

Interactive comment on “Modelling of the photooxidation of Toluene: conceptual ideas for validating detailed mechanisms” by V. Wagner et al.

Anonymous Referee #1

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General Comments

This paper reports a new strategy for chemical mechanism analysis in tropospheric chemistry taking the very complex gas-phase oxidation of toluene as an example. OH radical balance and ozone formation were investigated under particular consideration of the different oxidation pathways of the hydrocarbon. The tasks performed were referred to a smog chamber experiment carried out in the European photoreactor EU-PHORE in Valencia, Spain. The paper content is appropriate for publication in ACP. The, mostly theoretical, work is of high quality. The way of system analysis regarding OH radical balance as well as ozone formation presented in this manuscript offers interesting information on the reaction mechanism treated and can be easily adapted to

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other systems. However, to my mind, a number of aspects need some improvement before the paper is finally released (see below).

Specific Comments

pages 2-3, "Introduction" Although Figure 1 gives a comprehensive overview of the reaction products of toluene oxidation, some few general structures and reactions reflecting the main pathways of the OH-initiated degradation of toluene would be helpful for those readers that are not too familiar with the chemistry described here.

pages 5-6, "The smog chamber experiment" Regarding the fact that the whole theoretical work and the conclusions of the present manuscript refer to only one smog chamber experiment, the information given for this EUPHORE study is rather poor. In my opinion, much more background information on this study is necessary. Which analytical devices were used? It is well known that the measurement of e.g. ozone and NO_x by commercial analysers (UV absorption and chemiluminescence, respectively) is often subject of interferences by various factors under "smog" conditions. Therefore it is recommended to obtain these concentrations by FTIR spectroscopy. The plots of Figure 2 indicate that this is the case here, but the authors have to clarify this point in the text. Were the results found for the experiment at 22/10/97 also obtained for further EUPHORE studies on toluene oxidation? To my knowledge, a high number of toluene experiments have been carried out in the EUPHORE facility during the last years. Accordingly, it should be possible to find more experimental data sets for a confirmation of the model results presented here. This would lift the outcome of the present work to a safer level.

pages 6-7, "Product yields" Does this section need to be so extensive? Since product measurements are not given in this manuscript, I would propose to integrate the information on product yields in a more compressed form into the "Introduction" section.

pages 10-11, "Time profiles of new OH production" It would be interesting to see the modelled c/t profiles for toluene, NO_x and ozone when the additional OH source was

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used. The authors should consider an additional corresponding figure for the revised manuscript. Due to its nature as a very effective radical precursor, an additional HONO source must be carefully set. Accordingly, the reader might be interested, on which basis the source strength of "background HONO" was estimated. At the end of this section, it is not clear to the reader whether the observed disparities in experimental and modelled toluene c/t profiles are mainly caused by a lack of mechanistic information, by unknown wall effects or by a combination of both. I know that this question is not easy to answer, but the authors should try to point out more clearly, which source of uncertainty appears to be the dominant one.

pages 13-14, "O₃ sensitivities" The calculation of ozone isopleths for smog chamber studies is an interesting aspect that is not part of the "usual" analysis of such experiments. However, it is not surprising to obtain isopleth profiles similar to those for the "real" troposphere. Regarding this, I am not sure if it is necessary to show Figure 9 in the present manuscript. However, if the authors decide to keep the isopleth section in the manuscript, they should remove the artefacts shown and explained in Figure 9, since they would only confuse the reader.

pages 15-16, "Conclusion and implications" The present study shows the well-known "dilemma" of mechanism validation based on smog chamber studies. In the real world, the reactants' concentrations are normally lower than in the chamber and the VOC/NO_x ratios are often different. Accordingly, mechanisms tested under chamber conditions might only yield acceptable results in urban (source-near) regimes. The authors should briefly discuss this in their concluding remarks. Furthermore, the community of mechanism applicants would be interested if the MCM3 toluene scheme can be used as a basis for revised condensed aromatic VOC degradation schemes. Regarding this, the authors should consider for future activities the application of the MCM3 toluene scheme to the smog chamber oxidation of a simple "surrogate" VOC mixture containing alkanes, alkenes and aromatics, which is currently the usual testing procedure for condensed tropospheric chemistry mechanisms.

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Concluding Remarks

The present manuscript describes an interesting and ũ to my knowledge ũ new way of analysing chemical mechanisms in tropospheric chemistry. In particular the method of determining the fractions of OH production caused by the different oxidation pathways of a VOC promises an effective tool for the improvement of understanding the reaction sequence of more complex hydrocarbons. The weak point of this manuscript is that it is not able to answer the final question, if the large disparities between modelled and experimental c/t profiles of toluene, NOx and ozone are due to mechanistic gaps or uncharacterised chamber effects. To my knowledge, this problem always occurs when single hydrocarbons are oxidised in a smog chamber, and both possible error sources, mechanistic gaps and chamber effects are added up to a maximum of uncertainty. That might be the reason why e.g. condensed tropospheric chemistry mechanisms (such as SAPRC, RADM2 or RACM) are traditionally tested versus the smog chamber oxidation of VOC mixtures. In such studies, only a small fraction of OH is consumed by each single VOC, which reduces the negative influence of uncertainties in the single degradation pathways. Recent studies have also shown that the influence of chamber effects is weaker when VOC mixtures are oxidised. However, this procedure is not the method of choice if the "real" oxidation pathway of a VOC has to be worked out.

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