**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.

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We are very grateful to Dr Zabel for alerting us to the likely alternative reaction of substituted acyl peroxy radicals of generic formula $RC(O)C(O)O_2$ with NO_2,

$$RC(O)C(O)O_2 + NO_2 \rightarrow RCO + CO_2 + NO_2 \qquad (R = H, alkyl)$$
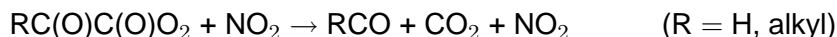
based on recent results from his group for $CH_3C(O)C(O)O_2$ and those of Orlando and Tyndall (2001) for $HC(O)C(O)O_2$. Dr Zabel also suggests that these reactions may explain the discrepancy between the observed and modelled concentration-time profiles for the toluene photo-oxidation experiment presented in our paper by contributing to cycles which lead to overall NO_2-to-NO conversion, and greater concentrations of OH through increased radical propagation chain lengths.

Although we feel it is important that the representation of these reactions is revised in future versions of our mechanism, the impact of such a revision on the simulated concentration-time profiles which appear in our paper is very minor and actually leads to slightly increased NO-to-NO$_2$ conversion and ozone formation. The minor impact results from flux through the key reactions being very small, which can be appreciated by consideration of the following points:

1. Despite being well-established products, the yields of glyoxal and methylglyoxal from the OH initiated degradation of toluene are well below unity.

2. Both glyoxal and methylglyoxal, are removed significantly by photolysis and reaction with OH (about 35% by OH reaction) under the conditions of the chamber experiment. Only the reactions with OH produce HC(O)CO and CH$_3$C(O)CO.

3. Both HC(O)CO and CH$_3$C(O)CO undergo thermal decomposition in competition with reaction with O2. Based on published experimental studies (e.g. Orlando and Tyndall, 2001), about 40% of HC(O)CO decomposes to HCO and CO, and a further 30% reacts with O$_2$ to generate CO+CO+HO$_2$. Thus only about 30% of the OH reaction yields HC(O)C(O)O$_2$. In the case of CH$_3$C(O)CO, decomposition to form CH$_3$CO + CO is assumed to dominate over reaction with O$_2$ in our mechanism, such that CH$_3$C(O)C(O)O$_2$ is not generated. This is based on evidence from published experimental studies on the oxidation of methylglyoxal (Green et al., 1990; Tyndall et al., 1995), and from the results of theoretical calculations on the relative importance of decomposition and reaction with O$_2$ in such systems (Méreau et al., 2001). The results of these studies are consistent with $\leq$ 5% of the loss CH$_3$C(O)CO being due to reaction with O$_2$ at 298K in 1 atmosphere of air. The above considerations are thus consistent with yields of about 10% HC(O)C(O)O$_2$ from glyoxal and $\leq$ 2% CH$_3$C(O)C(O)O$_2$ from methylglyoxal under the experimental conditions.
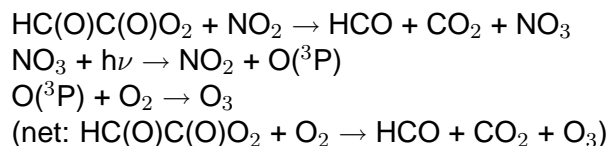
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After about 1.5 hours of experiment, the major reactions of $HC(O)C(O)O_2$ and $CH_3C(O)C(O)O_2$ are with NO_2. However, the net impact of these reactions suggested by Dr Zabel relies on photolysis of the product NO_3 via its minor channel (ca. 10%) to form NO and O_2, thereby leading to an overall flux of NO_2 to NO. In practice, the major irreversible sinks for NO_3 are (i) photolysis to form NO_2 and $O(^3P)$, (ii) reaction with organics such as cresols in the system, and (iii) reaction with NO. These processes lead either to direct ozone formation, or to indirect ozone formation following NO-to-NO_2 conversion.

The impact of implementing the revised products for the reaction of $HC(O)C(O)O_2$ with NO_2 was investigated by performing an additional simulation. In the current version of our mechanism, the reaction with NO_2 is assumed to generate a peroxyacyl nitrate, with a thermal lifetime comparable with that of PAN itself,
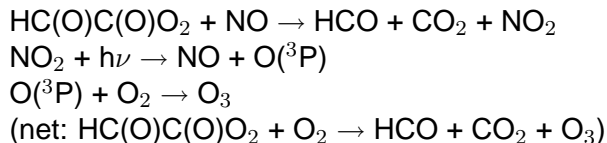
$HC(O)C(O)O_2 + NO_2 \rightarrow HC(O)C(O)O_2NO_2$
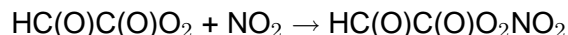
Revision of the products to $HCO + CO_2 + NO_3$, resulted in a very small increase (ca. 3%) in simulated O_3 at the end of the experiment and a negligible effect on the profiles for toluene, NO and NO_2. In some respects, the revised reaction has the same effect as the corresponding reaction involving NO, i.e. compare the ozone-forming cycle:

$HC(O)C(O)O_2 + NO_2 \rightarrow HCO + CO_2 + NO_3$
$NO_3 + h\nu \rightarrow NO_2 + O(^3P)$
$O(^3P) + O_2 \rightarrow O_3$
(net: $HC(O)C(O)O_2 + O_2 \rightarrow HCO + CO_2 + O_3$)

with the cycle:

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HC(O)C(O)O$_2$ + NO → HCO + CO$_2$ + NO$_2$
NO$_2$ + hν → NO + O(^{3}P)
O(^{3}P) + O$_2$ → O$_3$
(net: HC(O)C(O)O$_2$ + O$_2$ → HCO + CO$_2$ + O$_3$)

Compared with the alternative formation of a PAN analogue (which temporarily sequesters NO$_2$), implementation of the revised reaction products therefore leads to net O$_3$ formation.

Although Dr Zabel's suggestions do not improve the discrepancy between the chamber observations and our simulations, we reiterate that we are grateful for his input to this discussion and for alerting us to relevant mechanistic information.

References

Green M., Yarwood G. and Niki H. FTIR study of the Cl-atom initiated oxidation of methylglyoxal. International Journal of Chemical Kinetics, 22, 689-699, 1990.

Méreau R., Rayez M.T., Rayez J.C., Caralp F. and Lescalux R. Theoretical study on the atmospheric fate of carbonyl radicals: kinetics of decomposition reactions. Physical Chemistry Chemical Physics, 3, 4712-4717, 2001.

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