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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hydrogen isotope fractionation in the photolysis of formaldehyde" *by* T. S. Rhee et al.

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Preamble:

I refer to specific lines in the original manuscript as xxxxx-yy, where xxxxx is the page number and yy is the line number.

General comments:

The authors of this paper conducted careful experiments to measure the photolytic hydrogen isotope fractionation between CH2O and H2. They varied a range of parameters, such as actinic flux by using natural sunlight and a xenon arc lamp as light sources as well as quartz and glass reactors. They also varied the photolysis time and initial CH2O mixing ratios. The results are interpreted with the help of a box model,

to account for undesired photochemistry in the reactor. The results for the initial deuterium depletion of the H2 product (alpha_m) appear to be more robust than the implied fractionation factor for the radical channel. However, the uncertainty associated with alpha_m seems to be an underestimate, as explained below. There are also discrepancies between the box model simulations and the measurements, which make the implied fractionation in the radical channel more prone to systematic errors than suggested by the presently assigned values.

Although the authors varied a range of parameters, I personally would have preferred to do more than 25 runs to explore the influence of the various parameters more systematically. For example, all but 5 experiments were let to proceed to near complete conversions. The 5 experiments, for which the initial photolysis phase was investigated, have been carried out at CH2O mixing ratios that are one to two orders of magnitude higher than the other experiments (about 50 micromol/mol as compared to 0.4 to 2.6 micromol/mol). This was presumably due to obtain sufficient H2 for analysis, but it raises questions about the influence of wall effects and CH2O polymerisation. Although such effects have been discounted by a blank experiment (12719, 5-6), it is not clear whether the amount/pressure of CH2O that was added in this blank experiment corresponds to the higher or the lower mixing ratio used for the photolsysis experiment. Also, two days for the blank experiment is relatively short compared the experimental runs, which have lasted up to 16 days.

Given that the experiments have been conducted three to four years ago, it will probably be difficult to address the following points, which might help resolve some of the ambiguities of the experiments. Therefore, they probably need to be left for future studies and cannot be considered for a revised version of the present manuscript.

1) Experiments with the same initial CH2O mixing ratio and under the same actinic flux regime (same light source, same reactor), but various degrees of CH2O conversion. This would help discern the controlling parameters and prove the validity of the box-model used to interpret the results. The experiments should be conducted at a CH2O

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pressure range for which wall effects and polymerisation reactions have been shown not to play a role (see my comment abobve).

2) Measurements of the initial hydrogen isotope composition of the reactant CH2O by a different technique than mercury arc lamp photolysis, for example, pyrolysis. Rice & Quay (Anal. Chem. 78, 2006) demonstrated a precision of 0.5 per mille in deltaD for a 2.0 micromol/mol HCHO reference material. This would allow independent verification of the absence of any isotope effects in the conversion of CH2O to H2 by mercury arc photolysis. The chemistry that leads to H2 production in the radical channel under these harsh photochemical conditions could lead to artifacts. For example, there could be H2 formation from radical reactions with H2O adsorbed to the reactor walls and/or isotope exchange. It could be that the same artefacts occur in the sunlight and xenon arc lamp experiments, which would lead to the wrong conclusion that the deltaD value of the initial CH2O is identical to the final H2 product.

3) The isotopic composition of the residual reactant CH2O should be measured at the end of the experiment for various photolysis times. This would allow determining alpha_f and, potentially, its variation directly.

In addition, I have the following specific comments and technical corrections that should be addressed in a revised version of the paper.

Specfic comments:

1) Please consider using different symbols for "small" phi(H2), "capital" Phi(H2) and the "asymptotical value of phi(H2)". The present font makes it very difficult to distinguish between the various phi's. The "asymptotical value of phi(H2)" could, for example, be distinguished by an "infinity" sign as an index. The symbol for "capital" Phi(H2) should be set in italics, because it is a physical quantity.

2) These quantities should be defined exactly, for example phi(H2) = [H2]/[CH2O]_0 and Phi(H2) = d[H2]/d[CO], or, for only photolysis, Phi(H2) = [H2]/[CO] =

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[H2]/([CH2O]_0-[CH2O]=phi(H2)/(1-f), as implied by 12723-18.

3) Please add a glossary with symbols used for quantities such as phi(H2), Phi(H2), alpha values, etc. This would make it easier to follow the statements and calculations made in the paper.

4) The term "complete photolysis" has different meanings in this paper. For the experiments with the mercury arc lamp, it means that all CH2O has been converted by photolysis and by reactions with, presumably, H. For the sunlight and xenon arc lamp experiments, it means most CH2O has been photolysed, but a significant fraction has also reacted with H, OH or HO2. And in 12717-20, "complete photolysis" refers to the molecular channel of CH2O photolysis.

5) Use of ppb and ppm for mixing ratios is deprecated. Both units are not part of the IUPAC and SI system of units (see IUPAC Green Book Quantities, Units and Symbols in Physical Chemistry). Instead, mixing ratios should be given as nmol/mol, micromol/mol, etc. (ditto; Schwartz, S. E. and Warneck, P., 1995. Units for use in atmospheric chemistry. Pure and Applied Chemistry 67, 1377-1406).

6) 12716-6: The findings about alpha_m and the deltaD value of the final H2 product in themselves do not imply anything about the radical channel. In addition, the relative contribution of the reaction of CH2O with OH must be known, as the extensive discussion in section 4.2 shows.

7) 12719-3: What type of glass was used for the reactor? In Fig. 1, a quartz reactor is mentioned. What are its dimensions? Was it made entirely of quartz and what type of quartz was used?

8) 12719-28: What is the measurement uncertainty of deltaD values and mixing ratios of the Rhee et al. (2004) method?

9) 12720-1: What is the dominant emission line of the mercury arc lamp? 254 nm? 185 nm? It would be useful to show a comparison of the relative actinic fluxes of the different

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light sources (perhaps convoluted with the formaldehyde absorption spectrum).

10) 12720-5: Figure 4 shows four unlabelled data points near phi(H2) = 1.0. Do they correspond to mercurcy arc lamp photolysis? The corresponding points are missing in Figure 1. They suggest conversation ratios between 0.95 and 1. What are the associated uncertainties for the deltaD value of the reactant CH2O and what are the implications of the less than 100 % conversion?

11) 12720-8: STD in this paper is the mean isotope ratio of H2 produced by mercury arc lamp photholysis of CH2O.

12) 12722-18: Please define standard temperature and pressure or avoid this term. The definition of STP has changed various times over the years and could mean 25 žC, 0 žC, 101325 Pa, 100000 Pa, etc., with further differences arising for different scientific and engineering disciplines.

13) 12723-20; The authors gloss over the large discrepancy between model simulations and measurements, which imply an unrealistic SZA of 85ž. Shouldn't this be more cause for concern about the validity of the measurements? Even if the derived value for alpha_m was correct (it is actually confirmed independently by the measurements of Feilberg et al. 2007b), then the derived alpha_f value would be wrong, if the photochemical box model and the Phi(H2) value proved to be invalid. More experiments would be needed, as suggested above.

14) 12727-14 tp 12728-9: This could be shortened significantly: By definition of the fractionation factor, the isotope ratio of the initial H2 is equal to that of the initial CH2O times the fractionation factor.

15) 12727-19: The uncertainty of 20 per mille seems to be too small given that the uncertainty of the final product is 40 per mille (Table 2). SInce the final product of mercurcy arc lamp photolysis is the "reference material" for the present study, I would expect the uncertainty of alpha_m to be at least this large.

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16) 12728-9: "f approaching 1" - Eq. 13 is not defined for f = 1.

17) 12728-11: Under which conditions does "complete photolysis" (see my comments above) give the same isotope ratio for H2 as for the initial CH2O?

18) 12733-17: In an email to the authors of the present paper (sent on 9 November 2005), I pointed out that Eq. 20 and paragraph 28 in Rhee et al. (2006a) are wrong. My comment appears to be reflected by the corresponding Eq. 20 in the present paper, which is now correct. It would be nice if the authors acknowledged my contribution to the present work.

Technical corrections:

1) 12715-6: "Utrecht"

2) 12721-10 to 16: Repeated contents, needs rephrasing.

3) 12722-27: "was used to integrate the kinetic rate equations"

4) 12726-5: "-1" should be part of the exponent.

5) 12732-22: "photolysis in the molecular channel"

6) 12742, last row: "144 h" (the period from 5 June to 11 June is only 6 days).

7) 12742, Table 1: Please include the experiments with the mercury arc lamp here. How do you define daylight hours? SZA $>$ 90ž? SZA $>$ 96 ž?

8) 12743, Table 2: The uncertainty range for the photolys rates actually includes negative values.

9) 12745, Table A1: Please include the corresponding units for the rate coefficient, temperatures, pressures, etc.

10) 12746: The y-axis label phi(H2) should be in italics. What are the errors for the fit parameters? The symbols for the experiments do not match the dates given in Table 1 and the explanation in the figure caption. I would prefer to see all symbols explained

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in the figure legend (i.e. Quartz - March, May June; Glass, September; Glass - June). The caption mentions experiments in August, but there are none in Table 1. Please also add the data from the mercury arc lamp.

11) 12747: Local noon in Mainz is 11:27 GMT because Mainz is at 8ž16'E longitude. I would prefer to swap the axes for yield and photolysi rate to avoid the dark grey shaded areas crossing over the curves. It is confusing that the SZA at local noon are indicated on the x-axis, but the dark grey areas correspond to the daily mean values.

12) 12749: What are the triangles in the upper right corner of the figure? Mercury arc lamp experiments? The x-axis title phi(H2) should be in italics.

13) 12750: The data point for SZA = 90ž is mentioned in the caption, but not shown in the figure.

14) Grammar: There are a number of misplaced commas and the definite article ("the") is often used incorrectly.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 12715, 2007.