

Department of Environmental Sciences and Engineering

Gillings School of Global Public Health

BSPH – ENHS

Report of Undergraduate Honors Thesis Defense

Date: 4/11/2016

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Title of Thesis: **Investigation of the effect of aerosol acidity, oxidant type, and nucleation on MBO-derived SOA composition and yield**

We judge that the candidate has

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Passed with Honors

Passed with Highest Honors

Abstract

Fine particulate matter (PM_{2.5}, aerosol with aerodynamic diameters $\leq 2.5 \mu\text{m}$) has been classified by the U.S. Environmental Protection Agency (EPA) as an important air pollutant to mitigate due to its adverse impacts on human health, air quality and climate change. Prior research has shown that the atmospheric oxidation of 2-methyl-3-buten-2-ol (232-MBO), a volatile organic compound (VOC) emitted from coniferous trees, leads to the formation of PM_{2.5} in the presence of anthropogenic pollutants. The goal of this honors thesis work was to resolve the exact chemical formation mechanisms of secondary organic aerosol (SOA) derived from MBO ozonolysis in the presence of acidic sulfate aerosol. SOA is a type of PM_{2.5} that is formed from the oxidation of volatile organic compounds such as MBO. Experiments were conducted in a 10-m³ Teflon smog chamber. SOA constituents were characterized at the molecular level by using gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/quadrupole time-of-flight mass spectrometry equipped with electrospray ionization (LC/(-)ESI-QTOFMS) in the negative ion mode. Furthermore, total organic peroxide content of the SOA was determined using an iodometric spectroscopic method. Preliminary results indicate that the presence of acidic sulfate aerosol doubled the SOA mass loadings compared to less acidic sulfate aerosol. Characterization of the SOA at the molecular level revealed the formation 2-methylerythritol and 2-dihydroxyisopentanol, which might serve as potential tracer (marker) compounds for this type of SOA in PM_{2.5} collected from field studies. Analysis of peroxide content of select experiments showed that conditions that produced the highest concentration of peroxides were acidic seed in the presence of no OH scavenger.

Acknowledgements

I would like to thank Tianqu Cui for assisting me with research presented in this paper and for being an excellent mentor. I would also like to thank my committee: Dr. Jason Surratt, Dr. Louise M. Ball, and Dr. Avram Gold.

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1. Introduction

Atmospheric particulate matter (PM), which is as a form of aerosol, is either directly emitted from burning of fossil fuels and biomass or indirectly formed from the atmospheric conversion of natural and anthropogenic gaseous emissions.¹ PM_{2.5} are atmospheric aerosol particles that have aerodynamic diameters of less than 2.5 μm and contain liquid and/or solid phases. Sources of PM_{2.5} are important to understand since they can adversely impact human health, air quality, and the climate system.^{1,2} Decreases in the amount of PM_{2.5} in the atmosphere have been linked with increases in the life expectancy of individuals in the surrounding area.³ Seaton et al.⁴ reported that PM_{2.5} may aggravate lung illness by causing increased alveolar inflammation and by increasing the ability of the blood to form clots.⁴ PM_{2.5} has also been shown to directly reflect incoming solar radiation or indirectly lead to the formation of clouds, thus contributing to cooling on a local and global scale.⁵ The Intergovernmental Panel on Climate Change (IPCC) reported that the radiative forcing due to aerosol was -0.5 W/m² (the negative sign indicates that aerosols contribute to cooling rather than heating);⁶ however, this depends on the type of aerosol present and results in large uncertainties in the aerosol effect on the Earth's climate system.

The aerosol type that is of most interest to the research presented in this honors thesis is secondary organic aerosol (SOA). SOA is formed from the atmospheric oxidation of volatile organic compounds (VOCs), which leads to less volatile products that either nucleate or condense into the particulate phase. It is difficult accurately predict the amount of SOA in the atmosphere, and thus, the total amount of PM_{2.5} because the sources and formation mechanisms of SOA are not well known.²

SOA formation chemistry is highly complex due to the multitude of reactions that VOCs can undergo. Oxidation reactions of VOCs can then be divided into three different categories: hydroxyl radical (OH)-initiated reactions that occur during the day, nitrate radical (NO₃)-initiated reactions that occur during the night, and ozonolysis reactions that can occur during either day or night.¹ Furthermore, each of these reactions is influenced by the reactivity, volatility, and water solubility of each individual VOC and its respective oxidation products.⁷ SOA formation chemistry is further complicated by the fact that some of the oxidation products derived from the parent VOC can undergo particle-phase (multiphase) reactions. This makes it difficult to develop mechanisms that could be used to help document the total amount of SOA (or PM_{2.5}) in the atmosphere.

The following honor's research thesis focuses on the chemistry pertaining to 2-methyl-3-buten-2-ol (232 MBO). MBO (Figure 1) is of atmospheric relevance because it is one of the few biogenic volatile organic compounds (BVOCs) that are sufficiently reactive to contribute to the formation of SOA.⁸ Isoprene (2-methyl-1,3-butadiene) and other terpenoid compounds (such as monoterpenes and sesquiterpenes) are the two other major BVOCs that comprise a combined 55% of the total BVOC emission in the United States, which is 84 TgC year⁻¹.⁹ Global emissions of MBO have been reported to be 9.6 Tg year (11% of total emissions).⁸ On a regional scale, MBO constitutes 3.8% of the BVOC emissions in the United States (3.2 TgC year⁻¹).⁹ Although the overall emissions of MBO are lower in comparison to isoprene and terpenoid compounds, they could contribute a substantial amount to SOA production on a local scale. In areas where pines and firs dominate, MBO emissions have been reported to be as high as 6 ppb, which surpasses isoprene emissions in the same region.^{5,8}

Current literature surrounding MBO has dealt with OH-initiated oxidation and ozonolysis under natural conditions.^{8,9} Jaoui et al.⁸ allowed MBO to react with OH, nitrogen oxides (NO_x),

and sulfur dioxide (SO₂). Analysis of the gas-phase products resulted in the identification of (2-hydroxy-2-methylpropanal, Figure 2) 2-HMP, an indicator compound for MBO photooxidation. Formaldehyde, acetone, and methylglyoxal can be formed through OH oxidation or photolysis of 2-HMP. Jaoui et al.⁸ characterized products formed during the experiments, which led to the identification compounds such as acetone, glyoxal, formaldehyde, and 2,3-dihydroxyisopentanol (DHIP, Figure 3). Jaoui et al.⁸ suggested that NO_x had an inhibitory effect on SOA formation and that DHIP has the potential to be used as a tracer for MBO-derived SOA. Carrasco et al.⁹ conducted MBO ozonolysis experiments under dry and humid conditions. They observed the formation of three main carbonyl compounds: formaldehyde, acetone, and 2-hydroxy-2-methylpropanal (referred to as HMP_r instead of 2-HMP). These previous experiments utilized NO₂, which led to the conclusion that acetone and glycolaldehyde were formed in the presence of NO₂ and that HMP_r and formaldehyde were formed in its absence. Additionally, it was observed that acetone was not formed under humid conditions, and thus, not formed in the natural atmosphere. Yields of formaldehyde and HMP_r derivatives increased under humid conditions.⁹ OH radical chemistry, as opposed to ozonolysis, was observed to control daytime chemistry.⁹ Zhang et al.¹⁰ proposed that organosulfates could also serve as SOA tracers for MBO photooxidation. The organosulfate corresponding to mass-to-charge ratio (*m/z*) 199 (Figure 4) was found to be present in both laboratory experiments and air samples taken from the field.¹⁰

SOA formation is affected by a variety of factors, including oxidant type (OH radical and ozone (O₃)) and relative humidity (RH). The study conducted by Carrasco et al.⁹ examined O₃ and OH radical-initiated reactions of MBO. The investigators found that ozonolysis and OH radical-initiated reactions each yielded different amounts of products. For example, the production formation yields of HMP_r in the OH radical reactions was 31% ± 11% (dry conditions) and

43% ± 12% in the O₃ reaction.⁹ Zhang et al.¹¹ demonstrated that increased RH had suppressed SOA formation;¹¹ more specifically, they observed that the SOA yield was two times larger for the low RH (15-40%) experiments compared to the high RH (40%-90) experiments.¹¹ Carrasco et al.⁹ also examined the effect of RH on MBO ozonolysis chemistry. They found that acetone derivative compounds were less abundant under humid conditions (>20% RH), whereas HMP_r derivatives increased under humid conditions. After quantifying the production yields, it was observed that acetone, formic acid, and formic anhydride were only observed under dry conditions, whereas the production yield of HMP_r increased dramatically under humid conditions.⁹

Zhang et al.¹⁰ also investigated the effect of aerosol acidity on SOA formation from MBO. They found that the relationship between aerosol acidity and SOA formation for MBO was similar to that of isoprene and α -pinene. It was reported that increasing aerosol acidity was shown to increase MBO-derived SOA formation.¹⁰ However, few studies have experimentally characterized the SOA formation mechanisms and yields derived from the ozonolysis of MBO.

Zhang et al reported a diagram that represents what is currently known about the oxidation of MBO (Figure 4)¹⁰. The figure notes that it is believed that MBO forms SOA products through an epoxide intermediate. The exact mechanisms of how MBO is converted to this epoxide are unknown. The research presented this is directed looking at the mechanism of MBO ozonolysis and seeing how it might lead to the formation of the epoxide. The figure notes the potential importance of peroxides in the formation of SOA, by indicating peroxides as intermediates for the OH oxidation pathway to the formation of the epoxide.

This honor's thesis seeks to systematically characterize the SOA constituents derived from MBO ozonolysis using the UNC indoor smog chamber facility. Specifically, we examined the effects of oxidant type, seed aerosol acidity, and RH on MBO-derived SOA constituents and

yields. This thesis also seeks to provide new insights into SOA formation from MBO ozonolysis that might derive from nucleation processes.

2. Materials and Method

2.1 Chamber operation

The experiments were conducted in a 10-m³ indoor Teflon smog chamber. Prior to each experiment the chamber was flushed and purged using purified dry air for at least 24 hours. The experiments were conducted under dark conditions using a temperature maintained between 21-23 °C and RH of <5% for dry experiments. Neutral seed aerosol was generated in the chamber by atomizing a 0.06 M (NH₄)₂SO₄ (aq) stock solution made with ultrapure water. Acidified seed aerosol was generated in the chamber by atomizing 0.06 M (NH₄)₂SO₄ (aq) + 0.06 M H₂SO₄ (aq) stock solution that was also made with ultrapure water. Injections of seed aerosol were made using a mass flow controller with the flow rate set to 5 L/min. The mass flow controller was turned on for 2 minutes to allow for an initial detection of aerosol particles, after which purified air was turned on to aid in uniform mixing of the chamber. Aerosol concentrations were measured using a differential mobility analyzer (DMA, Brechtel Manufacturing, Inc. (BMI), Model 2002) coupled to a mixing condensation particle counter (MCPC, BMI, Model 1700). The target mass concentration for seed aerosol was between 55 and 60 μg/m³ assuming the seed aerosol density = 1.0 g/cm³. One hour was allotted for the seed concentration to stabilize and obtain a decay rate due to wall losses.

MBO (17.5 μL, converted to a mixing ratio of 400 ppb in chamber, ≥98%, Sigma Aldrich) was injected into the chamber through a 10 mL manifold heated to approximately 55°C. N₂ heated at 55°C was passed into the manifold to deliver MBO into the chamber at a rate of 4 L/min for 30 min. The MBO concentration was monitored using a gas chromatograph equipped with a 30 m

capillary column (Nonpolar, Grace AllTech, Econo-Cap-EC-5 Capillary Column) and interfaced to a flame ionization detector (GC-FID, Model CP-3800, Varian). The retention time of MBO was determined to be 12.5 min.

For selected experiments, 60 ppm diethyl ether was used as an OH scavenger in order to characterize SOA growth and formation that would occur with the absence of OH radical-initiated oxidation. The scavenger was injected into the chamber using the same equipment as the MBO injection; specifically, heated N₂ was used to assist in the injection at a flow rate at of 1 L/for approximately one hour. The GC-FID was also used to monitor the concentration of the diethyl ether, which was determined to have a retention time of 2.5 min on the column. The temperature program for the GC-FID was as follows: it started at 70°C and held for 2 minutes, after which the temperature increased at a rate of 10°C/min till it reached 120°C (7 min). This temperature was then held for 2.5 min. The oven temperature for the detector was 250°C and the sampling rate from the chamber was .45 L/min. The sample flow in the GC-FID was .03 L/min. The carrier gas used for the GC-FID for these experiments was helium and the fuel gas for the detector was hydrogen. The O₃ was injected into the chamber to trigger the reaction using an ozone generator (Model L21, Pacific Ozone) with a flow rate of 4.7 L/min for 45 seconds. The target ozone concentration in most of the experiments was 800 ppb. The O₃ concentration was continuously measured using an ultraviolet photometric ozone monitor (Thermo Electron, Model 49). During the experiments the temperature and RH were measured using a dew point meter (Omega Engineering).

When the maximum of SOA growth was observed, two Teflon filter samples (47-mm diameter, 1.0-µm pore size, Tisch Environmental) per experiment were collected for approximately 1.5 hours in order to characterize SOA constituents at the molecular level. This was

done placing the filter in a container that attached directly to the chamber. A line was attached from a pump to the container, which was used to pull air through the container. This allowed for the particles present in the chamber to be sucked onto the filter.

2.2 Filter extraction

The Teflon filters were extracted by 45 min of sonication in 22 mL of high purity methanol (LC-MS CHROMASOLV-grade (≥ 99.7), Sigma-Aldrich) for both analyses by gas chromatography/electron ionization mass spectrometry (GC/EI-MS) and ultra-performance liquid chromatography interfaced to a high-resolution quadrupole time-of-flight mass spectrometer equipped with electrospray ionization (UPLC/ESI-HR-QTOFMS). Filters that would be used for the iodometric spectroscopic method used to quantify total organic peroxides were extraction in a 20 mL 50:50 mixture of methanol and high purity ethyl acetate (LC-MS CHROMASOLV-grade (≥ 99.9), Sigma-Aldrich). After the scintillation vials were sonicated for 45 min, the solutions were transferred to separate vials.

2.3 GC/MS Analysis of DHIP and 2-Methylerythritol

The GC/EI-MS consisted of a Hewlett 5890 Packard Series II GC equipped with an Econo-Cap™-ECTM-5 column (30 m \times 0.25 mm \times 0.25 μ m) interfaced to an HP 5971A Series mass selective detector. For GC/MS analysis samples taken to dryness under a constant flow of N₂ and then the derivatizing reagents (100 μ L of BTSFA and 50 μ L of pyridine) were added. The samples were heated for one hour at 70°C, and then transferred to the GC auto-sampler amber vials. A previously obtained standard curve of 2-methylerythritol was used for the calibration of the GC/MS and quantification of DHIP and 2-methylerythritol. The concentrations used for generating the calibration curves were 2.5 ppm, 5 ppm, 10 ppm, and 25 ppm. Detailed operating conditions, including column temperature gradients, can be found in Zhang et al.¹¹

2.4 UPLC/ESI-HR-QTOFMS Analysis of MBO-derived Organosulfate (m/z 199)

As with the GC/EI-MS analysis, the aerosol extracts were dried using a steady N₂ flow at room temperature. The vials were reconstituted with 150 μL of a 50:50 mixture of high-purity methanol and high-purity water (Milli-Q, 18.2 MΩ). For this analysis an Agilent 6520 Series ESI-HR-QTOFMS was operated in the negative ion mode. The column used for the experiments was a Water Acquity UPLC HSS T3 column. The mobile phase consisted of a gradient of 0.1% acetic acid in methanol (solvent A) and 0.1% acetic acid in water (solvent B). Detailed operating conditions and procedures for the UPLC/ESI-HR-QTOFMS analyses can be found in Zhang et al 2011.¹¹

2.5 Iodometric Spectroscopic Method Used for Quantification of Total Organic Peroxides

For peroxide analysis, the filters were extracted in the 50:50 mixture of ethyl acetate and methanol by sonication. After being taken to dryness under a stream of N₂, samples were reconstituted with 2 mL of the ethyl acetate-methanol solvent, and then mixed with an additional 3 mL of reagent (0.53:0.27:0.20 acetic acid:chloroform:Milli-Q water). 50 mg Potassium iodide (KI) was then added under anaerobic conditions in order to titrate the total organic peroxides collected on the filter samples.

The 5 mL solutions of collected SOA constituents were purged with N₂ for approximately 5 minutes before KI was added, in order to remove dissolved O₂. After the KI was added, the solution was pressurized by adding ultra-pure nitrogen for 20 seconds and allowed to stand for 1 hr to allow the reaction to take place.

Analysis of the sample solutions was done through UV-VIS spectrometry (Spectrophotometer, U-3300, Hitachi). The quantification was done using benzoyl peroxide (reagent grade (≥98%), Sigma Aldrich) as a standard reagent at multiple concentrations.

3. Results and Discussion

Conditions and results from the 10 experiments conducted for this thesis are summarized in Table 1. All experiments shown in this table were conducted under dry conditions ($RH < 5\%$). The results for SOA formation and yield are plotted in Figure 1. Aerosol volume size distributions measured by the DMA were converted to total aerosol mass values by multiplying by the density of organic aerosol (1.4 g/cm^3). This density is typically assumed for organic aerosol,¹ but should be later corrected for the actual value. However, the actual value of the MBO-derived SOA density was not the focus of this thesis. SOA yields, corrected for chamber wall loss, were calculated using the SOA mass determined assuming a density of 1.4 g/cm^3 divided by the mass of MBO reacted during each chamber experiment. The correction for chamber wall loss was done by determining the equation for wall loss and subtracting the SOA values obtained from it from those observed using the DMA. As a result of the limited amount of data collected from peroxide analysis, results of the peroxide assay will not be presented in this paper. The experiment with the highest SOA formation was Experiment 9 ($31.81 \text{ } \mu\text{g/m}^3$), which had the corresponding experimental conditions of acidic seed and no OH scavenger.

3.1 Effect of Aerosol Acidity

Experiments 3 and 5 (acidic and neutral, respectively, in the absence of OH scavenger) and 4 and 6 (acidic and neutral, respectively, in the presence of OH scavenger) from Table 1 were used to examine the effect of aerosol acidity on MBO-derived SOA formation. From Experiment 3 ($26.16 \text{ } \mu\text{g/m}^3$ of SOA produced) and 5 ($25.82 \text{ } \mu\text{g/m}^3$ of SOA produced), it was observed that the effect of aerosol acidity on overall SOA formation from ozonolysis in the presence of OH radical was negligible. The effect of aerosol acidity on SOA formation from ozonolysis in the absence of

OH was also found to be negligible; 11.20 $\mu\text{g}/\text{m}^3$ in Experiment 4 (acidified seed + OH scavenger) and 12.02 $\mu\text{g}/\text{m}^3$ in Experiment 6 (neutral seed + OH scavenger).

Interestingly, effect of aerosol acidity on the profile of MBO-derived SOA constituents (or molecular tracers) was much different than observed for the total SOA mass described above. The mass concentrations of the DHIP⁸ and 2-methylerythritol were found to be much higher in the acidic seed experiments than in the neutral seed experiments. This also applies to the MBO-derived organosulfates at m/z 199. It was observed, that the overall contribution of the organosulfate to total SOA formation was small. The increase in the concentration of organosulfates with acidity supports the high correlation coefficient between acidity and MBO organosulfate concentration proposed by Zhang et al.¹⁰ Increases in the concentration of MBO-derived SOA molecular tracers due to the presence of acidic sulfate aerosol can be observed in the both experiments examining the co-presence of O₃ and OH radicals (Experiments 3 and 5) and to those experiments only using O₃ (Experiments 4 and 6).

3.2 Effect of OH Scavenger: OH vs. O₃ Dominated Oxidation

From Figure 1 it was determined that the amount of SOA formed and the SOA yields for the experiments without OH scavenger were greater than those with OH scavenger. Table 1 can be referred for the specific values for both SOA formation and SOA yields.

The purpose of using an OH scavenger was to inhibit OH radical-initiated oxidation chemistry of MBO, so that the SOA formation from ozonolysis could be isolated. The SOA formation in the experiments without OH scavenger represents a combination of both ozonolysis and OH radical- initiated oxidation. The amount of SOA formed from the acidic sulfate aerosol experiments without scavenger appears to be more than double that of the experiments with scavenger (26.16 $\mu\text{g}/\text{m}^3$ from Experiment 3 compared to 11.20 $\mu\text{g}/\text{m}^3$ from Experiment 4). This

trend also applies to the neutral sulfate aerosol experiments where SOA concentration for Experiment 5 (without OH scavenger) was $25.82 \mu\text{g}/\text{m}^3$ and the concentration of Experiment 6 (with OH scavenger) was only $12.02 \mu\text{g}/\text{m}^3$. This suggests that SOA contribution to total SOA formation from the OH radical-initiated oxidation is equivalent to that of ozonolysis.

3.3. Role of Nucleation

Nucleation is the formation of aerosol particles from precursor compounds without the presence of pre-existing aerosol surfaces on to which the gaseous products can condense. The data collected from experiments in the absence of pre-existing sulfate seed aerosol suggests that the amount of SOA produced from MBO ozonolysis in the absence of seed aerosol is comparable to the SOA production in the presence of seed present when OH scavenger was not used. In the presence of scavenger, the yield SOA decrease in yield was more striking - by a factor of ~ 3 , compared to the presence of seed. SOA production in Experiment 8 (no pre-existing sulfate aerosol and with OH scavenger present) was $5.22 \mu\text{g}/\text{m}^3$ (47%) while amount of SOA produced in Experiment 7 (no pre-existing sulfate aerosol and without OH scavenger) was $23.63 \mu\text{g}/\text{m}^3$ (1.89%).

Another observation that can be made from the experiments without seed aerosol is the effect of nucleation on mass concentrations of the MBO-derived SOA molecular tracers. Examination of both Figure 2 and Table 1 reveals that the experiment without sulfate aerosol and in the presence of OH scavenger yielded the highest mass concentration for DHIP ($14.91 \mu\text{g}/\text{m}^3$). This result suggests that the gas-phase chemistry (particularly gas-phase OH radical oxidation) may play an important role in the formation of DHIP. This does not apply to the SOA molecular tracer, 2-methylerythritol, since its mass concentration in the absence of sulfate aerosol without an

OH scavenger (Experiment 7) was similar to that of the neutral experiment without an OH scavenger (Experiment 5).

One concern is that part of the DHIP observed using the GC/MS may have been a byproduct of the acid-catalyzed trimethylsilylation reaction with peroxide rather than a SOA product originally from the ozonolysis of MBO.

3.4 Preliminary Peroxide Results

Table 2 provides the peroxide information collected from three experiments (8, 9, and 10). The data collected shows that the experiment with acidic seed and no OH scavenger (experiment 9) yielded the highest peroxide concentration ($50.71 \mu\text{g}/\text{m}^3$). Experiment 10, which involved no seed and OH scavenger yielded the smallest peroxide concentration ($17.05 \mu\text{g}/\text{m}^3$). In Table 2. The percent contribution of organic peroxides to total SOA mass is recorded. It was observed that for each of the experiments the percent contribution to total SOA mass was greater than 100 (experiment 8: 397%, experiment 9: 159%, experiment 10: 121%). These values were determined by dividing the peroxide concentrations by the total SOA formation. The mass used for the quantification of peroxides was 300 g/mol.

3.5 Atmospheric Implications

In the present report, the effects of aerosol acidity on SOA production from MBO ozonolysis along with the contributions of nucleation to SOA formation were examined. The experiments demonstrated that aerosol acidity can increase the mass concentrations of certain MBO-derived SOA constituents but not the total SOA mass. This was in agreement with previous studies.⁸

By comparing experiments containing mixtures of OH radical and O_3 with those experiments only containing O_3 , we were able to determine that OH radicals play an important and

even dominant role in the total amount of MBO-derived SOA mass produced. This information will be beneficial in developing explicit chemical mechanisms that produce MBO-derived SOA in the atmosphere. Although we understand that OH radical dominates the SOA production and which products can be produced in the aerosol phase, more work is needed to understand the explicit gas-phase chemistry occurring. The latter will require the use of novel analytical techniques like our group's iodide CIMS instrument.

In this report, SOA formation from nucleation was documented. Previous research has not attempted to quantify the amount of SOA formed from nucleation of oxidation products produced from MBO oxidation. Additionally, this study documented the differences between the SOA formed from nucleation when OH was present and when it was not. This study found that, when considering nucleation, the majority of SOA was formed from MBO reacting with OH radicals. This result has demonstrated the need for our group to conduct more experiments and monitor the gas-phase oxidation products responsible for nucleation (new particle formation) events and to fully quantify these characterized products in the gas phase.

One interesting observation was how the concentration of 2-methylerythritol changed between the different experimental conditions. 2-methylerythritol is a tetrol, so it is unclear how it is forming, considering that the other tracer compound of interest DHIP is only a triol. This is especially unusual considering that even in the experiments with OH scavenger, 2-methylerythritol is observed. This poses the question of where is the additional OH group coming from.

3.6 Limitations

Though comparisons were made between the experiments to help illustrate observations, it is necessary to point out that the initial concentrations of ozone and MBO between each experiment were not constant. This makes it difficult to derive accurate conclusions from these

comparisons, since the effects of the differences between the ozone and MBO concentrations are unknown. The small variability of temperature and RH, not reported in Table 1, between experiments is believed to have a negligible effect on SOA formation.

The mixing ratios of O₃ and MBO under which these experiments were conducted are larger compared to ambient levels (6 ppb for MBO).⁸ Carrasco et al conducted their studies using an MBO concentration of 200ppb.⁹ Thus, the measured SOA yields and mass concentrations for the chemical products presented in this report are much larger than would be observed in the atmosphere. Higher concentrations were used because of the detection limits of the analytical equipment (GC/EI-MS and UPLC/ESI-HR-QTOFMS). This allowed us to detect the MBO-derived SOA tracers and better understand the reaction conditions needed to form them.

Another limitation of this study is that the experiments were conducted only once. This means that results reported and subsequent conclusions have not been statistically reproduced. Biased observation could occur to one set of experiments, so it is imperative that these experiments be redone in the future before submitting our work for peer-review publication. It should be noted that since the iodide chemical ionization high-resolution time-of-flight mass spectrometer (Iodide CIMS) to detect low-vapor oxidation products was not available, and we were not able to correct SOA yields with losses of low-volatility products to chamber walls. This will be a focus of future work.

The observed percent contribution of peroxides to total SOA mass were over 100. This suggests that the mass used to quantify the peroxides (300 g/mol) was too high. Future analysis of peroxides at the molecular level using mass spectrometry will be done to determine the correct molecular weight to use in the quantification of peroxides.

4 Conclusions

The research presented in this report provides insight into the production of SOA from MBO ozonolysis under different environmental conditions. The MBO SOA formation data from “pure” ozonolysis experiments (OH scavenger molecules present) was compared to the MBO SOA formation data obtained from experiments in the presence of OH radicals (no OH scavenger molecules present) in order to see which of the two pathways dominated the particle-phase chemistry. The production of SOA from nucleation was also observed in these experiments. It appears from our data that OH-initiated oxidation of MBO enhances the amount of SOA produced, as well as the amount of the major SOA tracers (DHIP, 2-methylerythritol, and the MBO-derived organosulfate at m/z 199). In addition, OH-initiated oxidation of MBO also appears to favor the formation of new particles through nucleation of very low-volatile vapors produced from this reaction.

The results from these experiments has granted insight into the mechanism behind MBO ozonolysis. It was observed that acidity led to the increase of most of the tracer compounds. The presence of 2-methylerythritol indicates the potential for complex chemistry to be occurring in the gas phase. Additionally, the experiments have provided evidence to suggest that OH radical oxidation may contribute more to the formation of tracer compounds than ozonolysis and that the SOA contribution of nucleation is sufficiently large to warrant further investigation. Furthermore, higher RH experiments may also provide important information about organic peroxide formation. Recent work by Li et al.¹² states that 18% of the gaseous peroxides are adsorbed onto SOA particles in the presence of increased water vapor. Since 82% of the peroxides stay in the gas phase it is important that gas-phase experiments be done for both low- and high-RH experiments to examine what proportion of SOA mass comes from peroxides and to characterize the peroxides that form.¹² This work will require use of our group’s iodide CIMS. The iodide CIMS will also

be needed to correct our reported SOA yields for losses of low-volatility products to chamber wall surfaces. This will also be a focus of future work before publication is considered.

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Table 1. Summary of experimental conditions, SOA growth concentrations, SOA yields, and concentrations of major MBO-derived SOA constituents.

Expt. #	Seed	[OH-svg.] ₀	[MBO] ₀	[O ₃] ₀	Max SOA Growth	SOA Yield	DHIP	2-Me Erythritol	MBO OS at <i>m/z</i> 199
		ppmv	ppbv	ppbv	μg/m ³	%	μg/m ³	μg/m ³	μg/m ³
1	Acidic	-	250	361	3.36	0.73	0.15	0.33	0.05
2	Acidic	-	449	512	19.29	2.73	0.53	0.38	0.12
3	Acidic	-	451	903	26.16	2.92	2.37	1.52	0.12
4	Acidic	60	440	798	11.20	1.36	0.05	0.22	0.02
5	Neutral	-	431	800	25.82	2.23	3.01	0.36	0.02
6	Neutral	60	421	793	12.02	1.18	0.09	0.06	0.01
7	-	-	462	815	23.63	1.89	14.91	0.39	0.00
8	-	60	436	850	5.22	0.47	0.13	0.03	0.00
9	Acidic	-	485	795	31.81	3.94	1.72	0.37	0.22
10	Acidic	60	449	880	16.82	1.94	0.02	0.35	0.05

Max SOA Growth is the maximum net SOA growth after correction for wall loss and density of aerosol particles.

DHIP is the abbreviation for 2,3-dihydroxyisopentanol.

OS is the abbreviation for organosulfate.

Experiment Number	Description	Peroxides in (μg/m ³)	Percent Contribution to Total SOA Mass (%)
8	No seed, Scavenger	17.05	327
9	Acidified seed	50.71	159
10	Acidified, Scavenger	20.29	121

Table 2. Preliminary Peroxide Concentrations

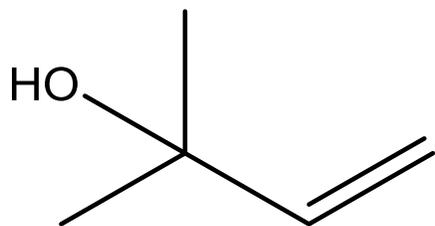


Figure 1. Structure of 2-methyl-3-buten-2-ol

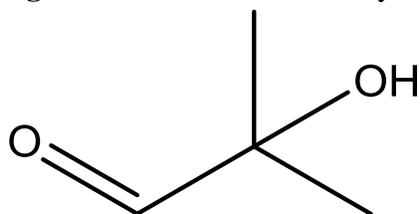


Figure 2. Structure of 2-hydroxy-methylpropanal

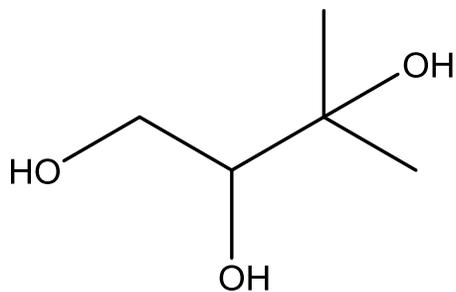


Figure 3. 2,3-dihydroxyisopentanol

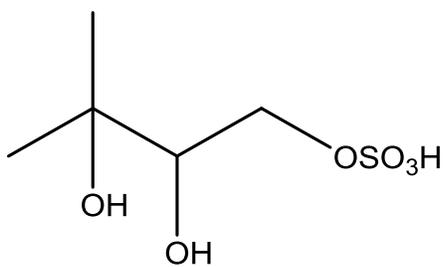


Figure 4. Organosulfate (m/z 199)

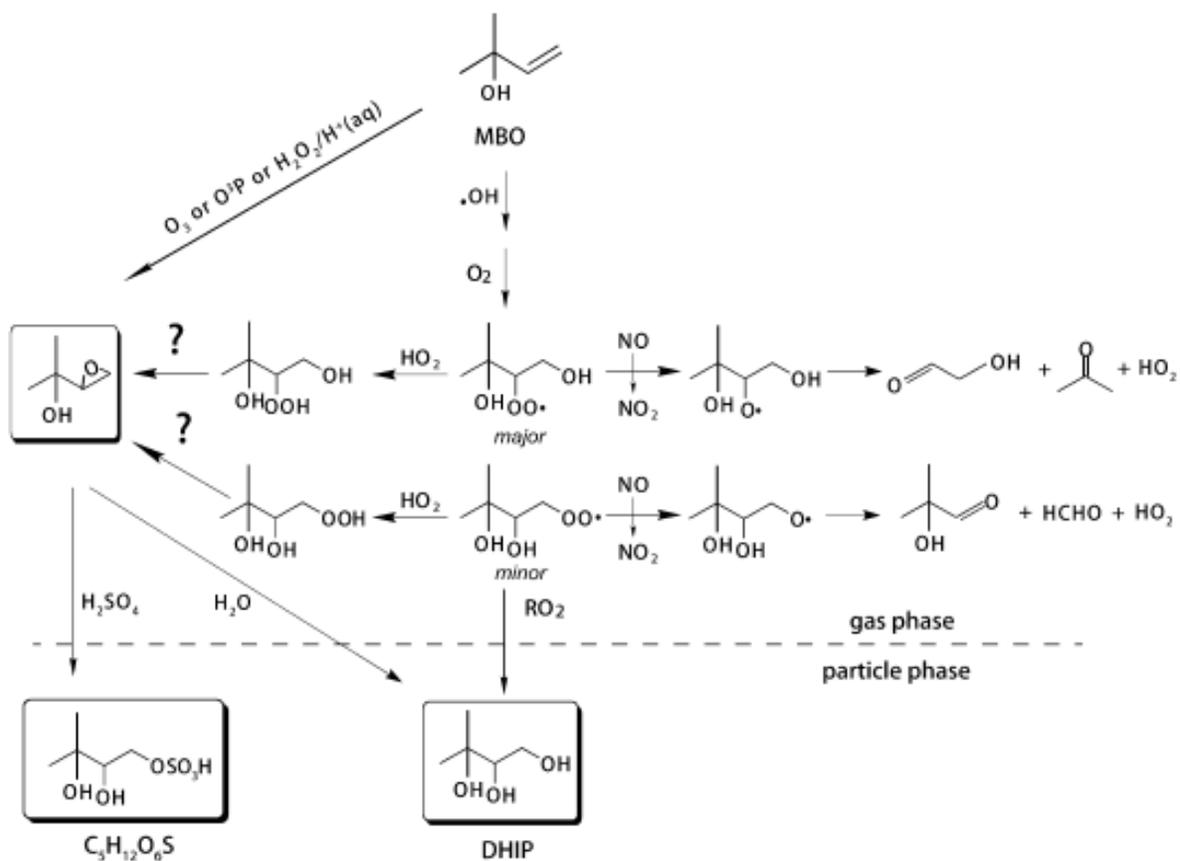


Figure 5. Present mechanism for formation of SOA from MBO oxidation

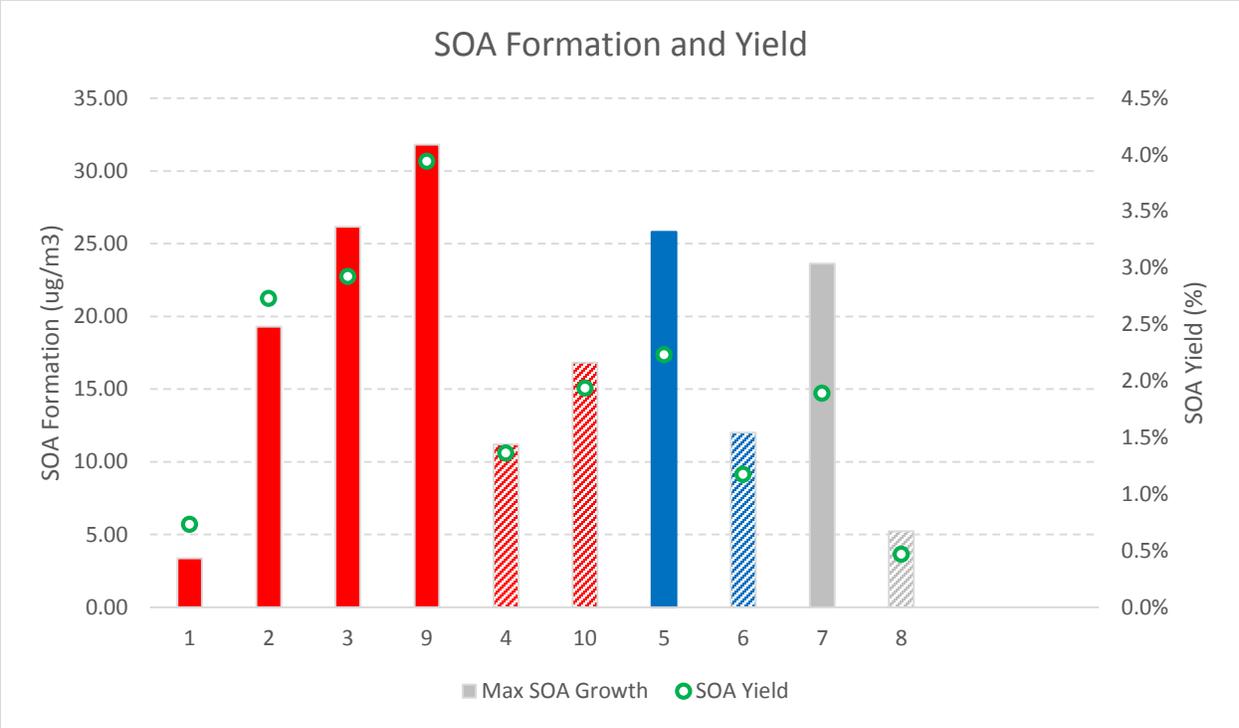


Figure 6. SOA growth values in $\mu\text{g}/\text{m}^3$ and associated SOA yield values. Red bars indicate experiments involving acidic sulfate aerosol particles, and blue bars indicate neutral sulfate aerosol experiments. Grey bars indicate seedless (or nucleation) experiments. The slashed colored bars indicate experiments that used OH scavenger.

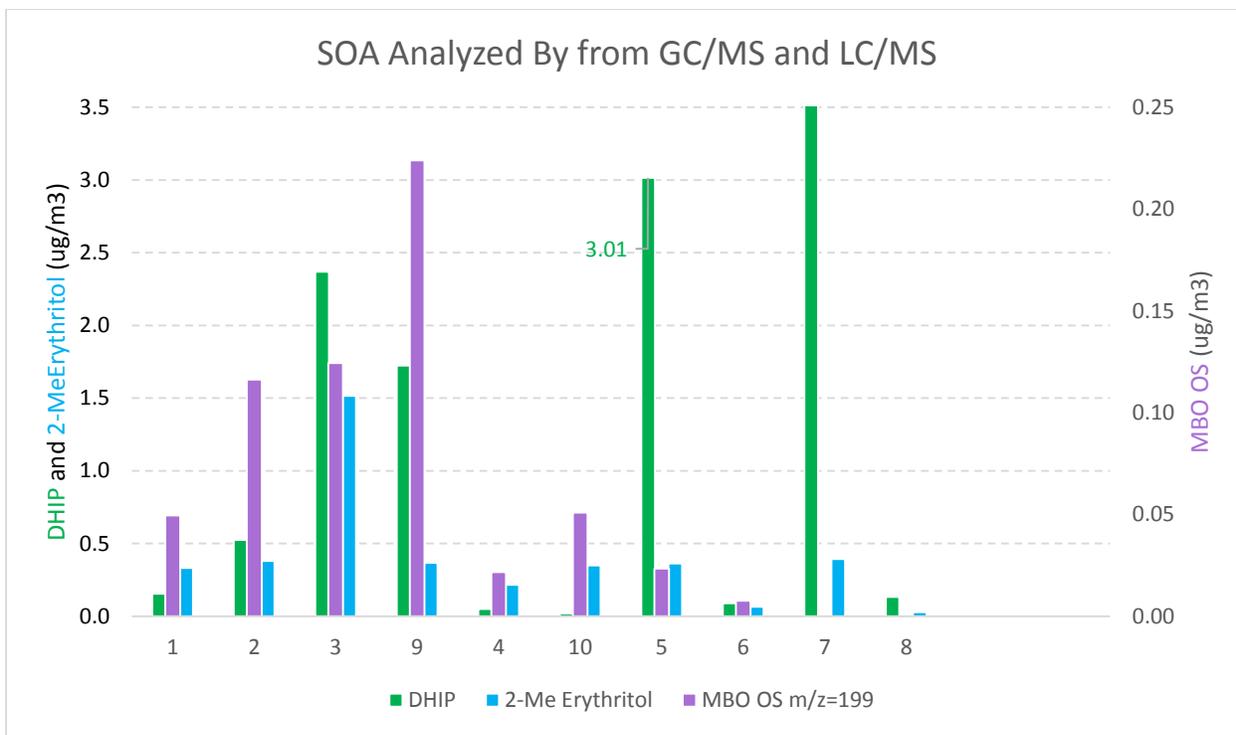


Figure 7. Quantification of MBO-derived SOA constituents.