

Interactive comment on “Evidence for a major missing source in the global chloromethane budget from stable carbon isotopes” by Enno Bahlmann et al.

M. S. Johnson (Referee)

msj@chem.ku.dk

Received and published: 8 October 2018

General Comments. This paper presents convincing experimental evidence and arguments supporting the view that earlier measurements of the KIE of the $\text{CH}_3\text{Cl} + \text{OH/Cl}$ were in error, the true value being 5 to 6 times smaller. This is based on experiments carried out in a 3500 L smog chamber coupled with offline IRMS analysis of canister samples. The analysis was further verified using GC-IRMS in two different laboratories. The conclusion is supported by the lack of a significant seasonal covariation in tropospheric $\text{d}^{13}\text{C}(\text{CH}_3\text{Cl})$ values. Further, comparisons are made with KIE's determined by experiment and theory in chemically similar systems, which would also seem

Printer-friendly version

Discussion paper



to indicate a revision in the accepted KIE. The revised KIE triggers an interesting and timely reanalysis of the atmospheric chloromethane budget.

Specific Comments. Accepting that other small molecules react with a smaller KIE, as argued at the bottom of page 6/top of page 7, this still does not account for the large KIE determined in the transition state theory study: As written in Sellevåg 2006, there will be a higher barrier to internal rotation in $\text{CH}_3\text{Cl} + \text{OH}$ than in $\text{CH}_4 + \text{OH}$. The authors note that they cannot find a flaw in these studies by Sellevåg and Gola; Sellevåg may have agreed with the experimental work of Gola 2005 by a kind of perverse luck. In which case we should thank the authors of this work for their careful re-analysis. I would feel better though if there was a corresponding theoretical reanalysis; the question remains unanswered. $\text{CH}_3\text{Cl} + \text{OH}$ certainly will have a more constrained transition state than $\text{CH}_4 + \text{OH}$.

Technical Corrections. I must complain a little bit about the use of units. 'micromole / mole' is fine, and I am often reading about 'ppm', but why use them both in the same paper? If you are going all in with IUPAC and SI notation then apply it consistently and use only the former and it's related forms, never the latter. (e.g. page 4 line 32, page 6 lines 11 and 12, etc.) Always put a space between number and unit (e.g. (page 1 line 22 = p1ln22), p4ln25, p4ln345, p11ln4, etc.) Are you using 'L' for the liter p1ln22 or 'l' p5ln33? Be consistent. p3ln2, 'CMC Instruments' Check p3ln23, p5ln6, p6ln9

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-855>, 2018.

[Printer-friendly version](#)[Discussion paper](#)