Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-819-RC1, 2020

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 #1

Received and published: 21 September 2020

Review of Priestly et al. “Chemical characterisation of benzene oxidation products under high and low NOx conditions using chemical ionisation mass spectroscopy.”

Synopsis of the manuscript. This study examines the products from the photooxidation of benzene in the presence and absence of nitrogen oxides (NOx) presumably with application to the ambient atmosphere. Mixtures of benzene, ozone, and water vapor in air with or without NOx are irradiated in a 1.45 m3 borosilicate glass chamber operated as a continuous stirred tank reactor (CSTR). For benzene to react in this relatively small environmental chamber, a robust source of hydroxyl radicals (OH) is needed. This is achieved through the photolysis of ozone at 254 nm giving O(1D) with then reacts with water present in the system to generate OH, although the photolysis of oxygen is also possible via the 185 nm Hg line. Once the system comes to steady-state at a chamber residence time (τ) of 2900 s, the gas-phase products are measured via a chemical ionisation mass spectrometer (CIMS) using I- and NO3- as the reagent ions. Multiple analysis methods to measure products, comparison with the Master Chemical Mechanism (MCM) model, a comparison of ring-fragmentation and ring retaining products, oxidation state analysis (OSA), and hierarchical cluster analysis (HCA) are used to interpret the CIMS product data. From the high resolution time-of-flight (TOF)-CIMS, empirical formulae for the ion peaks can be obtained with reasonable confidence which are then compared with stable MCM products and dozens of coincidences are observed. The OS developed almost exclusively for particle measurements (Kroll et al., 2011) are adopted for this work. The findings are all qualitative in that calibration factors are unattainable for the compounds of interest in this work. The interpretation includes findings for the volatility classification of the product distribution, differences in the importance of ring-fragmentation and ring-retaining products, and differences in the role of NOx in the mechanistic system.

Overall impressions. The findings are interesting and potentially valuable given the importance of benzene in the atmosphere. Moreover, the sophisticated instrumentation being used allows data to be obtained, which heretofore has been nearly impossible. The mechanisms of aromatic systems are extremely important for understanding both ozone and particle mass formation. Thus, the paper has great potential in adding to the body of mechanistic knowledge needed to predict these species. The paper is well written and reasonably well organized.

However, while the description of the findings in the abstract seems impressive, confidence in them quickly deteriorates upon further reading. For me that occurs at the beginning of Section 2. First, for the type of product study being undertaken, a 1.45 m3 reaction vessel is extremely small, which, of course, requires that the system be operated as a CSTR – a requirement more than just a means to homogenise the mixture. Since it was not stated, the vessel was probably uncoated and the OH wall loss must have been substantial and undoubtedly diffusion limited. This is an infinite sink thus, representing a constant gradient of OH in the system. Now we come to the production of OH. Creating OH from the photolysis of ozone at 254 nm followed by O(1D) + H2O strikes me as extremely dangerous for interpreting the data. Of course, the radiation is not only available to photolyze ozone but the other organics and the various nitrogen oxides in the chamber. Benzene has a strong absorption at 254 nm and likely being photolysed, depending on the quantum yield. The steady-state concentration of ozone is thus very important. Clearly, ozone does not react with benzene, but once fragmentation occurs, there are plenty of double bonds for ozone to react with, perhaps not as competitively as OH, but that only depends on the concentration of ozone being used. This leads to my first major complaint. Please give the concentrations or concentration ranges being used in the study. Better yet a table of the initial conditions: benzene, ozone, water (ppm), NO, NO2, chamber residence time is essential. A table of initial conditions should not be relegated to a supplementary section. It is ACP after all; there is no page limitation.

Onto the OH concentration in Table 1. I simply find it implausible that OH concentrations of 10(+8) molecules can be formed in what is basically a smog chamber. (Obviously, high concentrations of OH are generated in flowtubes operated on millisecond timescales. Not here.) There are just too many things for OH to do. As mentioned, walls and double-bonds are but two. This is all based on the p.5 equation for benzene loss and the low rate constant for irradiations over a period of minutes results in high calculated OH levels. First, I would call Column 3, benzene loss because that is what is measured. Second, the absolute benzene loss is irrelevant. Thus, either the initial benzene concentration in Table 1 caption or percent loss in the table should be given. In my opinion, the observed loss is some combination of reaction with OH and photolysis by 254 nm mercury radiation. This would thus lower the calculated OH concentration. However, if we take these concentrations seriously recognizing that the products are likely to be considerably more reactive than the parent compound, it is easy to believe that 3-5 generations of products are likely to be present in the chamber with the CIMS measuring all of them, and perhaps with increased oxidation, later generation products are being measured more sensitively than earlier generation products.

Of course, a major issue as noted in the manuscript is a lack of calibrations for products formed. This is unavoidable in these types of experiments. This is even worse when using a CIMS since the sensitivity of seemingly similar compounds can be one or more order-of-magnitude different. Therefore, to compare signal strength, as though implying, they are linearly related to concentration is a rapid path to misinterpretation. I would recommend that graphics based on signal strength should be treated very carefully and worded conservatively.

The comparison with MCM I find both tricky and the reverse of the experimental-deterministic model paradigm. First, given the complexity of MCM and the scarcity of quantitative data upon which later generation (beyond first) mechanisms are based I would describe the mechanisms at best as being tentative. It would be better to use the data in these experiments to provide some credence for later generation MCM product predictions, of course, not stating anything about predicted yields. Otherwise, it looks like “the blind leading the blind”.

Something needs to be added regarding the possible role of NO3 radicals in the system, especially given the number of oxidized nitrogen compounds being detected. Given what I expect to be a high ozone concentration (ppm), its reaction with NO2 is probably occurring to some non-negligible degree. I see no evidence provided that autooxidation plays an important role in the system. Perhaps, it does, but not from the data presented.

Of course, it may be that the authors have considered and addressed the issues above and similar issues. However, these issues are critical to understanding how the data are interpreted and must be included in the paper, if the study is to have any credibility.

Printer-friendly version

Discussion paper

Finally, I believe it would be valuable to show how the findings from this paper fit into the understanding of benzene oxidation. Thus, it is my opinion that this manuscript needs substantial work before it is published.

A few line-by-line comments.

Line 77. Johnson et al. 2005 is a rather poor reference. Dicarbonyl aldehydes were shown to be formed in aromatic systems by the mid-1980's (e.g., Dumdei and O'Brien, Science, 1983; Shepson et al. JPC, 1984; Dumdei et al, EST, 1988.)

Line 132. I am not sure what this sentence is saying. Mass closure, if that is ever possible, will require a lot more than complementary instruments. In fact, as these experiments are conducted, each product generation probably gets you further and further away from "mass closure". I would reword the sentence in a more realistic fashion and perhaps with a bit less jargon.

Line 148-49, Table 1. Is it true that the reacted benzene concentrations were identical to three significant figures for the experiments shown? The actual measured data would be more helpful together with the percent benzene loss.

Line 153. The sentence beginning in this line is a "red herring". Otherwise, reactions of benzene with ozone in the chamber would lead to product distributions being a complete mess. If benzene and ozone were introduced together, there would probably be less of a mixing issue.

Line 204. How about calibrations for the instrument sensitivity for the inorganic nitrogeneous compounds? Were any undertaken?

Line 246. I am not sure what the term "time series" means in the context of these experiments. They were all done under steady-state conditions.

Line 275. This would be an excellent place to include a table for the initial conditions. This would also allow us to see how many experiments the data is based on. One of my main questions is how many different residence times were tested. For example, it would have been helpful to have one experiment at τ=1450 s and another at τ=5800 s. (Note: I am not asking for any additional experiments if only one residence time was tested.)

Line 280. Again, I am not sure what “time-series behavior” means when conducting experiments in a steady-state reactor.

Line 283. The other studies mentioned were probably performed with the experiment(s) being conducted in a batch mode. However, for a CSTR used in reactive systems, a broad spike occurs at the beginning solely from the dynamics of a reacting system reaching steady state. Thus, three or four residence times are typically needed to achieve steady state. Moreover, I suspect the system is not fully homogeneous and certainly not at the beginning of the irradiation. OH is certainly a problem – high concentrations near the lamp and low concentrations near the wall. There is also the question as to whether the radiation is optically thin. I believe there are many factors leading to this “spiking” with gas-aerosol partitioning probably being a minor one.

Line 381. I find this section a bit too speculative and should be written more conservatively. I again repeat my comments regarding MCM and the CIMS data. Certainly, the CIMS data has no quantitative significance, since the sensitivities are typically all-over-the-map. This section would be a good place to consider what the uncertainties are present in these experiments.

Line 421. A consideration of the photolysis of the nitrogenated products at 254 nm might be considered in this section as well.

Line 470. The first sentence of the conclusion is totally unsupported. The sentence reads as though NOx is decoupled from OH. Experiments having steady-state OH concentrations near 10(+8) molec/cc have at best marginal relevance even with atmospherically plausible levels of NOx being tested. I would be far more circumspect in making atmospherically relevant statements from this dataset. At minimum, additional qualifying statements need to be provided in this paragraph. I would highly recommend simply leaving out the first paragraph.

Line 486ff. From this point on, I think the data is being overinterpreted.

Whilst it may be trivial, “whilst” strikes me as being rather anachronistic, perchance appropriate in poetry, less so in scholarly writing.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-819, 2020.