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Comment

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.

M. Jaoui et al.

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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 multifunc-

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tional 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.

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

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“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

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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, β -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.

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