

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 #3

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The paper presents isotope fractionation measurements of CH₃Cl for the reactions with hydroxyl and chlorine radicals and CH₄+OH. This is a valuable contribution to the hitherto scarce information on hydrogen kinetic isotope effect of reactions significant for the atmosphere. Isotopes deliver valuable adjunct information which can, together with other data, increase the understanding of the atmospheric processes. Therefore the paper is highly suitable to be published in the journal. The paper contains yet some weak points which need to be improved before publishing.

Major comment:

The major issue which should be made clearer to the reader is linked to the necessity

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of very accurate concentration and isotopic composition of the reactant during its degradation for delivering reliable epsilon values. Since during both oxidation reactions of CH₄ and CH₃Cl a similar temporal evolution of the concentration is observed, it should exist one order of magnitude difference in the produced OH concentration. For the former, this should be in the range of 10¹⁰ cm⁻³ range, which is very ambitious for the photooxidation of ozone method. The authors should give some more details about designing the experiments, for instance on ozone concentration, UV lamp intensity... To rule out any losses of the very small methane molecule (wall permeation, tightness), it would be helpful to add a figure (also as supplement) depicting a 'zero-run', i.e. the concentration evolution of methane in the FEP bag without reaction during the time of 10 h.

Other comments:

Page2Line62: The authors might consider to add a short statement on the significance of CH₃Cl losses into the stratosphere.

Page3Lines83-84: reformulate, the authors give themselves enough literature sources for hydrogen isotopic fractionation studies.

Page8Equation2: The authors should revise the consistency of this equation: they should keep 1000 also behind the second '='. This is dependent on the delta expression, and as it looks like (behind the first '='), this is in x10⁻³, permil, or the unusual murey.

Editorial revisions:

Page6Line 141: replace PFA by PFH

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