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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric deuterium fractionation: HCHO and HCDO yields in the CH_2DO+O_2 reaction" *by* E. Nilsson et al.

E. Nilsson et al.

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We would like to thank the referee for the very useful comments, including advice about the rate constants used in the model. The text below summarizes our responses to the referee’s report— in each case we have agreed with the referee and changed the manuscript accordingly.

Referee: Anonymous referee 2

This paper reports a study of the reaction of CH2DO with O2, specifically quantifying the yields of HCHO and HCDO. The results are consistent with this reaction leading to deuterium enrichment and, given that this reaction is a component step in the atmospheric oxidation of methane, help to explain observed enrichments in atmospheric hydrogen, for which methane-derived formaldehyde photolysis is the major source. The

methodology appears sound, and the results of the experiments are generally well described and discussed. Subject to consideration of a number of points outlined below, this paper is appropriate for publication in ACP. With the exception of the introduction, this paper is suitably concise.

1. In my opinion, the introduction is unnecessarily long, and could be shortened, probably to about 50% of its current size. Much of the introductory material seems to be somewhat peripheral to the required background for understanding the context of the reported work, and the key points about where the title reaction fits into the atmospheric methane oxidation mechanism, and the potential of the various steps for fractionating deuterium could be covered much more efficiently. For example, the extended discussion of the CH3O + O2 reaction mechanism on pages 10022 and 10023, whilst interesting, would seem more appropriate for a review paper, i.e. it is not a discussion of aspects of the reaction on which new information is gained in the current work. REPLY: Introduction shortened according to recommendations from referee. Some parts relevant for the discussion of the results are moved to Section 4.

2. Figure 1 should include the co-reagent species on the various conversion steps presented. REPLY: Figure not changed but the reader is now directed to Figure 1 for the full reaction mechanism.

3. Page 10026: The statement of that the impurity CH3ONO in the CH2DONO sample was checked by FTIR, and an upper limit assigned, has already been made on page 10024. REPLY: Omitted the unnecessary information on page 10026.

4. Although obvious to some, it should perhaps be pointed out somewhere in the paper that the relative yield of HCDO:HCHO on a statistical basis alone would be 66.7%:33.3% (probably on page 10028). REPLY: Information added on page 10028.

5. The appearance of CH3OH in Figure 2 and Table 1 does not appear to be explained. Is it impurity from the CH3ONO sample? REPLY: CH3ONO is synthesized from CH3OH. A comment on this is added to Section 3. The use of a model to ex-

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amine possible interferences in the result is sensible. Having said this, inspection of the mechanism listed in Table 1 reveals some unexpected omissions in the chemical scheme, and some erroneous rate coefficients. Although the major processes may be adequately represented, the authors should certainly consider if any of the following have an impact on their results, and refine their final branching ratio accordingly:

6. R3, R4, R26-R28: These reactions have been studied, and published rate coefficients are available. which differ from those used. These should be used. REPLY: Referee means reaction R5, not R3? Rate coefficients have been modified as follows: R4: Wilson et al from 2006. 6.37E-12 R5: Platz et al 1999. 6.7E-12 R26: Rowley et al 1992. 1.3E-14 R27: Rowley et al 1992. 7.7E-14 R28: Boyd et al 2003. 17.1E-12

11. R10: The PNA lifetime with respect to thermal decomposition (via the reverse reaction) at 300K is of the order of 10 seconds. This should be included, as irreversible loss of HO2 via R10 may distort the results. REPLY: Reverse reaction added to the model as R34.

12. R17 and R23: O2 co-product should be declared in the table for clarity (even if not in the simulation). Also, several reactions should have O2 reagent declared for clarity. REPLY: O2 reaction co- product and –reactants added to table for clarity.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10019, 2007.

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Interactive Comment