**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Analysis of high mass resolution PTR-TOF mass spectra from 1,3,5-trimethylbenzene (TMB) environmental chamber experiments" *by* M. Müller et al.

Anonymous Referee #2

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This paper describes an experimental study of the oxidation of 1,3,5-trimethylbenzene (TMB). The oxidation is carried out in a large environmental chamber, and reactants and products are monitored using a high-resolution proton transfer reaction mass spectrometer (HR-PTR-MS). Results are described in terms of both individual product species and bulk properties of the reaction mixture (total carbon, O:C, oxidation state), all of which are compared to results from the Master Chemical Mechanism (MCM). This is a very nice paper, utilizing a state-of-the-art analytical technique to better understand a highly complex chemical system. The experiments were carefully done, results are presented well, and the paper itself is clear and well-written. My main concern arises from quantification of the MS signal, which is not described in very much detail but is

important to most of the analysis and results. If this is addressed (along with other minor concerns), this paper certainly should be published in ACP.

Central to much of this work is the quantitative measurement of absolute concentrations of individual organic species. Such measurements require an accurate calibration of all mass spectrometric signal; however there is little discussion of the absolute accuracy of such measurements, and the description of the calibration approach (in the Supplement) is quite confusing. Some questions/concerns about this quantification: - A brief description of calculations of proton-transfer rate constants is provided, but then it is stated that "Calculated rates of the expected products were linked to experimental calibration results." What exactly does this mean? In other words, how do the use of rate constants and the use of acetone sensitivities relate? - A stated error of 30% for generic products is given – what data is this value based upon? - Based on Table S1, acetone seems to be detected more sensitively than nearly any other compound – meaning use of acetone as a calibration standard is likely to lead to an overestimate of most species' concentration (which would in turn lead to an overestimate of carbon balance). - All the species in Table S1 are monofunctional; how do the response factors change for multifunctional species (e.g., diols, diketones, etc)? - Were fragments (e.g., M+1-H2O) and clusters (e.g., M+1+H2O) included in the total ion signal when calculating concentrations? All these concerns should be addressed in the manuscript (and not just the Supplementary Information), since they relate directly to most of the results/conclusions of the work.

Other comments:

Section 3.1: The title of this section does not relate very well to the content – this section is mostly about comparing measurements of individual species (as determined with HR-PTR-MS) to MCM results.

Sections 3.1-3.2: Throughout these sections, experimental results are compared to MCM data. The similarities/differences are noted, but rarely commented upon. I think

it's important to at least acknowledge explicitly that the discrepancies could arise not just from experimental problems (e.g., fragmentation or clustering in the MS) but also because of shortcomings of the MCM scheme. As a first test of how well MCM describes the observed chemistry, agreement between simple modeled and measured chemical parameters - TMB, NOx, O3 – should be discussed.

25876, line 7 (also last sentence of the Supplement): it is mentioned that the different voltages allow for examination of clustering, but this is never discussed in the paper. (It might explain the very small differences in O:C in Figure 6a.)

Section 2.2: How were blank runs carried out? It is highly likely that NOx + light + "clean chamber air" would lead to some formation of secondary organics. A discussion of the role of these organics, and the subtraction from all PTR-MS data reported, is needed.

25878, line 4: It is stated that the MCM simulations are limited to 1st generation products only; how is this consistent with the decrease in some modeled concentrations (i.e., Fig 5b)? If the simulations are limited to 1 generation only, this seems like a major possible source of model-measurement discrepancy. Oxidation products of aromatic hydrocarbons tend to react with OH substantially faster than the parent hydrocarbons (due to the addition of OH and other activating groups to the aromatic ring), so the formation of 2nd- (and later-) generation products is more or less unavoidable. Moreover, the data (e.g., Figs. 2, 3, 5, 6b and 25885 lines 2-4) show clear evidence for multigenerational chemistry. Ignoring such chemistry is therefore a serious limitation of the model; this either needs to be corrected, or discussed in some detail.

25881, lines 3-8: here ions are assigned to specific species, with no discussion of the reason the assignment was made. It seems that isomers or fragments of larger species could also play a role. The wording here (and in other parts of the manuscript, such as the labels of Fig 2) should be changed to reflect the fact that these are molecular assignments of measured ions, not unambiguous measurements of individual species.

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25881, lines 8-11. The agreement between the data at different drift tube voltages does not necessarily mean that there is no fragmentation – it just means the amount of fragmentation is equal in both cases. An ion fragmentation channel that has a low activation energy could occur quantitatively in both cases.

25881, lines 25-26: These are the upper and lower bounds to PAN concentrations only if those are the only two (major) ions formed after protonation of the PAN. Has this been verified with an authentic standard?

25881, lines 22-27: the assignment of different ions to a single species can be constrained by comparing their temporal behavior. In the absence of matrix effects, a given molecule will produce all ions in fixed ratios – any deviations from this indicate contributions by other parent molecules. Can this sort of analysis be used to better constrain concentrations of PAN? How about for other species (as in lines 5-6)?

25882, lines 1-3: were these blank experiments carried out in the presence of NOx (and/or HONO)? That would seem to be the important point of comparison, not simply the irradiation of the chamber.

25882, line 7: the referenced paper by Praplan et al. (2011) is not in the References section.

25882, lines 17-20: The reader is referred to the Supplement for an explanation of why the data show "no significant amount of nitrates or anhydrides". However, the Supplement doesn't really address this question, other than saying that such species tend to have a neutral loss of HNO2 or HNO3. Given that, it would seem the PTR-MS cannot be used to assess the importance of oxidized-nitrogen-containing organic species, since the bulk of the ion signal would show up as $CxHyOz+$ ions. How then are the authors confident that no nitrates or anhydrides are formed? Also, what about nitroaromatic compounds – common products of aromatic oxidation that are chemically distinct from nitrates and anhydrides?

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25882, first paragraph in section 3.2, and Figure 4: Do these values (from both the experiments and the modeling) include particulate organics? What about losses of organics to the chamber walls?

25883, lines 6-7: It would seem the best comparison is between the summed PTR-MS measurements and the amount of carbon available (from the TMB reacted), rather than the modeled carbon available. Ideally the two are the same – that is, the modeled and measured TMB profiles agree. Is this the case? This agreement (which is actually very important for model-measurement comparison of product formation) should be discussed explicitly.

25884, lines 18-19: What concentrations of nitrogen-containing compounds does MCM predict?

25884 line 26-25885 line 18, Figures 6,7,9, and elsewhere: The manuscript should make more of a distinction between the two ways to calculate O:C(gas): with and without TMB. While including TMB can be useful for describing the entire system, excluding TMB is absolutely crucial whenever discussing reaction products, since much of the changes to O:C are driven by the loss of TMB. Thus I would recommend focusing more on the O:C calculated without the TMB. For example, lines 11-12 of the Abstract – "The O:C ratio in the particle phase was about twice the O:C in the gas phase" – seems to imply to that gas phase oxidation products are less oxidized than particle-phase products saying that O:C in the gas phase, when the opposite is actually true (p. 25885, line 26). Similarly, I think a version of Figure 9 that includes only products could be very interesting.

P. 2885, lines 16-18: In what way is this effect "obviously small"? The general agreement between the measurements and the MCM results doesn't necessarily tell us that the PTR-MS is measuring everything correctly, only that it's measuring what the MCM predicts – it is possible there are errors in both the model and the measurements.

Section 3.3: meaningful analysis of the O:C (or OSc) of the aerosol would require that

all (or at least most) of the SOA components are being measured by the PTR-MS. This can be verified by comparing total PTR-MS signal (scaled to the amount of material on the filter) to the real-time measurement of the aerosol mass (by an SMPS, AMS, etc). How good is this agreement?

Section 3.3: it should be noted here that the higher temperatures of the desorption could promote fragmentation of the analytes (forming H2O, CO2, etc), exacerbating the underestimate of the O:C of the particulate organics.

Throughout: there are seven individual references to the Supplementary Information, which is only 2 pages long! There is little reason this information needs to be in a separate document, and should be included in the main text.

Figure 2: an inset showing an HR mass spectrum at m/z 113, to demonstrate the separation of ions would be helpful here.

Figure 3: curves showing MCM predictions are needed here.

Figure 8: the y-axis label should be changed; it's listed as intensity but is actually a fraction.

Figure 10: Sizing the markers by ion intensity (or ppbC) could be useful. Also, there is clear evidence for species with more than 9 carbons (oligomers? Background organics) in the particle phase; these should be commented upon in the text.

Typos: 25886 line 14, 25888 line 15.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 25871, 2011.