

## ***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.***

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This paper describes some clever experiments to measure the H/D fractionation in the reaction of CH<sub>2</sub>DO with O<sub>2</sub>. Whilst this reaction is important in the atmospheric oxidation of deuterated methanes, in this case the radical was prepared by photolysis of CH<sub>2</sub>DONO. The reaction scheme provides a fairly direct measure of the relative yields of HCHO and HCDO, and hence the relative rates (or equivalently the KIE) for abstraction of the two hydrogen atoms. While I have some questions about the experimental analysis (see below), I do not think it affects the relative yields, in agreement with the authors.

The paper is pretty clear. The rationale for the experiments is well stated. The authors should probably also include a brief comment about the stratospheric significance of

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methane oxidation for the H<sub>2</sub> and H<sub>2</sub>O budget.

The experimental details should include more detail on concentrations and conditions. I was able to figure out what was going on from the figures, but either a range of concentrations or a summary table would have been useful. For example, Figure 5 shows HCDO concentrations increasing up to 400 ppm, which clearly should be 4 ppm, according to the data in Figure 6. However, I could have figured this out much more quickly with a table of concentrations. Please include the nitrite and cyclohexane concentrations, reaction times and percentage conversion of the nitrite.

Was NO added to the experiments, or simply the NO formed from nitrite photolysis? What about deuteromethanol? Was this left over from the synthesis?

Page 10028, line 25. The product of R(10) should be given as HNO<sub>4</sub> (PNA), not HNO<sub>3</sub>.

Rate constants in Table 1: R5: It is no longer believed that larger alkyl peroxy radicals react slowly with NO. This should probably be closer to 8E-12.

R8 and R9: The numerical values seem reasonable, but the footnote says they are 0.05% of the RONO photolysis rate. Presumably should be 5%.

R10: Should be reversible, especially if the NO concentration is low.

R13 and R14 are given as low pressure limits, both in Table 1 and in the model readout in the Supplemental material. If these were really treated as third order reactions, it leads to rate coefficients at 1 bar which are about a factor of 50 larger than the high pressure limit. This could overestimate the amount of methyl nitrate formed, and consequently reduce the amount of CH<sub>2</sub>DO reacting with O<sub>2</sub>. This should not affect the fractionation; however, since the carbon balance in Figure 6 looks quite good, I wonder just how much methyl nitrate was formed, and where the rest of the carbon goes if the rate coefficients R13 and R14 are reduced. Depending how the "extra" formaldehyde is lost (HO<sub>2</sub>, OH or photolysis) the fractionation could change.

R17: This is the value at zero pressure. Should be closer to 3E-12 at 1 bar.

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R27 and R28: It appears from the Table that cyclohexane is regenerated in the model (reactions R27 and R28) to provide a constant OH sink. This is fine, but the text says that loss of cyclohexane was on the order of  $10^{-5}$ . This is presumably an artifact of the model. Was there a measurable loss of cyclohexane? Maybe the residual spectrum at  $1730\text{ cm}^{-1}$  is cyclohexanone?

Furthermore, if cyclohexane does not decay in the model, this presumably suppresses the contribution of OH + HCHO. What happens to the fractionation if the cyclohexane is allowed to react away in the model?

None of these issues should affect the fractionation significantly, and simply running the model with corrected rate coefficients should take care of everything.

Overall, this is a very elegant piece of work, which could be improved by a little extra clarity in the description and explanation.

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