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Atmospheric Chemistry and Physics
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Discussions

Interactive comment on "Atmospheric oxidation of 1,3-butadiene: characterization of gas and aerosol reaction products and implication for $PM_{2.5}$" *by* M. Jaoui et al.

Anonymous Referee #1

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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 NOx 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,

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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. 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-NOx 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-NOx experiments into 1 table. Why did they do this? For chemical mechanism purposes, it would be more ideal to have separate tables for the

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NOx-free and NOx 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.

Specific Comments:

1.) Abstract and Table 2:

Can the authors state more specifically in the abstract how much of the organic aerosol they accounted for with their quantification for both the NOx and NOx-free experiments? Furthermore, if you do breakup Table 2 to keep the NOx and NOx-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.

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-NOx 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. Furthemore, 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.

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 flowtube 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 flowtube studies.

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.

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., MSn experiments)?

6.) NOx vs. NOx-free experiments and how this relates to RO2 chemistry:

For the NOx-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 13BD used in these studies. Furthermore, in the NOx 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 NOx and NOx-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 PM2.5 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.

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).

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.

9.) Figures and mass spectra for NOx-free experiments:

I suggest that the authors provide similar figures (i.e., chromatograms and mass spectra for SOA constituents) for NOx-free experiments. This information will be very helpful in understanding differences in the gas- and aerosol-phase chemistry. Minor Comments:

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)?

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)

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).

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.

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.

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!

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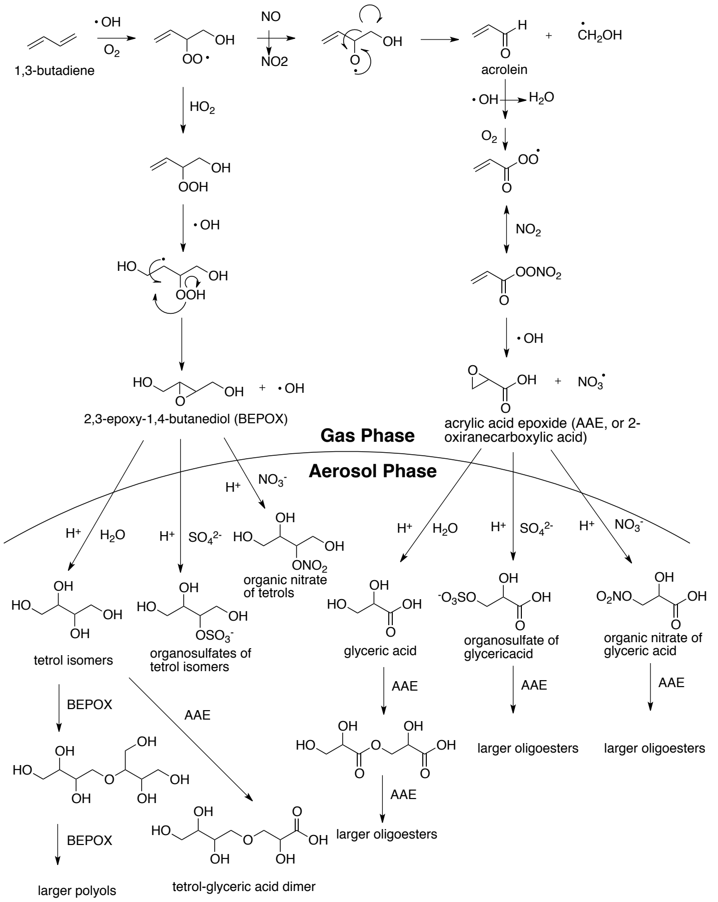

Fig. 1. Proposed gas- and aerosol-phase mechanism leading to 1,3-butadiene SOA formation