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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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General comment

The manuscript describes the update of isoprene oxidation mechanism according to the significant advancements that have been made in the last few years. It is important because of the central role of isoprene in tropospheric chemistry and because of widespread use of MCM in the community as a reference. The description of the updates is detailed and clear although in some places it is still obscure how reaction products were assigned. The points raised by by J. Peeters (reviewer) and J.-F. Müller need to be dealt with. In fact assuming the same rate constant for the 1,6-H-shift by CISOPAO2 and CISOPCO2 is against both the experimental and theoretical data. Below I list two other additional issues I found with this MCM update and a minor comment.

Major comments

1) HCOCO chemistry. In which way has Lockhart et al. (2013) been taken into account if no prompt HCOCO* dissociation of 60% is implemented? Moreover, Da Silva (2010) reports a personal communication with J. Orlando correcting the Orlando and Tyndall (2001) estimate of HCOCO thermal decomposition rate constat that is half the originally published one. Instead of 1.4E12*exp(-3160/temp) it should be 7E11*exp(-3160/temp).

2) C3MCODBCO3H and MC3CODBCO3H from C4MDIAL are actually the same as C5PACALD1 and C5PACALD2 although on the MCM website they are showed being E- and Z- geometric isomers, respectively. Even if this were the case, they should both undergo fast photolysis as proposed by Peeters et al(2010). However, C3MCODBCO3H and MC3CODBCO3H undergo an old and obscure chemistry. I find hard imagining how MC3CODBCO3H can yield CH3COCO3H by photolysis. Since C4MDIAL is a common oxidation product of isoprene and aromatics, an updated treatment of C3MCODBCO3H and MC3CODBCO3H would result in more OH-recycling for both VOCs. I would like to see the impact of such changes to the modelled HOx concentrations.

Minor comments

p.9733 l.20-24

This statement is confusing as no direct OH-regeneration from 1,6-H-shift of CISOPAO2 and CISOPCO2. Do the authors ascribe the OH generated by 1,4-H-shifts of C536O2 and C537O2 to the 1,6-H-shift of CISOPAO2 and CISOPCO2? If this is the case it would be more appropriate to assign this OH generation to 1,4-H-shifts. This way line (1) in Figure 11 is problematic. I suggest the authors to find a way to eliminate this source of confusion.

Technical comments

p.9719 l.19

It should be "Brégonzio-Rozier et al. (2015)" and not "Brégonzio-Rozier et al. (2014)"

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