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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Chemical characterisation of benzene oxidation products under high and low NO_x conditions using chemical ionisation mass spectrometry” *by* Michael Priestley et al.

Anonymous Referee #2

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This manuscript reported the measurements of benzene oxidation products with two CIMS using I- and NO3- as reagent ions. The discussions focus on (1) difference in products measured by I- vs NO3-; (2) difference in produces between one low-NOx experiment and one high-NOx one; (3) detected products vs the ones in MCM. The measurements are performed with the state-of-the-art instruments and the analysis in the manuscript is solid. However, the major issue is that the discussions are fragmented. Many interesting observations are presented, but it is a bit blurred how such detailed measurements of nearly 200 ions improve our understanding on the funda-

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mental oxidation mechanism of benzene, besides leaving the impressions that the benzene oxidation generates hundreds of products and the oxidation products are different between low- and high-NOx conditions. The manuscript can be largely improved if the detailed discussions can be synthesized in a coherent fashion. Overall, I recommend publication after major revision.

Comments 1. Many products more than 6 carbons (like C8, C9) have been detected. Please discuss the potential formation mechanisms of these compounds. 2. Some comparisons between measurement and MCM are not conducted in a meaningful way. For example, in Page 10 Line 351, it is claimed that compounds of formulae that match species in MCM compare 7.3% and 6.4% of the low and high NOx experiments, respectively. There are two issues in this comparison. First, the values depend on the extent of oxidation. For example, it is well-studied that the phenol yield in benzene oxidation $\sim$50%. MCM compounds should least comprise 50% of detected compounds when the secondary chemistry is negligible. Second, as the response factors in I-CIMS vary by orders of magnitude, the raw signal in Hz cannot represent the true product distribution. 3. Similarly, because of the two issues mentioned above (i.e., uncertainties in instrument sensitivity and extent of oxidation), it is unclear how meaningful the reported distribution of products is. The discussion on Page 10 Line 359 is one example. 4. Page 11 Line 375. How are these two values calculated? 5. Page 11 Line 396-397. This statement on the potential formation mechanism of C6H8O6, etc is too strong. The HOMs formation mechanism from benzene oxidation is unclear. For example, Garmash et al. 1 showed that the HOMs yield is higher in benzene oxidation than phenol oxidation. It lacks support to state that C6H8O6, etc can only be formed from phenol or catechol. 6. Table 1. Please include the initial concentration of benzene. I estimate that roughly 20-40% of initial benzene is oxidized in the experiments. Because benzene oxidation products are much more reactive than benzene, many detected products are likely from multi-generation chemistry. This should be clearly mentioned in the manuscript.

Reference 1. Garmash, O.; Rissanen, M. P.; Pullinen, I.; Schmitt, S.; Kausiala, O.; Tillmann, R.; Zhao, D.; Percival, C.; Bannan, T. J.; Priestley, M.; Hallquist, Å. M.; Kleist, E.; Kiendler-Scharr, A.; Hallquist, M.; Berndt, T.; McFiggans, G.; Wildt, J.; Mentel, T. F.; Ehn, M., Multi-generation OH oxidation as a source for highly oxygenated organic molecules from aromatics. Atmos. Chem. Phys. 2020, 20 (1), 515-537.

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