Atmos. Chem. Phys. Discuss., 10, C1699–C1702, 2010
www.atmos-chem-phys-discuss.net/10/C1699/2010/

Atmospheric
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Discussions

Interactive comment on "Impacts of mechanistic changes on HO_x formation and recycling in the oxidation of isoprene" *by* A. T. Archibald et al.

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Received and published: 15 April 2010

We have repeated calculations using a constrained non-diluting box model (sequential reaction model) according to reactions listed in our Table A3 (Karl et al., ACP, 2009) without and with changes in suggested RO2 and HO2 reaction rates (kisopdo2-ro2=1.4e-12 cm3/s; kisopbo2-ro2 = 4.8e-13 cm3/s kho2=1.7e-11 cm3/s). The model is initialized with constant isoprene emissions. NO, RO2, HO2, OH and O3 are held fixed. For OH, RO2 and HO2 radicals I adopted approximate concentrations listed in Figure 3 (Archibald et al.). The set of differential equations is run to steady state using a stiff solver. Figure A shows the evolution of the MVK/MAC ratio for different conditions similar to Figure 7 in Archibald et al. For conditions encountered during AMAZE (e.g. NO ~100 ppt) the MVK/MAC ratio is shifted somewhat as suggested (solid blue vs dashed

blue line). The combined effect of different RO2, HO2 reaction rates and lower NO concentrations (10 pptv) reduces this ratio (MVK/MAC ~ 4-6) by approximately a factor of two compared to previous results (Karl et al. 2009) (e.g. solid blue vs red line). This is still significantly higher than ratios reported by Archibald et al. (e.g. MVK/MAC ~ 0.6 – 1.8). The MVK/MAC ratio can be further reduced by significantly increasing RO2 radical concentrations (e.g. by a factor of 10 - green line). Conceptually this picture is consistent with the fast 1,6 isomerization reactions (Peeters et al., 2009) which largely outcompete HO2 and RO2 reactions and, initially, roughly impose an 8 to 1 ratio on the partitioning between MVK and MAC (e.g. 1,6 (Z14) and 1,6 (Z41) shifts are 1 s-1 and 8 s-1; see schematic figure B). Reactions with RO2 and HO2 will change this partitioning somewhat. For example Archibald et al. suggest kro2 x RO2 and kho2 x HO2 in the range of 0.0066 - 0.033 s-1 and ~0.12 s-1 respectively. I did not explicitly model the structural dependence of RO2 cross-reactions as suggested by Archibald et al. (e.g. primary + primary, primary + secondary, secondary + tertiary, etc.). However it appears that this is neither done by the MCM Leeds. For example from Figure 2 (Archibald et al.) I read that ISOPDO2 or ISOPBO2 react with the entire RO2 pool rather than with individual species of the RO2 pool according to peroxy radical permutation reactions (e.g. Madronich and Calvert, 1990).

References: Peeters et al., PCCP, 2009; Karl et al., ACP, 2009; Madronich and Calvert, JGR, 1990.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 5863, 2010.

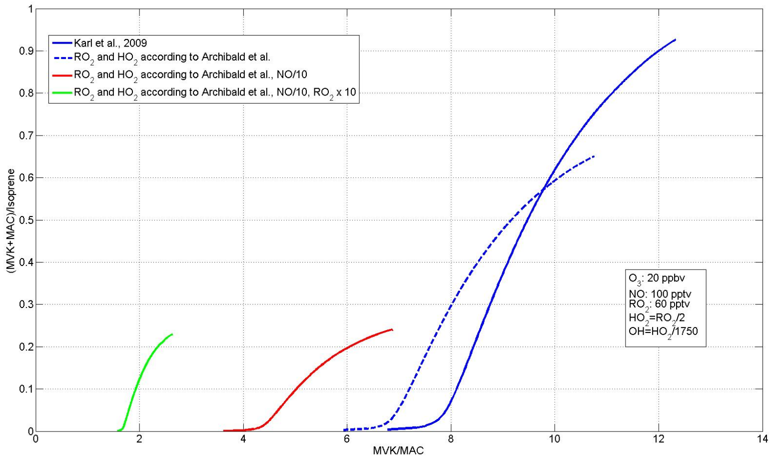

Fig. 1. Figure A: (MVK+MAC)/isoprene vs MVK/MAC. Each trajectory ends at the steady state limit for continuous isoprene supply.

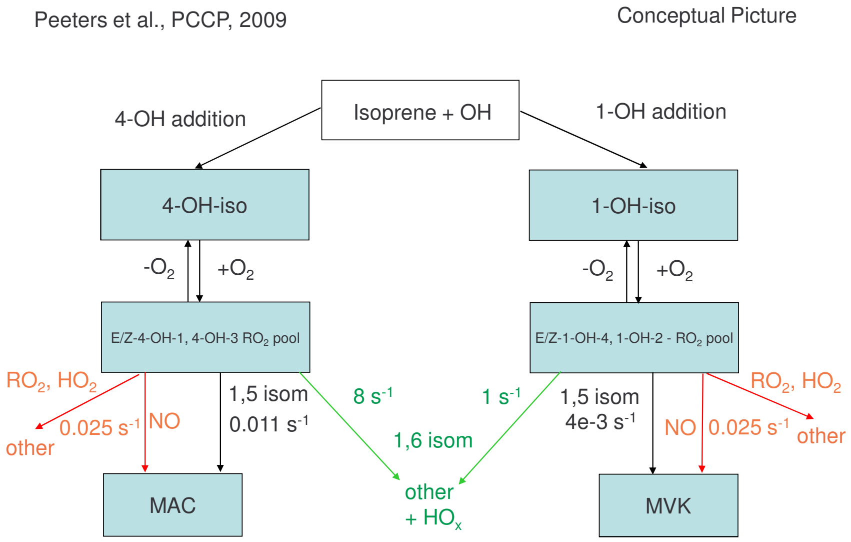

Fig. 2. Figure B: Conceptual picture proposed by Peeters et al., (2009)