

Interactive comment on “Isoprene photooxidation mechanism: resonance channels and implications for the production of nitrates and acids” by F. Paulot et al.

F. Paulot et al.

Received and published: 14 December 2008

We thank D. Taraborrelli for providing helpful comments on our manuscript

1/ 1a/ Very high values are given for the peroxy radicals that are internally double bonded and originates from MVK and MACR. No possible explanation is given about the significant deviations from previous and recent studies on similar peroxy radicals, e.g. Cassanelli et al. (Phys. Chem. Chem. Phys., 2007, 9, 4332-4337).

As suggested by Giacomelli, the data presented by Espada et al. may suggest a greater yield from nitrate with an alcohol group not in beta of the peroxy. The presence of the double bond in the isoprene peroxy may be responsible for large differences with the

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peroxy radicals originating from alkanes.

1b/ In Sect. 3.1.1 it is stated that OH addition to the double bond is mostly considered to take place yielding only the most substituted radical. The reason for that is apparently a lack of information or data. However, Peeters et al., (J. Phys. Chem. A 2007, 111, 1618-1631) provides a site-specific SAR for the OH addition to alkenes. For instance, the branching ratios of an isoprene-related alkene, that is internally double bonded, should be 65% occurring at C3 and 35% at C2. Therefore, the decomposition of other alkoxy radicals should be taken into account

Regarding Peeter's SAR, please refer to 8/ (Dibble).

Furthermore, the decomposition of alkoxy radicals from the C5-nitrates should depend significantly on the effect of the -ONO2 group. No decrease in the energy barrier due to this group is reported by Peeters et al., (J. Atmos. Chem. 2004, 48, 59-80) and nothing is mentioned in Paulot et al.. The -ONO2 group has unlikely a null effect and it would be useful to know which assumption has been made.

We do not make any assumption regarding the role of the ONO2 group in the decomposition of the alkoxy radical. Instead we attempt to constrain their fate using experimental constraint (cf. Reply to comment3/ of the first reviewer).

Finally, in Sect. 4.4.1 the products PROP_N and DHB are used to determine a NO_x- recycling efficiency for ISOPN(4,1) of 70%. In Sect. 4.2 the authors assumed that ISOPN(4,1) is the sole source of DHB. However, this is not correct since DHB is also produced from the degradation of the C5 peroxy acyl nitrate originating from what in the manuscript is indicated as HC5(1,4). How is the chemistry of this compound treated? Was this compound monitored during the experiments? If yes, how abundant was it? The above considerations pose some uncertainties on the significance of: - the NO_x- recycling efficiencies given in Table 1 of the manuscript - the source attribution of secondary nitrates like PROP_N,

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MACRN and MVKN.

HC5 (1,4) can indeed yield DHB but we followed Peeter's scheme to constrain the decomposition of the alkoxy radical which does not predict a substantial yield of DHB if only the addition on the main carbon is considered.

Both DHB ($m/z=189$ cluster) and HC5 ($m/z=185$) are monitored and their calibrated profiles reported in the manuscript.

2a/Early sources for formic and acetic acid are missed by the model.

Even though the mechanism for the formation of formic acid from isoprene nitrates, as presented in Paulot et al., is possible, other sources need to be considered. Many intermediates present patterns similar to hydroxyacetone and glycolaldehyde that could yield formic acid. Furthermore, the radical HOCH₂CO is responsible for most of HCOOH formed in the reaction of glycolaldehyde + OH (Butkovskaya et al(2006)) and it is the product of decomposition of some alkoxy radicals from isoprene oxidation. For instance, HOPL (HOCH₂COCHO) would do it at the right time scale. Are such HCOOH sources included in the model?

The formic acid profile is certainly not fully captured by the model but taking into account the uncertainties of the chemical processes involved, we believe it represents a substantial improvement over the chemistry traditionally implemented in kinetic mechanism.

If numerous compounds present patterns similar to HACET or GLYC, none of them is formed early enough to account for the formation of formic acid.

In the specific case of HOPL, the formation of formic acid is not taken into account but considering the predicted yield of this compound, its contribution to formic acid yield will be both very small and too late to contribute significantly to the early source of formic acid. Nevertheless for completion we will include them in the model using Butkovskaya et al branching ratios.

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2b/ In fact, for acetic acid other sources are the photolysis of pyruvic acid (Melouki and Mu, J. Photochem. Photobiol. A: Chem, 2003, 157, 295-300) and the reaction of CH₃CHOHCHO with OH similarly to glycolaldehyde as described in Butkovskaya et al, (J. Phys. Chem. A 2006, 110, 13492-13499). CH₃CHOHCHO should come from reactions of propene that in turn is produced by photolysis of MVK. Did the authors considered such sources? If not, they should include them.

Photolysis of pyruvic acid is included in the model and represents a very small source of acetic acid. Even though the photolysis of MVK is included, it represents a very small sink compared to its reaction with HO and O₃. Furthermore the yield of CH₃CHOHCHO is likely to be very small under our experimental conditions.

2c/

Its mixing ratio is slightly overestimated with a too early production by the model. The authors state that 15% should come from ozonolysis of MACR. The Criegee intermediate responsible for that should be CH₃C(OO)CHO. However, based on current knowledge, it is hard to imagine the production of pyruvic acid (CH₃COCO₂H) from this intermediate. On the other hand, ozonolysis of MVK can yield pyruvic acid through the reaction of the stabilised Criegee intermediate CH₃COCHOO with water. Hasson et al., (J. Geophys. Res. 2001, 106) report for a primary Criegee diradical an acid yield of 8% and a yield of 15% for the alpha-hydroperoxide that is an acid precursor. This would reasonably imply for CH₃COCHOO a direct 8% yield of pyruvic acid and 15% yield of CH₃COCH(OH)OOH. Apparently, if I am not mistaken, the authors missed a source of pyruvic acid from the ozonolysis of MOBA Z(1,4) (see below). This compound is shown in Fig. 7 to reach significant mixing ratios. Finally, the uncertainties on the chemistry of alkoxy radicals from the alkyl nitrates could be critical in this regard as well (see above).

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We thank the reviewer for pointing out that MACR should read MVK. This is corrected in the revised manuscript. A mechanism similar to the one presented by the reviewer is implemented. We followed IUPAC recommendations (Atkinson et al. (2006)) for the reaction of MVK with ozone.

2d/ The authors show a mechanism for the ozonolysis of MOBA isomers without providing any details. This is very unlikely, since primary ozonides decompose always giving two different Criegee intermediates in case of asymmetric alkenes. Moreover, the Criegee intermediates are produced with different geometries as syn- and anti- isomers. This affects their subsequent decomposition, for instance the OH yields. It is very likely instead that ozonolysis of MOBA isomers has OH and CO₂ yields much lower than 1. Since one of the foci the manuscript is on the acids from isoprene oxidation, it is worth to mention that pyruvic acid should be a major product of the ozonolysis of MOBA

In the absence of any experimental data on MOBA, we added a simple scheme in order to both account for the reaction of MOBA with ozone and limit the number of reactants and potential uncertainties such a reaction would add. As noted by the reviewer, this may be an oversimplification and pyruvic acid is very certainly a major product of MOBA photooxidation. Unfortunately, the uncertainties associated with pyruvic acid calibration are too large to reasonably test this hypothesis. We emphasize this uncertainty in the revised manuscript.

Specific comments

p. 14646 line 5: The authors should be cautious about their use of "concentration" and "mixing ratio": units like ppbv and ppmv are mixing ratios, whereas molec/cm³ is a concentration. These are mixed up here.

According to IUPAC, a concentration can be expressed in ppb

p. 14650 Sect. 3.1.1: Acyl radicals (RCO) with a tertiary alkyl group are predicted

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by Mereau et al(2001) not to decompose in the atmosphere. Only the presence of an hydroxy group can make such a radical decompose. For instance, about 80% of the $\text{HOC}(\text{CH}_3)_2\text{CO}$ radicals are predicted to decompose. This implies that the authors considered the reaction of $\text{MACR}_N + \text{OH}$ yielding 100% CO. Is that correct? If the authors considered the $-\text{ONO}_2$ group to have an effect similar to the one of the methyl group (CH_3-), for consistency they should apply the same assumption when predicting the decomposition of the alkoxy radicals from the alkyl nitrates (see Major comments, point 1b).

We applied Mereau's results to tertiary acyradical featuring a alcohol/carbonyl group in beta of the carbonyl. We extended Mereau's results to the nitrooxy group so that ETHNL is assumed to decompose before addition of O_2 . ISOPN are not affected by this hypothesis as they do not feature an acyl radical.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14643, 2008.

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