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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A consistent molecular hydrogen isotope chemistry scheme based on an independent bond approximation" *by* G. Pieterse et al.

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Title: A consistent molecular hydrogen isotope chemistry scheme based on simplified structure-activity relationship analysis Author(s): G. Pieterse, M. Krol, and T. Röckmann

This is an excellent paper that is useful to the community. The authors have built a rigorous conceptual framework and distinguish between the molecular isotope effect MIE, the kinetic isotope effect KIE and isotopic branching IB, and put this system to work in an atmospheric model. In this way they are able to identify the critical factors leading to the distribution of deuterium in atmsopheric trace gases. I provided detailed

comments to the authors at an earlier stage and am glad to see that many have been implemented. I recommend that it be published after slight revision.

The discussion leaves room for a significant amount of laboratory and theoretical work to explore the assumption that, as found on page 5686, 'The key assumption in the functional group approach is that the probability of abstracting a(n) H atom from a compound is independent of the presence of a heavy isotope at another location in this coumpound, i.e. that secondary isotope effects are negligible.'

On page 5688 near the top, It is not the interaction with a bond that is important, but rather the abstraction of an atom. Also, there is no reason to believe that the reactivity factor of 9 is universal for H/D abstraction reactions, far from it, for methanol it is around 2. Recommend rewriting as, 'This means that the rate for OH abstracting hydrogen from CH in methane is almost nine times larger than the rate of hydrogen abstraction from CD. This factor will vary from one compound to another.'

Equation 12. It is confusing to choose the superscript 'H' to represent 'Heavy' (that is, D), instead of 'Hydrogen' since H does mean hydrogen most other places in the manuscript.

5690, It is an oversimplification to only include the OH reactions of isoprene and ethene. This should be discussed more in the text, since O3 and NO3 will also be significant reaction partners for these compounds.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 5679, 2009.

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Interactive Comment