Role of aldehyde chemistry and NO\textsubscript{x} concentrations in secondary organic aerosol formation

A. W. H. Chan\textsuperscript{1}, M. N. Chan\textsuperscript{2}, J. D. Surratt\textsuperscript{1,\textdagger}, P. S. Chhabra\textsuperscript{1}, C. L. Loza\textsuperscript{1}, J. D. Crounse\textsuperscript{1}, L. D. Yee\textsuperscript{2}, R. C. Flagan\textsuperscript{1,2}, P. O. Wennberg\textsuperscript{2,3}, and J. H. Seinfeld\textsuperscript{1,2}

\textsuperscript{1}Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA
\textsuperscript{2}Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA, USA
\textsuperscript{3}Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA
\textsuperscript{\textdagger}now at: Department of Environmental Sciences and Engineering, The University of North Carolina at Chapel Hill, Chapel Hill, NC, USA

Received: 7 April 2010 – Published in Atmos. Chem. Phys. Discuss.: 19 April 2010
Revised: 13 July 2010 – Accepted: 16 July 2010 – Published: 4 August 2010

Abstract. Aldehydes are an important class of products from atmospheric oxidation of hydrocarbons. Isoprene (2-methyl-1,3-butadiene), the most abundantly emitted atmospheric non-methane hydrocarbon, produces a significant amount of secondary organic aerosol (SOA) via methacrolein (a C\textsubscript{4}-unsaturated aldehyde) under urban high-NO\textsubscript{x} conditions. Previously, we have identified peroxy methacryloyl nitrate (MPAN) as the important intermediate to isoprene and methacrolein SOA in this NO\textsubscript{x} regime. Here we show that as a result of this chemistry, NO\textsubscript{2} enhances SOA formation from methacrolein and two other \(\alpha,\beta\)-unsaturated aldehydes, specifically acrolein and crotonaldehyde, a NO\textsubscript{x} effect on SOA formation previously unrecognized. Oligoesters of dihydroxycarboxylic acids and hydroxynitrooxycarboxylic acids are observed to increase with increasing NO\textsubscript{2}/NO ratio, and previous characterizations are confirmed by both online and offline high-resolution mass spectrometry techniques. Molecular structure also determines the amount of SOA formation, as the SOA mass yields are the highest for aldehydes that are \(\alpha,\beta\)-unsaturated and contain an additional methyl group on the \(\alpha\)-carbon. Aerosol formation from 2-methyl-3-buten-2-ol (MBO\textsubscript{232}) is insignificant, even under high-NO\textsubscript{2} conditions, as PAN (peroxy acyl nitrate, RC(O)(OONO\textsubscript{2}) formation is structurally unfavorable. At atmospherically relevant NO\textsubscript{2}/NO ratios (3–8), the SOA yields from isoprene high-NO\textsubscript{x} photooxidation are 3 times greater than previously measured at lower NO\textsubscript{2}/NO ratios. At sufficiently high NO\textsubscript{2} concentrations, in systems of \(\alpha,\beta\)-unsaturated aldehydes, SOA formation from subsequent oxidation of products from acyl peroxy radicals+NO\textsubscript{2} can exceed that from RO\textsubscript{2}+HO\textsubscript{2} reactions under the same inorganic seed conditions, making RO\textsubscript{2}+NO\textsubscript{2} an important channel for SOA formation.

1 Introduction

Organic matter is ubiquitous in atmospheric aerosols and accounts for a major fraction of particulate matter mass (Zhang et al., 2007a). Most particulate organic matter (POM) is secondary in origin, comprising condensable oxidation products of gas-phase volatile organic compounds (VOCs) (Hallquist et al., 2009). Despite the importance of secondary organic aerosol (SOA), its sources and formation processes are not fully understood. Global modeling studies predict that oxidation of biogenic hydrocarbons dominates the global SOA burden owing to high emissions and efficient SOA production (Chung and Seinfeld, 2002; Kanakidou et al., 2005; Henze and Seinfeld, 2006). This is supported by observations of high levels of modern (hence biogenic) carbon in ambient particulate organic matter, even in urban centers such as Nashville, TN, Tampa, FL and Atlanta, GA (Lewis et al., 2004; Lewis and Stiles, 2006; Weber et al., 2007). However, field observations have repeatedly shown that SOA formation is highly correlated with anthropogenic tracers, such as CO and acetylene (de Gouw et al., 2005, 2008). A considerable body of laboratory chamber studies have investigated the dependence of SOA yields (mass of SOA formed per mass of hydrocarbon reacted) on NO\textsubscript{x} level, which can vary greatly between urban and remote...
areas. For photooxidation and ozonolysis of monoterpenes (Hatakeyama et al., 1991; Ng et al., 2007a; Zhang et al., 2007b; Presto et al., 2005), monocyclic (Song et al., 2005; Hurley et al., 2001; Ng et al., 2007b) and polycyclic aromatic compounds (Chan et al., 2009b), SOA yields are larger under low-NOx conditions; for sesquiterpenes, the reverse is true (Ng et al., 2007a). SOA formation from photooxidation of isoprene exhibits especially complex behavior depending on the NOx level (Kroll et al., 2006). The effect of NOx level on SOA formation has generally been attributed to the relative reaction rates of peroxy radicals (RO2) with NO and HO2 and the difference in volatilities of the products from the respective pathways (Kroll and Seinfeld, 2008). Under high-NOx conditions, RO2+NO dominates and leads to formation of fragmentation products or organic nitrates, which are generally volatile (Presto et al., 2005). On the contrary, the RO2+HO2 pathway, which is competitive only when [NO] ≲ 1 ppb, produces less volatile hydroxyhydroperoxides and peroxy acids, leading to higher SOA yields (Johnson et al., 2005). RO2+NO2 reactions have not been considered as important for SOA formation due to the short lifetime of peroxy nitrates (< 1 s); the notable exceptions are acyl peroxy nitrates (PANs) and perimetric acid (PNA). As a result, the so-called “high-NOx” yields (corresponding to urban NOx levels) have typically been measured under high-NO conditions. For example, the overall SOA mass yield for isoprene photooxidation ranges from 0.01–0.05 under low-NOx conditions (Kroll et al., 2006) to 0.002–0.03 under high-NOx (high-NO) conditions (Kroll et al., 2005a; Dommen et al., 2006). Owing to the large emissions of isoprene (Guenther et al., 2006), isoprene has been estimated to be the single largest source of SOA globally (Henze and Seinfeld, 2006; Carlton et al., 2009).

In a recent study of the mechanism of SOA formation from isoprene, it was shown that aerosol-phase 2-methylglyceric acid (2-MG) and its oligoesters are produced from methacrolein oxidation through the peroxy methacryloyl nitrate (MPAN) channel, as the SOA from MPAN oxidation is similar in composition to that from high-NOx oxidation of isoprene and methacrolein (Surratt et al., 2010). Since MPAN is formed from the reversible reaction of methacryloyl peroxy radicals with NO2, SOA formation can be highly sensitive to the NO2 concentration, an effect of gas-phase aldehyde chemistry that had previously not been recognized. Given the large emissions and the substantial fraction of isoprene reacting under high-NOx conditions (a recent modeling study predicts that globally up to two-thirds of isoprene reacts under high-NOx conditions (Paulot et al., 2009)), it is essential to understand more generally how gas-phase aldehyde chemistry and both NO and NO2 affect SOA yield and composition. Here we present the results of a systematic study of the effect of NO2/NO ratio on SOA formation from methacrolein and two other α, β-unsaturated aldehydes, acrolein and crotonaldehyde. In addition, other structurally similar aldehydes and alcohols are studied to provide insight into the reaction mechanism and to establish the role of PAN-type compounds as important SOA intermediates.

### 2 Experimental section

#### 2.1 Experimental protocols

Experiments were carried out in the Caltech dual 28-m3 Teflon chambers. Details of the facilities have been described previously (Cocker et al., 2001; Keywood et al., 2004). Before each experiment, the chambers were flushed with dried purified air for > 24 h (~4–6 air changes), until the particle number concentration < 100 cm−3 and the volume concentration < 0.1 μm cm−3. In all experiments, inorganic seed particles were injected by atomization of a 0.015 M aqueous ammonium sulfate solution. The parent hydrocarbon was then introduced into the chamber by injecting a known volume of the liquid hydrocarbon into a glass bulb, and the vapor was carried into the chamber with 5 L min−1 of purified air.

### Table 1. Hydrocarbons studied.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>OH rate constant, cm3 molec−1 s−1</th>
</tr>
</thead>
<tbody>
<tr>
<td>isoprene</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>1 × 10−10</td>
</tr>
<tr>
<td>methacrolein</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>2.9 × 10−11</td>
</tr>
<tr>
<td>acrolein</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>2.0 × 10−11</td>
</tr>
<tr>
<td>crotonaldehyde (cis and trans)</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>3.5 × 10−11</td>
</tr>
<tr>
<td>2-methyl-2-butenal (2M2B)</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>unknown</td>
</tr>
<tr>
<td>3-methyl-2-butenal (3M2B)</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>6.2 × 10−11</td>
</tr>
<tr>
<td>2-pentenal</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>unknown</td>
</tr>
<tr>
<td>4-pentenal</td>
<td><img src="image8.png" alt="Structure" /></td>
<td>unknown</td>
</tr>
<tr>
<td>2-methyl-3-buten-1-ol (MBO231)</td>
<td><img src="image9.png" alt="Structure" /></td>
<td>unknown</td>
</tr>
<tr>
<td>2-methyl-3-buten-2-ol (MBO232)</td>
<td><img src="image10.png" alt="Structure" /></td>
<td>3.9 × 10−11</td>
</tr>
</tbody>
</table>

\(^{a}\) Atkinson and Arey (2003); \(^{b}\) Magneron et al. (2002); \(^{c}\) Tuazon et al. (2005); \(^{d}\) Fantechi et al. (1998).
To study the sensitivity of aerosol yields and composition to relative concentrations of NO and NO₂, different OH precursors were used. Use of nitrous acid (HONO) and methyl nitrite (CH₃ONO) as OH precursors allows for SOA yield measurements over a wide range of NO₂/NO ratios. For “high NO” experiments, OH radicals were generated from photolysis of HONO. We refer to these experiments as “high NO” experiments because NO concentrations are sufficiently high that RO₂+NO+NO₂, most notably for acyl peroxy radicals, even though NO₂ concentrations are high (> 100 ppb). HONO was prepared by adding 15 mL of 1 wt% aqueous NaNO₂ dropwise into 30 mL of 10 wt% sulfuric acid in a glass bulb. A stream of dry air was then passed through the bulb, sending HONO into the chamber. During this process, NO and NO₂ formed as side products and were also introduced into the chamber. To achieve high NO₂ concentrations, CH₃ONO was employed as the OH precursor. These experiments are referred to as “high NO₂” experiments, as NO₂ concentrations are sufficiently higher than NO concentrations such that PAN formation is favored over reaction of acyl peroxy radicals with NO. CH₃ONO was vaporized into an evacuated 500 mL glass bulb and introduced into the chamber with an air stream of 5 L min⁻¹. The mixing ratio of CH₃ONO injected was estimated to be 200–400 ppb, based on the vapor pressure in the glass bulb measured using a capacitance manometer (MKS). In all experiments, varying amounts of NO and NO₂ were also added from gas cylinders (Scott Marrin) both to ensure high-NO and high-NO₂ conditions and to vary the NO₂/NO ratio. For the Cs unsaturated aldehydes and 2-methyl-3-buten-2-ol (MBO232), only high NO₂ experiments were conducted. Abbreviations, structures, and OH rate constants (Atkinson and Arey, 2003; Magneron et al.,...
2002; Tuazon et al., 2005; Fantechi et al., 1998) of the compounds studied are listed in Table 1, and initial conditions of the experiments are summarized in Table 2.

2.2 Materials

The parent hydrocarbons studied and their stated purities are as follows: isoprene (Aldrich, 99%), methacrolein (Aldrich, 95%), acrolein (Fluka, ≥99%), crotonaldehyde (Aldrich, 98%, predominantly trans), trans-2-pentenal (Alfa Aesar, 96%), 4-pentenal (Alfa Aesar, 97%), trans-2-methyl-2-butenal (Aldrich, 96+%), 3-methyl-2-butenal (Sigma-Aldrich, 97%), 2-methyl-3-buten-1-ol (Aldrich, 98%), and 2-methyl-3-buten-2-ol (Aldrich, 98%). CH$_3$ONO was synthesized following the method described by Taylor et al. (1980). 9 g of NaNO$_2$ was added to a mixture of 50 mL of methanol and 25 mL of water. 25 mL of 50 wt% sulfuric acid solution was added dropwise into the solution. The CH$_3$ONO vapor was carried in a small stream of ultra high purity N$_2$ through a concentrated NaOH solution and an anhydrous CaSO$_4$ trap to remove any sulfuric acid and water, respectively. The CH$_3$ONO was then collected in a cold trap immersed in a dry ice/acetone bath (−80°C) and stored under liquid N$_2$ temperature.

2.3 Measurements

Aerosol size distribution, number and volume concentrations were measured with a differential mobility analyzer (DMA, TSI, 3081) coupled with a condensation nuclei counter (TSI, CNC-3760). The volume concentration was corrected for particle wall loss by applying size-dependent first-order loss coefficients, obtained in a separate seed-only experiment, using methods described in Keywood et al. (2004). Aerosol volume concentrations are converted to mass concentrations assuming a density of 1.4 g cm$^{-3}$ (Kroll et al., 2005a). Concentrations of isoprene, methacrolein, methyl vinyl ketone (MVK), acrolein, and crotonaldehyde were monitored using a gas chromatograph with flame ionization detector (GC/FID, Agilent 6890N), equipped with an HP-LOT Q column (15 m × 0.53 mm ID × 30 µm thickness, J&W Scientific). For 2M2B, 3M2B, 2-pentenal, 4-pentenal, MBO231 and MBO232 experiments, the GC/FID was equipped with an HP-5 column (15 m × 0.53 mm ID × 1.5 µm thickness, Hewlett Packard). A commercial chemiluminescence NO/NO$_x$ analyzer (Horiba, APNA 360) was used to monitor NO and NO$_x$. Both HONO and CH$_3$ONO produce interference on the NO$_2$ signal from the NO$_x$ monitor. Concentrations of NO and NO$_2$ are estimated by photochemical modeling (see Appendix). Temperature, RH, and ozone (O$_3$) were continuously monitored.

A custom-modified Varian 1200 triple-quadrupole chemical ionization mass spectrometer (CIMS) was used to continuously monitor gas-phase species over each experiment. Details of the operation of the CIMS can be found in a number of previous reports (Crounse et al., 2006; Paulot et al., 2009). The CIMS was operated in negative ion mode, in which CF$_3$O$^-$ is used as the reagent ion, and in positive ion mode of proton transfer mass spectrometry (PTR-MS). In the negative mode, the reagent ion CF$_3$O$^-$ clusters with the analyte, R, forming ions at mass-to-charge ratios (m/z) MW+85 (R-CF$_3$O$^-$), or, with more acidic species, at m/z MW+19 (HF·R$^-_H$). In the positive mode, positively charged water clusters, n(H$_2$O)H$^+$, react via proton transfer with the analyte, R, to form the positively charged ion, R·n(H$_2$O)·H$^+$. In some cases, tandem mass spectrometry (MS/MS) was used to separate isobaric compounds. In brief, the parent ions selected in the first quadrupole undergo collision-induced dissociation (CID) in the second quadrupole. The parent ions of isobaric compounds can exhibit different CID patterns and yield different daughter ions. Hence, with the third quadrupole acting as a second mass filter for the daughter ions, this allows for separate measurement of these isobaric compounds (see Supplementary Material). The significance of this separation will be discussed in a later section.

Real-time particle mass spectra were collected continuously by an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (DeCarlo et al., 2006; Canagaratna et al., 2007), hereby referred to as the AMS. The AMS switched once every minute between the high resolution “W-mode” and the lower resolution, higher sensitivity “V-mode”. The “V-mode” data were analyzed using a fragmentation table to separate sulfate, ammonium, and organic spectra and to time-trace specific mass-to-charge ratios. “W-mode” data were analyzed using a separate high-resolution spectra toolbox known as PIKA to determine the chemical formulas contributing to distinct m/z ratios (DeCarlo et al., 2006).

Aerosol samples were also collected on Teflon filters and analyzed by offline mass spectrometry. Detailed sample collection and extraction protocol are described in Suratt et al. (2008). Filter extraction using 5 mL of high-purity methanol (i.e., LC-MS Chromasolv Grade) was performed by 45 min of sonication. The filter extracts were then analyzed by a Waters ACQUITY ultra performance liquid chromatography (UPLC) system, coupled with a Waters LCT Premier TOF mass spectrometer equipped with an ESI source operated in the negative (−) mode, allowing for accurate mass measurements (i.e., determination of molecular formulas) to be obtained for each observed ion. Operation conditions and parameters for the UPLC(−)ESI-TOFMS measurement have been described by Suratt et al. (2008).

3 SOA formation

The importance of isoprene as an SOA source was suggested by identification of 2-methyltetrols and 2-methylglyceric acid (2-MG) in both ambient POM (Claeys et al., 2004; Edney et al., 2005; Ion et al., 2005; Kourtchev et al., 2005)
and laboratory aerosol generated from isoprene photooxidation (Edney et al., 2005; Surratt et al., 2006; Szmigielski et al., 2007; Kleindienst et al., 2009). Methacrolein, a first-generation oxidation product of isoprene, has been shown to produce SOA upon further oxidation (Kroll et al., 2006; Surratt et al., 2006) and has been identified as the precursor to aerosol-phase 2-MG and its corresponding oligoester products (Surratt et al., 2006; Szmigielski et al., 2007). A recent study shows aerosol formation from methacrolein oxidation proceeds via subsequent oxidation of MPAN (Surratt et al., 2010). Here we focus our attention on photooxidation of methacrolein under high-NOx conditions to establish the effect of relative NO and NO2 concentrations on SOA yields and composition. Acrolein, crotonaldehyde, 2-methyl-2-butenal (2M2B), 3-methyl-2-butenal (3M2B), 2-pentenal, and 4-pentenal differ from methacrolein by one or two methyl groups, and studying their SOA formation provides insight into the mechanism of formation of low-volatility products. Furthermore, aerosol formation from photooxidation of 2-methyl-3-buten-2-ol (MBO232), an atmospherically important unsaturated alcohol (Harley et al., 1998), and structurally similar 2-methyl-3-buten-1-ol (MBO231) is studied to investigate the role of PAN-like compounds in SOA formation.

Fig. 1. Concentration profiles of gas-phase species during a typical methacrolein/high-NOx experiment (16/07/09). In this experiment, additional NO2 was injected prior to irradiation. Concentrations of NO and NO2 shown here are calculated from a photochemical model (see Appendix).

Fig. 2. Concentration profiles of gas-phase species during a typical methacrolein/high-NOx experiment (15/09/09). Additional NO (100 ppb) and NO2 (200 ppb) were injected prior to irradiation. Concentrations of NO and NO2 shown here are calculated from a photochemical model (see Appendix). As a result of the higher OH concentrations from CH3ONO than from HONO, more methacrolein was reacted and the concentrations of methacrolein nitrate relative to those of hydroxyacetone were lower than those in high-NOx experiments, owing to a more rapid consumption by OH.

3.1 Methacrolein

Figures 1 and 2 show typical concentration profiles of various gas-phase species in methacrolein/HONO (high NO) and methacrolein/CH3ONO (high NO2) photooxidation experiments, respectively. In all experiments, NO concentrations remain above 50 ppb during SOA growth, at which conditions RO2+HO2 or RO2+RO2 reactions are not competitive with those of RO2 with NO and NO2. Products of these reactions, such as methacrylic acid and methacrylic peracid, are not observed by CIMS. Instead, hydroxyacetone and methacrolein nitrate, products from RO2+NO reactions, are observed. During these experiments, RO2 and HO2 produced from methacrolein oxidation react with NO to produce NO2, which photolyzes to form ozone. As a result, ozone concentrations reach a maximum of up to 126 ppb. Despite relatively high levels of ozone, reaction rates of methacrolein and peroxy methacryloyl nitrate (MPAN) with ozone are still slow compared to those with OH, as efficient photolysis of HONO or CH3ONO leads to OH concentrations \( >3 \times 10^6 \) molec cm\(^{-3}\), estimated from the methacrolein decay. For high-NOx experiments, the initial decay of methacrolein slows down after 5 h, consistent with the HONO signal (CIMS (−) m/z 66) approaching zero. In
these experiments, more than 70% of the initial methacrolein is consumed before SOA growth ceases. In the high-NO\textsubscript{2} experiments, more than 90% of the initial methacrolein is consumed before SOA growth ceases.

Mass concentrations of SOA versus the concentration of methacrolein reacted, so-called “time-dependent growth curves”, are shown in Fig. 3. As reported previously, under high-NO\textsubscript{2} conditions (with HONO as the OH precursor), when additional NO is added before irradiation, aerosol formation (mass yield of 0.019) from photooxidation of 277 ppb of methacrolein is suppressed (Surratt et al., 2010). In contrast, SOA yields are higher when no additional NO is added (0.030 from 257 ppb methacrolein), and the highest when 350 ppb of additional NO\textsubscript{2} (instead of NO) is injected (0.052 from 285 ppb methacrolein) (Surratt et al., 2010). In all high-NO\textsubscript{2} experiments, the NO\textsubscript{2}/NO ratio remains low (<2), owing to presence of NO impurity in HONO synthesis and production of NO during HONO photolysis. The observed dependence of SOA yields on NO\textsubscript{2}/NO ratio is not a result of condensation of nitric acid from OH+NO\textsubscript{2}, as the experiments were conducted under dry (<10% RH) conditions. In confirmation of this conclusion, addition of gas-phase nitric acid in one experiment (31/07/09) did not lead to additional aerosol growth.

In the high-NO\textsubscript{2} experiments, CH\textsubscript{3}ONO was used as the OH precursor and lower NO concentrations are expected, owing to relatively pure CH\textsubscript{3}ONO synthesis and no net production of NO from CH\textsubscript{3}ONO photolysis (see Appendix). Higher SOA yields are observed at higher NO\textsubscript{2}/NO ratios; correspondingly, much lower concentrations of methacrolein are required to produce the same amount of SOA (see Fig. 3). Also, owing to the high concentrations of CH\textsubscript{3}ONO injected, more than 90% of the initial methacrolein is consumed before CH\textsubscript{3}ONO is depleted. For example, when 255 ppb of initial methacrolein is oxidized using CH\textsubscript{3}ONO as OH precursor (12/09/09), the SOA yields are more than 5 times larger than when a similar amount of methacrolein is reacted using HONO as OH precursor. This rules out a larger extent of reaction as the cause of the high observed SOA yields. HO\textsubscript{2} concentrations, quantified from the pernitric acid signal on the CIMS (m/z 98) and modelled NO\textsubscript{2} concentrations, do not exceed 60 ppt in all experiments. At organic loadings of 10–20 µg m\textsuperscript{-3}, SOA mass yields of methacrolein/high-NO\textsubscript{2} and methacrolein/high-NO\textsubscript{2} photooxidation are roughly 0.19 and 0.03, respectively.

### 3.2 Acrolein and crotonaldehyde

Figures 4 and 5 show SOA growth curves for acrolein and crotonaldehyde photooxidation, respectively. The SOA yields of these compounds are lower than those of methacrolein, with maximum yields of roughly 0.08 at the highest loadings (>100 µg m\textsuperscript{-3}). These compounds exhibit a similar dependence of SOA growth on NO\textsubscript{2}/NO ratio to that of methacrolein: SOA formation is suppressed with addition...
of NO, and enhanced with addition of NO$_2$. SOA yields are highest in the high-NO$_2$ experiments. Oxidation products analogous to those found in the methacrolein system, such as glycolaldehyde and hydroxynitrates, are observed in the gas phase at similar yields.

### 3.3 Other aldehydes and methylbutenols (MBO)

The growth curves for 2M2B and 3M2B photooxidation are shown in Fig. 6. Significant SOA growth is observed for 2M2B (277 ppb) photooxidation under high-NO$_2$ conditions, with mass yields exceeding 0.35. Similar to methacrolein, 2M2B contains a methyl group in the $\alpha$-position. Interestingly, photooxidation of 3M2B under similar NO$_x$ conditions and hydrocarbon loadings (207 ppb), produces less SOA (mass yield $<$0.01). 3M2B is a structural isomer of 2M2B with the methyl group in the $\beta$-position. The trend in SOA yields between 2M2B and 3M2B is consistent with that observed for methacrolein and crotonaldehyde, their C$_4$ analogs. The SOA yields from 2-pentenal, a straight-chain $\alpha,\beta$-unsaturated aldehyde, are higher than those from 4-pentenal, in which the olefinic bond is not adjacent to the aldehyde group (see Fig. 6).

We also carried out MBO232 and MBO231 photooxidation under high-NO$_2$ conditions. Both MBO’s are structurally similar to isoprene and, upon high-NO$_x$ photooxidation, produce an aldehyde (i.e., hydroxy-methylpropanal, HMPR) analogous to methacrolein. Previous results have shown that aerosol formation from MBO232 photooxidation under high-NO conditions is negligible, with mass yields of $<$0.001 (Carrasco et al., 2007; Chan et al., 2009a). Here we do not observe SOA growth even at high NO$_2$/NO ratios. Gas-phase compounds such as glycolaldehyde and HMPR are observed at molar yields of 0.6 and 0.3, respectively, consistent with those published in previous product studies (Carrasco et al., 2007; Chan et al., 2009a). On the other hand, MBO231, a structural isomer with the hydroxyl group in the 1-position, produces a significant amount of SOA (mass yields of 0.008–0.042) upon oxidation under high-NO$_2$ conditions, comparable to that of isoprene under similar conditions (see Fig. 6). Under high-NO conditions, no SOA is formed. The dependence of SOA yields from MBO231 on NO$_2$/NO ratio is therefore consistent with that observed in unsaturated aldehydes.

### 4 Chemical composition of SOA

#### 4.1 Offline chemical analysis

In previous work, offline chemical analysis of SOA from photooxidation of isoprene, methacrolein, and MPAN by UPLC/(−)ESI-TOFMS has been presented (Surratt et al., 2010). The same compounds are detected in the methacrolein experiments in this work under both high-NO and high-NO$_2$ conditions, and are summarized in Table 3. Four series of oligoester products from 2-methylglyceric acid (2-MG) and C$_4$-hydroxynitrooxycarboxylic acid are identified in the SOA. The compounds in the 2-MG oligoester series differ by 102 Da, corresponding to esterification of a 2-MG monomer unit (Surratt et al., 2006). The accurate masses of the identified ions confirm their elemental compositions, and their structures are proposed based on detailed characterization by tandem MS and GC/MS analyses with prior trimethylsilylation (Szmielinski et al., 2007).

All ions detected by UPLC/(−)ESI-TOFMS in acrolein and crotonaldehyde SOA are listed in the Supplementary Material. It is noteworthy that the identities of detected aerosol-phase products are the same regardless of the OH precursor used. The ions detected in acrolein SOA differ from those found in methacrolein SOA by one methyl group for every monomer unit, and those detected in crotonaldehyde SOA have the same exact mass and elemental composition as those in methacrolein SOA. Detected [M-H]$^-$ ions in SOA from 2M2B and 2-pentenal can also be found in the Supplementary Material. No filter sample was collected for MBO232 owing to low aerosol loading. Aerosol-phase products of methacrolein, acrolein, crotonaldehyde, 2M2B and 2-pentenal are structural analogs of each other, and the structures for the deprotonated ions are proposed based on those characterized previously in isoprene and methacrolein SOA (Surratt et al., 2006; Szmielinski et al., 2007). Interestingly, SOA produced from 4-pentenal is composed of entirely different products, and hence no structures are proposed at this stage.

![Fig. 5. Time-dependent SOA growth curves for crotonaldehyde photooxidation. Similar to methacrolein photooxidation, NO$_2$/NO ratios are computed from photochemical modeling (see Appendix).](https://example.com/figure5.png)
This oligoester series involves the esterification with formic acid.

Oligoesters Suggested by AMS high-resolution W mode

This oligoester series involves the esterification with acetic acid.

Detected in high-NO$_x$ experiments only. $^b$ This oligoester series involves the esterification with formic acid. $^c$ $C_{6}H_{11}O_{3}$ also detected. $^d$ This oligoester series involves the esterification with acetic acid.

Table 3. SOA constituents detected by UPLC/(−)ESI-TOFMS and AMS in methacrolein experiments. All ions were detected in both high-NO and high-NO$_x$ experiments, unless otherwise noted.

| Oligoester Series | UPLC/ESI-TOFMS Measured Mass | TOFMS Suggested Ion Formula | Error (mDa) | # of 2-MG Monomer Units (n) | Structure | [M – OH]$^d$ | AMS Suggested Ion Formula $^e$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2M2B vs 3M2B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>221</td>
<td>221.0661 $^{+}$</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{7}^{-}$</td>
<td>1.6</td>
<td>0.3</td>
<td>2</td>
<td>103</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{7}^{-}$</td>
</tr>
<tr>
<td>323</td>
<td>323.0979</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{6}^{-}$</td>
<td>0.1</td>
<td>22.6</td>
<td>3</td>
<td>205</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{6}^{-}$</td>
</tr>
<tr>
<td>425</td>
<td>425.1290</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{13}^{-}$</td>
<td>-0.5</td>
<td>48.0</td>
<td>4</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>527</td>
<td>527.1609</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{15}^{-}$</td>
<td>-0.3</td>
<td>3.7</td>
<td>5</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>266</td>
<td>266.0507</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$NO$_{5}^{-}$</td>
<td>-0.5</td>
<td>32.8</td>
<td>1</td>
<td>115</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$NO$_{5}^{-}$</td>
</tr>
<tr>
<td>368</td>
<td>368.0831</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$NO$_{13}^{-}$</td>
<td>0.2</td>
<td>11.4</td>
<td>2</td>
<td>232</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$NO$_{13}^{-}$</td>
</tr>
<tr>
<td>470</td>
<td>470.1149</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$NO$_{15}^{-}$</td>
<td>0.3</td>
<td>56.3</td>
<td>3</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>572</td>
<td>572.1510</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$NO$_{18}^{-}$</td>
<td>4.7</td>
<td>1.0</td>
<td>4</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>249</td>
<td>249.0616</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{7}^{-}$</td>
<td>0.6</td>
<td>2.7</td>
<td>2</td>
<td>131</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{7}^{-}$</td>
</tr>
<tr>
<td>351</td>
<td>351.0912</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{11}^{-}$</td>
<td>-1.5</td>
<td>46.9</td>
<td>3</td>
<td>233</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{11}^{-}$</td>
</tr>
<tr>
<td>453</td>
<td>453.1248</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{14}^{-}$</td>
<td>0.4</td>
<td>63.7</td>
<td>4</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>555</td>
<td>555.1610</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{17}^{-}$</td>
<td>4.9</td>
<td>3.0</td>
<td>5</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>263</td>
<td>263.0740</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{7}^{-}$</td>
<td>-2.7</td>
<td>4.7</td>
<td>2</td>
<td>149</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{7}^{-}$</td>
</tr>
<tr>
<td>365</td>
<td>365.1061</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{11}^{-}$</td>
<td>-2.3</td>
<td>54.9</td>
<td>3</td>
<td>247</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{11}^{-}$</td>
</tr>
<tr>
<td>467</td>
<td>467.1434</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{14}^{-}$</td>
<td>3.3</td>
<td>23.7</td>
<td>4</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>569</td>
<td>569.1711</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$O$_{17}^{-}$</td>
<td>-0.7</td>
<td>20.0</td>
<td>5</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>311</td>
<td>311.0333</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$N$<em>{3}$O$</em>{7}^{-}$</td>
<td>-3.0</td>
<td>58.9</td>
<td>0</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>413</td>
<td>413.0664</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$N$<em>{3}$O$</em>{14}^{-}$</td>
<td>-1.6</td>
<td>71.9</td>
<td>1</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>515</td>
<td>515.1039</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$N$<em>{3}$O$</em>{17}^{-}$</td>
<td>4.2</td>
<td>3.6</td>
<td>2</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
<tr>
<td>Other Oligoesters</td>
<td>458 $^{+}$</td>
<td>$^{+}$C$<em>{6}$H$</em>{10}$N$<em>{3}$O$</em>{15}^{-}$</td>
<td>2.7</td>
<td>3.3</td>
<td>n/a</td>
<td>$^{+}$</td>
<td>$^{+}$</td>
</tr>
</tbody>
</table>

$^a$ Observed by UPLC/(−)ESI-TOFMS. $^b$ Observed by AMS V mode. $^c$ Suggested by AMS high-resolution W mode.

$^d$ Not observed by AMS, most likely due to fragmentation of nitrate group, or below detection limit. $^e$ Detected in high-NO$_x$ experiments only. $^f$ This oligoester series involves the esterification with formic acid. $^g$ $C_{6}H_{11}O_{3}$ also detected. $^h$ This oligoester series involves the esterification with acetic acid.
time. The significance of this result will be discussed in a later section.

While the identities of the detected aerosol-phase compounds are independent of the OH precursor, the relative amounts vary greatly and exhibit a strong correlation with NO$_2$/NO ratio. Figure 7 shows the extracted ion signals for the oligoester products detected by UPLC/(-)ESI-TOFMS in the methacrolein high-NO experiments. The amount of identified aerosol-phase components shows the same dependence on NO$_2$/NO ratio as the total amount of SOA growth. In general, the abundance of each compound decreases when NO is added and increases when NO$_2$ is added.

4.2 Online AMS measurements

AMS V-mode organic spectra of SOA from high-NO$_2$ photolysis of isoprene and methacrolein are shown in Fig. 8. The mass fragments above m/z 200 likely contain more than 5 carbon atoms, and display a repetitive pattern, indicative of oligomer formation. In addition, 102 Da differences between major peaks were also observed, consistent with previous AMS and LC/MS results (Surratt et al., 2006). Elemental formulas based on accurate mass measurements are determined from high-resolution W-mode data for a number of the major ions observed, as shown in Fig. 9. The ions suggested by these elemental formulas differ from many of the ions detected by UPLC/(-)ESI-TOFMS by an O$^{2-}$ group. The observed AMS ions are consistent with loss of a hydroxyl group from the molecular ion (i.e. α-cleavage of a hydroxyl group under electron impact ionization). In UPLC/(-)ESI-TOFMS, these compounds are detected in their deprotonated form (loss of H$^+$). As shown in Table 3, the oligoesters are detected by both online and offline high-resolution mass spectrometry, and the agreement between the two techniques confirms that the oligoesters identified are indeed present in the SOA, and that the observations by offline aerosol analysis are not the result of filter sampling artifacts. AMS organic spectra of SOA from oxidation of acrolein and crotonaldehyde show similar features, and accurate mass measurements of a number of the major peaks correspond to the products analogous to those found in the methacrolein system (see Supplementary Material).

5 Effect of NO$_2$/NO ratios on SOA yield and composition

As mentioned in the Introduction, studies on the effect of NO$_x$ concentrations on SOA formation have shown that for most systems, SOA yields are inversely correlated with NO$_x$ concentrations (Hatakeyama et al., 1991; Hurley et al., 2001; Presto et al., 2005; Song et al., 2005; Zhang et al., 2007b; Ng et al., 2007a,b; Chan et al., 2009b). The “NO$_x$ effect” on SOA formation has been described as a competition of the chemistries for RO$_2$ between HO$_2$ (the high-yield pathway) and NO (the low-yield pathway), such that the ratio of HO$_2$ to NO is critical in determining the branching ratio between these two pathways (Kroll and Seinfeld, 2008; Henze et al., 2008). Aerosol yields from isoprene photolysis are also sensitive to HO$_2$/NO ratios, with higher yields measured under HO$_2$-dominated conditions (using H$_2$O$_2$ as OH source) (Kroll et al., 2006) than under NO-dominated conditions (using HONO or NO$_x$ cycling as OH source) (Kroll et al., 2005b; Pandis et al., 1991; Dommen et al., 2006). Addition of NO also suppresses SOA growth in low-NO$_x$ experiments, indicating that the RO$_2$+NO pathway yields
more volatile products, and hence less SOA (Kroll et al., 2006). However, under the experimental conditions in the present study, RO₂+HO₂ reactions are not expected to be significant. Rather, the dependence of SOA yield on the NO₂/NO ratio is consistent with analysis of SOA composition, which is consistent with MPAN, a product of the acyl peroxy radical+NO₂ reaction, being the intermediate in SOA formation. Although the absolute concentrations of NO₂ in these experiments are a factor of 10 higher than ambient levels, we expect the OH-adduct of alkenes and aldehydes studied here to react predominantly with O₂ to form alkyl peroxy or acyl peroxy radicals. Compounds with nitro functional groups (R-NO₂), such as those found in the aromatic systems (Calvert et al., 2002), were not detected in these experiments.

Based on the proposed mechanism shown in Fig. 10, the acyl peroxy radical formed from abstraction of the aldehydic hydrogen atom of an unsaturated aldehyde react with either NO or NO₂. The reversible reaction of RO₂ with NO₂ forms a PAN-type compound (MPAN for methacrolein), which, in the absence of competing reactions, reaches thermal equilibrium. The irreversible reaction of RO₂ with NO leads to fragmentation into CO₂ and a vinyl radical, which subsequently forms volatile gas-phase products, such as formaldehyde and CO (Orlando et al., 1999). At [OH]= 2 × 10⁶ molec cm⁻³, the reaction of MPAN with OH has a rate comparable to that of thermal decomposition (Orlando et al., 2002), and leads to formation of aerosol products. Hence, the SOA formation potential for this system depends critically on the NO₂/NO ratio. High NO₂/NO ratios shift the thermal equilibrium towards the unsaturated PAN, and SOA formation increases as the fraction of PAN reacting with OH radicals increases. At low NO₂/NO ratios, acyl peroxy radicals react predominantly with NO, leading to relatively volatile products.

Previous measurements of isoprene SOA yields under high-NOₓ conditions have been carried out using photoysis of HONO (Kroll et al., 2005a) or the recycling of HOₓ and NOₓ to generate OH (so-called classical photooxidation) (Pandis et al., 1991; Dommen et al., 2006). Low SOA yields were observed as NO concentrations remained high during the experiments. In fact, SOA growth occurred only after NO concentrations decreased to less than 10 ppb (Kroll et al., 2005a; Dommen et al., 2006). It was proposed that after NO has been consumed, aerosol formation commences as the RO₂+HO₂ pathway becomes competitive. However, such a mechanism is inconsistent with the major differences in composition observed between high- and low-NOₓ SOA products. High-NOₓ SOA from isoprene photooxidation is dominated by esterification products of C₄-carboxylic acids, whereas under low-NOₓ conditions, SOA is dominated by peroxides and C₅-tetrols (Surrett et al., 2006). It is more likely that the decrease in NO concentration (and increase in NO₂ concentration) leads to a transition from an RO₂+NO dominated regime to an RO₂+NO₂ dominated regime, resulting in significant SOA formation via the MPAN route.
At NO\textsubscript{2}/NO ratios (between 3 and 8) higher than in previous studies (and more relevant to urban conditions), SOA yields from isoprene are approximately 3 times larger than previously measured. The yields even exceed those under low-NO\textsubscript{x} conditions at the same organic aerosol loadings, as shown in Fig. 11. This is, in fact, consistent with observations from Kroll et al. (2006) that at very low NO\textsubscript{x} concentrations, addition of NO actually increases SOA yield. It is likely that under very low NO concentrations, the NO\textsubscript{2}/NO ratio increases rapidly, as NO is quickly converted to NO\textsubscript{2}. SOA yields are therefore higher than those in the absence of NO, as RO\textsubscript{2} (from methacrolein)+NO\textsubscript{2} forms SOA more efficiently than RO\textsubscript{2} (from isoprene)+HO\textsubscript{2}. However, further increasing NO decreases the NO\textsubscript{2}/NO ratio. RO\textsubscript{2} (from methacrolein)+NO becomes more dominant, forms volatile products and leads to a decrease in SOA yield. It must be noted that the effect of RO\textsubscript{2} radical chemistry on SOA formation is complex and can be unique to different systems (Kroll and Seinfeld, 2008). Also, the acidity of the inorganic seed can increase SOA yields significantly: Suratt et al. (2010) shows that SOA yields from isoprene low-NO\textsubscript{x} photooxidation can be as high as 0.29. Detailed knowledge of the chemical mechanism is required to predict the effect of NO\textsubscript{x} conditions on SOA production.

6 Role of PAN in SOA formation

6.1 Unsaturated aldehydes

One can infer from the shapes of the growth curves the relative timescales of the reaction steps of SOA formation. In all high-NO\textsubscript{2} experiments, a greater extent of reaction is achieved than in high-NO experiments, and SOA formation continues after the parent hydrocarbon is completely consumed; this behavior is characterized by a vertical portion (“hook”) at the end of the SOA growth curve. The presence of this vertical portion indicates that SOA formation results from further reaction of first-generation products, which is the rate-limiting step in the mechanism (see Figs. 3–5). This observation is consistent with our previous results showing that first-generation products of methacrolein, such as hydroxyacetone and MPAN, are themselves still volatile (Suratt et al., 2010). SOA is instead formed from the further OH reaction of MPAN, which has a comparable rate coefficient to that of methacrolein (Orlando et al., 2002).

Formation of dihydroxycarboxylic acids (e.g. 2-MG), hydroxynitrooxycarboxylic acids, and corresponding oligoesters appears to be important SOA formation pathways for the five \(\alpha,\beta\)-unsaturated aldehydes studied here (methacrolein, acrolein, crotonaldehyde, 2M2B, 2-pentenal). All of the SOA constituents detected by offline UPLC/(–)ESI-TOFMS in these systems are structural...
Fig. 10. Proposed mechanism to form aerosol-phase products from \( \alpha, \beta \)-unsaturated aldehydes. The pathways highlighted in red are favored under high \( \text{NO}_2/\text{NO} \) ratios and lead to aerosol formation. The pathways highlighted in blue are favored under low \( \text{NO}_2/\text{NO} \) ratios and lead to fragmentation into volatile products. Aerosol formation from OH-reaction of unsaturated PANs can proceed via 3 possible routes (routes 1–3), and detailed investigation of each route is discussed in the main text.

- Route 1: Formation of hydroxynitrate-PAN, the supposed SOA intermediate in all these systems, does not correlate with the amount of aerosol formed. Substitution of the \( \alpha \)-carbon atom by methyl groups (from crotonaldehyde to methacrolein, or from 3M2B to 2M2B) leads to an increase in the amount of SOA formed by more than a factor of 4, but no increase in gas-phase signal of the hydroxynitrate-PAN is observed (see Fig. 12), implying that it is unlikely the SOA-forming channel.

- Route 2: Hydroxyl groups (Sato, 2008) to form 2-MG and high-MW oligoesters (Route 3 in Fig. 10). However, gas-phase abundances of \( \text{C}_4 \) (for methacrolein and crotonaldehyde) or \( \text{C}_5 \) (for 2M2B, 3M2B and 2-pentenal) hydroxy nitrate-PAN, the supposed SOA intermediate in all these systems, do not correlate with the amount of aerosol formed. Substitution of the \( \alpha \)-carbon atom by methyl groups (from crotonaldehyde to methacrolein, or from 3M2B to 2M2B) leads to an increase in the amount of SOA formed by more than a factor of 4, but no increase in gas-phase signal of the hydroxy nitrate-PAN is observed (see Fig. 12), implying that it is unlikely the SOA-forming channel.

- Route 3: In the experiment with 21% \( \text{O}_2 \) (17/12/09), no increase in aerosol formation after addition of \( \text{O}_2 \) to the double bond in MPAN the OH-adduct undergoes intramolecular rearrangement before addition of \( \text{O}_2 \), leading to formation of 2-MG and oligoesters (Route 1 in Fig. 10). Such isomerization can be competitive with \( \text{O}_2 \) addition, as the O-O bond in the peroxy nitrate moiety is weak. In one experiment (17/12/09), the chambers were flushed with nitrogen to lower the oxygen content to 2%, thereby slowing down addition of \( \text{O}_2 \) by a factor of 10. Compared to another experiment with 21% \( \text{O}_2 \) (16/12/09), no increase in aerosol formation is observed, suggesting that SOA formation likely involves \( \text{O}_2 \) addition to the MPAN-OH adduct, though it is also possible that the intramolecular rearrangement reaction...
SOA formation is correlated with \( \text{SOA} \) mass yield. This intermediate is likely short-lived, even though 3M2B has an equal or higher molecular weight. This suggests that an interaction responsible for producing low-volatility species occurs between the peroxy nitrate functional group and the \( \alpha \)-carbon (likely a radical species) that our experiments are not able to precisely reveal. We hypothesize that the peroxy radical undergoes self cyclization to form a highly reactive dioxoketone intermediate, which subsequently reacts with \( \text{H}_2\text{O} \) or \( \text{HNO}_3 \) heterogeneously to form the low-volatility products observed in the SOA (see Fig. 10). This intermediate is likely short-lived, and further work is required to identify this species and its role in SOA formation.

One possible explanation for the higher SOA yields observed from methacrolein and 2M2B is that for these compounds SOA formation is favored by steric hindrance. With an additional methyl group on the \( \alpha \)-carbon, steric repulsion causes the methyl group to move away from the neighbour- ing peroxy nitrate functional group by rotation of the C-C bond. As a result, the intramolecular reaction leading to SOA formation can be enhanced, consistent with the relatively higher SOA yields. For the other \( \alpha, \beta \)-unsaturated...

![Graph showing SOA mass yields from isoprene photooxidation under neutral seed conditions as a function of organic loading. The solid markers indicate SOA yields measured in this study, using CH\(_3\)ONO as the OH precursor under high NO\(_2\)/NO ratios (between 3 and 8). The SOA yields for methacrolein (solid red triangles) have been multiplied by 0.25 to account for the gas-phase product yield of methacrolein from isoprene high-NO\(_x\) oxidation. The SOA yields measured under high-NO\(_2\)/NO conditions are higher than both high-NO (open red circles) and low-NO\(_x\) conditions (open blue circles) under neutral seed conditions. With an acidified seed, SOA yields can be as high as 0.29 (Surratt et al., 2010).

![Graph showing time trends of (a) gas-phase CIMS m/z 311 and (b) SOA growth during high-NO\(_2\) photooxidation of methacrolein (red) and crotonaldehyde (purple). m/z 311 corresponds to the unit mass adduct of C\(_4\)-hydroxynitrate-PAN. The observed gas-phase signals of C\(_4\)-hydroxynitrate-PAN in both experiments are within 20% of each other, but the amount of SOA formed from methacrolein photooxidation is about a factor of 4 higher. A similar difference was observed between 2M2B and 3M2B photooxidation. This suggests that C\(_4\)- and C\(_5\)-hydroxynitrate-PANs are not precursors to low-volatility aerosol-phase products.]}
aldehydes, this interaction is likely not favored, as the hydrogen atom on the \( \alpha \) carbon is in plane with the peroxy nitrate group in the most stable rotational conformer (see Fig. 14). The interaction between the peroxy nitrate group and the added functional group is reduced, corresponding to lower SOA formation. Thermodynamic calculations of the relative stabilities of the conformers are required to confirm this hypothesis.

6.2 Methylbutenols (MBO)

MBO232 is a biogenic hydrocarbon potentially important in forest photochemistry (Harley et al., 1998). The SOA yields of MBO232 photooxidation have been shown to be negligible, under both high- and low-NO\(_x\) conditions (Carrasco et al., 2007; Chan et al., 2009a). In this study, SOA formation from MBO232 photooxidation is below detection limit, even at high NO\(_2\)/NO ratios (which would favor any PAN formation). This is likely linked to the lack of PAN products from MBO232 oxidation. The fate of the alkoxy radical formed from OH-initiated oxidation of MBO232 is shown in Fig. 15. Scission of the C-C bond adjacent to the tertiary carbon is favored, leading to high yields of glycolaldehyde (\( > 0.6 \)). Formation of 2-hydroxymethylpropanal (2-HMPR) following scission of the C-C bond adjacent to the primary carbon is not the favored route, and hence the yields of 2-HMPR are relatively low (\( < 0.4 \)). Furthermore, OH oxidation of 2-HMPR proceeds by OH abstraction of the aldehydic hydrogen, but owing to the neighbouring hydroxyl group, decomposition to acetone and CO is favored over addition of O\(_2\) to form an acyl peroxy radical. Carrasco et al. (2006) found no PAN formation from photooxidation of 2-HMPR, despite high NO\(_2\)/NO ratios.

MBO231 photooxidation produces, in contrast, substantial amounts of SOA, at mass yields of 0.008 – 0.042. In MBO231, the hydroxyl group is in the 1-position and is not adjacent to the double bond. Decomposition of the analogous alkoxy radical therefore proceeds by scission of the C-C
In high-NO photooxidation of MBO231 and MBO232, 2010 Chan et al. 2009a Tandem mass spectrometry was used to distinguish those in MBO231 photooxidation. Also, following abstraction of 1-HMPR rapidly decomposes to CO and acetone. As a result, PAN formation is unlikely. For MBO231, 1-HMPR formation is favored from the decomposition of the alkyloxyl radical. Furthermore, OH reaction of 1-HMPR leads to an acyl peroxy radical, which reacts with NO$_2$ to form a C$_4$-hydroxy-PAN.

Fig. 15. Mechanism of MBO231 and MBO232 photooxidation under high-NO$_x$ conditions. The dashed lines indicate possible locations of C-C bond scission under decomposition of alkyloxyl radicals. For MBO232, 2-HMPR formation is relatively small, as scission of the C-C bond with the 4-carbon is not favored. In addition, the acyl radical from H-abstraction of 2-HMPR rapidly decomposes to CO and acetone. As a result, PAN formation is unlikely. For MBO231, 1-HMPR formation is favored from the decomposition of the alkyloxyl radical. Furthermore, OH reaction of 1-HMPR leads to an acyl peroxy radical, which reacts with NO$_2$ to form a C$_4$-hydroxy-PAN.

In this work, we systematically investigate the effect of relative NO and NO$_2$ concentrations on SOA formation from aldehyde photooxidation under high-NO$_x$ conditions. A strong positive correlation of SOA yields with NO$_2$/NO ratio is observed for methacrolein (a major oxidation product of isoprene responsible for SOA formation) and two related α,β-unsaturated aldehydes, acrolein and crotonaldehyde. Oligoester products from dihydroxyacarboxylic acids and hydroxynitrooxycarboxylic acids are also observed to depend on NO$_2$/NO ratio, confirming that PAN chemistry plays an important role in formation of these low-volatility products. Offline high-resolution aerosol mass spectrometry reveals that analogous oligoester products are major constituents in SOA formed from all α,β-unsaturated aldehydes studied here. By comparing SOA formation from structurally similar aldehydes, we establish that SOA formation is favored when the α-carbon is substituted by a methyl group and the olefinic bond is in the 2-position, such as in methacrolein and 2M2B. The experimental data suggest that SOA formation proceeds via an intramolecular reaction involving the peroxy nitrate functional group, following the addition of O$_2$ to the MPAN+OH adduct. No aerosol formation is observed from MBO232, an atmospherically important unsaturated alcohol, even at high NO$_2$/NO ratios, as PAN formation is structurally unfavorable.

Understanding the overall effect of NO$_x$ on SOA yields is important, as SOA yields can vary greatly depending on NO$_x$ conditions. In most photooxidation systems, addition of OH, followed by O$_2$, to an olefinic bond results in formation of a hydroperoxy radical. The competition between the RO$_2$+HO$_2$ pathway (which forms low-volatility hydroperoxides) and the RO$_2$+NO pathway (which forms volatile organic nitrates and fragmentation products) determines the SOA yields. In the isoprene-high-NO$_x$ system, owing to the MPAN chemistry, aerosol formation proceeds via OH abstraction of the aldehydic hydrogen from methacrolein. As a result, a competition exists between reaction of the acyl peroxy radical with NO$_2$, leading to formation of MPAN and SOA, and with NO to form volatile fragmentation products. The present work shows the importance of the RO$_2$+NO$_2$ pathway of unsaturated aldehyde photooxidation as a route leading to SOA formation. This could have important implications on SOA formation from...
other atmospheric compounds, especially those with conjugated double bonds. For example, photooxidation of aromatic compounds (Calvert et al., 2002) can lead to α, β-unsaturated aldehydes, which can form significant amounts of low-volatility products via a PAN intermediate. At atmospherically relevant NO2/NO ratios, SOA yields from isoprene are 0.031–0.074 at organic aerosol loadings of 3–47 μg m−3; these values are 3 times higher than those previously measured under high-NO conditions. The yields exceed even those measured under low-NOx conditions. An implication of these results is that atmospheric SOA formation from aldehydes may be significantly underestimated in current models, since an appreciable fraction of SOA is generated in areas where NO2/NO ratios are high.

Radiocarbon (14C) studies have repeatedly shown that ambient organic aerosol is dominated by biogenic carbon, suggesting that biogenic hydrocarbons are an important source of SOA. However, field measurements have shown that organic aerosol levels tend to be correlated with anthropogenic tracers such as CO and acetylene. From satellite observations one can infer that while the source of carbon in many regions is most likely biogenic, the aerosol formation from biogenic hydrocarbons is significantly enhanced by anthropogenic activities (i.e. NOx and SOx emissions; Goldstein et al., 2009; Carlton et al., 2010). The present work moves in the direction of reconciling these two seemingly contradictory observations of biogenic carbon versus anthropogenic enhancement. Here we show that the SOA yields from photooxidation of isoprene under atmospherically relevant NO2/NO ratios are significantly larger than those previously measured under lower NO2/NO ratios. Moreover, the SOA yields under these conditions are larger than those under low-NOx conditions, suggesting that SOA formation from isoprene, the most abundantly emitted non-methane biogenic hydrocarbon, can be more efficient in urban high-NOx plumes than in remote regions.

Appendix A

Photochemical modeling to estimate NO and NO2 concentrations

Owing to interference with the NO2 signal by HONO and CH3ONO in the chemiluminescence NOx monitor, we estimate NO and NO2 concentrations during chamber experiments by photochemical modeling. In experiments in which HONO is the source of OH, the photolysis rate of HONO is estimated from the first-order decay of the m/z 66 signal on the CIMS, which correspond to the HF-ONO− ion. The initial mixing ratio of HONO was estimated based on the decay of parent hydrocarbon and known rate constants (Atkinson and Arey, 2003; Magneron et al., 2002). Previous comparison to a GC/NO2 analyzer allows us to determine the HONO interference on the NOx signal, and hence the amount of NO and NOx produced during HONO synthesis (Chan et al., 2009b). The initial mixing ratio of NO2 is therefore the sum of the concentrations of NO2 impurity from HONO synthesis (calculated by multiplying the NO2 signal after HONO injection by a known factor) and additional NO2 injected (the increase in NO2 signal from direct injection). For unsaturated aldehydes, the photochemical model includes the following reactions:

![Figure 16](image)


\[ \text{HONO} + h\nu \rightarrow \text{OH} + \text{NO} \]

\[ \text{hydrocarbon} + \text{OH} \rightarrow 0.5 \text{RO}_2 + 0.5 \text{R'O}_2 \]

\[ \text{RO}_2 + \text{NO} \rightarrow 0.9 \text{fragmentation products} + 0.9 \text{NO}_2 + 0.1 \text{RONO}_2 \]

\[ \text{R'O}_2 + \text{NO} \rightarrow \text{fragmentation products} + \text{NO}_2 \]

\[ \text{R'O}_2 + \text{NO}_2 \rightarrow \text{MPAN} \]

\[ \text{MPAN} \rightarrow \text{R'O}_2 + \text{NO}_2 \]

\(\text{RO}_2\) denotes the peroxy radical produced by \(\text{OH}\) addition to the \(\text{C}=\text{C}\) double bond, followed by \(\text{O}_2\). \(\text{R'O}_2\) denotes the acyl peroxy radical produced by \(\text{OH}\) abstraction of the aldehydic hydrogen, followed by \(\text{O}_2\) addition. These two channels (\(\text{OH}\) addition and abstraction) have a branching ratio of 1:1 for methacrolein (Tuazon and Atkinson, 1990). Other reactions involving \(\text{O}_3\), \(\text{HO}_3\), \(\text{NO}_3\) are also included in the mechanism. For \(\text{MBO231}\) and \(\text{MBO232}\), the reactions described in Chan et al. (2009a) are used. The calculated \(\text{NO}_2/\text{NO}\) ratios averaged over the first 200 min of irradiation (the period during which \(\text{SOA}\) formation occurred, see Fig. 1) are listed in Table 2.

For the high-\(\text{NO}_2\) experiments, \(\text{CH}_3\text{ONO}\) was used as the \(\text{OH}\) precursor:

\[ \text{CH}_3\text{ONO} + h\nu \rightarrow \text{CH}_3\text{O} + \text{NO} \]

\[ \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \]

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]

The photolysis rate of \(\text{CH}_3\text{ONO}\) was estimated by the first-order decay of the \(\text{CH}_3\text{ONO}\) signal on GC/FID. The initial mixing ratio of \(\text{CH}_3\text{ONO}\) was determined from the measured vapor pressure of \(\text{CH}_3\text{ONO}\) in the injection bulb. The modeled decay of the hydrocarbon is consistent with that observed by GC/FID. FTIR analysis shows no \(\text{NO}\) or \(\text{NO}_2\) impurities are produced during \(\text{CH}_3\text{ONO}\) synthesis ([\(\text{NO}_2\]) was less than 0.6% of \([\text{CH}_3\text{ONO}])\). In the photochemical calculations, the initial \(\text{NO}\) and \(\text{NO}_2\) concentrations are determined from the increase in \(\text{NO}\) and \(\text{NO}_2\) signals from direct injection. The calculated \(\text{NO}_2/\text{NO}\) ratios averaged over the first 100 min of irradiation are listed in Table 2 (see Fig. 2).

**Supplementary material related to this article is available online at:**
http://www.atmos-chem-phys.net/10/7169/2010/acp-10-7169-2010-supplement.pdf

**Acknowledgements.** This research was funded by US Department of Energy Biological and Environmental Research Program DE-FG02-05ER63983, US Environmental Protection Agency STAR grant RD-83374901, US National Science Foundation grant ATM-0432377, and the Electric Power Research Institute. This publication has not been formally reviewed by the EPA. The views expressed in this document are solely those of the authors and EPA does not endorse any products mentioned in this publication. The authors would like to thank K. E. Kautzman and A. J. Kwan for experimental assistance, and F. Paulot for helpful discussion.

Edited by: M. Gysel

**References**


A. W. H. Chan et al.: High-NOx SOA formation from aldehydes

Orlando, J. J., Tyndall, G. S., Bertman, S. B., Chen, W. C., and Burkholder, J. B.: Rate coefficient for the reaction of OH with CH2=C(CH3)2C(O)OONO2 (MPAN), Atmos. Environ., 36, 1895–1900, 2002.

www.atmos-chem-phys.net/10/7169/2010/ Atmos. Chem. Phys., 10, 7169–7188, 2010