

## ***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 appreciate the comments and recommendations of referee #3 and are grateful for the general compliments towards the study. In the following we will address the specific comments:

### **Comment 1**

The authors might still find important information in the theoretical publications by Tonachini's group (at present not considered in the manuscript). If so, any (new) relevant theory-validated reaction for the ring-opening route in benzene should be taken into consideration in this work, and analogous pathways developed for toluene implemented in TOL\_MCM3a. The references are the following:

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Ghigo and Tonachini (1999), From benzene to muconaldehyde: investigation on some tropospheric oxidation channels, *J. Am. Chem. Soc.* 121, 8366-8372.

Motta et al. (2002), Oxidative degradation of benzene in the troposphere. Theoretical mechanistic study of the formation of unsaturated dialdehydes and dialdehyde epoxides, *J. Phys. Chem. A* 106, 4411-4422.

### Response 1

The authors have been aware of the above mentioned publication. The paper of Ghigo and Tonachini (1999) is a theoretical study on the initial reaction steps of the reaction of OH with benzene. Here the authors investigated the fate of the hydroxycyclohexadienyl peroxy radical and infer two major reaction pathways from their theoretical investigation: 1) at high NO concentrations the reaction with NO prevails resulting in the formation of an oxy-radical. This radical undergoes ring-opening and subsequently after reaction with O<sub>2</sub> muconaldehyde is produced. 2) At low NO concentrations their simulations indicate that a cyclisation reaction resulting in a peroxide bridge is favoured. At NO concentrations of about 1  $\mu\text{mol/mol}$  the reaction rates of the NO promoted ring-opening and the cyclisation are equal.

The paper of Motta et al. (2002) is a more comprehensive study on the initial reaction steps of the reaction of OH with benzene that also includes the breakdown of the peroxy-bicyclic radical. They come to the same conclusions as Ghigo and Tonachini (1999) that at high NO concentrations (several  $\mu\text{mol/mol}$ ) the hydroxycyclohexadienyl peroxy radical predominantly reacts with NO producing muconaldehyde. At NO concentrations that are comparable to the conditions of the 22/10/97 experiment (150 nmol/mol) their calculation predicts that the OH initiated oxidation of benzene will first result in a peroxy-bicyclic radical that rearranges to form an oxy epoxy intermediate and finally breaks down to an epoxidized muconaldehyde. According to their calculations glyoxal is only a minor primary product with a yield of far less than 1 %, independent of the NO concentration. These yields are in contradiction to the primary

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produced glyoxal yields of 35 % reported in a publication by Volkamer et al. (2001). In the experimental study of Volkamer et al. (2001) a DOAS instrument was employed to measure glyoxal c/t-profiles in benzene photooxidation experiments carried out in the large- volume outdoor smog-chamber EUPHORE (European Photoreactor). The initial concentrations of benzene and NO in their experiments were about 1  $\mu$ mol/mol and about 80 nmol/mol respectively. Motta et al. (2002) do not discuss the obvious contradiction between glyoxal yields inferred from their theoretical study and the measured values of Volkamer et al. (2001).

The epoxide-type primary products of aromatic oxidation as proposed by Motta et al. (2002) along with other theoretical studies (Garcia-Cruz et al., 2000; Bartolotti and Edney, 1995), have not yet been quantified in experimental studies. At present it is not clear how precisely theoretical studies can predict the intermediates of the early stages of the aromatic oxidation, but it has become obvious that further experimental work is needed to determine the main reaction pathways of the ring-opening routes in aromatic oxidation.

For the following two reasons the above papers were not referred to:

1) Both papers present quantum mechanical simulations on the initial reaction steps of benzene. At present it is not clear if these results can be transferred to toluene. The POCP values of toluene and benzene differ significantly and therefore the chemistry of the early stages of the benzene photooxidation might be significantly different from the chemistry of alkyl substituted aromatics.

2) In keeping the introduction as concise as possible the authors aimed to provide only information that is needed to understand the historic development of the MCM. For that reason we believe that a detailed discussion of the results of the above papers is beyond the scope of the introduction.

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However, on suggestion of referee #1 we have now added a further figure to illustrate the different reaction pathways of the toluene oxidation that have been proposed. This figure also includes the reaction of NO with the hydroxycyclohexadienyl type peroxy radical leading to muconaldehyde-type products. Furthermore we have added the following paragraph on page 1224 explaining this reaction route and referring to the above publications:

"The ring-opening pathways of the toluene oxidation proceed by a sequential addition of OH and O<sub>2</sub> resulting in a hydroxycyclohexadienyl type peroxy radical (Fig. 1). Depending on the NO concentration there are three proposed reaction pathways for this radical: 1) a cyclisation to form a peroxide bridged radical which is the precursor for both the carbonyl and the epoxide route (Jenkin et al., 2002), 2) an isomerisation and subsequent release of HO<sub>2</sub> to form cresol and 3) the reaction with NO resulting in the production of an oxy-radical that undergoes ring-opening and eventually results in the formation of muconaldehyde-type compounds. Ghigo and Tonachini (1999) and Motta et al. (2002) have investigated the photooxidation of benzene in theoretical studies. They both came to the conclusion that the NO promoted pathway can only compete with the cyclisation under polluted conditions. For NO concentrations of about 100 nmol/mol Ghigo and Tonachini (1999) estimate a branching ratio for the NO pathway of less than ten percent. Although this value was calculated for benzene, it can be taken as a tentative indication that the muconaldehyde route for aromatics in general is only of importance at NO<sub>x</sub> concentrations in the μmol/mol range. This is in line with experimental studies at moderate NO<sub>x</sub> levels in which only qualitative evidence for muconaldehyde type compounds as minor reaction products in the toluene system was found (Yu et al., 1997). On the basis of the results of the theoretical studies and the weak experimental evidence for the muconaldehyde route in the toluene system this reaction pathway is not implemented in the MCM v3."

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**Comment 2**

Concerning Olario's private communication (page 1223): there is now a published paper for more specific referencing:

Olariu et al. (2002), FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol, *Atmos. Environ.* 36, 3685-3697.

**Response 2**

We have updated the reference and refer now to the above publication.

**Response 3**

All technical corrections suggested by referee #3 have been addressed in the revised manuscript.

**References**

Bartolotti, L.J. and Edney, E.O.: Density functional theory derived intermediates from the OH initiated atmospheric oxidation of toluene, *Chem. Phys. Lett.*, 245, 119-122, 1995.

Garcia-Cruz, I., Castro, M., and Vivier-Bunge, A.: DFT and MP2 molecular orbital determination of OH-Toluene-O<sub>2</sub> isomeric structures in the atmospheric oxidation of toluene, *J. Comp. Chem.*, 21, 716-730, 2000.

Volkamer, R., Platt, U., and Wirtz, K.: Primary and secondary glyoxal formation from aromatics: Experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and p-xylene, *J. Phys. Chem. A*, 105, 7865-7874, 2001.

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

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