

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

Anonymous Referee #2

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1. General Comments

This paper describes a strategy to discover and elaborate deficiencies of reaction mechanisms for complex reaction systems, by comparing calculated with measured reactant and product concentrations and through a thorough analysis of modelled radical budgets. The photooxidation of toluene is taken as an example to present this strategy. The mechanism used in the model calculations is the Master Chemical Mechanism Version 3. The model results are compared with a single experiment performed in the EUPHORE environmental chamber at Valencia (Spain), called the 22/10/97 toluene experiment, and with literature data on product yields.

The abstract nicely summarizes the clear conclusions which could be drawn from the analysis of the model calculations:

- the modelled OH production is too low; 80% of the model calculated total OH has to be added by an artificial OH source in order to reproduce the measured decay of toluene; and
- the final ozone concentration as measured in the 22/10/97 toluene experiment is over-predicted by the model by 55%.

The model results are thoroughly analysed in terms of OH and ozone formation potentials of the various degradation channels and of individual intermediate products.

Still, the comparison of modelled and measured species concentrations (OH is too low and O₃ too high in the model, see Fig. 2) seems to provide the most direct and clear-cut information which can be used to discuss shortcomings of the reaction mechanism. However, the detailed analysis of the model calculations as presented in this paper, reveals additional new insights into the reaction mechanism. For example, this analysis shows that

- methylglyoxal is the most important radical source over the total course of the reaction;
- γ -dicarbonyls and epoxides are the most important radical sources in the early stages of the experiment;
- the sensitivity of the calculated O₃ yield to changes in the concentration of intermediates is highest at high NO_x concentrations. The tables and figures are appropriate and useful.

In addition, this paper presents an excellent review on the different degradation routes of aromatics which are presently discussed in the literature.

2. Specific comments

There are some additions and modifications to the text which might be able to improve the manuscript:

1. On p. 5 it is mentioned that 22/10/97 is one of the smog chamber experiments with the largest data set - are there other products which have been measured in this particular experiment, except of O₃, NO, and NO₂? Since the yields of several major product species existing in the literature scatter significantly, it would be useful to see, in an additional figure, the measured time dependencies of the concentrations of some other selected species like glyoxal, methylglyoxal and PAN. This is interesting, for example, with reference to the accelerated decrease of chainlength and conversion factor γ_{RO_2} at around 10.45 and 13.00 h (Fig. 4). Since the missing $\sum OH_{new}$ values in Fig. 6 probably reflect an error in the model, the calculated $\sum OH_{new}$ from individual radical sources might be much more helpful when compared to experimental profiles of carbon containing products.
2. Since glyoxal and methylglyoxal are partly lost by photolysis and reaction with OH and actually represent major OH radical sources in the course of the experiment, the discussion on the relative yields of both compounds should include a short remark on the (relative) rate constants of the reactions of OH and hn with glyoxal and methylglyoxal.
3. In Table 1 experimental and modelled yields of first generation products are compared. The experimental product yields (column "Literature") include first, second and third generation products whereas the model can differentiate between the different generations. The major products glyoxal and methylglyoxal are formed in all product generations. Are the model yields of glyoxal and methylglyoxal listed in this table the total yields from the first - third generation or only the fractions of the first generation?

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4. The phrase "transformation of NO_3 into a RO_x species" might be explained (p.8, line2).
5. To this referee, the stated percentage yields are unclear (e.g. the figure 80% in the abstract is misleading, erroneously suggesting that $[\text{OH}]_{total,exp.}:[\text{OH}]_{total,model} = 5:1$): On p. 6: "The model predicts a toluene decay that is about 28% too low compared to the experiment". I understand this statement in the way that the experimental value is taken as 100%. So do the authors as may be seen from the first panel of Fig. 2. However, the same expression on p. 10: "...the modelled OH production of 380 nml/mol (see also Fig. 3) is around 80% too low compared to experiment" is based on the modelled value = 100%, as may be deduced from the text on p. 10. Accordingly, the reader has to find out by himself in each case if the authors refer to the experimental or modelled value as being 100%; e.g. later on p. 10: "... $\sum \text{H}_{new}$ production in the model is too low by at least 50%". Inspection of Fig. 6-2 suggests that here again the model value is set to 100% because otherwise the value of Missing/Model would be ≥ 1 all the time, in contrast to Fig. 6-2. The model value being 100%, on the other hand, corresponds to Missing/Model ≥ 0.5 , but even this is not true for the time before about 11.10 h. In addition, unravelling what the authors actually mean by "at least 50%" is made more difficult by their time scale in Fig. 6-2 which is slightly different from the time scales in Figs. 6-1, 6-3 and 6-4 (see starting and end point in 6-2 as well as the points where missing and model values are equal).
6. There is a sudden increase of NO_2 at the beginning of the experiment - is this an NO_2 impurity in the added NO , or has it been added in order to accelerate HONO and thus OH formation (see Fig. 2)? Is, in the experiment, the light on all the time (also when gases are introduced into the chamber)? Is, in the model calculation, the mentioned 500 pmol/mol HONO added as a single event at zero time? What is the "general increase of the "background" production rate for $\sum \text{OH}_{new}$ of about 50%" (p. 11) and how is it introduced into the model - by

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increasing the rate constant of HONO production from NO_2 on the chamber walls by 50%?

7. Isn't CO_2 a major product of the degradation of methylglyoxal (via $\text{CH}_3\text{C}(\text{O})\text{CHO} \Rightarrow \text{CH}_3\text{C}(\text{O})\text{CO} \Rightarrow \text{CH}_3\text{CO} \Rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 \Rightarrow \text{CH}_3 + \text{CO}_2$) which is missing in Fig. 1?
8. The Sørensen et al. (1998) reference is presented in a different way in the text (p. 4) and under "references".

3. Concluding remark

This paper presents an excellent overview on the atmospheric degradation of toluene. The described method of analysing the results of model calculations is very useful in pointing to the deficiencies of the reaction mechanism and in assisting to design suitable experiments which are able to validate new ideas concerning the reaction mechanism. In addition, the discussion of calculated radical budgets seems to be a very suitable tool to improve the understanding of complex reaction mechanisms.

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

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