OH scavenger ($[C_2H_4] = 2.9$ ppmv and $[O_3] = 4.5$ ppmv), and the blue lines with cyclohexane (same as that in Figure 4). The spectra in panel a are obtained by subtracting spectra before adding O₃ to initiate the reaction. FA, 2-HEHP, and HPMF denote formic acid, 2-hydroxyethyl hydroperoxide, and hydroperoxymethyl formate, respectively. OS1 and OS2 denote the oligomer series 1 and 2, respectively (see text).

time of 1 h. All peaks observed in the presence of cyclohexane (blue line) were also observed without the OH scavenger (pink line). This confirms that these peaks are attributable to products from the ethylene ozonolysis. In addition, a series of peaks starting from m/z 113 (115) were observed. In the absence of a scavenger, the OH radicals produced during ozonolysis can contribute to the ethylene oxidation reaction. The OH oxidation of ethylene can produce HOCH₂CH₂OOH (2-hydroxyethyl hydroperoxide, 2-HEHP) with MW of 78 as follows:⁷

$$CH_2 = CH_2 + OH \rightarrow HO - CH_2CH_2$$
 (6)

$$HO-CH_2CH_2 + O_2 \rightarrow HO-CH_2CH_2 - OO$$
(7)

$$HO-CH_2CH_2-OO + HO_2$$

$$\rightarrow \text{HO}-\text{CH}_2\text{CH}_2-\text{OOH}+\text{O}_2 \tag{8}$$

where HO₂ in eq 8 can be produced by reactions such as O₂ reacting with an H atom, which can be formed from decomposition of an excited Criegee intermediate, CH₂OO*. Thus, the peaks at m/z 113 (115) can be attributed to 2-HEHP. The series of peaks at m/z 113 (115) + 46 n (n = 1 - 3) are attributed to compounds with MW of 78 + 46 n, another series of oligomers that are composed of 2-HEHP and n CH₂OO. Hereafter, these species are denoted as OS2.

Figure 5b shows a typical Cl⁻-CI mass spectrum obtained without an OH scavenger (pink line) together with that obtained with the addition of cyclohexane (blue line). From the

comparison of these two mass spectra, OS2 production is clearly seen in the absence of OH scavengers. Additionally, the peaks at m/z 151 (153) and 197 (199) disappear in the absence of cyclohexane. This is consistent with the mass assignments in the presence of cyclohexane, in which the peaks at m/z 151 (153) are attributed to cyclohexyl hydroperoxide (c-C₆H₁₁OOH) produced from the reaction of OH and cyclohexane, and the peaks at m/z 197 (199) to an addition product of CH₂OO to c-C₆H₁₁OOH. The observed product peaks in the absence of an OH scavenger are also summarized in Table 1.

To confirm that SCI was involved in the gas-phase oligomer formation, experiments with the addition of methanol as an SCI scavenger were performed. Figure 6a shows a typical



Figure 6. Typical mass spectra of gas-phase products in the ethylene ozonolysis obtained by SO_2CI^- -CIMS (a) and CI^- -CIMS (b) 1 h after initiation of the reaction. The green lines in both the panels show the spectra with an SCI scavenger ($[C_2H_4] = 2.9$ ppmv, $[O_3] = 4.5$ ppmv, [cyclohexane] = 350 ppmv, and [methanol] = 1300 ppmv), and the blue lines with cyclohexane (same as that inFigure 4). The spectra in panel a are obtained by subtracting spectra before adding O_3 to initiate the reaction. FA and HPMF denote formic acid and hydroperoxymethyl formate, respectively. OS1 denotes the oligomer series 1 (see text).

 SO_2CI^- -CI mass spectrum obtained with the addition of both cyclohexane and methanol as the green line.

For comparison, a mass spectrum with only the addition of cyclohexane is shown in blue. Again, both spectra are taken as the difference between the mass spectra before and after reaction. By comparing these two mass spectra, the peaks attributed to HPMF and OS1 observed with the addition of cyclohexane only (blue line) are found to disappear in the presence of methanol (green line), clearly indicating that the CH₂OO species plays a predominant role in oligomer formation. It is also found that the peaks attributed to formic acid were suppressed by adding methanol, implying that at least some fraction of the formic acid is produced from SCI through

decomposition of the CH_2OO reaction products, such as the secondary ozonide formed in eq 1.

Figure 6b shows a typical Cl⁻-CI mass spectrum obtained under the same experimental conditions. In addition to the disappearance of the peaks corresponding to HPMF and OS1 described above, the peaks at m/z 151 (153) were found to be suppressed by adding methanol. This is because OH radicals produced from ethylene ozonolysis are partly scavenged by methanol as well as by cyclohexane. However, new peaks at m/z 113 (115) were found to appear with the addition of methanol. As described above, peaks at m/z 113 (115) were observed also in the total absence of OH scavengers and were attributed to 2-HEHP produced from OH oxidation of ethylene. However, 2-HEHP can be ruled out in this case because the OH radicals are sufficiently scavenged by cyclohexane and methanol. Instead, these peaks can be attributed to another hydroperoxide, which is produced from the reaction between methanol and CH₂OO as follows:^{6,26}

$$CH_2OO + CH_3OH \rightarrow CH_3O - CH_2OO - H$$
 (9)

The product, CH₃OCH₂OOH, has MW of 78 and is expected to be detected as a Cl⁻ adduct at m/z 113 (115) in CIMS. In the presence of methanol, peaks at m/z 99 (101) and those at m/z 145 (147) were also observed. They are assigned to (CH₃OH)₂Cl⁻ and (CH₃OCH₂OOH)(CH₃OH)Cl⁻, respectively. These cluster ions were observable because of the extremely high concentration of methanol. These peaks are summarized in Table 1.

Proposed Mechanisms for the Oligomer Formation in the Gas Phase. As described above, our results suggest that oligomeric species composed of CH_2OO as a chain unit are produced in the gas phase. Oligomer formation involving Criegee intermediates from alkene ozonolysis has been reported by Sadezky et al.^{27,28} They observed oligomers in the aerosol phase using ESI-MS analysis techniques and suggested that these oligomers are produced in the gas phase. Our results represent the first direct observation of oligomers formed in the gas phase and support their suggestion.

Sadezky et al.²⁸ proposed an oligomer formation mechanism involving initiation by the reaction of an alkylperoxy radical and an SCI, sequential addition of SCIs, and termination by reaction with the HO_2 radical to produce an oligomeric hydroperoxide. According to their mechanism, oligomer formation from the ethylene ozonolysis can be described as follows:

$$RO_2 + CH_2OO \rightarrow ROO - CH_2OO$$
 (10)

 $ROO-CH_2OO + (n-1)CH_2OO$

$$\rightarrow \text{ROO}\left(\text{CH}_2\text{OO}\right)_{n-1}\text{CH}_2\text{OO} \tag{11}$$

$$\operatorname{ROO}\left(\operatorname{CH}_{2}\operatorname{OO}\right)_{n-1}\operatorname{CH}_{2}\operatorname{OO} + \operatorname{HO}_{2} \rightarrow \operatorname{ROO}\left(\operatorname{CH}_{2}\operatorname{OO}\right)_{n} \operatorname{H} + \operatorname{O}_{2}$$
(12)

where RO_2 denotes alkylperoxy radicals. The formation of OS2 species observed in our studies can be rationalized by the above mechanism by assigning RO_2 in eq 10 as the 2-hydroxyethylperoxy radical, $HOCH_2CH_2OO$, which is produced from the reaction between C_2H_4 and OH^7 as shown in eq 7. However, the formation of OS1 cannot be explained by the above mechanism since the formation of radicals with MW of 45 or 91, which are unlikely produced in ethylene ozonolysis, would be required. Instead, we propose a new mechanism for the oligomer formation, in which CH_2OO reacts with hydroperoxides as follows:

$$ROOH + CH_2OO \rightarrow ROO - CH_2OO - H$$
(13)

$$ROO-CH_2OO-H + (n-1)CH_2OO \rightarrow ROO\{CH_2OO\}_n H$$
(14)

The first step of this mechanism is the direct addition of the Criegee intermediate, CH_2OO , to a hydroperoxide, ROOH, which is analogous to the reaction of CH_2OO with hydrogen peroxide.⁵ Importantly, the first step generates a hydroperoxide, ROOCH₂OOH, to which another CH_2OO can add. In this way, CH_2OO adds sequentially to resultant hydroperoxides as shown in eq 14, and finally, oligomeric hydroperoxides are formed. The formation of OS1 can be explained based on this mechanism with HPMF as ROOH:

$$\begin{array}{c} O \\ HCO-CH_2OO-H + nCH_2OO \\ O \\ \rightarrow HCO-CH_2OO \left\{ CH_2OO \right\}_n H \end{array}$$
(15)

This same mechanism can be used to explain not only the formation of OS1 but also the formation of OS2. In the OS2 formation, 2-HEHP plays the role of ROOH:

$$HO-CH_2CH_2-OOH + nCH_2OO \rightarrow HO-CH_2CH_2-OO \left(CH_2OO\right)_n H$$
(16)

This mechanism can also be invoked to explain the formation of other products observed by NI-CIMS. For example, the peaks at m/z 197 (199) observed in the Cl⁻-CIMS spectra with the addition of cyclohexane can be attributed to the addition compound of CH₂OO to cyclohexyl hydroperoxide through eq 13. Thus, the newly proposed mechanism can fully explain the formation of all of the hydroperoxides and oligomers observed as gas-phase products. However, the radical chain reaction mechanism^{26,27} shown in eqs 10–12 cannot be ruled out. Very recently, the radical chain reaction mechanism was supported by *ab initio* calculations, where the sequential addition reactions proceed over a submerged energy barrier.²⁹

SOA Formation from Ethylene Ozonolysis. In our investigation of ethylene ozonolysis, SOA formation was observed. Figure 7 shows time profiles of the particle volume concentrations obtained from the SMPS measurements.

The pink, blue, and green circles show the particle volume concentrations without scavengers, with cyclohexane, and with cyclohexane and methanol, respectively. It should be noted that our Teflon bag experiments potentially underestimate volume concentrations because of possible particle deposition onto the inner surface of the bag. Thus, only a relative change in the measured concentrations is discussed here. First, the result shown by the blue circles suggests that either SOAs are formed via ethylene ozonolysis in the absence of OH radicals or that the reaction between OH and cyclohexane may contribute to the SOA formation. This will be discussed on the basis of the particle-phase analysis in the next subsection. It is seen in Figure 7 that particle concentrations for the reactions without scavengers are higher than those with the addition of cyclohexane. This indicates that OH oxidation of ethylene serves as an additional contributor to SOA formation in ethylene ozonolysis. Finally, Figure 7 shows that aerosol formation is strongly suppressed with the addition of methanol, as shown by the green circles. This clearly indicates that the SCI, CH₂OO, plays a critical role in SOA formation, as well as gas-phase oligomer formation, in ethylene ozonolysis.

Analysis of Particle-Phase Components. As described in the experimental section, particles formed during the reaction



Figure 7. Time profiles of the particle volume concentration measured by SMPS. Pink circles, without scavengers ($[C_2H_4] = 2.9$ ppmv and $[O_3] = 4.5$ ppm); blue circles, with cyclohexane ($[C_2H_4] = 2.9$ ppmv, $[O_3] = 4.5$ ppmv, and [cyclohexane] = 350 ppmv); and green circles, with cyclohexane and methanol ($[C_2H_4] = 2.9$ ppmv, $[O_3] = 4.5$ ppmv, [cyclohexane] = 350 ppmv, and [methanol] = 1300 ppmv).



Figure 8. Typical mass spectra of particle-phase components in the ethylene ozonolysis with and without an OH scavenger obtained by SO₂Cl⁻-CIMS (a) and Cl⁻-CIMS (b) 1 h after initiation of the reaction. The pink lines in both panels show the spectra without an OH scavenger ($[C_2H_4] = 2.9$ ppmv, $[O_3] = 4.5$ ppm), and the blue lines with cyclohexane ($[C_2H_4] = 11.6$ ppmv, $[O_3] = 18$ ppmv, and [cyclohexane] = 1400 ppmv). The spectra in panel a are obtained by subtracting the blank spectra. OS2 and OS3 denote the oligomer series 2 and 3, respectively (see text).

were collected on a PTFE filter, which was then heated at 403 K. The vaporized species from the collected particles were introduced into NI-CIMS and analyzed similarly to the gas-phase products. Figure 8a,b shows mass spectra for the particle-phase products, and Table 2 lists the observed peaks and their possible attribution.

m/z	MW ^a	w/ <i>c</i> -hexane ^b	w/o OH scavenger ^b	attribution ^c
81(83)	46	0	0	FA
97(99)	62	nd	0	
99(101)	64	O^d	O^d	HMHP^d
113(115)	78	nd	0	2-HEHP
115(117)	80	nd	0	
127(129)	92	0	0	HPMF
129	94	0	0	
143(145)	108	nd	0	OS3 $(n = 0)$
145(147)	110	0	0	$CH_3O(CH_2OO)_2H$
151(153)	116	0	nd	cyclohexane–OH ^e
159(161)	124	nd	0	OS2 $(n = 1)$
165(167)	130	0	nd	$cyclohexane-OH^{e}$
173(175)	138	nd	0	OS1 $(n = 1)$
181(183)	146	0	nd	cyclohexane–OH ^e
183(185)	148	0	nd	cyclohexane–OH ^e
187(189)	152	nd	0	
189(191)	154	nd	0	OS3 $(n = 1)$
203(205)	168	nd	0	
205(207)	170	nd	0	OS1 $(n = 2)$
211(213)	176	0	nd	cyclohexane–OH ^e
213(215)	178	0	nd	cyclohexane–OH ^e
217(219)	182	nd	0	
229(231)	194	0	nd	cyclohexane–OH ^e
233(235)	198	nd	0	
235(237)	200	nd	0	OS3 $(n = 2)$
249(251)	214	nd	0	
251(253)	216	nd	0	OS2 $(n = 3)$
297(299)	262	nd	0	OS2 $(n = 4)$
			1	

Table 2. Summary of Peaks Observed in the Particle-Phase

Analysis by NI-CIMS 1 h after Initiation of the Reaction

^{*a*}Obtained by subtracting 35 (37) from m/z. ^{*b*}nd: not detected. ^{*c*}OS1: m/z = 127 + 46 n. OS2: 113 + 46 n. OS3: 143 + 46 n. ^{*d*}Observed in the Cl⁻-CIMS mode only. ^{*e*}Peaks are attributed to the OH oxidation products of cyclohexane.

Note that all the spectra in Figure 8a are obtained by subtracting blank spectra recorded in the same setup without a PTFE filter.

The pink line in Figure 8a shows a SO_2Cl^- -CI mass spectrum obtained without an OH scavenger. Among the peaks that were observed in the gas-phase mass spectrum, those attributed to formic acid, HPMF, and OS2 were clearly observed, while those attributed to OS1 had very weak intensities. It is noteworthy that the chain length of OS2 species detected in the particlephase analysis (n = 1-4) was longer than those detected in the gas-phase analysis (n = 1 - 3). This suggests that OS2 produced in the gas phase can contribute to SOA formation through partitioning into the particle phase because of their low vapor pressures. In addition, many peaks that were not observed in the gas-phase analysis were observed in the particle-phase spectra. While it is presently difficult to assign most of the peaks solely from the observed mass-to-charge ratios, we found a series of the peaks starting from m/z 143 (145) with an interval of 46 Da. This series is attributed to compounds with MW of 108 + 46 n (n = 0-2), which is referred to as OS3. One can suppose that it might result from thermal decomposition of oligomeric species in the particle phase upon heating at 403 K for vaporization. Alternatively, it might be produced from an addition reaction of formaldehyde to 2-HEHP and OS2 in the particle phase, considering that the compound with MW of 108 has a mass 30 Da higher than 2-HEHP. A possible route would

be via an acid-catalyzed reaction producing a peroxyhemiacetal or hemiacetal compound. The NI-CIMS analysis shows the production of formic acid, which could act as a catalyst for the reactions. Peroxyhemiacetal formation has been proposed as a particle-phase reaction in SOAs from 1-tetradecene ($C_{13}H_{26}$ = CH_2) ozonolysis.³⁰ Sato et al. also suggested that hemiacetal and peroxyhemiacetal oligomers are formed in SOA from the photooxidation of toluene.³¹

The pink line in Figure 8b shows the Cl⁻-Cl mass spectrum obtained without an OH scavenger. The peaks observed in the SO₂Cl⁻-Cl mass spectrum were also observed in the Cl⁻-Cl mass spectrum. In addition, peaks at m/z 99 (101) were observed. These peaks are possibly attributed to HMHP, which has been reported to be produced from the reaction between CH₂OO and water as shown in eq 2. Because it was not observed as a gas-phase product, HMHP is not likely formed from a gas-phase reaction, but instead from a heterogeneous reaction on/in the particles. The peaks at m/z 145 (147) were also newly observed and are attributed to a compound composed of HMHP and CH₂OO.

The blue lines in Figure 8a,b display typical SO₂Cl⁻- and Cl⁻-CI mass spectra for aerosol-phase products obtained with cyclohexane as an OH scavenger. It should be noted that these spectra were obtained from experiments with much higher concentrations to obtain sufficient signal intensities of particle components: The concentrations of ethylene, ozone, and cyclohexane were 12, 18, and 1400 ppmv, respectively, which are approximately four times higher than the typical conditions used in this study. Under this higher concentration condition, the volume concentration reaches 0.8×10^9 nm³ cm⁻³ after a reaction time of 1 h, which is comparable to that measured in the experiments without OH scavengers under the typical conditions.

It is found from the comparison of the blue and pink lines in Figure 8a that OS2 and OS3 peaks almost disappear in the presence of cyclohexane. This supports the proposed mechanism for formation of OS2, which involves gas-phase OH oxidation of ethylene. Also, it is consistent with the presumption that OS3 might be produced from 2-HEHP and OS2. Conversely, several peaks not observed in the absence of OH scavengers were observed with the addition of cyclohexane (see Table 2). Although individual peak assignment is difficult, we believe these peaks do not arise from ethylene ozonolysis, but come instead from unidentified processes, including the reaction between cyclohexane and OH. Recently, Sato et al. detected aerosol components derived from OH radical scavengers in their investigation of SOA formation in isoprene ozonolysis.³² In the presence of cyclohexane as an OH scavenger, they identified hexanedioic acid (C₆H₁₀O₄, MW 146) and detected three other compounds with molecular formulas $C_6H_{12}O_4$ (MW 148), $C_7H_{12}O_5$ (MW 176), and $C_8H_{14}O_5$ (MW 190) in the LC/TOF-MS analysis. The particle-phase analysis in the present study also detected mass peaks attributed to compounds with MW of 146, 148, and 176 at m/z 181 (183), 183 (185), and 211 (213), respectively. These peaks are consistent with the LC/TOF-MS analysis by Sato et al. and confirm that cyclohexane itself is involved in SOA formation during ethylene ozonolysis. In addition, several peaks attributed to OH oxidation products of cyclohexane were observed with an interval of 46 Da, implying that species derived from OH oxidation of cyclohexane may interact with CH₂OO.

SOA Formation Chemistry from Ethylene Ozonolysis. Our experimental results demonstrate that the SCI, CH₂OO, produced from ethylene ozonolysis plays a central role in gasphase oligomer and subsequent SOA formation. Without OH radical scavengers, the oligomers formed from reactions between CH₂OO produced from ethylene ozonolysis and 2-HEHP produced from OH oxidation of ethylene contribute to SOA formation through partitioning into the aerosol phase. This indicates that coupling between OH oxidation and ethylene ozonolysis plays an important role in SOA formation. In studies where cyclohexane was added as an OH scavenger, aerosol-phase products, which would arise solely from the ethylene ozonolysis, could not be detected. However, we cannot rule out the possibility that ethylene ozonolysis could contribute to SOA formation even without OH radicals because there may be key species that cannot be detected by CIMS employed in this study. Meanwhile, SOA components derived from cyclohexane were detected, indicating that OH radical scavengers could affect SOA formation through partitioning of their oxidation products into the aerosol phase.

CONCLUSIONS

This study examined ethylene ozonolysis using a Teflon bag reactor. SOA formation was observed by SMPS, and gas- and particle-phase products were analyzed by SO_2CI^- and CI^-CIMS . Oligomeric hydroperoxides composed of CH_2OO as a chain unit were observed as both gas- and particle-phase products, suggesting that the oligomeric hydroperoxides formed in the gas phase are incorporated into the particle phase. The addition of methanol as a stabilized Criegee intermediate scavenger strongly suppressed both the gas-phase oligomer formation and SOA formation, indicating that CH_2OO plays a key role in the formation of oligomeric hydroperoxides, followed by SOA formation, in ethylene ozonolysis.

We propose an oligomerization mechanism initiated by the reaction of CH₂OO with ROOH, while Sadezky et al.^{27,28} proposed another mechanism initiated by the reaction of CH₂OO with RO₂. In the latter mechanism, the CH₂OO + RO₂ reaction may be limited to the daytime when photochemistry is active and by the low concentration of RO₂ in the atmosphere. Conversely, the CH₂OO + ROOH reaction does not have these limitations because atmospheric concentrations up to several ppbv have been reported for some selected hydroperoxides,³³ although our understanding of organic hydroperoxides in the troposphere is still lacking.

As described in the introduction, recent observations¹⁷ suggest that SCIs including CH₂OO may be involved in chemical processes in the troposphere through bimolecular reactions with species other than H₂O. However, we cannot discuss the importance of the oligomer and SOA formation from CH₂OO to tropospheric chemistry at the present stage because information on reaction rates and SOA yields were not obtained in this study. Further investigations on the kinetics of CH₂OO with atmospheric species such as hydroperoxides are required to estimate accurately the atmospheric impact of the oligomer and SOA formation observed in this study.

Meanwhile, the findings obtained in this study for ethylene ozonolysis will be extended to ozonolysis of other unsaturated hydrocarbons relevant to SOA formation in the atmosphere. Recent laboratory and field studies suggest that dimer esters generated from ozonolysis of monoterpenes, an important class of biogenic hydrocarbons, participate in new particle formation in forested regions.^{34–38} Dimeric species of an SCI combined with other reaction products have also been proposed^{21,39} and identified as SOA components by laboratory studies on monoterpene ozonolysis.^{40,41} The oligomer formation mechanism presented in this study may operate for larger SCIs than CH₂OO including those from monoterpene ozonolysis. The NI-CIMS

technique is expected to be applied to gas- and particle-phase analysis in that it can detect acids and hydroperoxides that play a critical role in SOA formation in the atmosphere.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Grant-in-Aid for Scientific Research on Innovative Areas (Grant No. 20120003) from the Ministry of Education, Culture, Sports, Science, and Technology in Japan. Y.S. was supported by a research fellowship from the Japan Society for the Promotion of Science for young scientists.

REFERENCES

(1) Johnson, D.; Marston, G. The Gas-Phase Ozonolysis of Unsaturated Volatile Organic Compounds in the Troposphere. *Chem. Soc. Rev.* **2008**, *37*, 699–716.

(2) Su, F.; Calvert, J. G.; Shaw, J. H. A FT IR Spectroscopic Study of the Ozone-Ethene Reaction Mechanism in Oxygen-Rich Mixtures. *J. Phys. Chem.* **1980**, *84*, 239–246.

(3) Herron, J. T.; Huie, R. E. Stopped-Flow Studies of the Mechanisms of Ozone-Alkene Reactions in the Gas Phase. Ethylene. J. Am. Chem. Soc. 1977, 99, 5430–5435.

(4) Horie, O.; Moortgat, G. K. Decomposition Pathways of the Excited Criegee Intermediates in the Ozonolysis of Simple Alkenes. *Atmos. Environ.* **1991**, *25*, 1881–1896.

(5) Neeb, P.; Horie, O.; Moortgat, G. K. The Ethene–Ozone Reaction in the Gas Phase. J. Phys. Chem. A 1998, 102, 6778–6785.

(6) Wolff, S.; Boddenberg, A.; Thamm, J.; Turner, W. V.; Gäb, S. Gas-Phase Ozonolysis of Ethene in the Presence of Carbonyl-Oxide Scavengers. *Atmos. Environ.* **1997**, *31*, 2965–2969.

(7) Hasson, A. S.; Orzechowska, G.; Paulson, S. E. Production of Stabilized Criegee Intermediates and Peroxides in the Gas Phase Ozonolysis of Alkenes: 1. Ethene, *trans*-2-Butene, and 2,3-Dimethyl-2-butene. *J. Geophys. Res.* **2001**, *106*, 34131–34142.

(8) Neeb, P.; Horie, O.; Moortgat, G. K. The Nature of the Transitory Product in the Gas-Phase Ozonolysis of Ethene. *Chem. Phys. Lett.* **1995**, *246*, 150–156.

(9) Alam, M. S.; Camredon, M.; Rickard, A. R.; Carr, T.; Wyche, K. P.; Hornsby, K. E.; Monks, P. S.; Bloss, W. J. Total Radical Yields from Tropospheric Ethene Ozonolysis. *Phys. Chem. Chem. Phys.* **2011**, *13*, 11002–11015.

(10) Thamm, J.; Wolff, S.; Turner, W. V.; Gäb, S.; Thomas, W.; Zabel, F.; Fink, E. H.; Becker, K. H. Proof of the Formation of Hydroperoxymethyl Formate in the Ozonolysis of Ethene: Synthesis and FT-IR Spectra of the Authentic Compound. *Chem. Phys. Lett.* **1996**, 258, 155–158.

(11) Neeb, P.; Horie, O.; Moortgat, G. K. Gas-Phase Ozonolysis of Ethene in the Presence of Hydroxylic Compounds. *Int. J. Chem. Kinet.* **1996**, *28*, 721–730.

(12) Copeland, G.; Ghosh, M. V.; Shallcross, D. E.; Percival, C. J.; Dyke, J. M. A Study of the Ethene-Ozone Reaction with Photoelectron Spectroscopy: Measurement of Product Branching Ratios and Atmospheric Implications. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14839–14847.

(13) Qi, B.; Sato, K.; Imamura, T.; Takami, A.; Hatakeyama, S.; Ma, Y. Production of the Radicals in the Ozonolysis of Ethene: A Chamber Study by FT-IR and PERCA. *Chem. Phys. Lett.* **2006**, *427*, 461–465.

(14) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. A FT IR Study of a Transitory Product in the Gas-Phase Ozone-Ethylene Reaction. *J. Phys. Chem.* **1981**, *85*, 1024–1027.

(15) Neeb, P.; Sauer, F.; Horie, O.; Moortgat, G. K. Formation of Hydroxymethyl Hydroperoxide and Formic Acid in Alkene Ozonolysis in the Presence of Water Vapour. *Atmos. Environ.* **1997**, *31*, 1417–1423.

(16) Hatakeyama, S.; Kobayashi, H.; Akimoto, H. Gas-Phase Oxidation of Sulfur Dioxide in the Ozone–Olefin Reactions. *J. Phys. Chem.* **1984**, *88*, 4736–4739.

(17) Mauldin, R. L., III; Berndt, T.; Sipila, M.; Paasonen, P.; Petaja, T.; Kim, S.; Kurten, T.; Stratmann, F.; Kerminen, V. M.; Kulmala, M. A New Atmospherically Relevant Oxidant of Sulphur Dioxide. *Nature* **2012**, *488*, 193–196.

(18) Hirokawa, J.; Kato, T.; Mafuné, F. Uptake of Gas-Phase Nitrous Acid by pH-Controlled Aqueous Solution Studied by a Wetted Wall Flow Tube. *J. Phys. Chem. A* **2008**, *112*, 12143–12150.

(19) Hirokawa, J.; Kato, T.; Mafuné, F. In Situ Measurements of Atmospheric Nitrous Acid by Chemical Ionization Mass Spectrometry Using Chloride Ion Transfer Reactions. *Anal. Chem.* **2009**, *81*, 8380–8386.

(20) Seinfeld, J. H.; Pankow, J. F. Organic Atmosphric Particulate Material. *Annu. Rev. Phys. Chem.* **2003**, *54*, 121–140.

(21) Lee, S.; Kamens, R. M. Particle Nucleation from the Reaction of α -Pinene and O₃. *Atmos. Environ.* **2005**, *39*, 6822–6832.

(22) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Volume II, Gas Phase Reactions of Organic Species. *Atmos. Chem. Phys.* **2006**, *6*, 3625–4055.

(23) Atkinson, R. Kinetics of the Gas-Phase Reactions of OH Radicals with Alkanes and Cycloalkanes. *Atmos. Chem. Phys.* 2003, *3*, 2233–2307.

(24) Horie, O.; Moortgat, G. K. Gas-Phase Ozonolysis of Alkenes. Recent Advances in Mechanistic Investigations. *Acc. Chem. Res.* **1998**, *31*, 387–396.

(25) Grosjean, E.; Grosjean, D. Carbonyl Products of the Gas Phase Reaction of Ozone with Symmetrical Alkenes. *Environ. Sci. Technol.* **1996**, *30*, 2036–2044.

(26) Klotz, B.; Barnes, I.; Imamura, T. Product Study of the Gas-Phase Reactions of O_3 , OH and NO_3 Radicals with Methyl Vinyl Ether. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1725–1734.

(27) Sadezky, A.; Chaimbault, P.; Mellouki, A.; Römpp, A.; Winterhalter, R.; Le Bras, G.; Moortgat, G. K. Formation of Secondary Organic Aerosol and Oligomers from the Ozonolysis of Enol Ethers. *Atmos. Chem. Phys.* **2006**, *6*, 5009–5024.

(28) Sadezky, A.; Winterhalter, R.; Kanawati, B.; Römpp, A.; Spengler, B.; Mellouki, A.; Le Bras, G.; Chaimbault, P.; Moortgat, G. K. Oligomer Formation during Gas-Phase Ozonolysis of Small Alkenes and Enol Ethers: New Evidence for the Central Role of the Criegee Intermediate as Oligomer Chain Unit. *Atmos. Chem. Phys.* **2008**, *8*, 2667–2699.

(29) Vereecken, L.; Harder, H.; Novelli, A. The Reaction of Criegee Intermediates with NO, RO_2 , and SO_2 , and Their Fate in the Atmosphere. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14682–14695.

(30) Tobias, H. J.; Ziemann, P. J. Thermal Desorption Mass Spectrometric Analysis of Organic Aerosol Formed from Reactions of 1-Tetradecene and O_3 in the Presence of Alcohols and Carboxylic Acids. *Environ. Sci. Technol.* **2000**, *34*, 2105–2115.

(31) Sato, K.; Hatakeyama, S.; Imamura, T. Secondary Organic Aerosol Formation during the Photooxidation of Toluene: NO_x Dependence of Chemical Composition. *J. Phys. Chem. A* **2007**, *111*, 9796–9808.

(32) Sato, K.; Inomata, S.; Xing, J.-H.; Imamura, T.; Uchida, R.; Fukuda, S.; Nakagawa, K.; Hirokawa, J.; Okumura, M.; Tohno, S. Effect of OH Radical Scavengers on Secondary Organic Aerosol Formation from Reactions of Isoprene with Ozone. *Atmos. Environ.* **2013**, *79*, 147–154.

(33) Lee, M.; Heikes, B. G.; O'Sullivan, D. W. Hydrogen Peroxide and Organic Hydroperoxide in the Troposphere: a Review. *Atmos. Environ.* **2000**, *34*, 3475–3494.

(34) Müller, L.; Reinnig, M. C.; Warnke, J.; Hoffmann, T. Unambiguous Identification of Esters as Oligomers in Secondary Organic Aerosol Formed from Cyclohexene and Cyclohexene/ α -Pinene Ozonolysis. *Atmos. Chem. Phys.* **2008**, *8*, 1423–1433.

(35) Camredon, M.; Hamilton, J. F.; Alam, M. S.; Wyche, K. P.; Carr, T.; White, I. R.; Monks, P. S.; Rickard, A. R.; Bloss, W. J. Distribution of Gaseous and Particulate Organic Composition during Dark α -Pinene Ozonolysis. *Atmos. Chem. Phys.* **2010**, *10*, 2893–2917.

(36) Yasmeen, F.; Vermeylen, R.; Szmigielski, R.; Iinuma, Y.; Böge, O.; Herrmann, H.; Maenhaut, W.; Claeys, M. Terpenylic Acid and Related Compounds: Precursors for Dimers in Secondary Organic Aerosol from the Ozonolysis of α - and β -pinene. Atmos. Chem. Phys. **2010**, 10, 9383–9392.

(37) Gao, Y.; Hall, W. A.; Johnston, M. V. Molecular Composition of Monoterpene Secondary Organic Aerosol at Low Mass Loading. *Environ. Sci. Technol.* **2010**, *44*, 7897–7902.

(38) Kristensen, K.; Enggrob, K. L.; King, S. M.; Worton, D. R.; Platt, S. M.; Mortensen, R.; Rosenoern, T.; Surratt, J. D.; Bilde, M.; Goldstein, A. H.; et al. Formation and Occurrence of Dimer Esters of Pinene Oxidation Products in Atmospheric Aerosols. *Atmos. Chem. Phys.* **2013**, *13*, 3763–3776.

(39) Bonn, B.; Schuster, G.; Moortgat, G. K. Influence of Water Vapor on the Process of New Particle Formation during Monoterpene Ozonolysis. *J. Phys. Chem. A* **2002**, *106*, 2869–2881.

(40) Heaton, K. J.; Dreyfus, M. A.; Wang, S.; Johnston, M. V. Oligomers in the Early Stage of Biogenic Secondary Organic Aerosol Formation and Growth. *Environ. Sci. Technol.* **2007**, *41*, 6129–6136.

(41) Tolocka, M. P.; Heaton, K. J.; Dreyfus, M. A.; Wang, S.; Zordan, C. A.; Saul, T. D.; Johnston, M. V. Chemistry of Particle Inception and Growth during α -Pinene Ozonolysis. *Environ. Sci. Technol.* **2006**, *40*, 1843–1848.