Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-161-RC1, 2020

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluation of the Chemical Composition of Gas and Particle Phase Products of Aromatic Oxidation" *by* Archit Mehra et al.

Anonymous Referee #1

Received and published: 10 April 2020

This paper reports results of mass spectral analyses of gas- and particle-phase products formed in the reactions of several C9 alkylbenzenes and 1-methyl naphthalene with OH radicals in the presence and absence of NOx. The products are identified by mass and the atomic numbers corresponding to the masses, but other structural information is not provided. A large number of products are observed, with carbon numbers ranging from 2 to the number of carbons in the starting compound, and although the product distributions differ depending on the compound and NOx levels, the contributions of products that are unique to any given compound are relatively small. The product distributions are discussed in terms of extent of oxidation, whether the product is likely to be from fragmentation or ring retaining (based on atom numbers), the ex-

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Discussion paper

tent to which the products are consistent with MCM, and how the product distributions compare with what is observed in the atmosphere.

This paper gives potentially useful information on products formed from aromatics, but I have some concerns about how representative the experiments are of atmospheric conditions and the correspondence between the ion signals and actual product yields. In addition, I think the presentation and discussion of the results could be improved, especially with regard to mechanistic implications. The major issues I see are discussed below, followed by a summary of other issues or suggestions.

Major comments

There should be more discussion of how their experimental system differs from the atmosphere, and also the extent of secondary reaction of products formed. Can the very low wavelength UV light they use to generate the radicals (and NOx) photolyze the reactants or products and cause products to be formed that would not formed in the lower atmosphere or deplete products that otherwise be important? They give an "OH exposure" number for their experiments and state that it is similar to "Chinese megacities", but they do not give the range of OH exposure numbers in Chinese cities or elsewhere or citations for them. What is the fraction of initially present aromatic hydrocarbon that reacts during an experiment? Do they have an estimate of how much of observed products are from multi-generations of reaction? Have they attempted to model their experimental conditions to obtain information about representativeness?

The major results are presented primarily as figures giving fractions of ion signals that have various characteristics, plus some summary information given in the text. The paper has a "Supplementary Data" (SD) section to give additional information, and ideally it should have the information that is summarized or shown graphically in the text, so the reader can examine it in more detail, to either to verify the discussion in the paper or perhaps to gain other insights. The SD does have 20 tables giving the "top 20" product distributions for each of the 2 types of experiments with 2 analysis

methods and 5 compounds, but it only has the information regarding the ion detected and true/false flags indicating whether it is common or unique among the compounds studied and whether it has the same molecular formula as a product predicted by MCM. That is not the most interesting information they could present. These tables should include at least the relative ion signal intensity, and ideally also the classifications as ring-scission, ring-retaining, HOM, DBE, and other classifications they discussed or summarized. Instead of just indicating that this may be predicted by MCM, they should give the name and structure of the products(s) corresponding to this molecular weight. This would make the tables much more interesting and greatly increase the value of this work and information content of the paper.

The discussion of MCM and mechanistic implications could be improved. It is not surprising that MCM does not predict the full range of products they observe, expecially HOM, because (1) the version of MCM that is currently online does not have autooxidation reactions that are now believed to be important, and (2) it employs lumping or reduction methods when it gets to 3+ generation products of the compounds represented. What might be more interesting would be high yield products that MCM predicts that they DO NOT observe. These should be listed, or it should be stated that there are no such products if that is in fact observed. One way to do this would be to run MCM to model the conditions of the experiments, summarize the yields predicted, and list these against the observed relative ion signals of products with the same molecular weight in the experiments. Are the products observed more consistent with the revised mechanisms predicted by Wang et al (2017)?

The tables in the SD indicate that no signals were observed for glyoxal (C2H2O2), which is known to be formed in significant yields from all products (and is predicted by MCM). Also, methyl glyoxal (C3H4O2) should also be seen as a product from the trimethylbenzenes and propyl glyoxal (C5H8O2) should be formed from propyl benzene. Does this method not work for alpha-dicarbonyls? If so, state this. Or are they all rapidly photolyzed away by the high UV in their system? This gives me some doubt

about the credibility of the experimental system.

It is stated that they did not correct for sensitivity of the ion signals to the actual concentrations in their analyses, apparently because of the complexities involved. However, since they are using the ion signal as a surrogate for the yields, it would be useful to estimate the uncertainty or potential for error when not making this correction.

Other Comments

The abstract should state what they mean by "product signal" and describe the analysis methods in a few words.

The statement in the abstract that the MCM "highlights" missing product pathways, but it is not clear from that statement if it is the MCM that is missing something (which is the case), or the experiments aren't finding something that MCM predicts (which may or may not be the case – see comments above – but is probably not what the authors meant to say).

The observation that "A large proportion of the ring scission products observed in the particle phase are more oxidised than those previously reported" is significant and should be included in the abstract.

Was there only a single experiment of each of the 10 types listed on Table 1, or are the concentrations given there the averages of several experiments. If the latter, indicate the number of experiments?

The legend on the top right on Figure 1 should be moved to where it doesn't get in the way of the data being shown.

The labels indicating the compounds on Figure 3 need to be larger and easier to read. Right now they are in a very tiny font hugging the axes and are hard to see.

Could they use a different color on Figure 3 to indicate N-containing ions?

Table 2 would have more impact if it were shown as a bar-plot figure. It clearly shows

n-propyl benzene as an outlier among the alkylbenzenes in terms of NOx effects. (I would have thought isopropyl benzene would be more likely the outlier, since the autooxidation proposed by Wang et al (2017) may be more important for this compound.) It might be useful to also include their estimates of ring-retaining and ring-scission fractions on this same table or figure, since there are also discussed in the text.

It is not clear what is the purpose of table 3, giving MCM branching ratios for various types of reactions, since they give no comparison of this with their data. If they can identify their products by the classifications on this table, why don't they give the relative amounts derived from their data? If not, why include this table and discussion?

The "Authors Contributions" section does not list all the authors.

The supplement document does not identify the title, authors, and journal of the manuscript it goes with.

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