

Interactive comment on “Mainz Isoprene Mechanism 2 (MIM2): an isoprene oxidation mechanism for regional and global atmospheric modelling” by D. Taraborrelli et al.

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The reduced mechanism presented here has 50% of OH addition occurring at C2, consistent with the MCM. Several lines of evidence indicate that, in contrast to the MCM, almost all OH adds to C1 and C4. If the first step of the MCM OH + isoprene mechanism is wrong, it is hard to see how the MCM is an appropriate starting point for further model reductions.

Notes on the branching ratios of the reactions leading to peroxy radicals are presented below:

- 1) The MCM mechanism for isoprene is stated to be based on a reduced version of that
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by Jenkin and Hayman (1995) and Jenkin et al. (1998). But Jenkin, et al., assumed OH addition to C2 (leading to R3O2) and C3 (leading to R4O2) each occurred with a branching ratio of only .047.

2) Structure-Reactivity relations: Peeters et al published (EUROTRAC Symposium '96) an SAR suggesting OH addition to C2 and C3 were minor pathways (15% in total, I believe).

3) Computational Chemistry: Lei, et al., Chem. Phys. Lett. 326 (2000) 109-114 computed branching ratios for OH addition to C1, C2, C3, and C4, as 0.56, 0.023, 0.046, and 0.37, respectively. The Lei, et al., 2000 paper is superseded by the much more rigorous work of Greenwald, et al., (J. Phys. Chem. A 2007, 111, 5582-5592), which obtained 0.67, 0.02, 0.02, and 0.29. Greenwald, et al., considered the uncertainties in their model parameters, and obtained fairly small error bars (0.01-0.03).

Moreover, Park et al, (PCCP 2003, 5, 3638-3642) indicate that the isoprene-OH adduct resulting from OH addition to C2 of isoprene is quantitatively converted to pent-4-en-2-one, so no peroxy radical is formed. The analogous adduct from OH addition to C3 only yields the corresponding peroxy radical in ca. 50% yield, the balance being 3-methyl-but-3-enal. Subsequent experimental work with 1,3-butadiene (J. Phys. Chem. A, 109, 7915-22, 2005) provides support for the theoretical work of Park, et al.

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