

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

V. Wagner et al.

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We are grateful for the comments of referee #1 and address the points raised in the following.

Comment 1

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.

Response 1

We have now added an additional figure showing the intermediates of the early steps

of the toluene oxidation as discussed in current literature.

Comment 2

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.

Response 2

2.1) To give more detail on the analytical techniques employed during the 22/10/97 experiment we have added the following paragraph to section 3.1:

"The experiment providing the most suitable dataset is the 22/10/97 toluene- NO_x system studied at the large-volume outdoor smog-chamber EUPHORE, located in Valencia, Spain. The hemispherical chamber consists of FEP (fluorine ethene propene) foil and has a volume of 195.5 m^3 . The experiment was conducted as a classical smog-chamber run in which toluene (482 nmol/mol) and NO (134 nmol/mol) were injected into the dark chamber. To start the reaction the protective housing was

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retracted so that the chamber was exposed to sunlight photoinitiating the toluene oxidation. The concentrations of toluene, NO, NO₂, and ozone were measured with a FTIR Spectrometer (Nicolet Magna 550) in combination with an open path white cell (optical path length, 526 m). For the measurement of the photolysis rates of O₃, NO₂, HCHO and HONO a spectroradiometer (Bentham DM300) was employed."

2.2) The conceptual study presented in our paper was part of the EXACT project (March 2000 - March 2003) that aims to further develop and to validate the aromatic mechanisms of the MCM. It was stated right at the beginning of the project and one of the objectives was to investigate current shortcomings in the toluene mechanism and to set the baseline for two extensive validation campaigns that took place in September 2001 and June 2002 at the EUPHORE smog-chamber. To find a suitable dataset for our model study all toluene experiments carried out at the EUPHORE chamber, that were available at that time, were considered.

The main requirements that need to be fulfilled for the validation experiment are the following: 1) The concentration of toluene and NO_x have to be moderate to be as close as possible to atmospheric conditions. 2) It must be a classical smog-chamber experiment in which, once NO_x and toluene are injected and the cover of the chamber opened, all parameters of the system are left unchanged. 3) It must be an experiment with no additional radical sources or radical scavengers added. 4) A complete data set is needed for toluene, O₃, NO_x, and photolysis rates, preferably obtained by FTIR measurements.

Indeed, from experiments that were available at the time our study was carried out only the 22/10/97 fulfilled all of the above requirements. For that reason, currently, we cannot present any other quantitative model-experiment comparisons for toluene. However we have analysed 4 further experiments for which at least two or three of the above criteria were fulfilled and for all of them the model-experiment comparison shows the same qualitative behaviour as for the 22/10/97 experiment: The model strongly under-predicts the oxidation capacity of the system and over-predicts the O₃

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production by up to a factor of two.

The two extensive EXACT campaigns, mentioned above, aimed to generate high quality datasets for the validation of aromatic mechanisms. In these campaigns the design of the experiments was to a great extent based on results from our model study and the experiments were tailored to retrieve the maximum information on shortcomings in the current mechanisms. The datasets of the EXACT campaigns are now in a state of analysis and although final results are not yet available preliminary qualitative analysis shows very similar model-experiment discrepancies as for the 22/10 /97 experiment. For this reason the authors are confident that the results presented for the 22/10/97 experiment are on a very sound level. It is planned to publish results of the EXACT campaigns including detailed analysis of model- experiment comparisons for toluene-NO_x systems sometime 2003.

Comment 3

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.

Response 3

The authors believe that this section is important to give the reader an impression how little is currently known about the intermediates of the toluene system and how ambiguous information on product yields still is. The yields of intermediates in aromatic systems is one of the pillars of information needed for the development of detailed mechanisms. For that reason we believe that the section on product yields is necessary and appropriate. The introduction is kept very concise and focussed on the development and the emergence of new theories on degradation routes. Owing to the encouraging comments of referee #2 on the introduction we like to keep it as concise as it is and prefer not to mix the "introduction" section with information given in section 3.2.

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Comment 4

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 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.

Response 4

4.1) We have added the model run with the artificial OH source to Fig. 2.

4.2) Further information on the background HONO source is now given in section 3.2 "The model simulation" (p 6.):

"Another side effect of the injection of NO into the chamber is the production of traces of HONO, which is almost certainly generated from the reaction of the newly formed NO_2 at the chamber wall (see discussion in section 4.2). In the 22/10/97 experiment the initial HONO concentration was below the detection limit of the FTIR instrument of around 5 nmol/mol. From earlier experiments in which HONO formation has been investigated, we know that the initial HONO concentration depends on the history of the chamber and the NO_x loading. Based on information from those chamber characterisation studies we have estimated a HONO background concentration of 0.5 nmol/mol for the 22/10/97 experiment and have initialised the model accordingly."

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4.2) To clarify the point of whether chamber effects have a significant influence on the radical budget in the 22/10/97 experiment we have added the following paragraph p 10:

"The analysis of the radical budget also gives information on the importance of chamber effects for the radical turnover in a toluene experiment. Based on characterisation measurements at the EUPHORE chamber the radical production caused by wall reactions can be described by a process in which gas-phase NO_2 is transformed into HONO. Thus, the rate of HONO production on the walls is a function of the NO_2 concentration in the chamber. For this process ($\text{NO}_2 \rightarrow \text{HONO}$) an average rate coefficient $k_{\text{HONO},\text{wall}}$ of $(1.15 \pm 0.45) \cdot 10^{-5} \text{ s}^{-1}$ has been established for the EUPHORE chamber. Unfortunately HONO formation is not a constant but also depends on the history of the chamber, so that the actual source strength of HONO production for a particular experiment is not known. However, the average value for $k_{\text{HONO},\text{wall}}$ gives a good first guess for wall production of HONO and was used in the simulations of the 22/10/97 experiment.

Over the whole course of the 22/10/97 experiment the total OH production by the photolysis of HONO resulting from wall reactions is only 9 nmol/mol compared to a total OH production in the toluene system of 371 nmol/mol. Even if we double the rate constant for the conversion of NO_2 to HONO, OH production by chamber effects would still be less than 5 % of the OH production of the toluene system.

For conditions such as those in the 22/10/97 experiment the effect of wall produced radicals on the OH production in the early and middle stages of the experiment is certainly minor and cannot explain the model-experiment discrepancies in the OH production and the toluene decay. However, as over the course of an experiment a complex mixture of highly reactive organics and NO_y species are transferred to the walls, at the end of an experiment (final 1.5 h) the situation becomes more uncertain. There might be a variety of wall related processes producing radicals, which so far have not been considered. Therefore, it cannot be ruled out that at the end of an experiment chamber effects have indeed a significant impact on the radical production

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in the system."

4.3) For the early and middle stages of the experiments it is most likely that a misrepresentation of the chemistry in the ring-opening routes is responsible for the model- experiment discrepancies. This is pointed out by the authors in the second paragraph on page 11.

Comment 5

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.

Response 5

Isopleth plots have turned out to be a very helpful tool for the design of smog-chamber experiments in particular for the design of validation experiments. They allow finding of appropriate initial conditions for running an experiment in a particular regime (NO_x, VOC limited). As this is a new approach for the design of smog-chamber experiments that has not been reported elsewhere, the authors believe that this is an important piece of information that should be kept in the paper. We have re-run the calculation for the O₃ isopleths to be able to generate a plot without gridding artifacts. The isopleth plot in the revised manuscript is updated accordingly.

Comment 6

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

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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.

Response 6

6.1) As pointed out in the introduction, the broader aim of our paper is to give an overview of the status of toluene modelling based on a master chemical mechanism. We have applied a novel method to analyse the radical budget of a smog-chamber experiment. Based on radical budget calculations we were able to identify key areas of uncertainty in the toluene mechanism and with this to deliver crucial information for future validation experiments. Therefore, the key objective pursued in our study is to show how much information can be retrieved from a detailed analysis of the radical budget of a smog-chamber experiment.

A second issue is how much mechanisms validated against smog-chamber experiments are suited for modelling the rural or remote atmosphere. This is certainly a very important point concerning validation strategies for atmospheric models. In fact this problem was addressed during the above mentioned EXACT campaigns in which toluene experiments were carried out with a novel experimental technique that allowed the NO_x concentration throughout the experiment to be kept in the one figure nmol/mol range. It is planned to discuss these experiments in forthcoming papers on the EXACT campaigns. Hence, we came to the conclusion that the issue raised is not of direct relevance to our model study and feel that a discussion would be beyond the scope of

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this publication.

6.2) At present the aromatic schemes of the MCM v3 are in a state of revision. As mentioned above two campaigns were undertaken at EUPHORE to obtain data needed for the validation of aromatic mechanisms. It is planned to publish the results of the mechanism validation and to update the aromatic mechanisms of the MCM v3 sometime 2003. Those who want to use the aromatic mechanisms of the MCM v3 to revise condensed schemes might consider waiting until the revised schemes of the MCM v3 are available.

6.3) VOC mixtures containing alkanes, alkenes, and aromatics are not suitable for testing the performance of an oxidation mechanism of a single compound. By using such mixtures information on the aromatic would be lost and literally smeared out by the chemistry of accompanying compounds. That means, model-experiment deviations can no longer be used to retrieve specific information on shortcomings of the aromatic system under investigation.

Actually smog-chamber experiments with VOC mixtures (ethene, butane, toluene and α -pinene) have already been used for model validation of the MCM (Carslaw, N., Pilling, M.J., Jenkin, M.E., and Hayman, G.D., Simulations of EUPHORE and field experiments using a master chemical mechanism, Combined US/German Ozone/Fine particle science and environmental chamber workshop, Riverside, California, October 1999.). These simulations show good agreement between model and experimental c/t-profiles for all key species in the system. From these results it was erroneously inferred that the fundamental chemistry of the aromatic mechanisms of the MCM is correct. In fact as the system was dominated by the chemistry of non-aromatics the shortcomings of the toluene mechanism were masked.

We believe that it is essential for detailed mechanisms that they are validated first against single-component experiments. Once they perform well for those systems the second step will be further testing against multi-component experiments to make sure

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that no cumulative or non-linear effects have been overlooked that might reduce the performance of the mechanism for complex mixtures.

Concluding Remarks

The present manuscript describes an interesting and to my knowledge 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, NO_x 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.

Response on concluding remarks:

Finally we would like to respond to the following statement in the concluding remarks of referee #1: "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, NO_x and ozone are due to mechanistic gaps or uncharacterised chamber effects".

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As pointed out above, this study aims to give an overview of the status of toluene modelling based on a master chemical mechanism and to present a couple of model tools which are helpful for analysing smog-chamber systems. A further objective of our paper was to develop new ideas for the design of future validation experiments. We have shown that radical production by chamber effects is small compared to the radical production of the toluene system and therefore in the early and the middle stages of the experiment chamber effects do not significantly influence the radical budget of the toluene system.

This study did not aim to find the "holy grail" of smog-chamber research, the ultimate description and quantification of all chamber effects. We are working towards a better understanding of chamber effects and the application of detailed mechanisms for chamber characterisation studies might become a milestone for a more quantitative treatment of chamber related processes. For these reasons, we cannot agree with the above comment on our study.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 1217, 2002.

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