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

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Commentary on Hydrogen Isotope Fractionation in the Photolysis of Formaldehyde

There is clearly a great deal of hard work behind this paper which concerns a critical step in the photochemistry of the atmosphere. I suggest that the paper would be more useful to the readers of ACP if the following points were to be addressed.

The terms 'incomplete photolysis' (R1) and 'complete photolysis' (R2) are defined in the introduction, referring to the H + HCO and CO + H2 product channels in formaldehyde photolysis respectively. This terminology is confusing, because the experimental procedure relies on the complete photolysis of an HCHO sample to products, presumably involving some amount of both the 'complete' and 'incomplete' pathways. These

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two reactions are usually called the radical channel and the molecular channel. For example, page 12749, caption to Figure 4, it is written '...that the complete photolysis of CH2O yields H2 with a dD value that is the same as that of the initial CH2O.' It is unclear whether this means '100% photolysis of CH2O via R1 and R2 but leading to 100% yield of molecular hydrogen' or 'Photolysis only at wavelengths that can produce H2 via R2'

The introduction should contain a reference to J. Troe's recent work on the photolysis of formaldehyde, Troe, J., Analysis of quantum yields for the photolysis of formaldehyde at lambda > 310 nm. Journal of Physical Chemistry A, 2007. 111(19):p. 3868 - 3874.

There are significant uncertainties in the experimental procedure that are not discussed adequately in the text:

1. What is the role of heterogeneous reactions in the photolysis cell? Many pathways are possible, for example: formation of paraformaldehyde; isotopic fractionation in the photolysis of paraformaldehyde, trimeric formaldehyde or surface-adsorbed formaldehyde; isotopic exchange between hydrogen and water (either surface-adsorbed water present at the beginning of the experiment or water formed by R3, R6, R11, R17, R24, R26, R28); isotopic exchange between hydrogen and formic acid or hydrogen peroxide; isotopic fractionation due to diffusion of hydrogen through the glass; isotopic fractionation occuring due to radical recombination reactions on the surface. It is known that isotopic exchange will take place when hydrogen is stored in a flask with water.

2.The authors have made a significant technical advance in developing a procedure for measureing the absolute concentration of hydrogen gas in a sample and are able to combine this with a measurement of dD(H2). This is not an easy measurement. The mercury arc lamp will produce H2, but also H and HCO, and a complex secondary chemistry will ensue. It is very important that the authors present the raw data concerning the absolute hydrogen concentrations produced in the 'complete photolysis' experiments. For one thing this will document how much if any hydrogen is lost through

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conversion to H2O, H2O2, HCOOH, etc., which would alsmost certainly involve iso-topic fractionation. In addition the uncertainty in the hydrogen measurement must be combined with the uncertianty in the pressure gauge measurement of HCHO concen-tration to give the uncertainty in the in the dD of the original HCHO. Also the accuracy of the hydrogen concentration measurement must be ca. 3%. It is inadequate to simply argue that there is 100% conversion given the number of complicating issues that are present. It is hard to be convinced that the uncertainty in the determinatin of the dD of the original HCHO is 4 per mil. Also 12728, 11, 'Given that complete photolysis of CH2O yields H2 that has the same isotopic ratio as that of the initial CH2O...' This topic is fundamental to the paper and should be discussed in more detail. Was there any evidence of H2O, HCOOH or HOOH formation (for example, were these measured, could they be seen in the cold trap used to clean the H2 sample?) Also note 12732, 6-8, '...follows from the fact that the isotopic compositions of the inital CH2O and of the H2 that are formed from complete photolysis are identical.' Here the assumption has become a fact. 'Identical' is rather strong given the complexity of the photochemistry and the difficulty of the measurements. It would be better to present a proper error analysis than to assume.

The spectral distribution of the actinic flux is a key parameter in this paper, as is the spectral distribution of light from the lamps. Are measurements available of the spec-tral flux distribution for the solar photolysis experiments? It would be useful to add UV spectra of the glasses used in the experiments as supplementary information to the paper– e.g. the Schott duran and quartz glasses used. The UV transmission of quartzes varies and the cutoff is not simply 'ca. 200 nm' for all types.

At the top of page 12723 it is written that 'the unique source of H2 in the reactor is CH2O photolysis' but according to the model presented in Table A1, molecular hy-drogen is produced by R2, R4, R10 and R16. Please present model results for what fraction of the H2 is coming from these other sources.

On page 12723, line 11, 'there are substantial differences between the measurements

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and the model predictions at longer photolysis periods.' The model is not able to reproduce the experiments, i.e. the photochemistry in the cell is not captured by the model. Why is this? In addition to differences in the gas phase, there are likely to be reactions occuring on the surface. These uncertainties should be included in the final result. Another indication of problems is that while the solar zenith angle for the experiments was 27 to 48 degrees, the model predicts that the sza would need to be 85 degrees to match the results (12723, 20). It appears that too much molecular hydrogen is being produced in the experiment relative to the model, which could be a sign of radical recombination reactions on the surface or other kinds of surface photochemistry.

12731, 28, what is not direct about the spectroscopic measurement?

12732, 1-4, these factors are accounted for in the error analysis of this paper.

12732, 5, what is the relevance of the comment 'performed at the level of natural deuterium abundance'? It is true that Feilberg et al. use enriched samples but this has nothing to do with the veracity of the result.

12743, it is great that the authors have done a sensitivity analysis of the model since this is the key to the data analysis. There are a few comments.

1. The uncertainty parameter in the relative photolysis rates of $H_2O_2$ and $CH_2O$ is 4 percent of the ratio. This seems too low, the absorption cross sections themselves of both of these compounds are likely to be in error by at least this much, not to mention uncertainty/changes in the spectral distribution of the actinic flux.

2. The kinetic isotope effect of $CH_2O + OH$ has been measured, but the KIEs of the $CH_2O + H/HO_2$ reactions have not been measured. The $CH_2O + HO_2$ reaction is an association reaction (as opposed to abstraction) and a guess of 1 with a large error bar would be better than the current guess.

3. The sensitivity analysis has included the uncertainty in the KIEs of the H, OH and $HO_2$ reactions, as discussed, but it has not included uncertainty in the concentrations

of these radicals. This is a serious point. The lifetimes of the radicals will depend on many things including surface reactions, concentrations of reaction partners and other radicals, concentrations of impurities. It would not be unreasonable to assume that the modeled concentrations could vary from the true concentrations by more than 50%. This will clearly have an effect on the uncertainty of alpha r. (see also Figure 3).

Proofreading:

12716, 24, 'a wide large range' $->$ 'a large range'

12721, 26 to 29, unclear sentence, please rewrite.

12722, 2, I believe this capital phi should be a lowe case phi, since only the lower case phi is a measurable quantity

12722, 27, 'FACIMILE' $->$ 'FACSIMILE'

12723, 12, the sentence beginning 'In particular...' cannot be understood, please rewrite. What is the phrase beginning 'that are based on most likely values' referring to?

12727, 5-6, 'By the same way' $->$ 'Similarly'; 'results in a same relations' $->$ 'results in similar expressions'

12733, 3, subscript '-H2'

12738, 13-15, this paper is now published, the full reference is, K. L. Feilberg, M. S. Johnson, A. Bacak, T. Röckmann and C. J. Nielsen, Relative tropospheric photolysis rates of HCHO and HCDO measured at the European Photoreactor Facility, Journal of Physical Chemistry A, 111 (37), 9034 -9046, 2007.

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