



August 26, 2014

Dr. James M. Roberts

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Dear Dr. Roberts,

Thank you for the prompt review and consideration of our submission to Journal of Atmospheric Chemistry and Physics (Manuscript No. acp-2014-323) entitled: "**Atmospheric oxidation of 1,3-butadiene: characterization of gas and aerosol reaction products and implication for PM_{2.5}.**" We wish to extend our sincere appreciation to you and the reviewers for the time and effort spent in evaluating this manuscript. The comments have been very helpful in improving the manuscript. The evaluation by the reviewers was very positive regarding the manuscript.

We have carefully considered the comments from the reviewers, and our revisions have been made to reflect these comments. We have addressed each point separately in the attached response to reviewers. The comments are delineated as Issues and this is followed by a Response which note changes made to the manuscript. A copy of the review is appended to this letter (see end of this letter) which we have numbered for ease of cross-referencing to our response.

Thank you again for considering this manuscript. For any additional issues, I can be reached by phone at (919) 541-7728 or e-mail at jaoui.mohammed@epa.gov.

Sincerely,

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Reviewer# 1.

This reviewer said:

General Comments and Recommendation

“The authors systematically examine secondary organic aerosol (SOA) formation from the hydroxyl radical (OH)-initiated oxidation of 1,3-butadiene (13BD) in the presence or absence of NO_x using ammonium sulfate seed aerosol. More specifically, this study examined this chemistry in the EPA 14.5-m³ smog chamber facility operated in both dynamic (flow or continuous) and static (batch) mode. Gas- and aerosol-phase products were chemically characterized using prior derivatization methods and coupled to HPLC-UV and GC/ion trap MS, respectively. **This group has been one of the leaders in uncovering novel tracer compounds in various SOA systems (e.g., isoprene, toluene, beta-caryophyllene, alpha-pinene, and naphthalene) over the past decade using similar approaches as described here.** The main focus of this manuscript was to identify unique tracer compounds that could be used in source apportionment of ambient aerosol, especially in urban areas where 13BD emissions are high.”

This reviewer goes on to say:

“**Although this manuscript is an excellent contribution to the literature**, I fear the authors fell short in utilizing a great opportunity to probe in more detail the actual gas- and aerosol-phase chemistry that produces SOA from 13BD and relating this to prior work. Moreover, I was a bit disappointed to see the authors failed to cite many previous studies (I’ll be more specific in my specific comments below) that have focused on elucidating the exact gas- and aerosol-phase chemistry from isoprene oxidation that yields SOA. Since isoprene and 13BD only differ by 1 methyl group, it is likely they share similar gas- and aerosol- phase chemistries that yield SOA. In fact, recent work by Surratt et al. (2010, PNAS) and Chan et al. (2010, ACP) showed that 2,3-epoxy-1,4-butanediol (BEPOX) and the PAN of acrolein (APAN) are direct precursors to explain the formation of the tetrols and glyceric acid monomers, respectively, as well as their respective oligomers (the authors are encouraged to visit the supplementary information of both of those papers) from 13BD. As described in those papers, the chemistry is exactly the same as that from isoprene under initially low- and high-NO_x conditions. Shown in Figure 1 attached here, I have provided a detailed gas- and aerosol-phase reaction mechanism that leads to some of the SOA constituents the authors listed in Table 2. Notably, the authors will see that I have added the fact that once APAN is formed in the gas phase its subsequent oxidation by OH likely leads to the formation of acrylic acid epoxide (AAE), with the latter being exactly similar to recent findings by Lin et al. (2013, PNAS). I was a bit surprised the authors didn’t include enough discussion in the manuscript about the likely SOA formation mechanism based on prior research and also proposing a tentative mechanism as a figure. The authors are welcome to modify my version as they see fit. Furthermore, the authors seemed to combine all the compounds detected from both low- and high-NO_x experiments into 1 table. Why did they do this? For chemical mechanism purposes, it would be more ideal to have separate tables for the NO_x-free and NO_x experiments, as I suspect important differences about the chemical composition of the SOA will arise. In addition to these major concerns, I have a number of specific and minor (technical) comments below that I would like to request that the authors address before publication can be fully considered. At this time, I must recommend this manuscript be accepted with major revisions.”

Response (General Comments and Recommendation).

First we would like to thank this reviewer for the time and effort spent in reading and evaluating this manuscript. We thank the reviewer for his suggestions and comments. This reviewer is supportive of this work, and has given a very positive view of the manuscript and says that this

manuscript is an excellent contribution to the literature. Below, are our response to issues and comments raised by this reviewer.

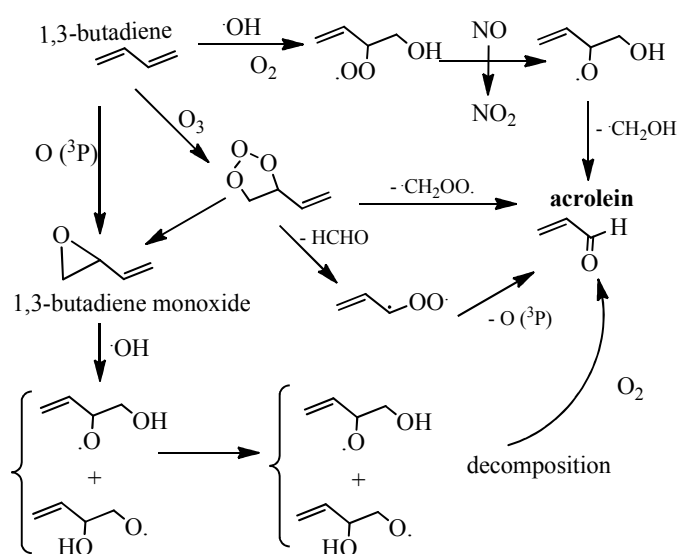
As mentioned by the reviewer, isoprene and 1,3-butadiene only differ by one methyl group, and both have two double bonds. Both compounds may share similar gas- and aerosol-phase chemistries that yield SOA. However, based on computational chemistry there is a fundamental differences between both molecules. Isoprene is an asymmetric molecule compared to 1,3-butadiene which is symmetric due to the absence of methyl group. They may lead after their atmospheric oxidation to similar end products but intermediates pathways may be different and more computational work is needed to elucidate if any difference exists. However, to reflect the reviewer concerns, a section related to 1,3-butadiene chemistry is added to the manuscript and reads:

Mechanism of Product Formation

Recent studies (Surratt et al., 2010; Sato et al., 2011; Lin et al., 2012, 2013; Pye et al., 2013; Birdsall et al., 2013, 2014) show the importance of epoxide chemistry in isoprene SOA formation. Methacrolein (MAC), methacryloylperoxynitrate (MPAN), and methacrylic acid epoxide (MAE) were proposed to be key intermediates in understanding mechanistic pathways leading to some isoprene reaction products either under low or high NO_x conditions. Of particular importance, species observed recently in isoprene-SOA including: 2-methylglyceric acid, 2-methyltetrols, 2-methylglyceric acid-oligomers, nitric acid esters, and sulfuric acid esters (Edney et al., 2005; Surratt et al., 2007; Szmigielski et al., 2007; Gomez-Gonzalez et al., 2008; Jaoui et al., 2008; Chan et al., 2010a, b; Nguyen et al., 2011; Hatch et al., 2011; Zhang et al., 2011). For example, MAE formed through MPAN chemistry (Surratt et al., 2010) was proposed to be key precursor to the formation of 2-methylglyceric acid and others oligoesters observed in isoprene aerosol (Lin et al., 2013; Birdsall et al., 2013, 2014). Since isoprene and 1,3-butadiene only differ by one methyl group, it is likely they share similar gas and aerosol phase chemistries that yield SOA. 1,3-Butadiene presents a higher degree of symmetry than isoprene and may leads to a simpler set of mechanistic pathways. The detection in smog chamber experiments of similar end products from isoprene and 1,3BD oxidation (e.g. methyltetrols vs tetrols, methylglyceric acid vs. glyceric acid, methacrolein vs. acrolein, methyl-oligoesters vs. oligoesters etc) suggests that the atmospheric oxidation of these two hydrocarbons may be similar.

Time profiles from the static experiment (ER442: Table 1) involving 1,3BD photooxidation in the presence of NO_x (Figures 4, 5) show an increase in the concentration of SOA compounds as ozone concentration increases. This indicates that ozone reaction is likely involved in the formation of SOA compounds, although under atmospheric conditions 1,3BD oxidation with OH radicals is believed to be dominant. In the following discussion, tentative mechanistic pathways leading to some major products

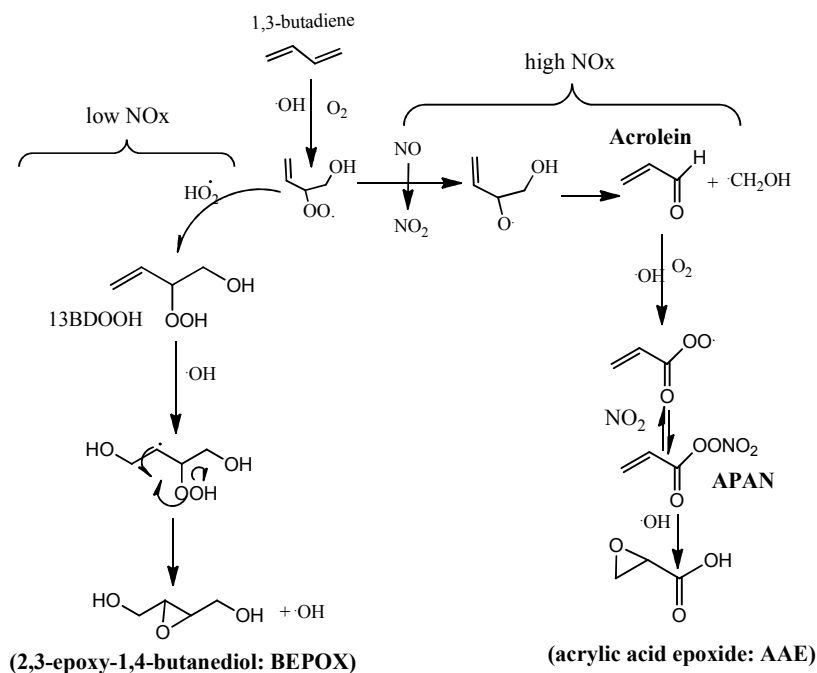
observed in the gas and particle phase are shown, based on either OH and/or ozone reactions. These mechanistic pathways are similar to those reported recently for isoprene. Acrolein, one of the major first generation product, was proposed to be formed through 13BD reaction with OH radical, ozone, or O(³P) as shown in Scheme 1 (Liu et al., 1999). Other mechanistic pathways leading to some gas phase products observed in this study, including formaldehyde, glyoxal, glycolaldehyde, butenedial, malonaldehyde, have been reported (Liu et al., 1999) through either O₃ or OH reactions with 13BD and are not presented here.



Scheme 1. Acrolein formation from 1,3-butadiene oxidation

Recent studies show that epoxide species (e.g. IEPOX [low NO_x] and MAE [high NO_x] for isoprene) play an important role in understanding SOA formation (Paulot et al., 2009; Lin et al., 2013; Birdsall et al., 2014; Nguyen et al., 2014). Similar to isoprene chemistry, two epoxides (acrylic acid epoxide (AAE); and 2,3-epoxy-1,4-butanediol (BEPOX)) formed in the gas phase through the reaction of 13BD with OH radicals are proposed to be keys intermediates in SOA formation. Scheme 2 shows reaction pathways leading to the formation of acrylic acid epoxide (AAE: right side) and 2,3-epoxy-1,4-butanediol (BEPOX: left side) under high and low NO_x condition, respectively. These mechanistic pathways are similar to those proposed for isoprene (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2013; Nguyen et al., 2014; Birdsall et al., 2014) for the formation of MAE and IEPOX, respectively. Under low NO_x conditions, BEPOX is proposed to be formed through OH radical addition to one of the external positions of the double bonds to form hydroxyhydroperoxide (13BDOOH). Subsequent addition of OH radicals to the other double bond of 13BDOOH yields dihydroxyepoxide (BEPOX) as shown in

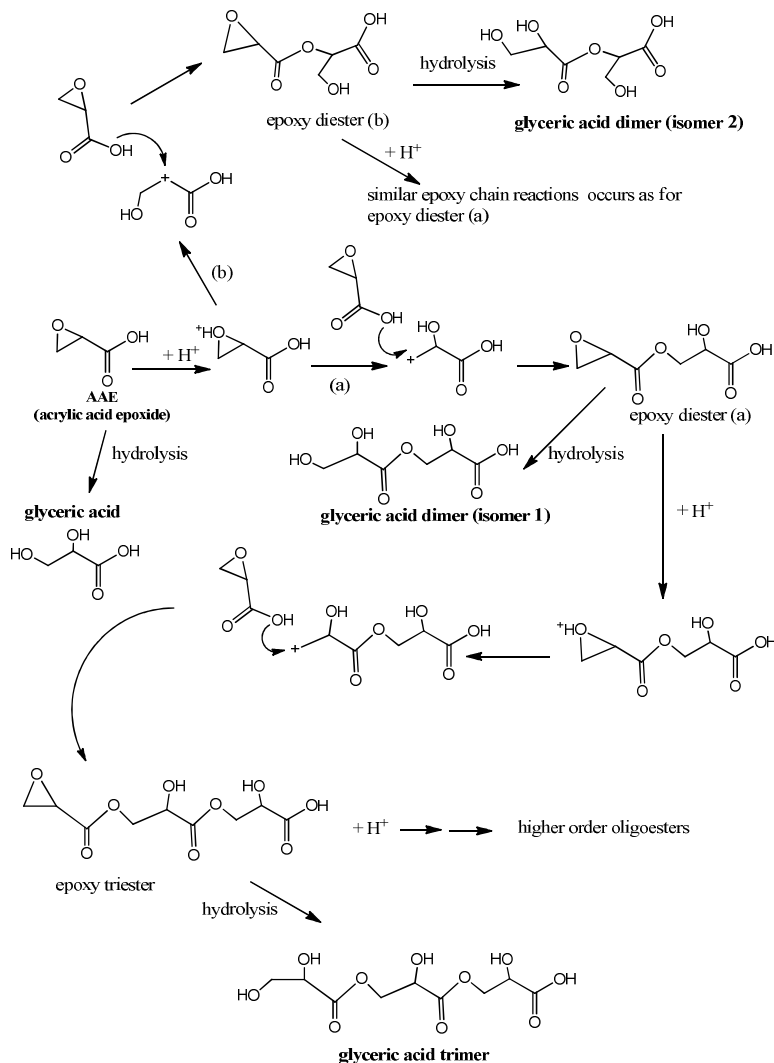
left side (Scheme 2). In addition, 1,4-anhydroerythritol compound was detected in 1,3-BD SOA (Table 2). This compound is similar to 3-methyldihydroxytetrahydrofurans formed from the oxidation of isoprene through IEPOX oxidation via acid-catalyzed rearrangement on sulfate aerosol (Zhang et al., 2011; Lin et al., 2012). 1,4-Anhydroerythritol observed here may be formed through similar reactions starting from BEPOX, and presents further evidence that BEPOX is being formed from the oxidation of 1,3-BD and playing a role in SOA formation. In the presence of NO_x, Scheme 2 (right side) shows the formation of acrolein through 13BD reaction with OH radicals yielding hydroxyperoxy radicals, then acrolein (see also Scheme 1). Acrolein reacts with OH radicals, and in the presence of NO, yields the formation of APAN (Scheme 2: right side). Similar to MPAN (Lin et al., 2013), APAN is proposed to react with OH radicals leading to AAE compound.



Scheme 2. Proposed mechanism for AAE and BEPOX formation from 1,3-butadiene oxidation

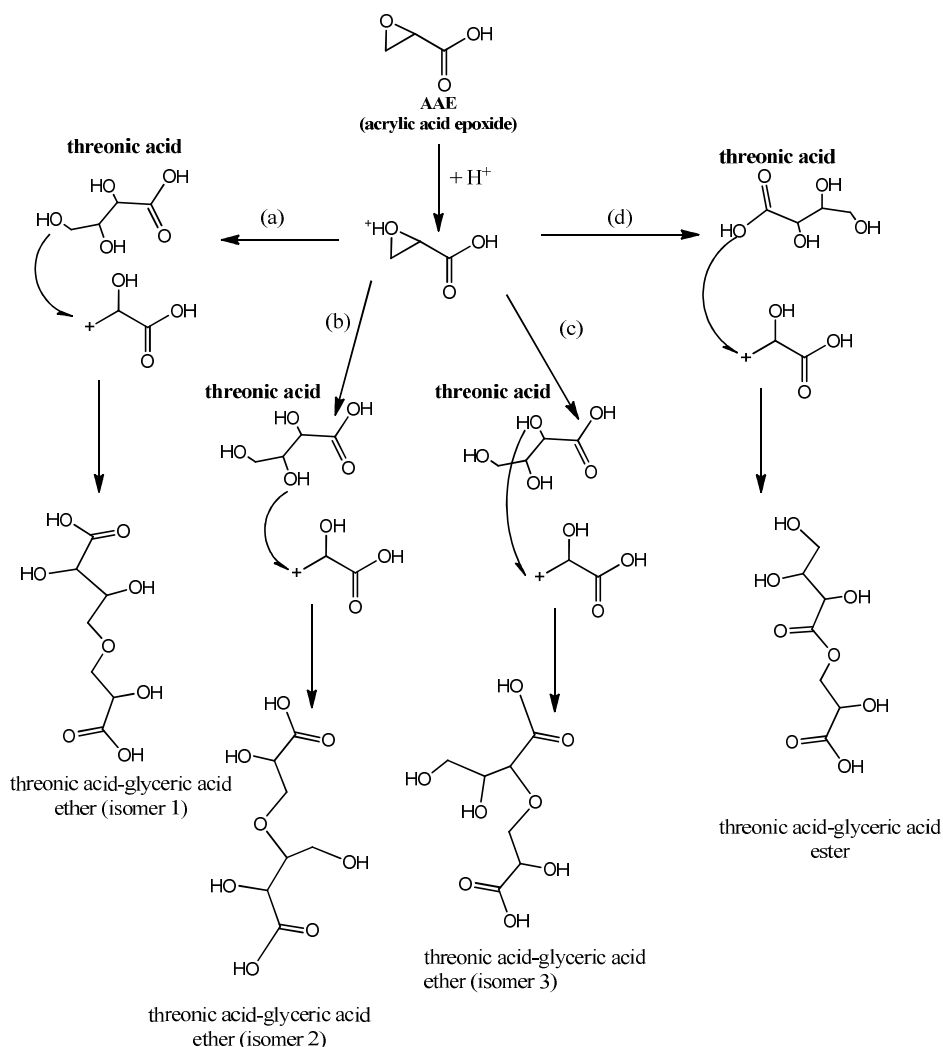
Mass spectra obtained from GC-MS analysis of SOA originated from experiments involving NO_x show the presence of a series of monomeric compounds as well as oligoesters structurally related to these monomers (Table 2). Although important advances has been made recently for isoprene chemistry to understand key intermediates species (epoxides) leading to SOA formation (Birdsall et al., 2014), the conditions necessary for their formation (e.g. acidity, water content, inorganic ions, etc) and the specific chemical mechanisms by which these compounds are formed remain unknown. Lin et al. (2013) and Birdsall et al. (2014) show the importance of MAE in the formation of methylglyceric acid as well as a

wide range of oligoesters structurally related to 2-methylglyceric acid. For oligoesters formation, Birdsall et al. (2014) presented data suggesting that acid catalyzed nucleophilic addition of MAE is kinetically feasible in the atmosphere mainly under acidic conditions but much slower than the epoxide chain reaction. In addition, Birdsall et al. (2014) show that a series of nucleophile reactions may occur in the atmosphere including self-reaction of MAE as well as MAE reaction with other nucleophilic compounds (water, acids, and alcohols). In this study, a series of oligoesters were observed and their formation may follow similar mechanistic pathways as those proposed by Birdsall et al. (2014) for isoprene reaction. Scheme 3 shows a proposed mechanism for AAE oligomerization via epoxy chain reaction. In the presence of H^+ , AAE undergoes nucleophilic addition leading to series of epoxy glyceric acid oligomers. Two pathways (a, b) are shown in Scheme 3 showing the formation of two isomers (e.g. glyceric acid dimer 1, and glyceric acid dimer 2). Each epoxy compounds may undergo hydrolysis leading to the corresponding monomer or oligomers.



Scheme 3. Proposed mechanism for AAE oligomerization via epoxy chain reaction leading to glyceric acid, and glyceric acid oligoesters

The detection in the aerosol phase of a series of oligoesters with structure characteristics of a combination of an alcohol and an acid compound (Table 2), suggests that reactions in the aerosol phase between monomer compounds bearing alcohol and acid groups may occur. Recent work by Birdsall et al. (2013) show that classical esterification reactions involving reaction of organic acid and alcohol under atmospheric conditions is too slow to occur and cannot accounts for all the oligoesters observed in chamber experiments. Based on his work and prior work (Surratt et al., 2010; Lin et al., 2013), Birdsall et al. (2014) provided evidence that nucleophilic reaction between MAE and a series of nucleophilic



Scheme 4. Proposed mechanism for AAE + threonic acid via nucleophilic addition reaction leading to ethers (3 isomers) and one ester

compounds yields a series of oligoesters including ethers, esters, and diols. By analogy to MAE, we proposed in this study similar nucleophilic reactions between AAE and a series of nucleophilic products observed in this study

(Table 2) (e.g. acids (oxalic acid, malic acid, threonic acid); alcohols (tetrols, glycerol etc)). As an example, Scheme 4 shows proposed mechanism of AAE and threonic acid reaction via nucleophilic addition. The nucleophilic addition of threonic acid, a trihydroxy acid, to AAE involves all three alcoholic OH groups leading to the formation of three ethers compounds (pathways a, b, and c), as well as the carboxylic COOH group leading to the formation of an ester (pathway d).

None of these oligoesters were detected in ambient samples analyzed using the same derivatization techniques suggesting that oligoesters may be formed mainly under laboratory conditions where high concentration of AAE and other nucleophile species are present. In addition, under atmospheric condition, water and other non-epoxide nucleophile compounds may limit the formation of oligoesters due to competitive hydrolysis pathway when epoxides are formed (Scheme 3). This is consistent with the work reported by Birdsall et al. (2014) involving MAE nucleophilic reactions.

The following references were added to the revised manuscript:

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Lin, Y.-H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L., Knipping, E. M., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene epoxydiols as precursors to secondary organic aerosol formation: Acid-catalyzed reactive uptake studies with authentic compounds, *Environ. Sci. Technol.*, 46, 250–258, 2012.

Lin, Y.-H., Zhang, H., Pye, H. O. T., Zhang, Z., Marth, W. J., Park, S., Arashiro, M., Cui, T., Budisulistiorini, S. H., Sexton, K. G., Vizuete, W., Xie, Y., Luecken, D. J., Piletic, I. R., Edney, E. O., Bartolotti, L. J., Gold, A., and Surratt, J. D.: Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides, *P. Natl. Acad. Sci. USA*, 110, 6718–6723, doi:10.1073/pnas.1221150110, 2013.

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Szmigielski, R., Surratt, J. D., Vermeylen, R., Szmigielska, K., Kroll, J. H., Ng, N. L., Murphy, S. M., Sorooshian, A., Seinfeld, J. H., and Claeys, M.: Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry, *J. Mass Spectrom.*, 42, 101–116, 2007.

Gómez-González, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C., Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(–) electrospray ionization mass spectrometry, *J. Mass Spectrom.*, 43, 371–382, doi:10.1002/jms.1329, 2008.

Jaoui, M., Edney, E. O., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Surratt, J. D., and Seinfeld, J. H.: Formation of secondary organic aerosol from irradiated α -pinene/toluene/NO_x mixtures and the effect of isoprene and sulfur dioxide, *J. Geophys. Res.*, 113, D09303 doi:10.1029/2007jd009426, 2008.

Chan, A. W. H., Chan, M. N., Surratt, J. D., Chhabra, P. S., Loza, C. L., Crouse, J. D., Yee, L. D., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Role of aldehyde chemistry and NO_x concentrations in secondary organic aerosol formation, *Atmos. Chem. Phys.*, 10, 7169–7188, 25 doi:10.5194/acp-10-7169-2010, 2010a.

Chan, M. N., Surratt, J. D., Claeys, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. M., Eddingsaas, N. C., Wennberg, P. O., and Seinfeld, J. H.:

Characterization and quantification of isoprene-derived epoxydiols in ambient aerosol in the southeastern United States, *Environ. Sci. Technol.*, 44, 4590–4596, 2010b.

Nguyen, T. B., Roach, P. J., Laskin, J., Laskin, A., and Nizkorodov, S. A.: Effect of humidity on the composition of isoprene photooxidation secondary organic aerosol, *Atmos. Chem. Phys.*, 11, 6931–6944, doi:10.5194/acp-11-6931-2011, 2011.

Hatch, L. E., Creamean, J. M., Ault, A. P., Surratt, J. D., Chan, M. N., Seinfeld, J. H., Edgerton, E. S., Su, Y., and Prather, K. A.: Measurements of isoprene-derived organosulfates in ambient aerosols by aerosol time-of-flight mass spectrometry – Part 1: Single particle atmospheric observations in Atlanta, *Environ. Sci. Technol.*, 45, 5105–5111, doi:10.1021/es103944a, 2011a.

Hatch, L. E., Creamean, J. M., Ault, A. P., Surratt, J. D., Chan, M. N., Seinfeld, J. H., Edgerton, E. S., Su, Y., and Prather, K. A.: Measurements of isoprene-derived organosulfates in 15 ambient aerosols by aerosol time-of-flight mass spectrometry – Part 2: Temporal variability and formation mechanisms, *Environ. Sci. Technol.*, 45, 8648–8655, doi:10.1021/es2011836, 2011b.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proc Natl Acad Sci USA* 107(15):6640–6645, 2010.

Zhang, H., Surratt, J. D., Lin, Y.-H., Bapat, J., Kamens, R. M.: Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions. *Atmos. Chem. Phys.* 11(13): 6411–6424, 2011.

Paulot, F., Crouse, J. D., Kjaergaard, H. G., Kürten, A., St. Clair, J. A., Seinfeld, J. H., and Wennberg, P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene, *Science*, 325, 730–732, 2009.

Nguyen, T. B., Coggon, M. M., Bates, K. H., Zhang, X., Schwantes, R. H., Schilling, K. A., Loza, C. L., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds, *Atmos. Chem. Phys.*, 14, 3497–3510, 2014.

Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R. A., Varutbangkul, V., Flagan, R. C., Seinfeld, J. H.: Contribution of First- versus Second-Generation Products to Secondary Organic Aerosols Formed in the Oxidation of Biogenic Hydrocarbons, *Environ. Sci. Technol.*, 40, 2283-2297, 2006.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hofmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prev'ot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

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Specific Comments:

Comment # 1. “Can the authors state more specifically in the abstract how much of the organic aerosol they accounted for with their quantification for both the NO_x and NO_x-free experiments? Furthermore, if you do breakup Table 2 to keep the NO_x and NO_x-free experiments separate, can you add a column that lists how much mass was quantified for each compound? Lastly, you might want to add another column that lists the derivatized MW so it helps readers less familiar with derivatization methods in understanding your GC/MS mass spectra.”

Response. The majority of reaction products (monomers) observed in this study do not have authentic standards available commercially. In addition, no standards are available for any oligoesters observed. Most “quantitative analysis” was based on surrogate compounds, therefore we believe it’s not relevant to present the amount of organic aerosol accounted for in this study.

As suggested by the reviewer we added a column to Table 2 that lists derivatized MW as BSTFA derivatives.

Only SOA originated from experiments involving NO_x were GC-MS analyzed, because (1) NO_x is coemitted with 1,3 BD; (2) the rate constant for OH + 1,3 BD is extremely high and its lifetime is therefore dominated by the NO_x pathways.

To reflect the reviewer concern, we added the following sentence to Table 1 title and reads:

“GC-MS analysis was done only when NO_x was present in the system.”

Comment # 2. “Introduction, Page 14249, Lines 24-26:

These oligoesters were likely derived from the further oxidation of APAN. Chan et al. (2009,

ACP), which is not cited here, studied the OH-initiated oxidation of acrolein in the presence of increasing levels of NO₂/NO. With increasing NO₂/NO ratios, SOA yields were significantly enhanced and the SOA composition was very similar to the high-NO_x SOA previously characterized in detail by Surratt et al. (2006, JPCA) and Szmigielski et al. (2007, JMS). The authors should visit Table S1 in the SI section of the Chan et al. (2010, ACP) paper. The authors will see the exact same oligomers were observed as you found in your study here. Furthermore, MPAN was recently shown by Lin et al. (2013, PNAS) to yield methacrylic acid epoxide (MAE), which is now believed to be the direct precursor for these oligoesters. As shown in Figure 1 attached here in this review, I proposed that acrylic acid epoxide (AAE) forms and its subsequent reactive uptake (or heterogeneous) chemistry yields SOA.”

Response. In the new section added to the original manuscript (see previous comment), a detailed analysis of mechanistic pathways leading to most observed compounds in this study from 13BD oxidation was added as suggested by this reviewer. We thank the reviewer for the time and effort putting together this figure.

Comment # 3. “Introduction, Page 14250, Lines 12-13: I would be very careful with this statement. The authors are inferring that these compounds are substantially lost from the aerosol phase due to heterogeneous oxidation by OH. However, this prior study was a flow tube study that had very high concentrations of OH, and thus, although substantial loss was observed how this translates to the atmosphere remains unclear as OH levels are not as high in these flow tube studies.

Response. To reflect the reviewer comment, the following sentence was deleted from the manuscript:

“However, heterogeneous oxidation of pure erythritol with OH radicals was found to lead to a substantial volatilization of products to the gas phase (Kessler et al., 2010).”

Kessler et al. (2010) reference was deleted from the revised manuscript.

Comment # 4. “Table 1: Can the authors add how much ammonium sulfate seed aerosol was actually present in these experiments? This wasn’t exactly stated in the materials and methods section, but I think it would be more helpful for readers if this information was incorporated into Table 1.”

Response. This was done as suggested by the reviewer.

Comment # 5. “Table 2: For your oligoester structures shown in Table 2, you need to denote that the structures listed are likely only 1 possible isomer. Since detailed tandem MS data are not presented or examined in the present manuscript, you cannot fully justify these isomers as the main isomers. By the way, are the authors planning to publish a subsequent study that plans to carefully examine the fragmentation data by using the capabilities of their ion trap MS (i.e., MS_n experiments)?”

Response. This was done as suggested by the reviewer.

Comment # 6. “NO_x vs. NO_x-free experiments and how this relates to RO₂ chemistry: For the NO_x-free experiments, the authors likely have a lot of HO₂ radicals being produced from the OH + H₂O₂ reaction in the gas phase, and thus, their experiments are likely RO₂ + HO₂ dominant; this condition likely leads to a large amount of BEPOX being formed in the gas phase. However, RO₂

+ RO₂ reactions cannot be ruled out owing to the VERY high mixing ratios of 1,3BD used in these studies. Furthermore, in the NO_x experiments, as the authors carefully describe in the time profile section, the nitric oxide (NO) levels quickly drops to zero. Once this occurs, NO₂, O₃, acrolein and APAN form as well as SOA. However, at this time, RO₂ + NO stops being the dominant pathway for the RO₂ radicals and now either RO₂ + RO₂ or RO₂ + NO₂ likely dominates, with the latter likely producing AAE from APAN + OH reactions. I think it is incredibly important for the authors to provide more insights into which RO₂ reaction pathway dominates under the NO_x and NO_x-free experiments and how this likely relates to the most abundant aerosol products measured. Further, if RO₂ + RO₂ dominates in your experiments, how does this really relate to the RO₂ chemistry in the atmosphere? As the authors know, the current thinking in the research community is that RO₂ + RO₂ cross-reactions are likely not substantial in the atmosphere. Since many of the most abundant aerosol products measured in these experiments were also detected in the ambient PM_{2.5} samples, I think this discussion is warranted and will likely provide much richer insights into the actual atmospheric chemistry that might produce these aerosol constituents.”

Response. The main objective of this study was the analysis of compounds in the presence of NO_x since (1) NO_x is coemitted with 1,3 BD; (2) the rate constant for OH + 1,3 BD is extremely high and its lifetime is therefore dominated by the NO_x pathways. Experiments conducted under low NO_x condition (Table 1) were analyzed for bulk parameters (see Tables 3 and 4). We agree with the reviewer the importance of chemistry under low condition; however, we believe data presented in this manuscript is of high importance to the atmospheric community.

Comment # 7. “Section 3.1.2. Oligoesters, Page 14261, Lines 6-8: Classical organic esterification (i.e., condensation reactions involving an organic acid and alcohol) was recently shown not to be kinetically favorable at atmospheric conditions by the Elrod Group (Birdsall et al., 2013, ACP). These recent kinetic results by the Elrod group provide credibility to the epoxide (i.e., AAE) pathway proposed here in Figure 1 by this reviewer, which is based on prior work (Lin et al., 2013, PNAS; Surratt et al., 2010, PNAS, Chan et al., 2009, ACP).”

Response. Birdsall et al. (2013, 2014) suggest that esterification reaction are slow under atmospheric conditions (studies were specific to 2-methylglyceric acid oligomers). To reflect the reviewer comment, we added the following sentences to the manuscript at the end of section 3.2.1 and reads:

“However, recent work by Birdsall et al. (2013) show that esterification reactions involving organic acid and alcohol under atmospheric conditions is too slow to occur and cannot accounts for the oligoesters observed in chamber experiments. Based on his work and prior work (Surratt et al., 2010; Lin et al., 2013), Birdsall et al. (2014) provided evidence that methacrylic acid epoxide (MAE) through hydrolysis reaction plays key role in isoprene-SOA composition.”

We also changed the following sentence from

”Furthermore, a series of oligoesters were detected and found to be produced from esterification reactions among compounds bearing alcoholic groups and compounds bearing acidic groups.”

To

” Furthermore, a series of oligoesters were detected and found to be produced through chemical reactions occurring in the aerosol phase between compounds bearing alcoholic groups and compounds bearing acidic groups. Time profiles are provided for selected compounds.”

We agree with the reviewer of the importance of epoxide chemistry and its role in SOA formation. The new section added to the manuscript provide detailed epoxide chemistry in the case of 13BD oxidation.

Comment # 8. “Field measurements and Figure 9: Can the authors be more specific as to how much of the SOA mass these novel tracers account for in Bakersfield? Furthermore, do the authors suggest using these tracers in the Kleindienst et al. (2007, Atmos. Environ.) SOA tracer method for future field studies? I’m sure readers will be curious about this and wondering if you will provide an updated tracer method paper that includes 13BD? I really did not see the point or need of Figure 9. The authors do not really explain this figure well in the main text, so unless they can clarify more exactly why it is needed I would suggest removing from the manuscript.”

Response. This is an important comment and work is underway to incorporate 1,3-butadiene in the tracer method reported by Kleindienst et al., 2007.

Comment # 9. “Figures and mass spectra for NO_x-free experiments: I suggest that the authors provide similar figures (i.e., chromatograms and mass spectra for SOA constituents) for NO_x-free experiments. This information will be very helpful in understanding differences in the gas- and aerosol-phase chemistry.”

Response. See our response to comment # 6.

Minor Comments.

Comment # 1. “Introduction, Page 14247, Line 19: Why not cite a more recent review article, such as Hallquist et al. (2009, ACP) instead of Kanakidou et al. (2005, ACP)?”

Response. Done as suggested by the reviewer.

Comment # 2. “Introduction, Page 14248, Lines 8-11: I think you should also cite the following articles and breakup the citations in order to correspond to each specific VOC: For isoprene: Kroll et al. (2006, ES&T), Surratt et al. (2006, JPCA), Surratt et al. (2010, PNAS). For MBO: Zhang et al. (2012, ES&T) and Zhang et al. (2014, ES&T Letters). For 13BD: Angove et al. (2006, Atmos. Environ.), Surratt et al. (2010, PNAS)”

Response. Done as suggested by the reviewer. New references were added to the reference section.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, 40, 1869–1877, 2006.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical

composition of secondary organic aerosol formed from the photooxidation of isoprene, *J. Phys. Chem. A*, 110, 9665–9690, 2006.

Zhang, Z., Lin, Y. H., Zhang, H., Surratt, J. D., Ball, L. M., and Gold, A.: Technical note: Synthesis of isoprene atmospheric oxidation products: Isomeric epoxydiols and the rearrangement products cis- and trans-3-methyl-3,4-dihydroxytetrahydrofuran, *Atmos. Chem. Phys.*, 12, 8529–8535, doi:10.5194/acp-12-8529 2012, 2012.

Zhang, H., Zhang, Z., Cui, T., Lin, Y. H., Bathela, N. A., Ortega, J., Worton, D. R., Goldstein, A. H., Guenther, A., Jimenez, J. L., Gold, A., and Surratt, J. D.: Secondary organic aerosol formation via 2-methyl-3-buten-2-ol photooxidation: evidence of acid-catalyzed reactive uptake of epoxides, *Environ. Sci. Technol. Lett.*, 1 (4), pp 242–247, 2014.

Comment # 3. “Introduction, Page 14249, Lines 2-3: Is it worth noting the study by Doyle et al. (2004, EHP) here? Specifically, this study showed that photochemically oxidized 13BD produced products in the gas phase, such as acrolein, that lead to cytotoxicity and inflammation (i.e., potential human health effects).”

Response. Done as suggested by the reviewer.
The following reference was added to the reference section:

Doyle, M., Sexton, K. G., Jeffries, H., Bridge, K., and Jaspers, I/: Effects of 1,3-butadiene, isoprene, and their photochemical degradation products on human lung cells, *Environ Health Perspect.* 112(15), 1488–1495, 2004.

Comment # 4. “Materials and Methods, Page 14251, Line 18: Should this citation be removed? It is a “pet peeve” of mine with my post docs and graduate students not to cite papers that reviewers (and readers) are not able to find and carefully read.”

Response. Although the paper is not publically available it has been submitted to APCD and is expected to be in print should this paper be accepted. We have given the reference as “(Submitted to *Atmos. Chem. Phys. Discuss.*)”.

Comment # 5. “Section 3.2 Time profile of gas-phase and SOA products, Page 14262, Lines 21-23: You need to provide citations for this sentence.”

Response. Done as suggested by the reviewer.

Comment # 6. “Section 3.3 Field measurements, Page 14264, Lines 6-9: You should add citation to Chan et al. (2010, ACP). They showed that APAN could in fact yield SOA including the same oligomers you observed here!”

Response. Done as suggested by the reviewer.

Comment # 7. “I had one further comment about this manuscript in regards to the 1,4-anhydroerythritol (MW 104) compound observed in the 1,3-BD SOA. The authors should recall work conducted by Lin et al. (2012, ES&T) and Zhang et al. (2012, ACP) by the UNC group. They showed the IEPOX from isoprene oxidation undergoes an acid-catalyzed rearrangement on sulfate aerosol to form cis- and trans-3-methyldihydroxytetrahydrofurans, which are exactly the same as the 1,4-anhydroerythritol found here (minus the methyl group). This is further evidence that 2,3-epoxy-1,4-butanediol (BEPOX) is being formed from the oxidation of 1,3-BD in these experiments and playing a role in forming the SOA constituents found in this study.”

Response. See our response to the first comment. The following sentences were included in the new section and reflect the reviewer comments:

“In addition, 1,4-anhydroerythritol compound was detected in 1,3-BD SOA (Table 2). This compound is similar to 3-methyldihydroxytetrahydrofurans formed from the oxidation of isoprene through IEPOX oxidation via acid-catalyzed rearrangement on sulfate aerosol (Zhang et al., 2011; Lin et al., 2012). 1,4-Anhydroerythritol observed here may be formed through similar reactions starting from BEPOX, and presents further evidence that BEPOX is being formed from the oxidation of 1,3-BD and playing a role in SOA formation.”

Reviewer# 2.

This reviewer said:

“(General Comments).

In this manuscript, the authors describe the characterization of particle and gas-phase oxidation products from a series of 1,3-butadiene oxidation experiments performed in a smog chamber. The authors examined the influence of oxidation condition (i.e. NO_x/HO_x ratios, RH and particle acidity) on product formation using the smog chamber that was operated in either a batch reactor or flow reactor mode. The authors applied appropriate derivatization methods to identify multifunctional gas- and particle phase products.”

This reviewer goes on to say:

“Overall, I found this manuscript meet the scope of the journal and the quality of analytical work is sound. However, I feel that the manuscript is not written in a clear enough fashion to deliver the message to potential readers. In particular the current version of the manuscript does not highlight the difference between high-NO_x and low- (or no) NO_x SOA chemistry in the 1,3-butadiene oxidation from the results obtained from the authors’ extensive analytical work. This is unfortunate. **Nevertheless, the topic the authors dealt with is of great interest to the community** and I recommend the publication of the manuscript after the authors address the following comments and the excellent comments made by the other reviewer. In addition, I fully support the other reviewer’s comments about missing citation and they should be rectified in a revised manuscript.

Response.

We would like to thank also this reviewer for the time and effort spent in reading and evaluating this manuscript. We thank him for his suggestions and comments. This reviewer is also very supportive of this work, and has given a very positive view of the manuscript. Below, are our response to issues and comments raised by this reviewer?

Specific comments

Comment # 1. “Page 14257 “Characterization of SOA products”: I suggest moving the descriptions of fragmentation patterns to supporting information (or summarize in a table) and concentrate on the difference in product distributions between high-NO_x and low-NO_x experiments.”

Response. One of the main objective in this study is the identification of reaction products from the oxidation of 1,3-butadiene using the different derivatization techniques reported in this manuscript. We feel that this section is important since it’s the first time these compounds were identified and a discussion about mass spectra fragmentations is important.

Comment # 2. “Page 14265 Line 10: I recommend the authors to add a section titled “Summary”, “Conclusions” or “Atmospheric Implication” here and highlight the message of this study.”

Response. As recommended by the authors a section was added to the manuscript and reads:

“Summary

In the present manuscript, laboratory experiments were conducted to investigate SOA formation from the oxidation of 1,3-butadiene in the presence and absence of NO_x. Chamber aerosol collected under these conditions have been analyzed for organic mass to organic carbon ratio, effective enthalpy of vaporization, and aerosol yield. In addition, the chemical composition of the gas phase and SOA was analyzed using derivative-based methods followed by gas chromatography–mass spectrometry or high-performance liquid chromatography analysis of the derivative compounds. More than 60 oxygenated organic compounds in the gas and particle phases were observed, of which 31 organic monomers were tentatively identified. The major products identified are glyceric acid, *d*-threitol, erythritol, *d*-threonic acid, *meso*-threonic acid, erythrose, malic acid, tartaric acid, and carbonyls including glycolaldehyde, glyoxal, acrolein, malonaldehyde, glyceraldehyde, and peroxyacryloyl nitrate (APAN).

Two epoxides compounds, BEPOX and AAE, are proposed in this study to be key intermediates for the formation of an important class of 13BD-derived compounds including glyceric acid and oligoesters found in SOA. Similar to isoprene oxidation (Birdsall et al., 2014), the mechanism proposed is based on epoxide chain reaction of AAE, as well as AAE reaction with a number of nucleophile species including water, carboxylic acids and alcohols. The BEPOX channel is also an important pathway leading to ambient SOA formation. However, none of these oligoesters were detected in ambient samples, suggesting that oligoesters may be formed mainly under laboratory conditions where high concentration of AAE and other nucleophile species are present. These oligoesters under ambient conditions may be not

stable and after their decomposition could be possible sources of glyceric acid, threonic acid and tetrols found in ambient aerosol.

The results of this study potentially have atmospheric implications for areas impacted by 1,3-butadiene oxidation and contribute to understanding the formation of ambient SOA from small anthropogenic precursors. For instance, several compounds were detected and identified in both field and smog chamber SOA (e.g. malic acid, glyceric acid, erythritol, erythrose, and threonic acid) and suggest that they might be responsible for the formation and/or the growth of the aerosol in region impacted by 13BD emission. The presence of nucleophile compounds (acids, alcohols, epoxides) and aldehyde including dicarbonyls (e.g. glyoxal), and their potential for heterogeneous and multiphase processes is also very interesting. However, in the absence of authentic standards, it is difficult to accurately quantify the contribution of SOA originating from 13BD to ambient PM_{2.5}. Due to the health risks associated with 13BD and its reaction products, this work indicates the importance of increasing the inclusion of detailed chemistry of 13BD into photochemical models and local, regional and global models used to investigate ozone and SOA formation and health concerns to rural and urban areas.”

Comment # 3. “Table 2: I suggest the authors to add information about the experiments that they were found (i.e. high-NO_x or low-NO_x) and the concentrations for those compounds that the authors quantified.”

Response. See our response to comment # 6 (reviewer 1)

Comment # 4. “Figure 6: What are the reasons for the steep increase in the yield when 95% of the 1,3-butadiene is reacted? Is it because later generation oxidation products partition into the particle phase? The authors should this observation in a revised manuscript.
N. L. Ng, J. H. Kroll, M. D. Keywood, R. Bahreini, V. Varutbangkul, R. C. Flagan, J. H. Seinfeld, A. Lee, A. H. Goldstein, Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons. Environ. Sci. Technol. 40, 2283-2297 (2006)”

Response. To reflect the reviewer comment, the following sentences were added to the original manuscript and read:

“This growth curve can be divided in three regions (Figure 6). The first region is characteristic of no or very low aerosol formation. After ozone starts building up in the chamber (region II), more aerosol is formed as 13BD is reacted. After 13BD is completely reacted (region III), aerosol continue to increase, probably due to the oxidation of first and potentially second/third generation products resulting in a vertical section. Ng et al. (2006) reported a similar trend for compounds bearing two or more double bonds (isoprene, α -terpinene, γ -terpinene, terpinolene, limonene, myrcene, α -humulene, β -caryophyllene, and linalool).”

Ng et al. reference was added to the reference section.

Comment # 5. “Figure 9: This figure does not add much information to the manuscript. Do the concentrations of these compounds correlate well in ambient samples? Are the ratios of these compounds similar to what the authors found in chamber samples? If so, are they similar to high-NO_x or low-NO_x experiments?”

Response. We agree with the reviewer, figure 9 was deleted from the revised manuscript.