Atmospheric Chemistry and Physics Discussions

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 favourable general comment of referee 2 and we appreciate the specific comments that have helped to improve the manuscript and to increase it's readability. We have addressed the points raised in the following:

Comment 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 O_3, NO, and NO_2? 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_{RO2} at around 10.45 and 13.00 h (Fig. 4). Since the missing ΣOH_{new} values in Fig. 6 probably reflect an error in the model, the calculated ΣOH_{new} from individual radical sources might be much more helpful when compared to experimental profiles of carbon containing products.

Response 1
The phrase "largest dataset" is indeed misleading, we meant "the most suitable dataset" and have changed the text accordingly. We completely agree with referee #2 that c/t-profiles of NO_y species (e.g. PAN and HNO_3) and reaction products of the toluene oxidation are necessary to unravel the reasons for the model-experiment discrepancies and it is planned to retrieve crucial information on the uncertain parts of the toluene oxidation mechanism through a comparison of the calculated missing ΣOH_{new} with c/t-profiles of carbon containing products.
However, the 22/10/97 experiment was not carried out with the primary aim to validate a detailed toluene mechanism, rather to check on more general issues such as the ozone production as function of the NO_x concentration. The conceptual study published in the above 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. Our study started 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. At the time of this study we had to utilize existing toluene experiments carried out at EUPHORE. We analysed all experiments available and selected the 22/10/97 experiment as the most suitable for several reasons: 1) the toluene and NO_x concentrations are comparatively low for smog-chamber experiments 2) a set of photolysis rates was available 3) the experiment was a classical smog-chamber experiment in which once NO_x and toluene were injected and the cover of the smog- chamber opened all parameters of the system were left unchanged. 4)

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toluene, NO, NO$_2$ and O$_3$ were measured by FTIR technique.

As the 22/10/97 experiment was not carried out for model validation purposes the number of species measured is small compared with the large amount of intermediates produced during the toluene photooxidation. Apart from the species shown in Fig. 2 there are also data available on PAN and HCHO. However, we did not wish to discuss these in detail as a more complete dataset for NO$_y$ and intermediates is necessary for a thorough analysis of the shortcomings of the toluene mechanism. More comprehensive datasets are now available from the two EXACT campaigns that were particularly designed for validating detailed aromatic mechanisms and that provide high quality data for many species including glyoxal, methylglyoxal and selected C4 and C5 compounds of the ring-opening routes. These datasets are currently being analysed and used for the validation of the aromatic mechanisms of the MCM v3. It is planned to publish the results of the campaigns including detailed analysis of model-experiment comparisons for toluene sometime 2003.

Comment 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.

Response 2

At 12.00 h the model calculates branching ratios for the photolysis channels of glyoxal and methylglyoxal of 0.51 and 0.5 respectively. The complements to one are the branching ratios for the OH reaction channels with minor contributions, less than one percent, of the NO$_3$ reactions. We agree that these figures are of importance for a detailed discussion of the radical turnover in the toluene oxidation system. However, there is more information needed for a thorough understanding of the

radical production. If we take glyoxal as an example, only 25 % of the total photolysis produces HO_2, whereas molecular channels resulting in CO, HCHO and H_2 account for 75 %. The latter do not contribute directly to radical production in the toluene system. The situation is further complicated as different OH channels show differences in their efficiency to propagate radicals depending on the type of the peroxy radicals formed. To be consistent the radical production not only of glyoxal and methylglyoxal but for all important radical sources in the toluene system should be discussed in appropriate detail. However, such a discussion would be very lengthy and does not align with the main focus of the paper, which is to present and describe a new method of determining radical flows in a photooxidation system. To keep the paper as concise and readable as possible we do not wish to add further discussion of specific radical sources. Rather we would prefer to reference to the MCM web page from which information on the branching ratios and radical yields can be retrieved (http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html).

Comment 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?

Response 3
The model yields for glyoxal and methylglyoxal listed in Table 1 refer to first generation production. The total model yield, including all generations of production for glyoxal and methylglyoxal, is 63.7 % and 33.1 %, respectively, calculated at 15.00 h. We would like to add, that all literature values shown in Table 2 are expected to be yields for primary production. The ring-retaining products (cresol, benzaldehyde) are only

produced via first generation processes. According to a recent publication of Volkamer et al. (J. Phys. Chem. A, 105, 7865-7874, 2001) secondary and higher generation production of glyoxal and methylglyoxal are negligible. Hence, measured glyoxal and methylglyoxal yields in the toluene oxidation systems are assumed to be first generation production yields. The listed yields for the co-products of α-dicarbonyls, 4-oxo-pentenal and α-angelicalactone published by Smith et al. (1998) are measured in a dynamic reactor. These experiments were set-up in a way that only primary reaction products in the toluene system were measured.

Comment 4
The phrase "transformation of NO_3 into a RO_x species" might be explained (p.8, line2).

Response 4
For clarification we have added the following text (p. 8, line 4):
"Furthermore the reaction of NO_3 with VOC produces RO_x radicals and thus acts as a link between the NO_x and RO_x radical families. RO_2 production through reactions such as $RH + NO_3 + O_2 \rightarrow RO_2 + HNO_3$ is also classified as new radical production."

Comment 5
To this referee, the stated percentage yields are unclear (e.g. the figue 80% in the abstract is misleading, erroneously suggesting that $[OH]_{total,exp}$:$[OH]_{total,model}$ = 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: "...

ΣOH_{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 $\geq$ 1 all the time, in contrast to Fig. 6-2. The model value being 100%, on the other hand, corresponds to Missing/Model $\geq$ 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).

Response 5

5.1) Indeed, we have inconsistently taken the model value as 100% for describing the model- experiment discrepancy for the total OH production. We have corrected this inconsistency so that the deviation between model and experimental OH production is now always expressed with reference to the experimental value as 100 % (p 1, p 10, p 15). That means the model- experiment deviation for $[OH]_{total}$ is now given as 44 %. For clarification we have added the following text on p 6: "(for all model experiment comparisons the experimental value is taken as 100 %)".

5.2) Fig 6, panel 2, does not show a percentage value but the fraction Missing ΣOH_{new}/Model ΣOH_{new}. That means it looks from a model point of view at the missing ΣOH_{new} and indicates how much the ΣOH_{new} production in the model has to be increased to match the experimental oxidation capacity. For clarification we have added the following sentence (p. 10, paragraph 4) "If we consider the discrepancies from a model point of view it becomes clearer how much the OH production in the model has to be increased to match the radical production in the experiment."

5.3) (p. 10, paragraph 4) The statement "is too low by at least 50 %" is wrong and has been corrected to "is too low by at least 25 %".

5.4) The time scale in Fig. 6, panel 2, is indeed different from the time scales of the other panels. The time scales of Fig. 6 have been adjusted, accordingly.

Comment 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 ΣOH_{new} of about 50%" (p. 11) and how is it introduced into the model - by increasing the rate constant of HONO production from NO_2 on the chamber walls by 50%?

Response 6
6.1) The 22/10/97 experiment is a classical smog-chamber experiment in which all precursors, in this case toluene and NO, are injected into the chamber under dark conditions, that is when the cover of the chamber is closed. The sudden increase in NO_2 at 9.15 h is due to the injection of NO at this time. NO is introduced into the chamber with a syringe. At the point of injection the NO concentration is extremely high and NO_2 is produced by a termolecular reaction with O_2 ($NO + NO + O_2 \rightarrow NO_2 + NO_2$). Due to this process, the NO_2 concentration rises from 0.1 to about 15 nmol/mol. The injection of NO is also the reason for the "background" HONO concentration of about 0.5 nmol/mol. The mechanism of HONO formation is not completely under-stood, but it is very likely that NO_2 wall reactions are the predominant source. The concentration of HONO at the beginning of experiment is below the detection limit of the FTIR spectrometer of about 5 nmol/mol, so that the HONO concentration had to be estimated. Based on information from earlier chamber characterisation experiments we estimated an initial concentration of HONO of 0.5 nmol/mol and initialised the model accordingly. For further explanation we have added the following text (p 6)

"For the simulation of the 22/10/97 experiment the model was initialised with concentrations of toluene, NO, NO_2 and HONO. The high NO concentrations in the chamber at the point of NO injection led to production of NO_2 by a termolecular reaction (2 NO + $O_2 \rightarrow$ 2 NO_2), giving an initial concentration of NO_2 in the chamber of 14 nmol/mol. 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."

(p. 10, paragraph 5) For clarification we have further changed "... "background" HONO (an estimated 500 nmol/mol), produced by wall reactions of NO_2, "...by "background" HONO (an estimated 0.5 nmol/mol), produced during the injection of NO into the chamber".

6.2) (p. 11, line 8) The percentage figure in the statement "...a general increase of the "background" production rate for new OH of about 50 % is necessary to describe the oxidation capacity in the experiment." is wrong and has been corrected to 25 % (see response 5.3). In this context "background" means that an increase in the OH production is needed at all times and on top of that at certain times (around 12.00 h and after 13.30 h) an additional distinctive increase of the OH production is necessary to match the oxidation capacity in the smog-chamber experiment.

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Isn't CO_2 a major product of the degradation of methylglyoxal (via $CH_3C(O)CHO \rightarrow CH_3C(O)CO \rightarrow CH_3CO \rightarrow CH_3C(O)O_2 \rightarrow CH_3 + CO_2$) which is missing in Fig. 1?

Response 7
CO_2 is a major degradation product not only of methylglyoxal but also of most other intermediates in the toluene system. This is mentioned on page 5. However, we did not show CO_2 in Fig. 1, as it has no impact on the reactivity of the system. Furthermore, it cannot be taken as a tracer for the degradation process of toluene in smog-chamber experiments owing to the high background concentration of CO_2 in ambient air. We have added a phrase to the figure caption (Fig. 1) pointing out that CO_2 as reaction product is not shown.

Comment 8
The Sørensen et al. (1998) reference is presented in a different way in the text (p. 4) and under "references".

Response 8
The Sørensen et al. (1998) reference has already been corrected in the ACPD version of the manuscript (first review stage).

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

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