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

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I am aware of the fact that the following comment does not affect the aim of the paper of Wagner et al.; however, it might be of general interest for all those modelling the atmospheric degradation of aromatics. I would like to suggest that reaction (1), (1) $RO_2 + NO_2 => RO + NO_3$, be included in the toluene oxidation system for R = HC(O)CO and R = $CH_3C(O)CO$. Without this reaction, the reactions of ozone formation are: (2) $RO_2 + NO => RO + NO_2$, (3) $NO_2 + hv => NO + O$, (4) $O + O_2 + M => O_3 + M$, (5) net: $RO_2 + O_2 => RO + O_3$. Inclusion of reaction (1) gives (simplified, neglecting the second (major) NO_3 photolysis channel): (1) $RO_2 + NO_2 => RO + NO_3$, (6) $NO_3 + hv => NO + O_2$, (7) net: $RO_2 + NO_2 => RO + NO + O_2$. The main

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effect of including reaction (1) is that an RO2 to RO conversion step is accompanied by consumption of NO2 via reactions (1) and (6) rather than by formation of O3 via reactions (2)-(4). This is exactly what makes the difference between the EUPHORE experiment and the model calculations. In detail, the following discrepancies between experiment and model result as documented in Fig. 2 of the paper of Wagner et al. can possibly be explained by reaction (1): (i) Since NO favours chain propagation and NO2 favours formation of reservoir or stable species, the re-formation of NO from NO2 in reactions (1) and (6) leads to faster toluene consumption. (ii) For the same reason, the toluene consumption rate changes parallel to the NO2 concentration. (iii) O3 formation per RH consumed is considerably larger in the model without reaction (1). (iv) The relatively good agreement between experiment and model during the first 1.5 hours is in line with reaction (1) since glyoxal and methylglyoxal have to accumulate until degradation of these compounds and thus RO2 formation with R = HC(O)CO and CH3C(O)CO reaches a considerable level. (v) The NO2 concentration peaks earlier in the experiment since it is consumed in reaction (7) after glyoxal and methylglyoxal have accumulated. What makes reaction (1) particularly attractive is that it is not speculative but has already been proposed in two experimental studies: (i) Orlando and Tyndall [1] explained the observed N2O5 formation in their experiments on the photolysis of mixtures of HC(O)CHO, Cl2, O2, and NO2 by the existence of reaction (1). (ii) Jagiella and Zabel [2] explained the formation of CO2 and N2O5 in the photolysis of mixtures of CH3C(O)CHO, Br2, O2, and NO2 by the occurrence of reaction (1) [2]. In their work, the NO3 formation via NO2 photolysis was avoided by the use of long-wavelength photolysis lamps (above 500 nm). Of course, the RO2NO2 $<=>$ RO2 + NO2 reaction is still the "normal" reaction of RO2 and NO2; however, for certain R (e.g. R = HC(O)CO and CH3C(O)CO), the RO-ONO2 bond may be weaker than the ROO-NO2 bond, thus giving rise to reaction (1).

References [1] J. J. Orlando and G. S. Tyndall, The Atmospheric Chemistry of the HC(O)CO Radical, Int. J. Chem. Kinet. 33(2001)149-156. [2] S. Jagiella and F. Zabel, Thermal Stability of the Methylglyoxyl Radical, 17th Int. Symp. Gas Kinetics, August

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