

Interactive comment on “Isotope effect in the formation of H₂ from H₂CO studied at the atmospheric simulation chamber SAPHIR” by T. Röckmann et al.

Anonymous Referee #2

Received and published: 25 January 2010

Isotope effect in the formation of H₂ from H₂CO studied at the atmospheric simulation chamber SAPHIR.

These experiments add to our knowledge of the deuterium kinetic isotope effects in the photolysis of formaldehyde. A new estimate of KIE_{mol} is provided that is near other recent determinations. However, the authors argue that KIE_{rad} and KIE_{mol} are likely not as different as described in the literature. As detailed below, these arguments lack an accounting of sources of statistical uncertainty, and a quantification of the overall effect of these factors on KIE_{mol} and KIE_{rad}. It is likely that the error in KIE_{mol} will be adjusted upwards by a significant amount, and, unfortunately, that the error in KIE_{rad}

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will be so large that the result is not useful. In addition, there is a good mechanistic reason not to expect that KIE_{mol} and KIE_{rad} should be the same. The mechanism of photodissociation is very different in these two channels. The quantum yield in the radical channel does not show a pressure dependence, while that in the molecular channel DOES. As described in ACPD 9, 24029, 2009, when the effect of pressure on KIE_{mol} is removed, the low pressure KIE_{mol} is actually equal to the (pressure independent) KIE_{rad}. So what is actually going on would seem to be the opposite, and there is no problem with the atmospheric pressure KIE_{rad} and KIE_{mol} being different. It is important to extract as much information as possible from the experiments, but not to overstate what has been learned. According to the discussion on page 25198 lines 11 to 13, the confidence interval was set at 0.03 'to account for possible differences between KIE_{mol} and KIE_{rad}.' It would be much better to have an error bar that is based on the uncertainties in the experimental data, the fits to the data and the sensitivity of the model. I do not find the article fit for publication; after significant revision this may be possible. Please see further discussion below.

25188, 6, 'the radical channel has only a second order effect' - this lacks precision. Second order in what? Effect on what? The radical channel accounts for 1/4 to 1/2 of formaldehyde photolysis, depending on actinic flux spectrum and choice of absorption cross section/quantum yield, and so at first examination, it is not a second order effect. Please clarify.

25188,10, There are significant uncertainties in the experimental data as described below, and this is compounded by the uncertainty of the model. Therefore it may not be justified to conclude that 'it is likely that KIE_{mol} and KIE_{rad} are not as different as described previously in the literature.' What is meant by 'likely'? Instead, please try to quantify this likelihood and if it cannot be quantified it should not be highlighted as a main conclusion in the abstract.

25188, 16, 'Since H₂ production only produces H₂O' - note that H₂ USE produces H₂O, whereas H₂ production consumes H₂O.

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25189, 1-2, water vapor in the stratosphere from H₂ will also affect mid-latitude stratospheric aerosol loading, impacting albedo and perhaps more importantly, mid-latitude ozone depletion via hydrolysis of N₂O₅/heightened sensitivity to HO_x and ClO_x.

25189, 9, reason 2, rather than 'atmospheric oxidation reactions', in situ production is due to one single reaction, the photolysis of formaldehyde.

25191, 2, please include error in KIEOH

25191, 6, please include error in KIE_{mol} and KIE_{rad}

25191, 8, please include error in KIE_{mol} and KIE_{rad}

25191, 10, 'in none of the experiments this KIE was measured directly'. The argument is good but please be specific about whether this refers to KIE_{tot}, KIE_{mol} or KIE_{rad}. Note that Feilberg et al. measured KIE_{tot} directly.

25192, 2, It is more usual to use 'matrix' for solids. 'Bath gas' is the accepted term.

25192, 9, The starting material was paraformaldehyde. I assume this was vaporised by heating with a flame? (Please describe). It is common that hot formaldehyde recondenses in the inlet, before it reaches the chamber. This can cause two kinds of problems. One is simply that the initial concentration of formaldehyde in the chamber is not as high as would be predicted based on the mass of paraformaldehyde. The second is that the inlet then serves as a hidden source of additional formaldehyde throughout the experiment. Please describe how the gas phase concentration of formaldehyde was determined since this is a central piece of information used to calculate the main results. Was it by FTIR, or UV-DOAS, or ?? If so, what cross sections were used to calibrate the measurements? UV and IR cross sections have recently been redetermined by Gratien et al. JPCA 2007, resulting in some cases in significant revisions. Due to the difficulty of working with formaldehyde even a very good spectroscopic measurement would be accurate to 5 %, probably more like 10% and possibly more than 20%. How does this error propagate through the model?

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25193, 6, Did these measurements include the actinic flux spectrum? (Is this what is meant by photolysis frequencies?) That would be very valuable, in order to predict the quantum yields in the molecular and radical channels. Otherwise this partitioning is based on assumptions. The actinic flux spectrum will change from day to day due to the solar zenith angle and atmospheric conditions such as cloudiness. The double layer of teflon will very likely change the spectrum, especially in the UV. What then is the error in the predicted quantum yields in the molecular and radical channels, and how does this error affect KIE_{rad} and KIE_{mol}?

25193, 6, Please present the data for the temperature, RH, pressure, photolysis frequencies, ozone, nitrogen oxides, carbon monoxide, HCs and HCHO, as supplementary information. This is important for evaluating the model. For example the chamber will produce OH and HO₂, and these radicals will interfere with the experiment by consuming HCHO. How much will depend on UV flux, ozone and NO_x, etc.

25193, 24, change '5A' to '5 Å'.

25194, 13 - 17, the error in determining [H₂] is 2%, and the error in determining dD of the formaldehyde is 2%. How do these errors propagate?

25194, 23, what is the error in the value 1.28 and how does this impact the results?

25194, section 2.1 The model is central to this paper because it allows the main results, KIE_{mol} and KIE_{rad}, to be estimated based on the experimental determinations. Therefore more detail must be provided concerning the model (as table of reactions or reaction diagram, and including model output, in supplementary information if necessary), most importantly the reactions concerning formaldehyde. Without this list it is not possible to check independently if the chemistry is correct. It is also important since additional reactions have been added to the model that these appear in the published paper so other scientists can build on this work.

The authors state that the model includes the KIE of the reaction of formaldehyde with

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OH. What concentration of OH is predicted in the chamber by the model, and what fraction of the formaldehyde is being removed by this reaction? How accurate is the model's estimation of OH - perhaps 50%? What is the uncertainty in KIE_{mol} introduced by uncertainty in [OH] and KIE_{OH}?

The reaction mixture included 500 ppm of CO to quench OH, and this may indeed prevent OH from reacting with formaldehyde - but the model will say for sure. The reaction is: $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ followed by $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$. Also, HCHO photolysis will produce H, and HCO. H will be converted to HO₂ as above, and $\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$. Therefore significant amounts of HO₂ will be generated in the chamber, and HO₂ is not quenched by CO. As described for example in Nilsson et al. 2007 (cf. Fig 2), HO₂ reacts reasonably fast with formaldehyde giving formic acid as the main product. What is the HO₂ concentration predicted by the model, was the HO₂ + HCHO reaction included in the model, and how much of the formaldehyde is being removed by this reaction? What KIE is used for the HO₂ + CH₂O reaction? How will errors in these numbers affect KIE_{mol}?

It is well known that the walls of reaction chambers produce formaldehyde, in particular when exposed to sunlight. For example the EUPHORE chamber produces ca. 1 ppb per hour (Zador et al., J. Atm. Chem. 2006; Feilberg et al. 2007b). There is no reason to think SAPHIR will be any different. Were measurements made of the background source of formaldehyde? It may not seem large however it does make a significant difference by the end of the experiment, when the integrated emission is larger and the concentration of formaldehyde is at its lowest. Feilberg found that the background source of formaldehyde gave a significant correction to the EUPHORE results. Assuming that the background source is 1 ppb per hour, how much would this change KIE_{mol}? Please add to uncertainty estimate.

25196, 16, the authors note that 'the system is underdetermined, since we only have one measurable, dD(H₂), but two unknowns, KIE_{mol} and KIE_{rad}.' In addition, at 25197, 8 - 14, it is noted that the model is relatively insensitive to changes in KIE_{rad},

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but somewhat sensitive to changes in KIE_{mol}, the difference in sensitivity being a factor of five. Further, at 25198, 7 it is argued that KIE_{rad} must be ≥ 1 because the ZPE of HCDO is lower than that of HCHO. While it is true that the ZPE of HCDO is lower it does not follow that KIE_{rad} must also be lower, for a few reasons. The ZPE argument rests on the reflection principle, see for example Yung and Miller's article in Science 1997. A key assumption for the reflection principle is that the system undergoes direct photodissociation. This is not the case for formaldehyde which undergoes an indirect dissociation confounded by multiple electronic surfaces and exit channels. A key piece of evidence for this is the highly structured UV absorption band. In addition formaldehyde has complicated dissociation dynamics with curve crossing and a competition between radical channel, molecular channel and collisional deactivation. Jumping over the discussion about how these dynamical processes change with isotopic substitution one could ask how the process of photoexcitation, that is the rate of absorption of light, changes with isotopic substitution. Rather than rely on the ZPE model which is not accurate even for direct dissociations, it is better to simply look at the absorption cross sections of HCHO and HCDO in the UV which have been measured by Gratien et al. JPCA 2007. They find that 'The integrated UV absorption cross-sections of HCHO, HCDO, and DCDO are equal to within the experimental uncertainty.' The bottom line is that there is not sufficient experimental or theoretical knowledge to justify this assumption. This is even more important because this limiting value is what determines the authors best guess result that KIE_{mol} = 1.63 and KIE_{rad} = 1. Given the uncertainties in the results and the insensitivity of the model to KIE_{rad}, it seems that the error bar of KIE_{mol} must be increased, and that either nothing at all can be said about KIE_{rad}, or that it can only be said in connection with a large error bar.

25197, 10, 'This is because both channels remove HCHO at roughly comparable rates (60%;40%).' Please provide actinic flux spectrum and state which cross sections/quantum yields were used in this calculation. What is the error in this calculation (plus or minus 5%??); how much does the actinic flux change from one day to the next; what is the effect of this error on KIE_{mol}?

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25197, 27, I see no reason other than convenience to assume that $KIE_{mol} = KIE_{rad}$. In fact, the mechanisms of the two channels would seem to argue against them being equal. Further, this error estimate does not take into consideration the points that have been raised above which will clearly have an effect.

25197, 29 to 25198, 1, 'do not agree on the magnitude or even the direction of the effect', please define what effect - the deviation of KIE_{rad} from KIE_{mol} ?

25198, 25 to 27, It cannot be concluded that 'it is impossible to quantitatively reconcile the results of Feilberg 2007b with the new dataset' because quantitative error bars have not been presented in the present work. Given the sources of error detailed above, it may be that the conclusion of this study is for instance $KIE_{mol} = 1.63$ plus or minus 0.16, and then this work and Feilberg are clearly in agreement. In addition for the reasons outlined above, I am not yet convinced that anything can be said about KIE_{rad} from this study, because of uncertainties in the experimental data, and of the data the model is based on, and even more because as the authors write the model is insensitive to KIE_{rad} and therefore we would not expect it to be able to provide a very accurate result.

25199, 19, The authors note that $dD(HCHO)$ was determined by the model, but was not measured in the photoreactor. Another reason to be concerned about the background/chamber wall source of formaldehyde is that there is no reason to assume it has the same dD as the synthetic paraformaldehyde that was used. If by the end of the experiment 1/5 of the formaldehyde comes from the background source, and this formaldehyde has a dD value that differs from the synthetic formaldehyde by say 100 per mil, it is easy to see that this would affect KIE_{rad} and KIE_{mol} .

25199 - 25200, Discussion. '...the values of KIE_{mol} , KIE_{rad} and KIE_{tot} reported in Feilberg 2007 are not consistent with the recommended relative photolysis yields of the molecular channel and radical channel.' This is true if it is assumed that 60% of the photolysis is in the molecular channel, and 40% in the radical channel. However, by

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taking the actinic flux spectrum published in the supplementary information of Feilberg, in combination with the JPL cross sections and quantum yields, it is seen that the split is not 60/40, but rather 72/28. Using the correct numbers it is seen that the numbers do in fact make sense - they are consistent with recommended values and they are self consistent. This underlines the need to publish the SAPHIR actinic flux spectrum with this paper, and shows that any uncertainty in the 60/40 branching will be associated with an uncertainty in KIE_{rad} and KIE_{mol} . These uncertainties do not seem to have been included in the analysis.

25201, 3 to 6, it does not seem that a reevaluation is called for.

25202, 8, 'Whereas the partitioning between KIE_{mol} and KIE_{rad} in Feilberg 2007 may be erroneous.' as written above, there is no evidence to support this statement.

25203, 'Pieterse 2009 already noted that in a simple box model of the isotopic composition of atmospheric H_2 it was difficult to close the isotope budget with the original values from Feilberg 2007.' Nor should one expect that that would be the case. It is erroneous to assume that results for KIE_{tot} , KIE_{mol} and KIE_{rad} obtained at atmospheric pressure can be used throughout the atmosphere. Please see ACPD 9, 24029, 2009 for a discussion of the pressure dependence of KIE_{mol} .

25209, Table 1, please include estimate of errors in these concentrations/delta values.

25211, Figure 1, Please provide a better description of the experiments in section 2. What the reader learns is that the experiments were begun at 10.00 and ended at 17.00. By inspecting the figure however it looks like H_2 was added already at 7.30 and $HCHO$ at 9.30? Was the chamber open for the entire period from 10 to 17, or only for a portion of this time? What is the cause of the break in the $HCHO$ and H_2 concentration data at 16.00? If this is when the chamber was closed to sunlight, I do not understand why $HCHO$ drops just after this event. One would expect rather that the formaldehyde would be lost more slowly in the dark.

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The lower right panel shows that there is very little difference between $KIE_{mol}=KIE_{rad}=1.63$ and $KIE_{rad}=1 KIE_{mol} = 1.63$. Given all the uncertainties, I do not find convincing evidence here for revising estimates for KIE_{rad} or arguing that either Feilberg or Rhee are in error. We know already that the two results do not agree - is there any additional information that this study can provide regarding KIE_{rad} , given no measurement of $dD(HCHO)$, significant errors that have not been taken into account and a model that is insensitive to variation in KIE_{rad} ?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 25187, 2009.

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