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Interactive comment on "The MCM v3.3 degradation scheme for isoprene" *by* M. E. Jenkin et al.

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This article is important as it presents a quite comprehensive mechanism for isoprene which will surely be widely disseminated and used in the community interested by the impact of isoprene. Given the large number of reactions involved, it is to be expected that many issues, questions and problems remain, in spite of the impressive work which has been done to incorporate the recent relevant mechanistic updates. Besides the points raised by Jozef Peeters, I have the following remarks which I hope can contribute to improve the manuscript and possibly the mechanism.

p. 9720 and Fig. 5 : The 1st generation nitrate yields in MCMv3.3 follow more or less an average of different experimental studies. Note that in atmospheric conditions

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(relatively low NO), two isomers are largely dominant: ISOPN-1,2 (ISOPBNO3) and ISOPN-4,3 (ISOPDNO3). But the MCM assumes a twice higher nitrate yield (14% vs 7%) for the ISOPDO2+NO reaction than for the ISOPBO2+NO reaction. This is in line with the experimental study of Lockwood et al. But very serious doubts can be raised regarding the Lockwood et al. results since it provided a completely wrong determination of the ozonolysis rate constant for the 1,2 nitrate : 10^{-16} cm^3 molec^{-1} s^{-1} i.e. a factor of 20-40 above the experimental value determined by Lee et al. 2014 for the very similar 4,3 nitrate. This suggests a wrong identification of the different isomers by Lockwood et al. in particular for the 1,2 isomer. Therefore I would recommend ignoring the Lockwood results in this context, and adopting identical nitrate yields for 1,2 as for 4,3.

p. 9722-9723 : In the MCM reaction file, the reaction of HMML with OH produces CH3CO3 + HCOOH. I guess the MCM protocol was followed here, but given the recent interest in the atmospheric sources of formic acid, it would be worthwhile to provide some more details on how these products are formed.

p. 9724, lines 4-5 : From the MCMv3.3 reaction file, k(ISOPDNO3+O3) = $7 \cdot 10^{-19}$ cm^3 molec^{-1} s^{-1}, which is well above the range given by Lee et al. (2014) i.e. $(2.5\text{-}5) \cdot 10^{-19}$ cm^3 molec^{-1} s^{-1}. Is there a reason for that?

p. 9725, on the photolysis of carbonyl nitrates : the photolysis rates of carbonyl nitrates in the MCM reaction file are given as the photorate of nitrooxy acetone multiplied by a scaling factor deduced from Table 3 in Müller et al. (2014), which is reasonable. For the β-nitrooxy aldehydes, however, for which no photorates were presented in Müller et al. (2014), the MCM scaling factor is taken to be the same as for the β-nitrooxy ketones (0.91). Due to the much higher absorption cross sections of aldehydes compared to ketones, the scaling factor for β-nitrooxy aldehydes should be much higher. I estimate a factor of 4 using assumptions similar as for the other carbonyl nitrates. Note that MCM-type expressions of the photolysis rates can be derived for the carbonyl nitrates, based on a fit of TUV estimations at three zenith angles (0, 30 and 60 degrees). Based

on such calculations (assuming 300 DU ozone), I obtain the following expressions:

$$J(NO3CH2CHO) = 2.119E-04 \times (COSX^{0.672}) \times EXP(-0.328/COSX)$$

$$J(MACRNO3) = 4.926E-04 \times (COSX^{0.637}) \times EXP(-0.312/COSX)$$

$$J(C58NO3) = 2.182E-04 \times (COSX^{0.779}) \times EXP(-0.378/COSX)$$

$$J(MVKNO3) = 8.949E-05 \times (COSX^{0.799}) \times EXP(-0.385/COSX)$$

$$J(HMVKANO3) = 5.594E-05 \times (COSX^{0.946}) \times EXP(-0.454/COSX)$$

where COSX is the cosine of the zenith angle, NO3CH2CHO is ethanal nitrate, MACRNO3 ($OCHC(CH_3)(ONO_2)CH_2OH$) is a model compound for most α-nitrooxy aldehydes, C58NO3 ($OCHCH(OH)C(CH_3)(ONO_2)CH_2OH$) a model compound for β-nitrooxy aldehydes, MVKNO3 ($CH3C(O)CH(ONO_2)CH_2OH$) a model compounds for α-nitrooxy ketones, and HMVKANO3 ($CH3C(O)CH(OH)CH_2ONO_2$) a model compound for β-nitrooxy ketones.

p. 9726-9727 : the oxidation mechanism of IEPOXB is largely based on the mechanism presented by Bates et al. (2014). However I note that the 1,5-H shifts of the peroxy radicals proposed by Bates et al. (their Fig. 7) were neglected in the MCM (Fig. 8). This might be very well justified, but I'm wondering on what basis those processes were neglected in the MCM.

p. 9729 lines 10-14: the compounds HVMK and HMAC are assumed to photolyze as MVK and MACR, respectively, which means that photolysis is simply negligible for those compounds in MCM, due to the known very low photolysis quantum yields of MVK and MACR. But HVMK and HMAC are ketone-enols, with highly specific properties due to H-bonding, very different from the simple unsaturated carbonyls MVK and MACR. As outlined in Peeters et al. (2014), and by analogy with the case of

acetylacetone for which laboratory data is available, the ketone-enols are expected to photolyze into OH and a strongly stabilized radical at a rate of about $(2\text{-}3)\cdot 10^{-4}$ s^{-1}, assuming a quantum yield close to unity. The latter assumption is justified by the allowed type of transition and much lower wavelengths involved in the photodissociation of ketone-enols compared to the cases of MVK and MACR (forbidden transition). As a consequence, the photolysis of HVMK and HMAC should be far from being negligible.

In the MCM reaction file, the photolysis of the nitrooxy enal NC4CHO (O=CH-CH=C(CH$_3$)CH$_2$ONO$_2$) (formed in large amounts from the oxidation of isoprene by NO$_3$) generates as products C4MDIAL + HO2 + NO2, where C4MDIAL is the unsaturated dialdehyde O=CH-C(CH$_3$)=CH-CH(=O) . But if we assume that NC4CHO photolysis proceeds by NO$_2$ expulsion (as apparently assumed here), the oxy radical co-product is the same as the radical formed in the photolysis of C5HPALD2. We would therefore expect the same subsequent chemistry as outlined in Sect. 2.2.4 and Fig. 9.

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