

Interactive comment on “Mass spectrometric measurement of hydrogen isotope fractionation for the reactions of chloromethane with OH and Cl” by Frank Keppler et al.

Anonymous Referee #2

Received and published: 21 February 2018

Summary of the manuscript

The authors studied hydrogen kinetic isotope fractionations of CH₃Cl occurring in its reactions with OH and Cl by measuring change of $\delta^2\text{H}$ of CH₃Cl in a smog-chamber, in which CH₃Cl contained in the filled air was destroyed with time. As expected from the Rayleigh equation for kinetic isotope fractionation, the authors observed clear relationships between $\delta^2\text{H}$ and mixing ratio of CH₃Cl, by which they estimated the kinetic isotope fractionation factors.

General comment

CH₃Cl is the most abundant chlorine containing gas in the atmosphere, but it is not
C1

the target species of the Montreal protocol since emission regulation is not effective for stratospheric ozone recovery, given that its main sources are natural. An improved global budget estimate for CH₃Cl is important for reducing uncertainties of future ozone prediction. In particular, the globally largest source, vegetation, is unknown in many aspects, emitting plant species, processes, mechanisms and global emission magnitude etc.

As examined for relatively “major” trace gases such as CO₂, CH₄ and CO, isotopic mass balance is a powerful tool to separate different source categories and sink processes in the global budget. General approach is that atmospheric isotope ratio is considered to equal to sum of isotopic fluxes from all sources corrected for kinetic isotope fractionations that happen in sink processes. For this purpose, accurate values for the all terms of the mass balance equation are required. Measurement of isotopic composition of CH₃Cl is a difficult technical challenge and thus many of necessary terms in the isotopic mass balance are lacking. In this context, this study addresses the sink terms and it indeed gives an important contribution.

New data presented in this study is significant and overall the paper is well organized and concise. I would recommend publication of this manuscript in ACP after some of concerns and questions below are considered.

1. One earlier study Sellevåg et al. (2006) reported more ²H enrichments for the all reactions addressed in this study e.g. CH₃Cl + OH, CH₃Cl + Cl and CH₄ + OH. Although the authors avoid deeper discussion and it may be difficult to identify the dominant cause now, maybe can they specify potential sources that could systematically bias either experiment? Any difference in smog chamber settings or production of OH/Cl radical? Use of different measurement method (FTIR versus IRMS)? In particular, spectroscopy measurements (FTIR) do not require chemical conversion of sample gas, but IRMS measurements need chemical conversion from CH₃Cl or CH₄ to H₂ which could cause isotope fractionation.

2. Estimation of the kinetic isotope effect in this study relies on simple regression of the data (Figure 2–4). Lower remaining fraction f at the end of the experiment would cover wider range of the X axis and more frequent sample collection would increase the number of data, both might change the regression result. What is the limitation factor in the experiment? Beside this, the regression in principle should start from the point of origin ($X=0$ and $Y=0$), but the authors do not taken into this account. Why?

3. Section 2.4 is an important introduction. I would move this section into section 1 with some reformulation. Section 1 could be enriched so that readers could better understand overview of the global isotopic mass balance for CH_3Cl and importance of KIE to close the budget. I would reformulate P3 L65–L89. The authors might present mass balance equations (mass balances for mixing ratio, $\delta^{13}\text{C}$ and $\delta^2\text{H}$) and then readers could clearly find the key role of the KIE in estimating the budget using isotopes. This would also help the authors for discussions in section 5.

4. I am not sure how the new unit “mUr” would be accepted in the research community, because people are used to see the conventional unit ‰. In reality, I was very confused throughout the manuscript. The authors might want to share the newly suggested unit in the manuscript, but in my opinion the authors should choose one that would advance scientific discussion more smoothly under the current situation. It might be too early to use the new unit in a scientific paper even if it alters the conventional one in the future (I am not sure for this though).

Specific comments

P3 L65–L89: As in the earlier comment, I would like to suggest to reformulate the paragraphs so that readers could get the principle framework of the global isotope budget and how determination of the KIEs contributes to it.

P3 L81: “in view of the unexpected isotope fractionation” Please elaborate what this phrase means. What is expected and what is unexpected? Do you expect that FTIR measurements could be somehow biased?

C3

Sections 2.1 and 2.2: Please describe traceability of mixing ratio measurements (both CH_3Cl and CH_4). Samples are measured against the working gases, but those working standards were calibrated ultimately to what type of standards or scales?

P6 L141: What is “PFA”?

P6 L157: “relative trueness” I am not familiar with this wording. Does it mean that a sample is measured against the working standard gas (H_2) that were calibrated independently? Please reword. Otherwise please define “trueness” and “relative trueness”.

P6 L159: typo “LSVEC”, but description about NBS22 and LSVEC is not necessary, because $\delta^{13}\text{C}$ measurement is out of scope.

P6 L167: It appears to me that the SD magnitude is not in relation to the absolute $\delta^2\text{H}$ value but that it depends on the relative “distance” from the value of the working standard. In such a large range of $\delta^2\text{H}$ values determined by extrapolation, the IRMS response could not be linear any more or cause a significant system-dependent bias.

P7 L170–174: Please refer to my general comment no 4.

P7 L175: Please see my comment to P6 L167.

P7 L194: Same comment as above (P6 L167). This sentence should be reworded as the authors also mention to the possible error in the IRMS calibration. The current sentence is misleading as in my earlier comment.

Section 2.4: I would move this to section 1 or at least before section 2.1 since the content is the principle of this study rather than measurement methods which constitute large part of section 2.

P8 L218: might be more specific i.e. the heavier CH_2DCI or CH_3D .

Figure 2: See my general comment no 2. Also the authors should specify significant digits in the annotation of the graphs.

C4

Figures 2–4: “~10 (or 6) ppmv”. How precisely/accurately was the CH₃Cl mixing ratio measured? This relates to transparency of the error bars given in the figures.

P10 L10: What is the “limited analytical resources”? The information might help following researchers.

P14 L306–309: As in the earlier comment, I would like to see a bit deeper discussion. The authors might be able to specify possible or potential sources of the biases.

P14 L310ff: The authors might want to validate their results by comparing to previous measurements and to indicate advantage over Sellevåg et al. (2006). Even supposing that the KIE of the CH₄ + OH reaction are in good agreement, the fact might support validity of the chamber set-up (common in all the experiments in this study) but not of the IRMS measurement including preparation steps that are not identical for CH₃Cl and CH₄. Please clarify this point in the manuscript.

P14 L331: “cmu” capitalized?

P15 L354: “excellent agreement” looks a bit exaggerated. This study’s result agrees to some of previous measurements within the range of uncertainty. Skeptical eyes could see this study’s result for CH₄ + OH reaction being at less negative end among previous measurements (Table 1) and this possible trend is also the case for CH₃Cl + OH/Cl reactions.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-8>, 2018.