

Interactive comment on “Deuterium fractionation in formaldehyde photolysis: chamber experiments and RRKM theory” by E. J. K. Nilsson et al.

Anonymous Referee #2

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This paper presents observations of the kinetic isotope fractionation that occurs during the photolysis of D₂CO (relative to CH₂O). The authors then use RRKM theory to help interpret their results, and conclude that a theory falls short of explaining the observations.

This paper does not really discuss the theoretical framework behind RRKM theory beyond using a canned model result to compare with observations. This is really a paper that presents new measurements. So, first, the observations. The authors use FTIR to monitor the relative reaction rates of the isotopologues in a photolysis reaction chamber, at different pressures. From these data they get Figure 2. Figure 2 is the meat of the paper; Table 2 is derived from Figure 2. In figure 2, the log-log plot of the ratios of each species is plotted. A slope is then derived. The slopes are reported in Table 2 and

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the authors claim the uncertainty in those slopes is essentially insignificant. However, this is a problem with the units. Figure 2 is a log-log plot. So an uncertainty of a few percent in the slope, as reported, is a little bit misleading. Take, for example, the data at the 400 mb and the 200 mb pressures. There is clearly a significant deviation between observations the slope of the lines in the figure. Are the authors really claiming that the uncertainties associated with those two slopes at those two pressures to be near 0? I get 0 because the authors say ‘errors include an additional 3% error to account for uncertainties in reference spectra’. But the values are 1.7+/-0.05 and 2+/-0.06. So the reported errors are equivalent to about 3% of the value, which means the error in the calculated slope is about 0. As can be seen in Figure 2, there is a large deviation of the slopes from the data. A linear regression, or 95% confidence interval, would result in a much larger uncertainty than is reported in Table 2. Of course, the work reports a very large KIE across the board, so the more accurate errors won’t change the mean values much.

The authors use a fairly standard model approach to compare results with theory. Other than they don’t match (no surprise there), there is no insight given .

The authors claim these results don’t support the results from Rhee et al. 2008. But they don’t back this up. An enhanced discussion with Rhee’s results would be great. It is not obvious from Table 1 whether these results are, or are not, consistent with the previously reported results. Furthermore, the authors claim these results support the observations that show an enrichment in the minor isotopologues of H₂ with altitude; but this is a rather glib statement that doesn’t take into account any other production (and no removal) mechanism for atmospheric hydrogen. Without a proper modeling study that constrains the system, one cannot back up this statement.

Overall, the paper lacks any sort of detailed discussion. The paper refers too heavily on the author’s earlier publication for the method used and for the results. Even if this is an identical paper, the authors need to expand more on the methods here rather than referring to a different paper. Furthermore, if this paper is so close to the other paper,

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one wonders the value of this incremental step, without a more detailed discussion comparing and contrasting the two different isotopologues CHDO and CD₂O.

I wonder how variations in bath gas composition might affect the observations.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 10303, 2013.

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