

## ***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 #1**

Received and published: 19 October 2011

The authors describe photo oxidation experiments of trimethylbenzene (TMB) in a 27 m<sup>3</sup> smog chamber using a novel PTR-TOF instrument. They compare the measured gas phase products with simulations using the master chemical mechanism (MCM) and find generally good agreement between the MCM predictions and the measured species. This part of the manuscript I find interesting and well documented –worth of being publishing in ACP. However, I have major concerns about the analysis of aerosol filter samples which are also presented as part of this study. There are two reasons why I ask for major revisions:

- 1.) From the current manuscript it is not clear if blank filters have been analyzed.

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Background contamination certainly exists and has to be subtracted properly. Fig 10 reveals that many peaks with more than 9 carbon atoms (i.e. the carbon number of TMB) have been detected in the filter measurements. Does this signal really come from collected SOA? I suspect that these peaks are due to background contamination and should not be accounted for in the analysis. Similarly, all other analyzes done with filter measurements could be significantly biased if no proper background correction has been applied.

2.) The authors do not provide a quantitative analysis of the detected SOA species. The total SOA mass can be estimated - for example from SMPS data. The fraction of SOA detected with the PTR-TOF should be constrained and reported.

If the authors can provide the requested analysis the SOA part can be a valuable addition. Otherwise I suggest to remove the SOA related part and to concentrate on the interpretation of the gas phase.

Specific comments:

P25876

19: give the corresponding pulse time for m/z 600

23-24: the sentence 'Co-addition . . .' is not clear and understandable.

27-28: what do you mean by 'duty cycle correction'? More explanation needed.

P25877

4: typo 'o'

Section 2.1.2: within the accuracy of 20 ppm it is hard to imagine that the attribution of an empirical formula was always unequivocally (for example in *Atmos. Chem. Phys.*, 10, 10111-10128, 2010 the authors found up to four possible identifications for mass peaks obtained with a similar instrument). This needs discussion!

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Section 2.2.1. add date and time of the experiments.

ACPD

Section 2.2.3: see major comments above.

P25878

17: give the size of the PTFE filter.

21: give the size of the aliquot that was inserted into the oven.

P25879

1-2: the statement is misplaced and should be moved to section 2.1.1 or to the supplement.

18-21: I was not able to follow this discussion.

Section 2.4: there is no information on how N-containing compounds (PAN!) were treated.

Section 3.1: The title is not appropriate. The section largely discusses the observed VMRs. Comparison with PTR-MS is a minor aspect.

P25881

12 and 14:  $\text{C9H13O}^+$  should actually be  $\text{C2H5O3}^+$ , shouldn't it?

Section 3.3: Another reason for declining O/C with temperature could be charring.

P25886

10-11: '... somewhat less oxidized ...' is not correct. Fig 8b shows that the number of O atoms is actually increasing with higher temperature. I suggest '... somewhat lower oxidation state ...'

Section 3.4: I find the discussion of the van Krevelen diagram rather weak. What do we learn from this analysis?

11, C10587–C10590,  
2011

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14-15: I guess that the authors refer to Fig 9.

14-15: Fig 9 does not show a higher O:C of exp 2 as compared to exp 1!

Table 1: add a column giving start date and duration of all experiments

Table 2: it is impossible to understand the meaning of numbers 1134 and 324 in the last column.

Table 3: improve layout. It is not always clear to which species the numbers in the last two columns refer to.

Figure 1: This scheme is not necessary and can be omitted. It is only used to show the 3 initial reaction pathways. These pathways are explained in the text anyway. Together with Table 2 this provides sufficient information.

Figure 4a: what is the bold black line.

Figure 6b: I am not sure this presentation really makes the point. Furthermore it contradicts the statement made in the text: e.g. O/C 0.5-0.55 peaks after 4 hours while O/C 0.65-0.7 already peaks after 2.5 hours.

Figure 10: CO is displayed in the plot. This is not a common PTR-MS compound. How was it measured? For the filter measurements detection of CO could be another indication of charring.

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

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