

## ***Interactive comment on “Atmospheric deuterium fractionation: HCHO and HCDO yields in the CH<sub>2</sub>DO+O<sub>2</sub> reaction” by E. Nilsson et al.***

### **Anonymous Referee #2**

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This paper reports a study of the reaction of CH<sub>2</sub>DO with O<sub>2</sub>, 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. 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

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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  $\text{CH}_3\text{O} + \text{O}_2$  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.

Figure 1 should include the co-reagent species on the various conversion steps presented.

Page 10026: The statement of that the impurity  $\text{CH}_3\text{ONO}$  in the  $\text{CH}_2\text{DONO}$  sample was checked by FTIR, and an upper limit assigned, has already been made on page 10024.

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

The appearance of  $\text{CH}_3\text{OH}$  in Figure 2 and Table 1 does not appear to be explained. Is it impurity from the  $\text{CH}_3\text{ONO}$  sample?

The use of a model to examine 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:

R3, R4, R26–R28: These reactions have been studied, and published rate coefficients are available. which differ from those used. These should be used.

R10: The PNA lifetime with respect to thermal decomposition (via the reverse reaction)

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at 300K is of the order of 10 seconds. This should be included, as irreversible loss of HO<sub>2</sub> via R10 may distort the results.

Also:

R17 and R23: O<sub>2</sub> co-product should be declared in the table for clarity (even if not in the simulation). Also, several reactions should have O<sub>2</sub> reagent declared for clarity.

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

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