Low-volatility compounds contribute significantly to isoprene SOA under high-NO conditions

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Abstract. Recent advances in our knowledge of the gas-phase oxidation of isoprene, the impact of chamber walls on secondary organic aerosol (SOA) mass yields, and aerosol measurement analysis techniques warrant re-evaluating SOA yields from isoprene. In particular, SOA from isoprene oxidation under high-NO conditions forms via two major pathways: 1) low-volatility nitrates and dinitrates (LV pathway) and 2) hydroxymethyl-methyl-α-lactone (HMML) reaction on a surface or the condensed phase of particles to form 2-methyl glyceric acid and its oligomers (2MGA pathway). These SOA production pathways respond differently to reaction conditions. Past chamber experiments generated SOA with varying contributions from these two unique pathways, leading to results that are difficult to interpret. This study examines the SOA yields from these two pathways independently, which improves the interpretation of previous results and provides further understanding of the relevance of chamber SOA yields to the atmosphere and regional/global modeling. Results suggest that low-volatility nitrates and dinitrates produce significantly more aerosol than previously thought; the SOA mass yield from the LV pathway is $\simeq 0.15$. Sufficient seed surface area at the start of the reaction is needed to limit the effects of vapor wall losses of low-volatility compounds and accurately measure the complete SOA mass yield. Under dry conditions, substantial amounts of SOA are formed from HMML ring-opening reactions with inorganic ions and HMML organic oligomerization processes. However, the lactone organic oligomerization reactions are suppressed under more atmospherically relevant humidity levels, where hydration of the lactone is more competitive. This limits the SOA formation potential from the 2MGA pathway to HMML ring-opening reactions with water or inorganic ions under typical atmospheric conditions. Due to the high isoprene SOA mass yield from the LV pathway measured in this work, we now roughly estimate that the LV pathway produces moderately more SOA mass than the 2MGA pathway under typical atmospheric conditions (RH = 70%, T = 298K, NO_2/NO = 6, NO = 0.05 ppb, isoprene = 5 ppb, and OH = 1.5 x 10^6 molec cm^{-3}). This suggests that in the atmosphere low-volatility compounds such as organic nitrates and dinitrates may contribute to isoprene SOA under high-NO conditions significantly more than previously thought, and thus deserve continued study.

1 Introduction

In the atmosphere, submicrometer particulate matter is composed of a significant fraction of organic aerosol (Zhang et al., 2007). There are two forms of organic aerosol: primary, which is directly emitted into the atmosphere, and secondary, which is formed when gas-phase compounds partition to the particle phase. Processes governing secondary organic aerosol (SOA) formation are particularly complex (Kroll and Seinfeld, 2008; Hallquist et al., 2009). SOA yields, the ratio of the mass of SOA formed to the mass of the parent volatile organic compound (VOC) reacted, are measured in environmental chambers and are used in models to reduce the complexity of SOA formation.

Isoprene is the dominant non-methane biogenic VOC emitted into the atmosphere. Because of the large flux of isoprene ($\sim$535 Tg yr^{-1}) into the atmosphere (Guenther et al., 2012), oxidation of isoprene is a significant source of SOA even though SOA yields measured in chambers are relatively low (Carlton et al., 2009). Despite numerous experimental studies of isoprene SOA formation under varying conditions (Pandis et al., 1991; Edney et al., 2005; Kroll et al., 2005; Dommen et al., 2006; Kleindienst et al., 2006; Kroll et al., 2006; Ng et al., 2006; Paulot et al., 2009; Chan et al., 2010; Chhabra et al., 2010; Surratt et al., 2010; Nguyen et al., 2011; Zhang et al., 2011, 2012; Lin et al., 2013; Nguyen et al., 2014b; Xu et al., 2014; Krechmer et al., 2015; Lambe et al., 2015; Nguyen et al., 2015; Bregonzio-Rozier et al., 2015, etc.), a consensus on the magnitude of SOA formed from isoprene oxidation by the hydroxyl radical (OH) is still lacking (Carlton et al., 2009; Bregonzio-Rozier et al., 2015). This lack of consensus in the experimental data leads recent global modeling studies (Marais et al., 2016; Stadtler et al., 2018) to implement SOA schemes that produce significantly different overall isoprene SOA yields. Isoprene SOA yields have been shown to depend on a variety of factors including RO$_2$ fate, NO$_2$/NO ratio, relative humidity, degree of oxidation, temperature, seed surface area, particle acidity, and chamber irradiation source (Carlton et al., 2009). These experimental conditions have not always been controlled or reported, which is likely a major reason for the variability seen in past isoprene SOA yields. By measuring isoprene SOA yields while controlling for seed surface area, RO$_2$ fate, NO$_2$/NO ratio, relative humidity, and temperature, we seek to resolve uncertainties in SOA formation in past yields.

Recent advances have improved our understanding of how chamber SOA yields should be measured and analyzed. This includes accounting carefully for particle wall deposition (Loza et al., 2012), vapor wall deposition (Zhang et al., 2014; Ehn et al., 2014), and particle coagulation (Nah et al., 2017). Advances have also taken place in the data processing of aerosol size distribution measurements by the differential mobility analyzer coupled to a condensation particle counter (DMA-CPC), the main instrument used to measure SOA yields (Mai and Flagan, 2018; Mai et al., 2018). Because isoprene SOA yields tend to be relatively small, the DMA data inversion technique and correction for CPC response time are quite important.

Additionally, there have been major recent advances in our understanding of isoprene gas-phase oxidation (Wennberg et al., 2018) and the processes governing isoprene SOA formation. The present work focuses on the production of SOA from OH-initiated isoprene oxidation under high-NO conditions, which occurs via two major chemical pathways (Figures 1 and 2). The first we define throughout as the low volatility (LV) pathway representing all aerosol formed from the equilibrium gas/particle partitioning of compounds with sufficiently low volatility, which mostly include functionalized nitrates and dinitrates (e.g., red

compounds in Figure 1). The second we define as the 2-methyl glyceric acid (2MGA) pathway representing aerosol formed from 2MGA and its oligomers (blue compounds in Figure 2).
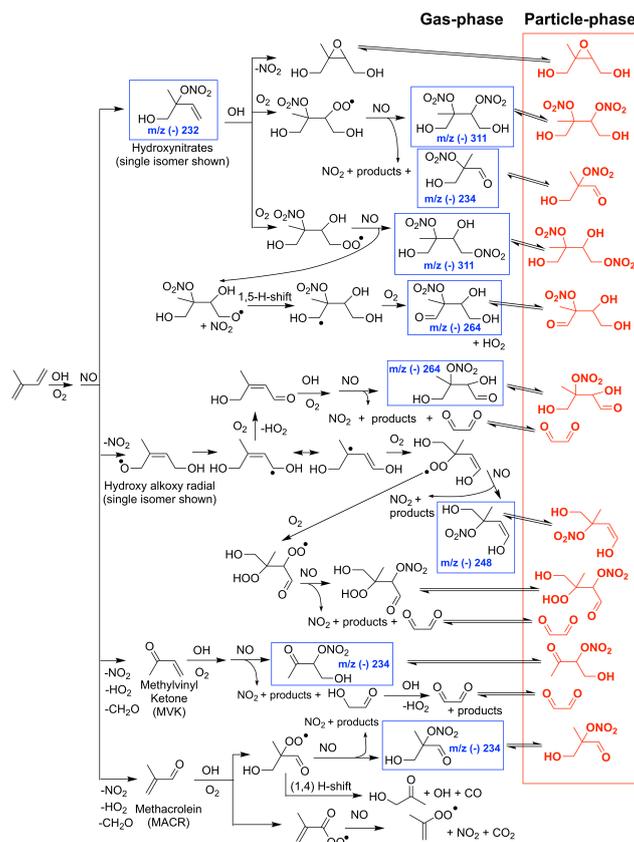
Figure 1. Simplified chemical mechanism of isoprene OH-initiated oxidation under high-NO conditions emphasizing SOA generated from the LV pathway, which includes low-volatility organic nitrates and dinitrates in red. Compounds detected in the gas phase by the chemical ionization mass spectrometer (CIMS) are highlighted with a blue square.

Aerosol from the LV pathway is believed to be composed largely of isoprene dihydroxy dinitrates, which are produced from the first-generation hydroxy nitrate reacting with OH to form a peroxy radical that then reacts with NO. The gas-phase
5 yield of isoprene dihydroxy dinitrates is quite uncertain (Lee et al., 2014). In general, the nitrate yields from highly functionalized RO_2 radicals have not been well studied (Wennberg et al., 2018) due mostly to difficulties in measuring such low volatility compounds. Aerosol from the 2MGA pathway forms when methacrolein is oxidized under high-NO_2 conditions to form methylacryloyl peroxynitrate (MPAN). MPAN reacts with OH to form hydroxymethyl-methyl-α-lactone (HMML), and HMML either decomposes in the gas phase to form hydroxy acetone or interacts with a wet surface to form 2-MGA (Kjaergaard
10 et al., 2012; Nguyen et al., 2015). A minor channel to form methacrylic acid epoxide (MAE) also exists from methacrolein oxidation (Lin et al., 2013), but not from pure MPAN oxidation (Nguyen et al., 2015). Nguyen et al. (2015) demonstrated that
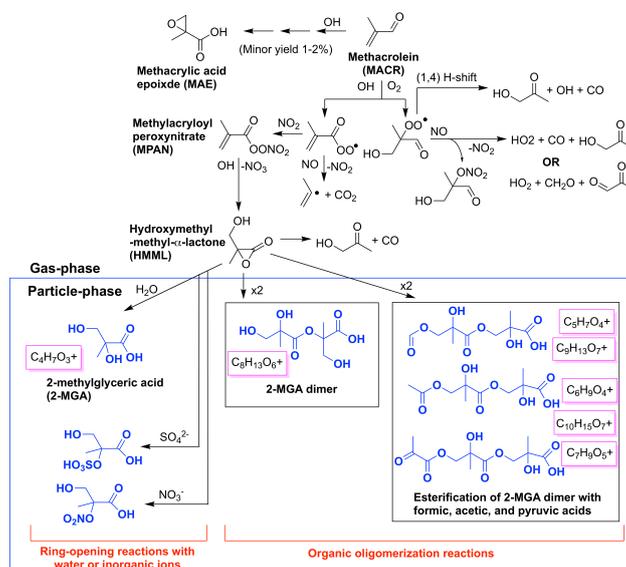
Figure 2. Simplified chemical mechanism of methacrolein OH-initiated oxidation under high-NO conditions emphasizing SOA generated from the 2MGA pathway including 2-methylglyceric acid (2MGA) and its oligomers in blue. Aerosol mass spectrometer (AMS) fragments likely corresponding to each compound are boxed in magenta.

MAE does not easily undergo ring-opening reactions to form particles. Thus, the yield of MAE from MACR oxidation reported in Lin et al. (2013) should be adjusted to include only MAE detected in the gas phase, which corresponds to a yield of ∼1-2%.

Because SOA formed from the LV and 2MGA pathways is chemically distinct in both route of formation and composition, the experiments reported here probed these chemical pathways separately. This experimental design is aimed to resolve in-
5 consistencies associated with previously reported isoprene SOA yields (Carlton et al., 2009) and improve our understanding of isoprene SOA formation. Additionally, we seek to report updated isoprene SOA yields as well as trace the SOA yields to known gas-phase SOA precursors.

2 Experimental Methods

Chamber experiments were performed to study SOA formation from isoprene oxidation under high-NO conditions from two
10 distinct pathways: 1) low-volatility nitrates and dinitrates (LV pathway) and 2) 2-MGA and its oligomers (2MGA pathway). Experiments targeting the LV pathway were performed using isoprene as the precursor and an NO_2/NO ratio < 1.5 was maintained throughout the entire experiment (as verified by the kinetic mechanism) in order to favor the formation of nitrates and dinitrates and limit the formation of MPAN (Figure 1). Experiments targeting the 2MGA pathway were performed using methacrolein as the precursor and an NO_2/NO ratio > 11 was maintained throughout the entire experiment (as verified by the
15 kinetic mechanism) with the exception of experiment M9, which maintained an NO_2/NO ratio > 8. This high NO_2/NO ratio accentuated the formation of MPAN, and thereby 2MGA (Figure 2) and was important for reducing variability between the

experiments. If a lower NO$_2$/NO ratio was used, small fluctuations in the initial NO$_2$ or NO would result in large differences in the NO$_2$/NO ratio. In each case, the effect of seed surface area, temperature, and humidity on SOA formation was determined.

2.1 Experimental Conditions

Experiments (see Table 1) were conducted in the Caltech dual chamber facility using a 21 m^3 Teflon chamber. Prior to each
5 experiment, the chamber was flushed with dry, purified air for 24 h. For humid experiments, the chamber was humidified prior to all injections. 25°C ultrapure water (18Ω, Milipore) was recirculated through a Nafion membrane humidifier (FC200, Permapure LLC) while purified air was flowed through the humidifier and into the chamber. First, isoprene (99% purity) or methacrolein (95% purity) was injected into a glass bulb using a gas-tight syringe and was carried by a flow of dry nitrogen into the chamber.

10 Second, methyl nitrite (CH$_3$ONO) was injected into the chamber. CH$_3$ONO was synthesized using the technique described in Taylor et al. (1980) and Chan et al. (2010) and stored in liquid nitrogen. Prior to each experiment, an evacuated glass bulb was filled with CH$_3$ONO to the desired pressure, as measured by a capacitance manometer (MKS Baratron^{TM}). This bulb was then backfilled with nitrogen and flushed into the chamber. The bulb pressure was used to calculate the CH$_3$ONO mixing ratio in the chamber (see Table 1). After CH$_3$ONO was injected, pulses of purified air were added to the chamber to enhance
15 mixing. Once the chamber was adequately mixed, NO (501 ppm in N$_2$, Scott Specialty Gases) or NO$_2$ (488 ppm in N$_2$, Scott Specialty Gases) was injected into the chamber through a calibrated mass flow controller. Again the chamber was mixed by pulses of purified air.

Seed particles were generated from an atomizer using 0.06 M (NH$_4$)$_2$SO$_4$ seed solution. The seed aerosol was directed through a soft x-ray neutralizer (TSI Model 3088) prior to injection into the chamber to ensure a consistent initial particle
20 charge distribution for all experiments. For humid experiments, the seed aerosol was directed through a wet-wall denuder after exiting the neutralizer in order to ensure the particles were deliquesced. After seed injection, mixing air was turned on for 1 min to enhance mixing.

After injecting all gas-phase precursors and seed aerosol, photooxidation was delayed by 1 h for experiments with no initial seed aerosol and 4 h for experiments with initial seed aerosol. The rate of particle wall deposition was measured for each
25 experiment during this 4 h delay. Although NO$_2$ was not intentionally added for the LV pathway experiments, a modest NO$_2$ signal was observed to form during the 4 h delay and is reported in Table 1. This "NO$_2$" signal may be NO$_2$ itself or an interference in the NO$_x$ monitor from an NO$_y$ compound (e.g., organic nitrates, nitrous acid, and CH$_3$ONO). The small signal of NO$_2$, or other NO$_y$ compound, is not expected to influence the results given the significantly larger initial NO levels (Table 1). When NO$_2$ or CH$_3$ONO were injected into the chamber, an NO signal was observed on the NO$_x$ monitor. As the NO$_x$
30 monitor has few interferences for NO, a small fraction of NO was likely formed from NO$_2$ or CH$_3$ONO photolysis in the Teflon injection lines. Thus, the slight increase of NO with the NO$_2$ and CH$_3$ONO injection was assumed and reported to be initial NO (Table 1).

The Caltech chamber uses Ultraviolet (UV) broadband lights with the main emission peak centered at ~350 nm. Only 10% of full light capacity (j$_{NO2\ 10\%}$ = 4 x 10^{-4} s^{-1}) was used for these experiments because CH$_3$ONO photolyzes rapidly,

Table 1. Initial conditions and SOA yield for all experiments

Expt #	[VOC]$_0$ (ppb)	[NO]$_0$ (ppb)	[NO$_2$]$_0$ (ppb)	[CH$_3$ONO]$_0$ (ppb)	[Aer Vol]$_0$ (μm^3 cm^{-3})	[Aer SA]$_0$ (μm^2 cm^{-3})	Avg T (°C)	Avg RH (%)	OH (molec cm^{-3})	SOA Yield
Dry Control Experiments										
C1	NA	NA	NA	NA	37	788	25.1	10.7	NA	NA
C2	NA	NA	NA	NA	109	2130	25.2	8.3	NA	NA
C3	NA	NA	NA	NA	183	3360	24.7	5.6	NA	NA
C4	NA	NA	NA	NA	375	5390	25.5	7.3	NA	NA
Experiments optimized for LV pathway (VOC precursor is isoprene)										
D1	59	585	6	118	0	0	25.6	5.0	2.6E6	0
D2	58	526	20	117	54	1170	26.4	5.6	2.5E6	0.04
D3	57	519	17	117	183	3420	25.9	7.5	2.5E6	0.17
D4	58	518	18	116	337	5770	26.4	7.9	2.4E6	0.16
D5	55	506	20	117	159	2830	12.8	16.4	1.7E6	0.15
D6	56	541	16	118	152	2660	32.4	5.9	2.7E6	0.16
D7	40	527	18	117	197	3580	25.9	8.1	2.6E6	0.18
D8	60	519	20	118	109	1790	25.5	44.7	2.3E6	NA
D9	55	489	20	119	166	2750	25.6	78.1	2.5E6	NA
D10	58	516	17	111	85	1580	25.8	5.1	2.2E6	0.04
D11	56	490	17	115	264	4770	25.8	5.2	2.4E6	0.16
Experiments optimized for 2MGA pathway (VOC precursor is methacrolein)										
M1	49	14	376	234	0	0	25.8	6.3	4.3E6	0.10
M2	48	15	365	235	82	1640	25.9	8.9	4.7E6	0.34
M3	46	23	345	236	118	2260	25.1	6.8	4.7E6	0.52
M4	50	17	356	235	50	1040	12.9	12.6	3.4E6	0.27
M5	58	18	375	235	87	1740	31.8	4.5	5.1E6	0.34
M6	52	12	334	235	104	1720	25.6	47.1	4.4E6	NA
M7	53	14	339	233	134	2340	25.6	67.4	4.6E6	NA
M8	56	18	352	236	141	2510	25.4	81.0	4.3E6	NA
M9	57	29	298	229	95	1910	25.9	5.1	4.7E6	0.24

Acronyms are defined as follows: VOC = volatile organic compound, NO = nitric oxide, NO$_2$ = nitrogen dioxide, CH$_3$ONO = methyl nitrite, Temp. = temperature, and RH = relative humidity. OH is estimated from the VOC decay over the first 3 h of each experiment. The [Aer Vol]$_0$ is the particle wall loss corrected seed volume at the start of photooxidation, which is used to determine the uncertainty in the particle wall loss correction as explained in Section 4.1. The [Aer SA]$_0$ is the surface area of the seed aerosol at the start of photooxidation not corrected for particle wall loss, and is used to understand how the SOA yield changes depending on the surface area of the suspended particles (e.g., Figure 5). The SOA yield is the mass fraction after 10 h of photooxidation.

and the lower light intensity minimizes chamber temperature increases ($\sim$0.4 °C on average) caused by the UV lights. In all experiments, OH was produced by the photolysis of CH_3ONO as shown by the following reactions:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{R1}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{R2}$$

5   $$HO_2 + NO \rightarrow OH + NO_2 \tag{R3}$$

Relative to other OH precursors, CH_3ONO has a low Henry's law constant (15 M atm^{-1}, calculated by theory) (Sander, 2015). During experiments with high RH, unlike other OH precursors, CH_3ONO is not expected to enhance OH production in the particle phase beyond atmospherically relevant levels.

2.2   Instrumentation

10   Temperature and relative humidity (RH) were measured using a Vaisala HMM211 probe. NO and NO_2 were monitored using a Teledyne NO_x analyzer (T200). Because the Teledyne NO_x monitor detects CH_3ONO, organic nitrates, and other NO_y compounds as NO_2, only initial NO_2 measurements can be constrained with this instrument. For some experiments, NO_2 was also monitored using a luminol NO_2/acyl peroxynitrate analyzer developed by Fitz Aerometric Technologies. This instrument separates NO_2 via chromatography at room-temperature using a deactivated DB-5 column. NO_2 then reacts with luminol to
15   produce a chemiluminescence response (Gaffney et al., 1998).

A gas chromatograph with a flame ionization detector (GC-FID, HP 6890N, column HP-Plot-Q) was used to measure the decay of isoprene and methacrolein. The GC-FID was calibrated with $\sim$50-60 ppm of isoprene or methacrolein generated from analytical standards (Aldrich 95-99% purity) and cross-calibrated by fourier transform infrared absorption (FT-IR) spectroscopy (pathlength 19 cm) using the absorption cross sections measured by Pacific Northwest National Laboratory (PNNL)
20   for isoprene or methacrolein (Sharpe et al., 2004). Linearity in the GC-FID calibration was determined to an error of $\sim$1% across a factor of 150 in dilution.

Aerosol organic and inorganic composition was recorded in-situ using a high-resolution time-of-flight aerosol mass spectrometer (HR-AMS, Aerodyne Research, Inc.). The HR-AMS switched every 1 min between the high-resolution W-mode and the lower-resolution, higher-sensitivity V-mode. The data were analyzed with Igor Pro (Wave Metrics, Inc.), utilizing the Squir-
25   rel 1.56D and PIKA 1.15D analysis toolkits (from http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html). In-line filter runs conducted prior to each experiment were used to correct for air interferences (Aiken et al., 2008). Bulk SOA elemental composition was calculated following the methods and recommendations of Aiken et al. (2008) and Canagaratna et al. (2015).

Aerosol volume and number concentration were monitored using a differential mobility analyzer (DMA, TSI 3081 column) coupled with a condensation particle counter (CPC, TSI 3010), which measures all particles with a diameter between 20-800 nm. The voltage scan used by the DMA was 1 min hold at 15 V, 4 min increase to 9850 V, 1 min hold at 9850 V, and 0.5 min decrease back to 15 V. Only the upscan data were used for the analysis. The longer upscan and hold times used here, compared to previous studies (e.g., Loza et al. (2012) and Zhang et al. (2014)), reduced biases caused by mixing in the CPC. Such CPC mixing biases particularly impact the measurement of large particles, which are important in SOA yield experiments as they contribute significantly to the total SOA volume.

The DMA data analysis includes an improved data inversion and a correction for particle mixing in the condensation particle counter, which influences the CPC response time (Mai and Flagan, 2018; Mai et al., 2018). The inversion technique is applicable only to particles $\leq$ 600 nm. Particle concentration between 600-800 nm was calculated assuming a non-linear least squares Gaussian fit applied to particles from 400-600 nm. For experiments with no initial seed aerosol, the inversion inconsistently determined the presence of particles beyond 400 nm. Such large particles are unlikely to be the result of nucleation and more likely to represent an artifact of the inversion; thus, only particles <400 nm were used in the analysis of these experiments. Corrections to the DMA data for coagulation and particle wall loss are addressed in Section 4.1.

Isoprene oxidation products were measured using a CF_3O^- chemical ionization mass spectrometer (CIMS), which utilizes a custom-modified triple quadrupole mass analyzer (Varian 1200) (St. Clair et al., 2010). CF_3O^- interacts with a gas-phase compound (A) to form a complex that is detected at the molecular weight of A + 85 or, in some cases, to fragment. Various fragmentation products can form as explained in previous work (e.g., Paulot et al. (2009); Praske et al. (2015); Schwantes et al. (2017)). In this work, the CIMS results are only used to identify the presence of highly functionalized organic nitrates and not for quantification, so only signals from the complex (i.e., A $\bullet$ CF_3O^-) and not from fragmentation are reported.

3 Kinetic Mechanism

All relevant reactions included in the Master Chemical Mechanism (MCM) v3.3.1 (http://mcm.leeds.ac.uk/MCM) were used in the current kinetic model (Jenkin et al., 1997; Saunders et al., 2003). Isoprene oxidation chemistry was recently updated in MCM v3.3.1 by Jenkin et al. (2015). Additional reactions included in the kinetic model, but not in MCM v3.3.1 (e.g., CH_3ONO photolysis), are listed in Table 2. BOXMOX, a box-model software package using the Kinetic PreProcessor (Knote et al., 2015), was used to simulate the chamber experiments.

As shown in Table 1, the inferred OH concentration was larger in experiments with higher temperatures. Because the temperature dependence of the CH_3ONO absorption cross section and quantum yield are not well established, the CH_3ONO photolysis rate constant was calculated from the CH_3ONO decay curve as measured by the GC-FID. Unfortunately, the GC-FID sensitivity to CH_3ONO was low, so only the 2MGA experiments produced a sufficiently large signal for this approach. The average CH_3ONO photolysis rate constant from experiments M1-M3, M4, M5, and M6-M8 were used for dry $\sim$25°C (1.9 x 10^{-4} s^{-1}), dry $\sim$13°C (1.4 x 10^{-4} s^{-1}), dry $\sim$32°C (2.3 x 10^{-4} s^{-1}), and humid $\sim$25°C (1.9 x 10^{-4} s^{-1}) experiments, respectively. This approach accurately captured the reaction of isoprene and methacrolein with OH in all experiments (Figures

Table 2. Additional reactions and reaction rates included in the kinetic model, but not in MCM v3.3.1

Reaction	Reaction Rate cm^3 molecule^{-1} s^{-1}	Source
$CH_3ONO + h\nu \rightarrow HCHO + HO_2 + NO$	$(1.4\text{-}2.3)$ x 10^{-4} s^{-1}	NA [a]
$CH_3ONO + OH \rightarrow H_2O + HCHO + NO$	3 x 10^{-13} * 0.5	Nielsen (1991), Cox (1980), Jenkin (1988)
$CH_3ONO + OH \rightarrow HCHO + HO_2 + HONO$	3 x 10^{-13} * 0.5	Nielsen (1991), Cox (1980), Jenkin (1988)
$HO_2 + NO_2 \rightarrow HONO$	5 x 10^{-16}	JPL
$HO_2 + HCHO \rightarrow HOCH_2OO$	9.7 x 10^{-15} exp(625/T)	IUPAC
$HOCH_2OO \rightarrow HO_2 + HCHO$	2.4 x 10^{12} exp(-7000/T) s^{-1}	IUPAC
$HOCH_2OO + HO_2 \rightarrow HMHP$	5.6 x 10^{-15} exp(2300/T) * 0.5	IUPAC
$HOCH_2OO + HO_2 \rightarrow HCOOH$	5.6 x 10^{-15} exp(2300/T) * 0.3	IUPAC
$HOCH_2OO + HO_2 \rightarrow HCOOH + HO_2 + OH$	5.60 x 10^{-15} exp(2300/T) * 0.2	IUPAC
$HOCH_2OO \rightarrow HCOOH$	7 x 10^{-13} * RO_2	IUPAC
$HOCH_2OO \rightarrow CH_2(OH)_2$	7 x 10^{-13} * RO_2	IUPAC
$HOCH_2OO \rightarrow HCOOH + HO_2$	5.50 x 10^{-12} * 2 * RO_2	IUPAC
$HOCH_2OO + NO \rightarrow HCOOH + HO_2 + NO_2$	5.60 x 10^{-12}	IUPAC
$HMHP + OH \rightarrow HOCH_2OO$	3.1 x 10^{-11} * 0.12	Jenkin (2007)
$HMHP + OH \rightarrow HCOOH + OH$	3.1 x 10^{-11} * 0.88	Jenkin (2007)
$HMHP + h\nu \rightarrow HCOOH + HO_2 + OH$	2.0 x 10^{-7} s^{-1}	JPL
$OH + OH \rightarrow O$	6.2 x 10^{-14} $(T/298)^{2.6}$ exp(945/T)	IUPAC
$OH + NO_2 + M \rightarrow HOONO + M$	Termolecular	IUPAC
$HOONO + M \rightarrow OH + NO_2 + M$	Termolecular	IUPAC
$OH + OH + M \rightarrow H_2O_2 + M$	Termolecular	IUPAC
$OH + NO_2 + M \rightarrow HNO_3 + M$ [b]	Termolecular	IUPAC
$NO_2 + O_3 \rightarrow NO_3$ [c]	1.4 x 10^{-13} exp(-2470/T)*0.97	Cantrell (1985)
$NO_2 + O_3 \rightarrow NO$ [c]	1.4 x 10^{-13} exp(-2470/T)*0.03	Cantrell (1985)
$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	Termolecular	IUPAC
$N_2O_4 + M \rightarrow NO_2 + NO_2 + M$	Termolecular	IUPAC

Acronyms are defined as follows: HMHP = $CH_2(OH)(OOH)$. [a] CH_3ONO photolysis was calculated from the GC-FID measurements. [b] This reaction was included in MCM v3.3.1, but the rate constant has been updated to the most recent IUPAC recommendation. [c] The $NO_2 + O_3$ reaction was included in MCM v3.3.1, but here a small yield of NO is added (Cantrell et al., 1985).

S1 and S2), which implies that the simulated OH in the kinetic model is reasonably accurate even over varying temperature. All other photolysis rate constants are calculated from the absorption cross sections and quantum yields reported in Burkholder et al. (2015) and Jenkin et al. (2015). Additionally, the kinetic model captures NO and NO_2 reasonably well for both the LV and 2MGA pathway experiments (Figure S3).

5 4 Results

First, corrections for particle coagulation and particle wall deposition, which are required for accurate calculation of SOA yields, are addressed (Section 4.1). Next, SOA produced from the LV (Section 4.2) and 2MGA (Section 4.3) pathways are discussed.

4.1 Corrections for Particle Coagulation and Particle Wall Deposition

10 Past studies reporting particle wall deposition coefficients apply the measured particle number decay rate in each size bin to produce a wall deposition coefficient, ($\beta(D_p,t)$), that is a function of particle size (D_p) (Loza et al., 2012). Because larger seed particle number and surface area concentrations were used in these experiments, corrections to $\beta(D_p,t)$ that account for coagulation are needed (Pierce et al., 2008; Nah et al., 2017). The current work uses an approach similar to that of Nah et al. (2017) and Sunol et al. (2018) with updates to account for electrostatic charges on the chamber walls as described by Charan
15 et al. (2018). To reduce the experimental uncertainty associated with these processes, particle wall deposition was calculated during each experiment. This approach accounted for the day-to-day fluctuations in particle coagulation processes, chamber wall charging, and chamber mixing. We summarize these approaches and describe any changes required for this analysis in Section S2 of the Supplement.

Four particle wall loss experiments were performed under dry conditions (RH <10%) at varying seed surface areas as controls
20 to verify the technique used to correct for particle wall loss, particle coagulation, and electrostatic charges on the chamber walls. These particle wall deposition experiments were performed by injecting ammonium sulfate seed into the chamber, as described in Section 2.1. Mixing air was added, and the ammonium sulfate seed aerosol was monitored in the dark chamber for at least 14 h. These controls confirmed that the wall loss correction calculated over the first 3.5 h could be extrapolated for an additional 10 h. Beyond 10 h, the wall loss correction was more uncertain, so results only from the first 10 h of each experiment are reported.
25 The percent change between the aerosol volume over 10 h and the aerosol volume at the start of the control experiment was between +4% and -6% for all dry control experiments (Figure 3).

The results of these control experiments verified the robustness of the correction technique and provided an estimate for the uncertainty. The reported uncertainty for the particle wall deposition correction is +4% and -6% of the corrected aerosol volume at the start of photooxidation. Experiments with larger seed aerosol volumes exhibit larger uncertainty in the reported
30 SOA yield. However, such experiments are necessary despite the extra uncertainty, as larger seed surface areas minimize low biases in SOA yields due to vapor wall deposition of low-volatility compounds (Zhang et al., 2014; Ehn et al., 2014). For experiments with no initial seed aerosol, particle wall loss corrections were applied assuming the particles coagulated and
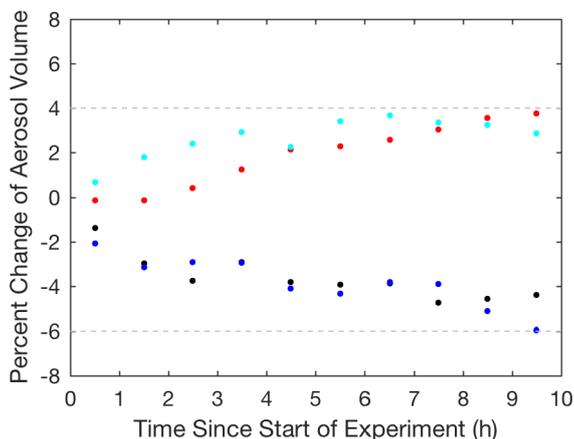
Figure 3. Percent change between the corrected aerosol volume over 10 h and the corrected aerosol volume at the start of photooxidation (60 min averages) for the following particle wall deposition control experiments: C1 (V = 37 $\mu m^3 cm^{-3}$, ●), C2 (V = 109 $\mu m^3 cm^{-3}$, ●), C3 (V = 183 $\mu m^3 cm^{-3}$, ●), and C4 (V = 375 $\mu m^3 cm^{-3}$, ●), respectively where V is the initial corrected particle volume.

deposited similarly to the lowest aerosol loading control experiment (C1). No uncertainty for the particle wall deposition correction was added to these experiments because the uncertainty derived here is applicable only to experiments with initial seed aerosol.

In experiments C1-C4, D1-D9, and M1-M8, electrostatic charges on the chamber walls were inferred to be present. After 5 these experiments were completed, new Teflon chambers were acquired with negligible electrostatic charges on the chamber walls (Charan et al., 2018) likely due to their smaller volume (18 m^3). Three additional new experiments (D10, D11, and M9) were completed using one of these new Teflon chambers to confirm that we had accurately corrected for the chamber wall charging effects. For the LV pathway experiments (Section 4.2), results for the new experiments were quite similar and within uncertainties of the old experiments. The new 2MGA pathway experiment produced slightly lower SOA yields than the old 10 experiments, but not necessarily because of the chamber wall charging corrections as described in Section 4.3.

Five control experiments were also performed under humid conditions. The DMA cannot measure hydrated particles owing to arcing in the DMA column at high RH. Thus, a Nafion dryer was used to dry particles before measurement. For the coagulation correction, the volume of the hydrated seed was calculated based on the dry DMA particle measurement, the RH in the chamber, and the hygroscopic growth curve for ammonium sulfate measured by Sjogren et al. (2007). The percent change for 15 the aerosol volume was higher and less consistent in the humid control experiments than in the dry control experiments. Also, the optimized value of the electric field ($\bar{E}$) was higher in many of the humid experiments than in the dry experiments (Section S1, Table S1). Increased humidity is expected to decrease the electrostatic charges on the chamber walls (e.g., Ribeiro et al. (1992)), but the inferred $\bar{E}$ suggests the opposite. Possibly, the humidifying process enhanced the electrostatic charges on the chamber walls, or nitric acid, which is enhanced in the particle phase in the humid experiments under high-NO conditions, 20 impacts the coagulation or particle wall loss processes.

The AMS data confirm that during the humid experiments, nitric acid partitioned to the particle phase and that organic aerosol was produced during photooxidation for all experiments. Nevertheless, the particle wall loss corrected volume measured by the DMA decayed below zero during photooxidation in the humid experiments. Potentially, this DMA volume decay suggests that nitric acid present in the particle phase changes the particle coagulation or wall loss characteristics. Even if we understood the impact of nitric acid on the particle coagulation or wall loss corrections, assessing how much of the particle growth is due to nitric acid versus organics would be difficult with the DMA, which measures only total aerosol volume and not composition. Further chamber characterization is required in order to assess isoprene SOA yields measured by the DMA from humid experiments under high-NO_x conditions. Thus, in this work, only the AMS results will be discussed for the humid experiments.

4.2 SOA Formation From the LV Pathway

The SOA mass yields from isoprene for all LV pathway experiments (i.e., experiments targeting low-volatility compounds) are shown in Figures 4 and 5. To convert aerosol volume measured by the DMA to aerosol mass, a density of 1.4 g cm^{-3} was assumed, consistent with past work (Dommen et al., 2006; Kroll et al., 2005, 2006; Bregonzio-Rozier et al., 2015). The kinetic mechanism suggests that in all experiments targeting the LV pathway, formation of the 2-MGA precursor was < 0.14 ppb even in experiments performed under cold conditions (13°C). The AMS results also confirm that 2MGA and its oligomers are not present in the LV pathway experiments (Section 5.2). Thus, the kinetic mechanism and AMS results verify that the experimental design correctly separates the two chemical regimes and 2-MGA is not substantially adding to the aerosol mass in the LV pathway experiments.

Aerosol growth in the absence of seed aerosols was not observed in the LV pathway experiments (Figure 4). As expected, SOA formed from gas/particle partitioning in the LV pathway exhibited a large dependence on seed surface area (Figure 5). Without sufficient seed aerosol, low-volatility nitrates partition primarily to the chamber walls, and the resulting SOA yields are biased low. Differences in SOA yield by varying temperature (13-32°C) lie within the experimental uncertainty. While vapor wall losses of LV compounds are expected to increase at colder temperatures (Zhang et al., 2015), the organic nitrate yields are also expected to be enhanced under colder temperatures (Orlando and Tyndall, 2012). Thus, the effects of these two temperature-dependent processes might cancel.

Consistent with past work (e.g., Kroll et al. (2005); Ng et al. (2006)), aerosol from the LV pathway is produced only after most of the isoprene is consumed, implying that aerosol from the LV pathway largely forms from later-generation chemistry (Figure 4). Thus, the extent to which later-generation products are oxidized (i.e., the degree of oxidation) impacts the SOA yield as demonstrated by the varying slope (i.e., SOA yield) during each experiment in Figure 4. We tested the OH/isoprene ratio on the SOA yield. Experiment D7 was performed with 40 ppb of isoprene compared to 55-60 ppb used in the other experiments, while the OH precursor concentration was kept constant. The kinetic model predicts that the SOA mass yield of dinitrates from experiment D7 is similar to the other experiments (Figure S4), and the empirical results are consistent with these predictions. Although a lower isoprene loading decreases the competition of isoprene with OH, other compounds also react with OH quickly (e.g., NO). Under the conditions used in this study, differences in isoprene loading are not expected to
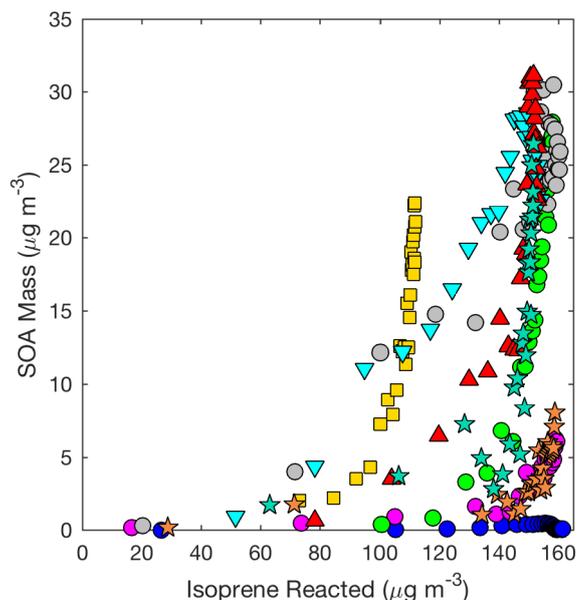
Figure 4. SOA mass yield (20 min averages) as measured by the DMA assuming a density of 1.4 g cm^{-3} for all LV pathway experiments: seed surface area - D1 (SA = 0 μm^{2}cm^{-3}, •), D2 (SA = 1170 μm^2 cm^{-3}, •), D3 (SA = 3420 μm^2 cm^{-3}, •), & D4 (SA = 5770 μm^{2}cm^{-3}, •), temperature - D5 (13 °C, ▼) & D6 (32 °C, ▲), isoprene loading - D7 (initial isoprene 110 μg m^{-3}, ◆), and new chamber with less wall charging - D10 (SA = 1580 μm^{2}cm^{-3}, ★) & D11 (SA = 4770 μm^{2}cm^{-3}, ★)

greatly influence the isoprene SOA mass yield. However, detailed kinetic modeling of past experimental conditions would be necessary to understand how the degree of oxidation of later-generation products in this study compares to other studies.

In summary, the results (Figure 5) suggest that one of the most important metrics for understanding the variability in SOA production from the LV pathway in various chamber experiments may be the initial seed surface area, instead of temperature or OH/isoprene ratio. Other parameters such as humidity and seed composition may also be important for SOA yields, but were not tested in this study. Future experiments examining SOA yields should report the initial seed surface area and use a sufficient seed loading to reduce the impact of vapor wall deposition.

4.3 SOA Formation from the 2MGA Pathway

The SOA mass yields from methacrolein for all 2MGA pathway experiments (i.e., experiments targeting 2MGA and its oligomers) are shown in Figures 6 and 7. Results from past experiments (Chan et al., 2010) have already demonstrated that fluctuations in the NO$_2$/NO ratio impacts SOA formation through the production of MPAN. In this work, the NO$_2$/NO ratio is kept as consistent as possible to isolate other influences on SOA production. The kinetic model suggests that the conditions for each experiment produce a consistent level of gas-phase 2-MGA precursor (Figure S4). Interestingly, because the experimental
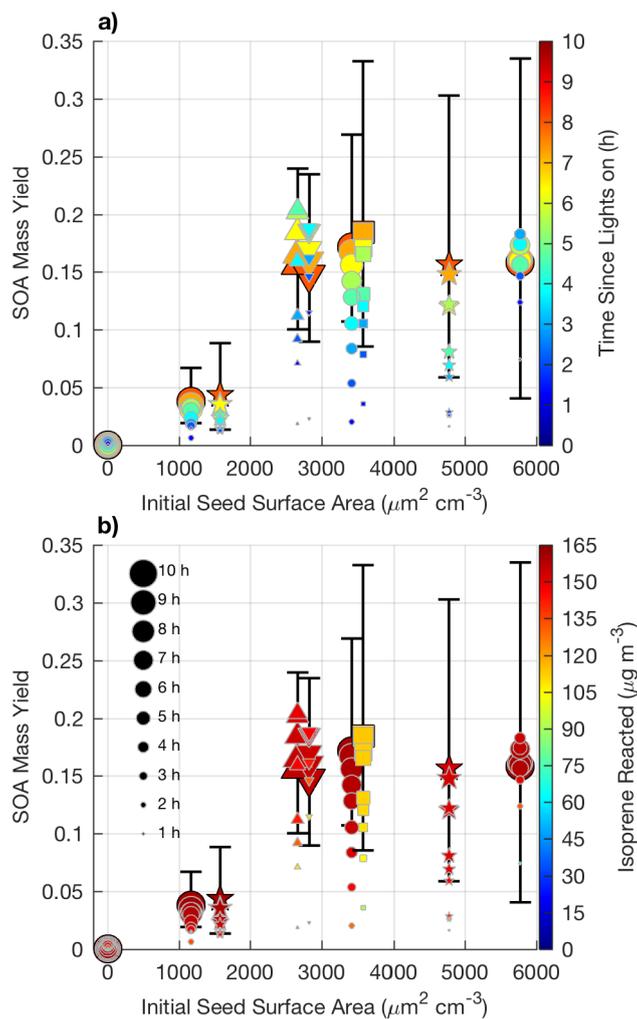
Figure 5. SOA mass yield (60 min averages) as a function of initial seed surface area for all LV pathway experiments. Colors represent time since lights on in panel a and extent of isoprene reacted in panel b. Marker size represents time since lights on. Uncertainty is shown in black lines as described in Section 4.1. Marker types indicate: 25-26°C (●), 13°C (▼), 32°C (▲), lower loadings of isoprene (■), and new chamber with less wall charging (★).

conditions heavily favored MPAN formation, the level of OH available to react with MPAN became the limiting reactant for aerosol formation in each experiment.
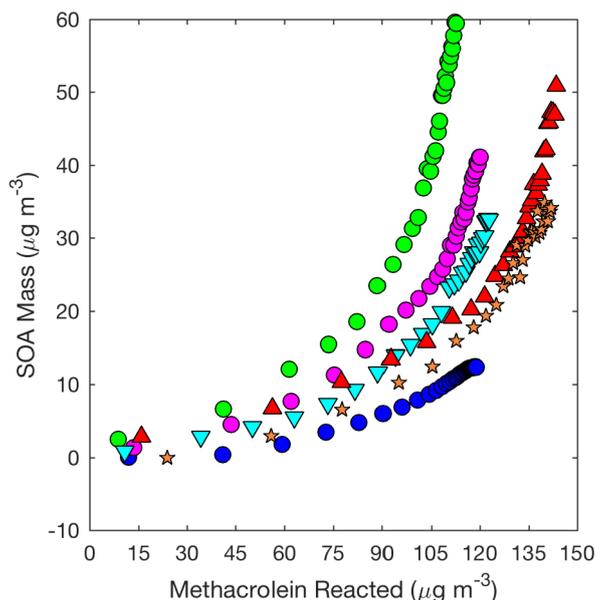
Figure 6. SOA mass yield (20 min averages) as measured by the DMA assuming a density of 1.4 µg cm^{-3} for 2MGA pathway experiments: seed surface area - M1 (SA = 0 µm^{2}cm^{-3}, ●), M2 (SA = 1640 µm^{2}cm^{-3}, ●), & M3 (SA = 2260 µm^{2}cm^{-3}, ●), temperature - M5 (13 °C, ▼) & M6 (32 °C, ▲), and new chamber with less wall charging - M9 (SA = 1910 µm^{2}cm^{-3}, ★).

Contrary to the LV pathway, SOA in the 2MGA pathway experiments do not require seed particles to form. The process of SOA formation from these two pathways is very different. Lactone SOA precursors may polymerize in the presence of organics

5 and water, which possibly explains why SOA from the 2MGA pathway readily forms particles without significant seed surface area, whereas in the LV pathway experiments volatility-based SOA formation results in aerosol yields that are particularly impacted by vapor partitioning. For the 2MGA pathway experiments, even though SOA formation occurred without initial seed aerosol, larger initial seed loadings still enhanced the SOA yield (Figure 7). Possibly, similar to the LV pathway, larger seed surface areas limit vapor wall loss of HMML or its oligomerization partners.

10 Temperature was varied between 13°C to 32°C. The NO$_2$/NO ratio was sufficiently high such that this temperature change did not greatly influence MPAN or HMML formation (Figure S4). Thus, these experiments only test whether aerosol properties and SOA yields are affected by the temperature, as MPAN thermal decomposition is minimized. Temperature does not impact SOA mass yield beyond given uncertainties (Figure 7).

Based on HMML production simulated by the kinetic mechanism under the conditions used in these experiments, ∼0.25

15 SOA mass yield from methacrolein is expected purely from the mass contained in HMML (MW = 102 g/mol, Figure S4). This represents about half of the SOA mass yield (∼0.5) measured from the experiment performed with the highest seed surface
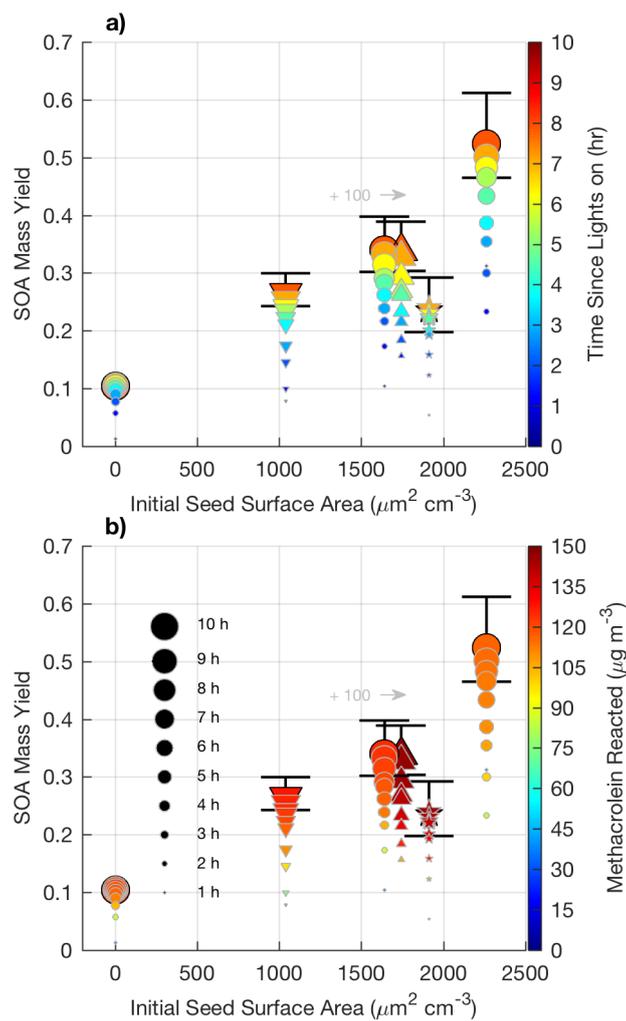
Figure 7. SOA mass yield (60 min averages) versus initial seed surface area for all 2MGA pathway experiments. Colors represent time since lights on (panel a) and extent of methacrolein reacted (panel b). Marker size represents time since lights on. Uncertainty is shown in black lines and described in Section 4.1. Markers represent: 25-26°C (●), 13°C (▼), 32°C (▲), and new chamber with less wall charging (★). Two experiments were performed at nearly the same seed surface area. To enhance viewing, experiment M6 (32°C, △) is shifted to the right by 100 μm² cm⁻³.

area. The rest of the aerosol is likely comprised of inorganic or organic compounds that react with HMML in the particle phase. For example, inorganic compounds such as water, nitrate, and sulfate can react with HMML through ring-opening reactions to produce total methacrolein SOA mass yields of ∼0.29, ∼0.40, and ∼0.49, respectively (Figure 2). Additionally, HMML can react with 2MGA and other organic compounds through oligomerization processes (e.g. Chan et al. (2010); Nguyen et al.

5 (2015); Zhang et al. (2011, 2012). Some of these organic oligomerization reactions bring into the particle phase additional organic compounds (e.g., organic acids) that ordinarily would exist primarily in the gas phase (Figure 2). The details of these particle-phase reactions are further discussed in Section 5.2.

In general, there is much greater variability in the SOA mass yields measured from the 2MGA pathway than the LV pathway. The additional variability is only partially explained by the initial seed surface area (Figure 7). Because the SOA yield is larger

10 for experiments in which less methacrolein is oxidized (Figures 6 and 7b), potentially, the extent of methacrolein oxidization contributes to this variability. The kinetic model suggests that formation of the gas-phase 2MGA precursor is similar for all of the experiments (Figure S4), but potentially slight variations in the NO_2/NO ratio and/or OH particularly near the end of each experiment are not well captured by the model. The kinetic model used here only simulates gas-phase oxidation. Chemistry occurring on surfaces such as the chamber walls or in the particle phase may be especially important for capturing the variability

15 in the 2MGA pathway experiments. Considering that the 2MGA pathway experiments are very susceptible to small differences in chamber conditions, regional and global models should parameterize SOA formation from the 2MGA pathway through gas-phase formation of HMML and subsequent particle-phase reactions.

5   Discussion

The gas-phase compounds measured by the CIMS (Section 5.1) and aerosol composition measured by the AMS (Section

20 5.2) provide important insight into isoprene SOA chemical composition formed from both the LV and 2MGA pathways. Additionally, comparison of the AMS and DMA results lends insight into possible biases in the AMS measurements of organic aerosol in Section 5.3. The SOA yields measured in this study are compared with past measurements in Section 5.4 and the atmospheric contribution of the LV versus 2MGA pathways toward SOA formation from isoprene OH-initiated oxidation under high-NO conditions is estimated in Section 5.5.

25 ### 5.1   Specific Low-Volatility Nitrates and Dinitrates Detected in the Gas-Phase

Numerous nitrates and dinitrates are detected in the gas phase by the CF_3O^- CIMS (i.e., compounds highlighted in blue boxes in Figure 1). Many of these nitrates have been identified in previous studies (e.g., Lee et al. (2014)). Yields for the low-volatility later-generation nitrates are either highly uncertain or unknown. Quantification is difficult for these low-volatility compounds due to high losses to sampling lines or chamber walls and lack of available standards. Lee et al. (2014), assuming a sensitivity

30 similar to standards of the first-generation isoprene hydroxy nitrates, measured a dinitrate yield of 0.03-0.04 from OH-initiated oxidation of the δ-1-hydroxy,4-nitrate isomer. However, these dinitrate yields are highly uncertain; Lee et al. (2014) assigned

an upper limit for the yield of dinitrates from the δ-1-hydroxy,4-nitrate isomer to 0.29 - 0.39 and the β-4-hydroxy,3-nitrate isomer to 0.18.

Although most past studies have focused on dihydroxy dinitrates as the main contributor to isoprene high-NO SOA, other low-volatility nitrates are likely also important. In Figure 8, the CIMS signals for the other low-volatility nitrates are comparable

5 or larger than the dihydroxy dinitrate signal. The relative sensitivities for these compounds are unknown, but these results suggest that detection and quantification of all low-volatility dinitrates and nitrates is important. The peroxy radical formed from OH-initiated oxidation of an isoprene hydroxy nitrate can undergo a 1,5 or 1,6 α-hydroxy H-shift to form a number of low-volatility nitrates that would occur in the ambient atmosphere (Wennberg et al., 2018). The NO concentrations are too high in these experiments for such shifts to occur. However, similarly, certain isomers of the alkoxy radical, formed from OH-

10 initiated oxidation of a isoprene hydroxy nitrate, can undergo a 1,5 or 1,6 α-hydroxy H-shift to form a dihydroxy carbonyl nitrate detected by the CIMS at m/z (-) 264 (Figure 1 and 8). Additionally, various low-volatility nitrates in the gas phase are detected, which are potentially derived from the delta-isoprene hydroxy alkoxy radical as depicted in Figure 1.

Further measurements of the yield of these low-volatility nitrates and dinitrates in the gas phase will be crucial for better understanding isoprene SOA formation under high-NO conditions. Although these low-volatility nitrates and dinitrates have

15 low molar yields from isoprene OH-initiated oxidation, their mass is substantially larger than isoprene and so their contribution to the isoprene SOA mass yield is significant. The nitrate yield from straight chain hydrocarbons is reasonably well understood, but few experimental measurements of the nitrate yield from highly oxidized compounds exist (Orlando and Tyndall, 2012; Wennberg et al., 2018).

5.2 Aerosol Composition of High-NO Isoprene SOA

20 Pieber et al. (2016) determined that inorganic aerosol such as ammonium nitrate or ammonium sulfate causes an interference on the AMS for the CO_2^+ ion signal. Although this interference is small for ammonium sulfate aerosol (<1%, (Pieber et al., 2016)), a correction may be needed for experiments with high initial seed aerosol loadings. Here organic signals from the AMS rise when ammonium sulfate seed is injected into the chamber. We expect this is due to the same interferences described in Pieber et al. (2016) and not due to contamination in ammonium sulfate solution or atomization technique. The background

25 organic signal caused by the ammonium sulfate is subtracted from the overall results to produce Figures 9, 10, and 11.

The AMS spectra from the LV pathway confirm that SOA formed from the LV pathway is not dominated by 2-MGA and its oligomers (cyan and red bars in Figure 9 and S11). This is an important confirmation that isoprene SOA formed from the 2MGA and LV pathways are distinct. A small yield of isoprene epoxydiol (IEPOX) is produced from OH-initiated oxidation of isoprene hydroxy nitrates (Jacobs et al., 2014) and IEPOX SOA can be formed when particle liquid water is present (Nguyen

30 et al., 2014a). NO levels remained high (> 100 ppb) throughout all LV pathway experiments (Figure S3), ensuring that the RO_2 fate in these experiments was always RO_2 + NO. AMS fragments associated with IEPOX, which were identified by Lin et al. (2012), are slightly enhanced under humid conditions in the LV pathway experiments (Figure 9). Some examples of organonitrate fragments ($C_xH_yNO_z^+$) are highlighted in Figure 9. Some of these organonitrate fragments are enhanced under
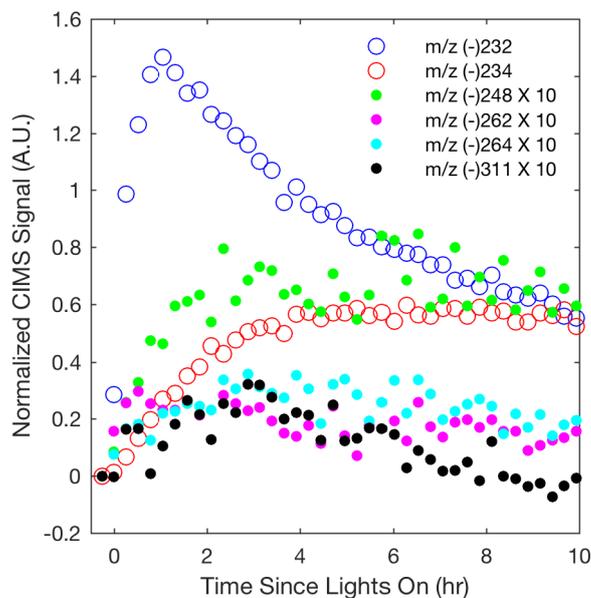
Figure 8. Normalized CIMS signal for known nitrates: C_5 hydroxy nitrate (m/z (-) 232 ○), methyl vinyl ketone/methacrolein nitrate (m/z (-) 234 ○), & C_5 dihydroxy dinitrate (m/z (-) 311 ●) and unknown nitrates, which are postulated in Figure 1 as C_5 dihydroxy nitrate (m/z (-) 248 ●), unknown (m/z (-) 262 ●), & C_5 dihydroxy carbonyl nitrate (m/z (-) 264 ●). As indicated in the legend, signals represented by filled circles are multiplied by 10.

humid conditions (e.g., CH_3NO^+). In general, the AMS spectra are similar between all LV pathway conditions (i.e. varied humidity-Figure 9 and varied temperature - Figure S11).

Prominent peaks in the AMS spectra from the 2MGA pathway clearly indicate that under dry conditions aerosol is comprised of various oligomerization products as mechanistically summarized in Figure 2. These oligomerization processes include 2-

5 MGA oligomerization with HMML (cyan bars in Figure 10a) and, possibly, esterification of 2-MGA with carboxylic acids including formic, acetic, and pyruvic acids (red bars in Figure 10a), which yield products that have been detected in numerous studies (Chan et al., 2010; Zhang et al., 2011, 2012). Based on the AMS spectra, 2-MGA oligomerization appears to be more dominant without the presence of ammonium sulfate seed aerosol (Figure S13). Varying temperature from 13-32°C does not appear to substantially change the extent of 2-MGA oligomerization (Figure S14).

10 Past studies have determined that HMML reaction with 2-MGA to form oligomers decreases under humid conditions while HMML ring-opening reactions with water and inorganic ions to form organic nitrates and organic sulfates increase (Zhang et al., 2011, 2012; Nguyen et al., 2015). Consistent with these past studies, the 2-MGA oligomer fragments on the AMS (cyan and red) are no longer prominent signals for all humid experiments (Figure 10 and Figure S12). 2-MGA oligomer fragments are not substantially different at 47%, 67%, or 81% RH, suggesting that the HMML oligomerization processes are impeded

15 as soon as aerosol particles become deliquesced. Because isoprene is mostly emitted in regions with relatively high humidity,
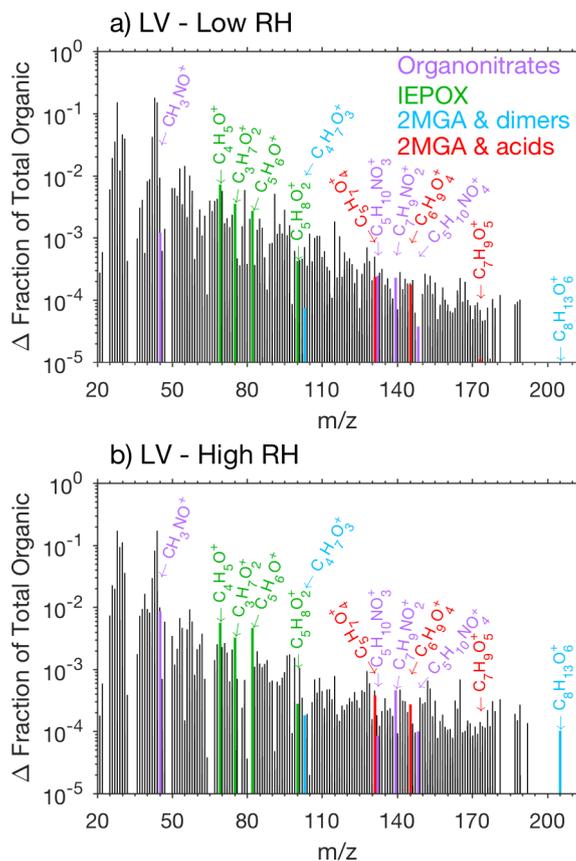
Figure 9. High resolution AMS mass spectra (averaged over 10h of photooxidation - the sulfate background) for experiment D3 (RH = 8%, panel a) and D9 (RH = 78%, panel b). Fragments are labeled as 2-MGA monomer/dimer (**cyan**), esterification of 2-MGA with acids (**red**), isoprene epoxydiol (IEPOX) tracers (**dark green**), and examples of organonitrate fragments - $C_xH_yNO_z$ (**purple**).

in the ambient atmosphere, HMML will more likely react with water and inorganic ions than undergo the various organic oligomerization reactions summarized in Figure 2.

5.3 Comparison of AMS and DMA Results

Based on the DMA measurements when assuming the same density, the SOA mass produced from the 2MGA pathway experiments is ∼2 times higher in magnitude than that from the LV pathway experiments (Figures 4 and 6). However, the AMS results (Figure 11) suggest that the SOA mass produced from the 2MGA pathway experiments is ≥8 times larger than that from the LV pathway experiments. This implies that the collection efficiency (CE) and/or the ionization efficiency on the AMS is quite different between these two regimes. Because the AMS is significantly more sensitive to aerosol formed from the 2MGA pathway, and not to SOA formed from the LV pathway, even ambient organic aerosol measurements have the potential
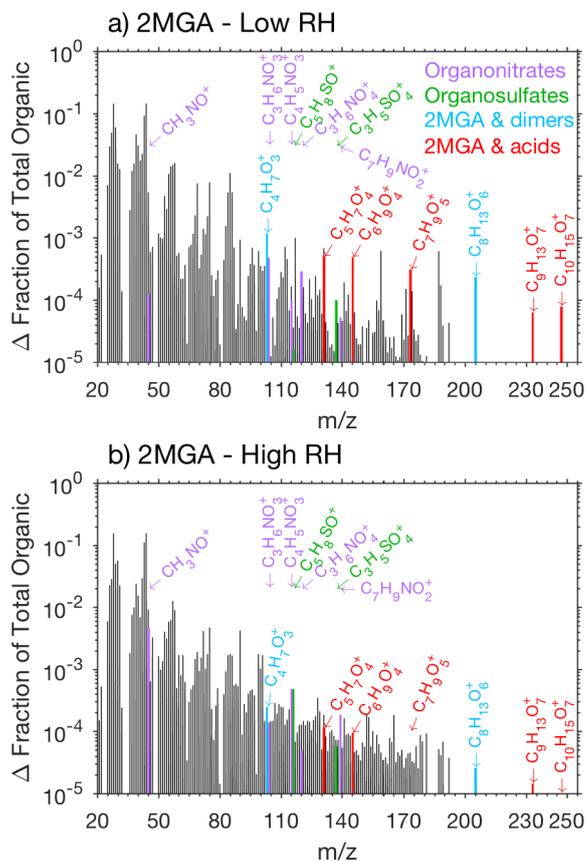
Figure 10. High resolution AMS mass spectra (averaged over 10h of photooxidation - the sulfate background) for experiment M2 (RH = 9%, panel a) and M8 (RH = 81%, panel b). Fragments are labeled as 2-MGA monomer/dimer (**cyan**), esterification of 2-MGA with acids (**red**), examples of organosulfate fragments (**dark green**), and examples of organonitrate fragments - $C_xH_yNO_z$ (**purple**).

to be impacted. Understanding whether the AMS is systematically underestimating organic aerosol from organic nitrates and dinitrates in general, or if this is only relevant to the isoprene system is crucial as the AMS is used throughout the world to quantify organic aerosol. Moreover, ambient measurements over the isoprene-rich Southeastern United States of particulate organic nitrates measured by the AMS are a factor of ∼5 lower than that measured by the thermal dissociation laser-induced
5   fluorescence instrument (TD-LIF) (Lee et al., 2016). The relative CE differences between the LV and 2MGA pathways in this study and these field campaign results suggest further AMS calibration of organic nitrates is necessary.

In this work, a CE of 0.5 is assumed for both regimes consistent with past work (Nguyen et al., 2014b). The exact CE is not relevant as no mass yields are reported here from the AMS. Docherty et al. (2013) determined that the CE could be estimated based on the f_{44}/f_{57} ratio. The f_{44}/f_{57} ratio for all experiments (2MGA and LV) is ≥ 6, which is where the CE vs f_{44}/f_{57} curve

plateaus at 0.2. Thus, the CE vs f_{44}/f_{57} relationship developed by Docherty et al. (2013) is not able to explain the large CE difference between aerosol formed from the LV and 2MGA pathways.
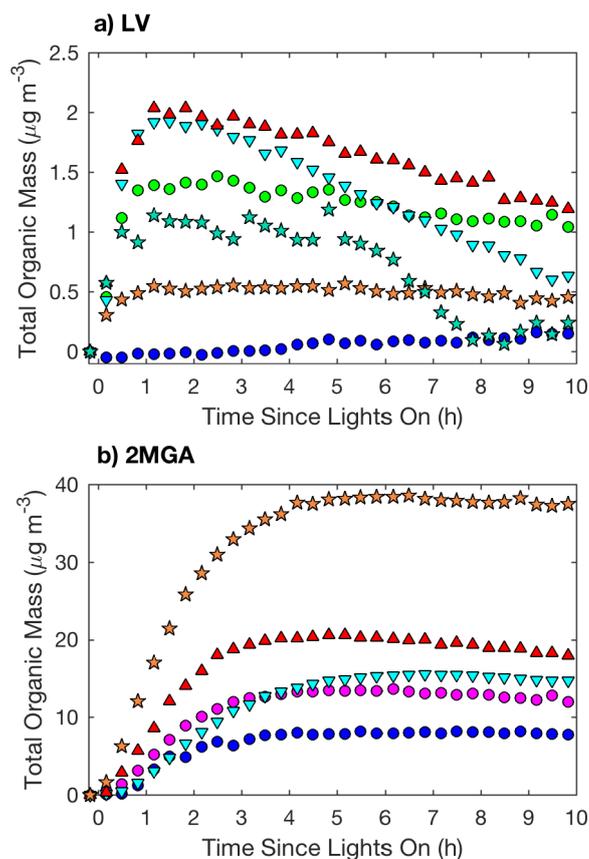
Figure 11. Total organic mass (20 minute averages) as measured by the AMS for LV pathway experiments (panel a): seed surface area - D1 (SA = 0 μm^2 cm^{-3}, ●) & D3 (SA = 3420 μm^2 cm^{-3}, ●), temperature - D5 (13 °C, ▼) & D6 (32 °C, ▲), and new chamber with less wall charging - D10 (SA = 1580 μm^2 cm^{-3}, ★) & D11 (SA = 4770 μm^2 cm^{-3}, ★) and 2MGA pathway experiments (panel b): seed surface area - M1 (SA = 0 μm^2 cm^{-3}, ●) & M2 (SA = 1640 μm^2 cm^{-3}, ●), temperature - M4 (13 °C, ▼) & M5 (32 °C, ▲), and new chamber with less wall charging - M9 (SA = 1910 μm^2 cm^{-3}, ★).

5.4 Comparison to Previously Reported SOA Yields

SOA mass yields reported from past environmental chamber studies of OH-initiated oxidation of isoprene under high-NO conditions vary over the range of 0-0.09, suggesting isoprene SOA yields are highly dependent on chamber conditions (Carlton et al., 2009). In Table 3, past reported SOA mass yields are summarized along with the chamber conditions for both isoprene and methacrolein OH-initiated oxidation under high-NO conditions. Only experiments that explicitly measure an SOA mass yield

are listed in Table 3. By varying a large number of conditions, our results lend insight into the variation in these experiments. Overall our results suggest that the initial seed surface area has the greatest impact on SOA yield. Unfortunately, the initial seed surface area was not commonly reported in past studies. The closest metric is aerosol volume, which can roughly be used to understand differences.

Table 3. Reported SOA mass yields and chamber conditions for isoprene and methacrolein OH-initiated oxidation under high-NO conditions

Study	Oxidant	$[VOC]_0$ (ppb)	$[NO]_0$ (ppb)	$[NO_2]_0$ (ppb)	Light Source	$[AS]_0$ ($\mu m^3/cm^3$)	Temp. (°C)	RH (%)	SOA Yield (fraction)
Isoprene									
Edney (2005)[a]	NO_x	1610-1680	∼630	0	UV	<0.6-24[b]	29.7	30	0.002-0.028
Kroll (2005)	HONO	25-500	75-138	98-165	UV	10-25	∼20	40-50	0.009-0.03
Dommen (2006)	NO_x	180-2500	0-700	40-806	X	0	20	<2-84	0.002-0.053
Kleindienst (2006)[a]	NO_x	1600	406-485	7-69	UV	0.1-27[b]	25	30	0.003-0.018 [c]
Chan (2010)	HONO or CH_3ONO	33-523	259-316	510-859	UV	11-19	20-22	9-11	0.031-0.074
Chhabra (2010)	HONO	81-286 [d]	518-591	374-434	UV	11-14	NR	<10	0.006-0.015
Zhang (2011)	NO_x	400-790	138-253	1-9	N	10-30	281-303	15-88	0.007-0.03
Nguyen (2011)	H_2O_2	∼250	600	100	UV	0	22-26	<2-90	∼0.07
Xu (2014)	H_2O_2	101-115	338-738	0	UV	0	∼25	<5	0.015-0.085
Bregonzio-Rozier (2015)	NO_x or HONO	439-846	14-143	<1-79	X	0-16	16-24	<5	0.001-0.01
Methacrolein									
Chan (2010)	HONO or CH_3ONO	20-285	164-725	365-799	UV	11-16	20-22	9-11	0.019-0.392
Bregonzio-Rozier (2015)	NO_x or HONO	396-927	19-123	4-100	X	0-15	19-24	<5	0.005-0.042

Acronyms are defined as follows: NR = not reported, UV = ultraviolet lights, N = natural, X = xenon arc lamps, and AS = ammonium sulfate seed aerosol volume. [a] Chamber was operated in dynamic mode (residence time = 6 h). [b] Ammonium sulfate was injected throughout the experiment to generate the lower limit of initial seed aerosol. SO_2 was added in some experiments to generate the upper limit of initial seed aerosol. [c] SOC is converted to SOA using factor (2.47) reported in Kleindienst et al. (2007). [d] VOC reacted was reported and tabulated instead of VOC initial.

5   Many of the past SOA yield measurements were performed with no seed aerosol. Consistent with past results, when no seed aerosol was injected into the chamber (experiments D1 and M1), the SOA mass yield for the LV pathway (0 from isoprene) and 2MGA pathway (0.1 from methacrolein) were quite low. Past experiments performed with no seed aerosol were only measuring SOA from the 2MGA pathway, which is very dependent on the NO_2/NO ratio (Chan et al., 2010). The NO_2/NO ratio varied greatly between these past studies (Table 3).

While the zero or low seed aerosol loading experiments in this study compare well with the past, SOA yields measured here using higher initial seed surface areas are substantially greater, especially for the LV pathway. The SOA yield from the LV pathway is $\simeq 0.15$ in this study, while past isoprene SOA yields are largely ≤ 0.07 with the exception of studies optimizing for high $RO_2 + NO_2$ reactions (Chan et al., 2010) or mixed regimes - $RO_2 + HO_2/NO$ (Xu et al., 2014). The higher yields measured in this study are not unexpected given that recent publications have recognized the importance of using high initial seed surface areas when measuring SOA yields to reduce the impact of vapor wall deposition (e.g., Zhang et al. (2014), Ehn et al. (2014)). The methacrolein SOA yields measured in this study from the 2MGA pathway are comparable to those measured by Chan et al. (2010), but larger than those measured by Bregonzio-Rozier et al. (2015).

The most recent isoprene SOA yield study, Bregonzio-Rozier et al. (2015), measured low isoprene (0.001-0.01) and methacrolein (0.005-0.042) SOA mass yields. They proposed that these lower yields were due to using xenon arc lamps as a light source, which are more representative of natural sunlight than the UV lamps used here and in most other studies. Dommen et al. (2006) also used xenon arc lamps and reported low yields. However, both of these studies used 0 or low levels of initial seed aerosol (0-16 $\mu m^3/cm^3$), which could also cause this low bias. Additionally, the stainless steel chamber used by Bregonzio-Rozier et al. (2015) may have higher vapor wall losses than the Teflon chambers used in other studies. Further work is necessary to understand how vapor wall losses compare across different types of environmental chambers.

As discussed by Carlton et al. (2009), isoprene SOA forms mostly from oxidation of 2nd and later-generation products (e.g., Ng et al., 2006). Towards the end of the experiment, SOA mass grows even when isoprene is no longer reacting (e.g., the characteristic hook in Figure 4). Differences in the level of oxidation of 2nd and later-generation products could also explain some of the discrepancies between our results and past results. The isoprene SOA mass yields from the LV pathway are particularly sensitive to the extent of oxidation. More studies measuring the gas-phase yields and formation processes of low-volatility nitrates and dinitrates will be critical for further understanding isoprene SOA.

Many of the previous studies listed in Table 3 report the VOC/NO ratio when comparing experiments. A more useful metric is understanding the RO_2 fate and RO_2 lifetime. Simply injecting NO and/or NO_2 and reporting the initial concentrations are not sufficient to confirm that SOA was dominantly produced from the $RO_2 + NO$ channel or in the case of HMML formation from the $RO_2 + NO_2$ channel. For example, if NO decreases to zero before the end of the experiment, SOA has formed in a mixed regime; $RO_2 + NO$ reactions dominate in the beginning and $RO_2 + HO_2$ reactions dominate at the end. If large initial VOC loadings are used in the beginning of the experiment without comparable increases in NO, $RO_2 + RO_2$ reactions may become dominant.

Experiments here are specifically designed to test two different RO_2 fates, and the kinetic mechanism is used to confirm the fate of the RO_2. In the LV pathway experiments, high NO levels are maintained such that NO_2/NO ratio remains < 1.5 throughout the entire experiment and RO_2 dominantly and consistently across the experiments reacts with NO. In the 2MGA pathway experiments, high NO_2 levels are used such that the acyl radical derived from methacrolein dominantly and consistently across experiments reacts with NO_2. By controlling for the RO_2 fate, the effects of temperature, seed surface area, and relative humidity on SOA formation become easier to resolve. Design of future experiments should optimize and report the

RO_2 fate for which the experiment was designed, in addition to key reaction parameters such as seed surface area, rather than simply reporting an initial VOC/NO ratio.

5.5 Estimating the Atmospheric Contribution of the LV versus 2MGA Pathways

A detailed global modeling study is needed to precisely capture the contribution of the LV versus the 2MGA pathways toward SOA formation from isoprene OH-initiated oxidation under high-NO conditions. However, in order to demonstrate the significance of the new isoprene SOA yield from the LV pathway measured in this work, we roughly approximate the contribution of each pathway under typical atmospheric conditions. We use the same kinetic mechanism described in Section 3, but hold the following constant: RH = 70%, T = 298K, NO_2 = 0.3 ppb, NO = 0.05 ppb, isoprene = 5 ppb, OH = 1.5 x 10^6 molec cm^{-3}, CO = 135 ppb, O_3 = 37 ppb, and HO_2 = 25 ppt (Sanchez et al., 2018; Feiner et al., 2016; Pajunoja et al., 2016). Then we simulate the formation of the gas-phase 2-MGA and dinitrate SOA tracers as done for the experimental results in Figure S4.

To estimate the aerosol contribution for the LV pathway, we assume that SOA from the LV pathway scales with the dinitrate tracer, so we multiply the dinitrate tracer by 7.1, which is the ratio of the measured SOA yield (Figure 5) versus the simulated SOA yield from the gas-phase dinitrate tracer (Figure S4). Then we convert to mass by multiplying by the molecular weight of dihydroxy dinitrate (226 g/mol). The dinitrate SOA tracer includes all dihydroxy dinitrates from isoprene OH-initiated oxidation. MCM v3.3.1 assumes a nitrate yield of 0.087-0.104 from NO reacting with the peroxy radical derived from OH + isoprene hydroxy nitrate. Low-volatility nitrates such as dihydroxy hydroperoxy nitrates form when HO_2 reacts with the peroxy radical derived from OH + isoprene hydroxy nitrate. Such products would not form in the chamber conditions used in this work where NO levels remained above 100 ppb, but would form in the ambient atmosphere. Considering these low-volatility species from mixed chemical regimes would further increase the SOA mass generated from the LV pathway. For the 2MGA pathway, we convert to mass by multiplying the gas-phase 2MGA tracer by the molecular weight of 2-MGA (120 g/mol), 2-MGA-nitrate (165 g/mol), and 2-MGA-sulfate (200 g/mol), which are the expected condensed-phase products under the high humidity levels in the atmosphere. The 2MGA tracer includes HMML and MAE, which in MCM v3.3.1 are produced in yields of 0.57 and 0.21, respectively from the reaction of MPAN + OH.

Then based on the assumptions above, the kinetic model estimates that under typical atmospheric conditions the fraction of the total SOA mass from isoprene OH-initiated oxidation under high-NO conditions is 0.7-0.8 from the LV pathway and 0.2-0.3 from the 2MGA pathway depending on whether HMML ring-opens to react with water, nitrate, or sulfate. Thus, in the atmosphere the LV pathway produces moderately more SOA mass than the 2MGA pathway and consequently deserves equal attention. The conditions chosen here represent average atmospheric conditions around noon as measured during the SOAS field campaign, which occurred in the isoprene-rich Southeastern United States (Sanchez et al., 2018; Feiner et al., 2016; Pajunoja et al., 2016). A more complete assessment using global and regional modeling is needed to more definitively determine the fraction of SOA formed via the LV versus 2MGA pathways as location, time of day, season, ambient aerosol concentration and composition, etc. will all impact the amount of SOA formed from each pathway.

6 Conclusions

SOA from OH-initiated isoprene oxidation under high-NO conditions forms from two major pathways: 1) low-volatility nitrates and dinitrates (LV pathway) and 2) 2-methyl glyceric acid and its oligomers (2MGA pathway). These SOA production pathways respond differently to experimental conditions, so this work examines the SOA yields from these two pathways independently. Results suggest that low-volatility nitrates and dinitrates produce significantly more aerosol than previously thought with the isoprene SOA mass yield from the LV pathway $\simeq 0.15$. Sufficient initial seed aerosol is necessary to reduce the impact of vapor wall losses of low-volatility compounds and accurately measure the entire SOA mass yield. Even though previous studies have assumed that isoprene high-NO SOA largely forms from 2-MGA and its oligomers (Chan et al., 2010; Zhang et al., 2011, 2012), results from this study confirm low-volatility compounds are also important for isoprene SOA formed under high-NO conditions. The fate of isoprene's RO_2 radicals and the environmental conditions will determine which pathways are active in the atmosphere at a certain time and location.

Under dry conditions, substantial amounts of SOA form from HMML reaction with 2MGA to produce oligomers. The AMS results confirm that under humid conditions, these low-volatility oligomers are diminished in favor of higher-volatility monomer formation (and potentially subsequent volatilization of 2-MGA) to reduce the SOA mass. Thus, under atmospherically relevant humid conditions, aerosol formed from the 2MGA pathway is limited to HMML reaction with water or inorganic ions such as nitrate and sulfate. The importance of SOA from the 2MGA pathway will also depend on the NO_2/NO ratio, while SOA formed from the LV pathway will be important under all NO_2/NO ratios. Under typical atmospheric conditions (RH = 70%, T = 298K, NO_2/NO = 6, NO = 0.05 ppb, isoprene = 5 ppb, and OH = 1.5 x 10^6 molec cm^{-3}), we now estimate that the LV pathway produces moderately more SOA mass than the 2MGA pathway due to the high isoprene SOA yield from the LV pathway measured in this work.

Given the high isoprene SOA mass yield from the LV pathway ($\simeq 0.15$) measured here, low-volatility compounds are as important as 2MGA-based compounds for isoprene SOA formed under high-NO conditions. Thus, further studies investigating the formation rates and yields of these low-volatility compounds are needed. Consistent with past work (e.g., Lee et al. (2014)), a number of low-volatility nitrates and dinitrates, which are likely important precursors for SOA formed from the LV pathway, were detected in the gas phase by the CF_3O^- CIMS (Section 5.1). These low-volatility compounds are likely derived from OH-initiated oxidation of the first-generation isoprene hydroxy nitrates. Synthetic pathways toward standards of many of the isoprene hydroxy nitrates exist (Lee et al., 2014; Teng et al., 2017). Now that this study has confirmed that low-volatility products contribute significantly to isoprene SOA, measuring SOA mass yields under varying RO_2 fate using these isoprene hydroxy nitrate standards as the initial precursor instead of isoprene could be particularly valuable for decreasing the uncertainty in isoprene SOA yields. Additionally, an improved mechanistic understanding of isoprene SOA is needed. This would include an improved understanding of gas-phase reactions including measurements of highly functionalized peroxy radical isomerization rate constants and quantification of nitrate and hydroperoxide yields from highly functionalized RO_2 radicals reacting with NO or HO_2, respectively.

There are some limitations for how results from this study should be interpreted. In the atmosphere, the RO_2 lifetime is longer than that in chamber experiments from this study and most past studies measuring SOA yields. Due to limitations in the sensitivity of the DMA and high NO levels needed to control the RO_2 fate, performing SOA yield chamber experiments at conditions that favor a long RO_2 lifetime is difficult. At longer RO_2 lifetimes, the hydroxy nitrate isomer distribution shifts

5   toward a higher percentage of β-isomers over δ-isomers (Teng et al., 2017). Additionally, NO_x emissions are decreasing across many regions of the world due to improvements in emissions controls creating mixed regimes in the ambient atmosphere where a later-generation gas-phase product could form from RO_2 + NO reaction during the 1st-generation and RO_2 + HO_2 during the 2nd-generation. Field measurements confirm the presence of such products. For example, Xiong et al. (2015) discuss the presence of dihydroxy hydroperoxy nitrates detected in the particle phase by Lee et al. (2016) during SOAS, a field campaign

10   that occurred during the summer in the Southeastern United States. Dihydroxy hydroperoxy nitrates likely form when hydroxy nitrates, produced from the RO_2 + NO pathway, react with OH and O_2 to form a peroxy radical that then reacts with HO_2. Additionally, because isoprene SOA from the LV pathway only forms once later-generation products get oxidized, the extent of oxidation is important, but also difficult to compare across different studies.

Comparisons of the DMA and AMS results imply that the collection and/or ionization efficiency on the AMS for SOA

15   formed from the LV pathway is significantly lower than that formed from the 2MGA pathway. This could have important consequences on the interpretation of ambient organic aerosol measured by the AMS. Further work calibrating organic hydroxy nitrates on the AMS is needed to better understand why the organic fraction analysis varied so significantly between the two pathways.

Results from this work combined with past work provide further insight into how isoprene SOA should be parameterized

20   in global and regional atmospheric chemistry models. Under humid conditions, SOA formation from the 2MGA pathway is produced mostly from HMML ring opening reactions to form monomer compounds 2-MGA, 2-MGA-nitrate, and 2-MGA-sulfate, which simplifies the parameterization of SOA from the 2MGA pathway as the organic oligomerization reactions can be ignored. The particle's liquid water and pH will be important to consider, as these metrics shift the equilibrium of 2MGA and its carboxylate and change the hydrolysis rates for the 2-MGA-nitrate and 2-MGA-sulfate. The gas-phase kinetics for

25   MPAN formation and reaction with OH to form HMML have been reasonably well studied (e.g., Orlando et al. (1999, 2002); Nguyen et al. (2015)). HMML formation and generation of SOA in the atmosphere would be best incorporated into models by directly forming SOA through the MPAN + OH reaction. This would best parameterize the effects of temperature and NO_2/NO ratio on MPAN formation and also the influence of OH on HMML formation. This study confirms the need to perform experiments with adequate seed aerosol to limit vapor wall deposition processes when measuring SOA yields from

30   the LV pathway. When regional chemical transport models use SOA yields that account for vapor wall deposition, there are differences in the contribution of isoprene to the total SOA budget and improvements in the agreement between simulated and observed total SOA and diurnal variability (Cappa et al., 2016). Incorporating the isoprene SOA yields from the LV pathway measured in this work into models will further improve the accuracy of simulated isoprene SOA. Moreover, the results from this study along with future experiments studying the formation of low-volatility nitrates and dinitrates on a mechanistic basis

35   will be important for incorporating more explicit SOA formation into global models as has recently been done (e.g., Marais

et al. (2016); Stadtler et al. (2018)), thus replacing previous parameterizations that typically were based on a single chamber condition (e.g.,Henze and Seinfeld (2006); Henze et al. (2008); Heald et al. (2008)).

Data availability. Data used within this work are available upon request. Please email Rebecca Schwantes (rschwant@ucar.edu).

Competing interests. The authors declare that they have no conflict of interest.

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