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Atmospheric
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Discussions

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

T. S. Rhee et al.

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We thank Jan Kaiser for the comments on our paper.

We reply the questions and comments on point-by-point basis as follows:

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.

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Q: 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.

R: We chose the uncertainty of alpha_m such that all the data measured is covered by the uncertainty. alpha_r could be prone to systematic errors due to incomplete simulation of measurements. To account for this, we ran a sensitivity analysis by changing in several parameters which are relevant to calculation of alpha_r in the box model.

Q: 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.

R: As mentioned in the reply to the other reviewers, heterogeneous reactions on the wall surface of the reactor and CH2O polymerization are not likely. As written in the line 14 of page 12719, the CH2O mixing ratios of stock air is ˜ 0.3 %. This means that the partial pressure of CH2O for the 'blank test' was ˜3 mbar. Several papers report that CH2O was not polymerized up to ˜10 mbar. In addition, note that the photolysis experiments were carried out at 50 or ˜ 2 ppm which is orders of magnitude smaller than the amount of CH2O for blank test. Thus, although the blank test ran only two days, this is enough to see if CH2O polymerization may occur during experiments. Furthermore, as shown in Figure 1, the lifetime (or e-folding time) of CH2O in the reactor is about ˜20 hours. Thus, it is not necessary to test the blank run for 16 days.

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

R: It is indeed impossible at the moment to conduct further experiments, but they are not necessary for the present paper. The aim of the present experiments is to determine the degree of isotopic fractionation occurring in the photolysis of CH2O under ambient conditions. It may be indeed interesting for future experiments to test what the reviewer suggests. However, as replied to all reviewers, it is not likely for polymerization or other heterogeneous reactions to significantly influence the present experiments.

Q: 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.

R: Of course it is necessary to verify the results from the present study by a different approach in future. As mentioned above, however, complete photolysis of pure CH2O produces only CO and H2. Isotope exchange between H2 and other compounds or intermediates are not likely (see the reply to M. Johnson).

Q: 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.

R: This is a good suggestion if CH2O can be isolated from other compounds produced in the photolysis. Isotope analysis on CH2O is still under development (Rice and Quay, 2006) and cannot be just added as a routine measurement.

Q: 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.

R: Notation, phi(H2), is replaced by 'capital' psi(H2) in the revised manuscript. The reviewer's suggestions are appreciated. However, we prefer not to use too many symbols in the manuscript. Furthermore, as the 'asymptotic value of phi(H2)' is not used in the mathematical or chemical expressions, we like to keep the descriptive expression. All symbols are set in italics.

Q: 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.

R: The definitions for Phi(H2) and Psi(H2) are clearly expressed with phrase in the revised manuscript. The mathematical expression of Phi(H2) above is not correct, since CO is produced from both the reaction CH2O + OH and the photolysis of CH2O in the reactor. As stated in the text, Phi(H2) is defined as the yield of the molecular channel in the CH2O photolysis and can be determined when CO and H2 are formed only by CH2O photolysis without their destruction in the reactor (in particular CO + OH). Even on this assumption, Phi(H2) = phi(H2)/(1 - phi(H2)) is wrong since the denominator of the equation does not result in ([CH2O]_0 - [CH2O]), but in (([CH2O]_0 - [H2]). The line 12723-18 should be read as that the asymptotic value of phi(H2) equals to the product of Phi(H2) and capital Gamma.

Q: 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.

R: We decline this suggestion because each notation has been explained wherever necessary.

Q: 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.

R: This point was also commented by M. Johnson and accordingly we revised it.

Q: 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,

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micromol/mol, etc. (ditto; Schwartz, S. E. and Warneck, P., 1995. Units for use in atmospheric chemistry. Pure and Applied Chemistry 67, 1377-1406).

R: We followed the conventional use of the units in atmospheric chemistry. Units of volume mixing ratios such as ppm or ppb are interchangeable with micromol/mol or nmol/mol (Warneck, 1999). The two expressions are identical in terms of dimensionless units.

Q: 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.

R: One should differentiate the laboratory experiment and implication to the atmosphere. As explained in detail in the present paper, the values of alpha_m and the deltaD of the final H2 are key parameters to estimate the isotopic fractionation factor for the radical channel in the experiment. The variability of OH concentration in the atmosphere only implies whether the H2 from CH2O photolysis produce H2 enriched in D or H.

Q: 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?

R: As written in the line 15 of the same page, all glasses used in the experiments are made of Duran (Schott). The volume of the quartz bulb is about 1 L and it is made of quartz (SiO2). We do not know the type of quartz.

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

R: The uncertainty of dD of H2 is less than 4 permil, and that for H2 mixing ratio is 2 % of the value.

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

R: According to the data sheet of the manufacturer (OSRAM), the dominant emission line of Hg short arc lamp (HBO 103W/2) is 366 nm. For the shake of comparison, the relative scale of light intensities is shown in Figure 1.

Q: 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?

R: The data represent the results from photolysis with the Hg short arc lamp. The uncertainties of the conversion is only related to the fraction of H2 produced by CH2O photolysis (phi(H2)), but not to the dD-H2 value, since the dD-H2 values are the same within their uncertainties (see Table 1). The values of phi(H2) were corrected for the conversion factor of the CH2O photolyzed with the Hg arc lamp.

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

R: For clarification we have added the following sentence: 'For convenience, we express the dD values relative to the isotopic composition of the parent CH2O.'

Q: 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 ÿC, 0 ÿC, 101325 Pa, 100000 Pa, etc., with further differences arising for different scientific and engineering disciplines.

R: The phrase is revised.

Q: 13) 12723-20; The authors gloss over the large discrepancy between model simulations and measurements, which imply an unrealistic SZA of 85°. 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.

R: We have further discussed this issue in the text. One thing to keep in mind is that the experiments under ambient conditions were carried out without the control of any parameters relevant to CH2O photolysis whereas in the model run we defined a specific value for each parameter relevant to CH2O photolysis.

Q: 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.

R: Shortening the phrases is welcome. And what the reviewer suggested is correct. However, here we deliberately derived the alpha_m at phi(H2) = 0 by means of Eq. (13) for clarification, whereas the reviewer counts on the definition of isotopic fractionation factor.

Q: 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.

R: The analytical uncertainty of dD values of H2 obtained from photolysis of pure CH2O is only 5 permil, which is less than 20 permil of uncertainty chosen for determination of the error of alpha_m. The uncertainty of the dD-H2 of the final product in Table 2 is from the results of photolysis experiments for the mixture of CH2O and synthetic air under ambient conditions.

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

R: The expression is revised.

Q: 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?

R: Here complete photolysis means the reach of asymptotic value of phi(H2). The ambiguity of the term complete has been removed, see above and the reply to M. Johnson&'s comments.

Q: 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.

R: I acknowledged already in Rhee et al. (2006a) and hope this is sufficient. I do not consider this comment appropriate in a public forum.

Technical corrections: 1) 12715-6: "Utrecht"

R: Revised.

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

R: The phrase explained findings and the reasons, but not repeated same content.

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

R: Revised the sentence.

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

R: Revised.

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

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R: The original expression seems to be fine.

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

R: Thank you for the reviewer's scrutiny. The photolysis had been conducted from May 31 to June 11, 2004 with a pause of 12 hours between June 4 and 5. Since the exact dates for photolysis with artificial light sources appear redundant, they are excluded in the revised table.

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

R: The results with the Hg arc lamp are included in the revised version. Daylight hours were calculated using astronomical parameters as indicated in the footnotes.

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

R: The prescribed value for J_CH2O is a weighted mean while the range was assumed to be half of the full range of the theoretical photolysis rate of CH2O (0° $<=$ SZA $<=$ 90°) under the photochemical conditions of Mainz. Now the uncertainty is revised such that the range of photolysis rate is between 0 and 7.67x10ˆ-5 as shown in Figure 2. capital Delta alpha_r is calculated with the largest value of uncertainty, 4.5x10ˆ-5.

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

R: Temperature and pressure are fixed at 298.15 K and 10ˆ5 Pa. The units of the rate coefficients are added in the footnote the table.

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 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.

R: The fitting curves are from model runs at the given values of photolysis rates (see Appendix A for the boundary conditions of the model). There is clearly an error in indexing the month to symbols. As the experimental dates are shown in Table 1, symbols are grouped only by material of the reactors and light sources in the revised figure. We did not conduct experiments with the Hg arc lamp to determine a yield of H2 from the photolysis of CH2O and synthetic air mixture.

11) 12747: Local noon in Mainz is 11:27 GMT because Mainz is at 8°16'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.

R: Here GMT indicates time zone to calculate SZA (Finlayson-Pitts and Pitts, 1999). We understand the reviewer's concern. However, different gray colors should avoid the confusion.

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.

R: The symbols are noted in the revision.

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

R: The figure caption is revised.

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

R: We revised it where to be necessary.

References:

Finlayson-Pitts, B.J. and J.M. Pitts, Jr.: Chemistry of the upper and lower atmosphere, 969 pp., Academic Press, San Diego, 1999.

Rice, A.L., and P.D. Quay: Anal. Chem. 76:6320-6326, 2006.

Warneck, P.: Chemistry of the natural atmosphere, 927 pp., Academic Press, San Diego, 1999.

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

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