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

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General comment

Paulot et al. presents very valuable and unique details on high-NOx isoprene chemistry. This could be made even more beneficial to the reader by providing a complete listing of the mechanism reactions as an Electronic Supplement, for instance.

A previous comment by Dibble (2008) focused on the initial branching ratios of OH addition to isoprene. Both experimental and theoretical work show significant uncertainties. Unfortunately, MACR and MVK were not measured in Paulot et al. as they would have provided an additional and important constrain. This stresses how critical are the as-

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sumptions on the initial branching ratios in affecting the subsequent conclusions on C5 carbonyls and alkyl nitrates, for instance.

Beyond this, I have additional comments and requests for clarification that, if answered, will greatly improve the manuscript.

Major comments

1) Alkyl nitrates

1a) Yields

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).

1b) Chemistry

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 6 alkoxy radicals should be taken into account.

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.

Finally, in Sect. 4.4.1 the products PROPN_N and DHB are used to determine a NOx-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 NOx-recycling efficiencies given in Table 1 of the manuscript - the source attribution of secondary nitrates like PROP_N, MACR_N and MVK_N.

If possible, the authors should assess the effects of these uncertainties on their results.

2) Acids

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

2a) Formic acid

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?

2b) Acetic acid

In fact, for acetic acid other sources are the photolysis of pyruvic acid (Mellouki and Mu, J. Photochem. Photbiol. 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.

2c) Pyruvic acid

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).

2d) MOBA

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 diffrent 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

Z(1,4). Addition of this source would be appropriate.

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.

p. 14650 Sect. 3.1.1: Acyl radicals (RCO) with a tertiary alkyl group are predicted 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 HOC(CH3)2CO radicals are predicted to decompose. This implies that the authors considered the reaction of MACR_N + OH yielding 100% CO. Is that correct? If the authors considered the -ONO2 group to have an effect similar to the one of the methyl group (CH3-), 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).

p. 14653 line 3-4: Dillon and Crowley (Atmos. Chem. Phys., 8, 4877-4889, 2008) should be cited. It reports the first direct observation of OH as a product of channel R12.

p. 14656 line 15,18 and 23: MACR and MVK are erroneously exchanged in the text that results in an inconsistency with Fig. 3.

p. 14670 line 11: The citation Ryzhkov et al., 2004 contains a mistake. Actually, the paper has just two authors. Furthermore, important experimental work on the formation of HMHP from the reaction of CH2OO with water is not cited, e.g. Gäb et al., 1995, Neeb et al., 1997, Hasson et al., 2001 and Sauer et al., 1999.

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