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Interactive comment on “Pressure dependent deuterium fractionation in the formation of molecular hydrogen in formaldehyde photolysis” by E. J. K. Nilsson et al.

Anonymous Referee #1

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This paper describes photolysis of formaldehyde, using an artificial light source, by FTIR detection of the rate of removal of HCHO relative to that of HCDO at varying bath gas pressures. Isotopic information may help to better understand certain aspects of the important oxidation pathway from CH₄ to H₂ and CO, and the fate of HCHO in general. Therefore these experiments are important, but after reading the manuscript, the reader is left with many questions. The extensive modelling of the isotopic chain of atmospheric HCHO by e.g. Mar et al. 2007 had shown that the fractionation for deuterium must be different in the stratosphere, but no parameter (pressure, light spectrum, temperature) could be identified. It now is likely that pressure plays a major role. Thus the fact that H₂ shows a nearly flat vertical profile, and stratospheric enrichment

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of D in H₂ can be better understood now. An important question is however why the present experiments are not compatible with results from other studies. Importantly the study by Feilberg et al.(2007) is from the same group. At the outset the reader is puzzled why there is no explanation given why this is the case. If comparison with other laboratories is difficult, one would expect a discrepancy or inconsistency of this sort to be given scrutiny.

The manuscript shows that several issues/statements need consideration or changes. The experiments are not as conclusive and uncertainties/confusions still remain.

The title should, if maintained in this form, at least be “Pressure dependence of..” because it now suggests that there is a pressure independent fractionation and a pressure dependent fractionation. The authors have not measured the hydrogen formed for its D/H ratio. To be clear, the title should state that it is the fractionation of deuterium in formaldehyde due to photolysis using lamp light.

Abstract. Why is the rate for HCHO given relative to that of HCDO (only ~0.03% of natural H₂CO)? The isotopic ratio is wisely given as the D/H ratio; that is the rare over the abundant isotope. Why then relate the reaction rate of the abundant isotopologue to that of the rare one? In this way, the isotope community makes it harder for non specialists to work with their data. Is the measurement uncertainty at 50 and 1030 mbar 0.1 in both cases? How accurate is an uncertainty estimate that the authors give 2 significant digits at 1030 mbar? The “extrapolation” of the lamp results to the stratosphere at 50 km seems premature. Written is that the ratio between the channels depends on actinic flux. Is this a result of this study? The abstract is not acceptable.

The introduction requires work. P24030, L22. Does the statement by Forster et al. pertain to the reaction of H₂ with OH, or also including the soil sink? The lifetime of CO is about 1 month and its concentration is about 80 ppb. H₂ has about 500 ppb, but its lifetime against OH is several years. The reviewer is not certain here, please check this. If the removal by soils is involved the statement has no value in the context of this

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paper.

P24030, L24. “the rest is removed by soil bacteria”. Because this is the larger fraction, one should state it the other way around, namely, “the rest is removed by OH” It also is an insult to the soil bacteria involved. Moreover, is it the bacteria, fungi, or perhaps mostly certain soil enzymes? Unless one is well informed it is safer to use the concept “soil sink”.

P24030, L25. The statement is badly formulated and hence useless, also because it is superfluous. I suggest to delete it.

P24031.L6. The quantifier “dramatic” is not a rational concept. Furthermore, in the same sentence, the meaning of the word “presumed” is no clear.

P24031.L8. “biogenic VOC is likely to be at least this depleted in deuterium”. Even though this is a citation, it raises questions. Atmospheric CH₄ is depleted in D because of several reasons, one is that bacterial CH₄ (wetlands, ruminants) is depleted. The reason can be understood on the basis of metabolic pathways. But for VOC it is not so clear. Is this statement based on atmospheric measurements? If so, it must be based on certain VOCs, these should then be mentioned. Is it based on isoprene (abundant species) D/H measurements?

P24031, L20. CH₃D reacts slower, why then are the products enriched in D? Why do the authors write “more slowly” and not (more objectively) slower? Also notice the semantic inconsistency that now results from the statement in the abstract (H relative to D, thus one would logically write “faster”, certainly not “more speedily..).

P24031.L23. “great” One may state that there are “great scientists or presidents” but for isotope fractionation, this qualifier is not appropriate.

P24031.L27. “these”, which ones exactly are meant?. “a depletion” or better “the depletion”

P24032.L6. “Roaming atom”. Going into detail, a question that arises is whether water

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clusters play a role in HCHO photolysis in the troposphere. This potentially is another factor that differs between lab experiments (reactors) and outside air.

P24032.L25. Table 1. The light source used by Rhee should be mentioned. Often in papers, the authors list their result in a table with results from others. Extending Table 1 would help readers to get a clearer impression, certainly because there are discrepancies.

P24032.L27. “similar ..even though.. statistically distinct” One more grey hair here, this is a sort of statement we read in newspapers.

P24033.L3. Why this statement? What is the H2 isotope scheme? What about the role of the “great deuterium enrichment”.

P24033.L14. Is the diameter of the reactor 25 cm? Why does it have stainless steel flanges? Stainless steel is a mixture of iron, nickel and more, and these elements are known to exhibit a wide range of catalytic properties. It seems to be an unwise choice, unless the flanges are coated or treated to render their surfaces inert. Is the tube made of quartz or of silica. Quartz is found in nature, often is not so pure, and rarely in the form of a tube.

P24033.L23. The inlet line was heated. Why this? Is the pressure in the inlet line so high that formaldehyde condenses on its wall? How can one be sure that only formaldehyde molecules enter the reaction chamber. When the tubing is heated, why then should the reactor not be heated? Furthermore, when for instance laboratory air enters such a reactor, several layers of water molecules form on its surface. These layers are very persistent. Was the reactor “baked” prior to the experiments? How is this for formaldehyde? Even one monolayer of formaldehyde represents an amount that can be significant. Could it be that HCDO is enriched on the wall of the reactor? How does HCHO stick to silica surfaces with abundant OH groups? Are hydrogen bridges involved? This could give a strong preference for the absorption of HCDO over HCHO. The authors correctly point out that small vessels may have stronger artefacts. How-

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ever the surface to volume ratio is basically a function of one dimension only, which means that surface effects are not orders of magnitude smaller. In particular in laboratory experiments and using FTIR much could have been verified that now intrinsically remains questionable. Perhaps the authors used a method similar to Gratien et al. (2007), which is a basis for confidence that pure gas phase results free of artefacts haven been obtained. One way to admit formaldehyde would be to expand it from an intermediate known volume, and ascertain that the pressure ratios are as expected for an ideal gas free of absorption problems. But perhaps the absorption problems are related to the amount of water on the walls of the reactor. It remains unsatisfactory, and the discord with other results (of what?) raises doubts. For how long did experiments typically last?

P24034, L2. Why does Table 2 not give the formaldehyde partial pressures (or ranges)? Why were these pressure selected (0.09 to 4.5 microbar)? How were these pressures measured? The authors write that their reactor is temperature controlled. Have they tried to raise the temperature and observe the change in the (initial) formaldehyde pressure?

P24034.L5. From Figure 1 it is not visible where the maximum light intensity is. What was the light intensity in the reactor?

P24034. Is it possible to use the FTIR spectra to check for the water content of the gas in the reactor? How high was it?

P24035.L25. “After convoluting with the photolysis lamp spectrum, recent work by Troe shows..” This is an interesting statement. Did Troe wait for Copenhagen?

P24035. Given the lamps used, what fraction is actually following the radical channel? There seems to be an (unavoidable) uncertainty here.

P24036.L20. In Figure 5, mistakingly Figure 4 is mentioned. Also note that in the literature we use the full stop as separator and not the comma. The authors can perhaps

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change the language setting in their Microsoft software, to get correct plots.

P24037.L3. Why exactly are such values unacceptable?

P24037.L23. The fit does appear not to fit. Why is this? Furthermore, Fig 6 and Fig 3 can be combined. To devote a figure to this fit seems unreasonable. Or is Figure 6 meant to be for atmospheric conditions, which cannot be true. Why is there such a large spread (similar but statistically different) in the measurement results displayed in Figure 3. Figure 3 has a very brief caption, that basically tells nothing more than we glean from the figure. What error bars are given, how were they determined? How do the authors explain the deviations?

P24039. It is unfortunate that the work is not convincing in many aspects, also because the reporting is poor. What was the surface to volume ratio here, and by others? Further... "including our analysis here" assumes the ratios to be wavelength independent. There is literature on isotope enrichment using laser light. Enrichment is attractive when there is a strong wavelength dependence.

In the end the authors recommend what has to be done, including using FTIR for checking the products. The biggest question mark is formulated as follows. When the present results are in conflict with earlier work in the same lab, why is this not discussed, and why is FTIR then not used to check product channels to avoid the uncertainty about the results.

Whereas both channels produce CO, only the molecular channel produces H₂. Even aliquot taken from the reactor could have been analysed for the D/H ratio of the H₂ formed.

When reading the paper, one gets the impression that the authors believe that the only reaction in the reactor is the photolysis of formaldehyde. What role did other photochemical reactions play, how much OH was formed? In the troposphere OH is formed directly by UV light photolyzing ozone. However, radical formation leads to a

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great deal of recycling of OH. Given the radical reactions in the reactor, can OH be excluded, H₂O₂ etc.?

The quantum yield of the molecular channel depends on pressure, but there are few data on this. What was the quantum yield under the conditions used? Has it been measured? Neither for the actual lamp conditions, and not at all for sunlight conditions is “ c (= kh/kH)” known, and the implications for the real atmosphere bear therefore large uncertainties. Note the disagreements with the various daylight experiments.

Compared to GC analyses, FTIR can do much more (we hope) and it remains strange that actually only 2 variables have been observed. If there would be no disagreements so far, one could justify the experiment, but when there is conflict one has to go further. In particular the presence of chemistry other than photolysis is not treated. Maybe the spectra still hold valuable information for a more complete analysis.

Remaining points. Why is in Table 2 “:” (unusual) used as separator and also “/”. Are the nominal ratios based on pressure readings or FTIR measurements? What is the meaning of the classifier “nominal”? The figure captions in general are not precise and informative enough.

It is my opinion, that the manuscript can unfortunately not be accepted. Because the work is pure laboratory work, should it, after changes be better submitted to a specialist journal?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24029, 2009.

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