

Interactive comment on “Atmospheric deuterium fractionation: HCHO and HCDO yields in the CH₂DO+O₂ reaction” by E. Nilsson et al.

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Received and published: 1 October 2007

We would like to thank the referee for useful comments, both for pointing out some obvious mistakes and for recommendations regarding content and rate constants. All comments have been considered as detailed in the text below.

Referee: G. Tyndall

This paper describes some clever experiments to measure the H/D fractionation in the reaction of CH₂DO with O₂. Whilst this reaction is important in the atmospheric oxidation of deuterated methanes, in this case the radical was prepared by photolysis of CH₂DONO. 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

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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.

1. The authors should probably also include a brief comment about the stratospheric significance of methane oxidation for the H₂ and H₂O budget. REPLY: Material added to introduction.

2. 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. REPLY: Clarifying details about concentrations and experiment added to beginning of Section 2.2. Figure 5 has been corrected.

3. Was NO added to the experiments, or simply the NO formed from nitrite photolysis? What about deuteromethanol? Was this left over from the synthesis? REPLY: The NO is all formed from nitrite photolysis. Deuteromethanol was left over from synthesis. Comment about this added to Section 3.

4. Page 10028, line 25. The product of R(10) should be given as HNO₄ (PNA), not HNO₃ REPLY: Changed according to comment from referee.

Rate constants in Table 1:

5. R5: It is no longer believed that larger alkyl peroxy radicals react slowly with NO. This should probably be closer to 8E-12. REPLY: R5: Platz et al 1999. 6.7E-12

6. 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%. REPLY: Changed 0.05% to 5%.

7. R10: Should be reversible, especially if the NO concentration is low. REPLY: Reverse reaction included in simulation and in Table 1 as R34.

8. R13 and R14 are given as low pressure limits, both in Table 1 and in the model read-out 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 CH₂DO reacting with O₂. 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 (HO₂, OH or photolysis) the fractionation could change. REPLY: New values valid for 1000mbar; R13: 2.34E-26 R14: 5.46E-26

9. R17: This is the value at zero pressure. Should be closer to 3E-12 at 1 bar. REPLY: Recalculated. New value: 2.3E-12.

10. 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 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? REPLY: Neither experiments nor model show that cyclohexane reacts away to a significant extent. Brief comment added in section 2.2.

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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