

Interactive comment on “Kinetic and mechanistic study of the reaction between methane sulphonamide (CH₃S(O)₂NH₂) and OH” by Matias Berasategui et al.

Anonymous Referee #2

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This paper describes original laboratory studies of the OH rate coefficient and atmospheric oxidation pathways for methane sulphonamide (MSAM), a molecule recently detected for the first time in ambient air by a subset of the co-authors. In general, this is an excellent study, and the subject of the work is clearly suitable for publication in ACP. Assumptions and limitations are clearly and logically presented and discussed. It is comforting to see detailed calibration curves presented in the supplement, kinetic simulations of the proposed mechanism carried out, etc. The observation of an anomalous rate of oxidation of SO₂ by OH is intriguing, and I look forward to hearing more about this issue in future work. Some questions and comments are given below, the first one of more significance than the remainder. It is my opinion that the paper will be

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publishable in ACP after these comments are addressed.

Main question: I did not get a good sense of how reproducible the MSAM IR cross sections or the product yields really are. How many experiments were actually carried out, and how were final values and uncertainties obtained? (At times, the section 3.4 reads as though one experiment only was done, which would not seem sufficient to me).

Minor comments and questions: I think most of the experiments (kinetics and product studies) were done in air – if so, it would help to state this early on (around line 45?).

Line 59 – space needed between ‘and’ and ‘SO₂’.

Line 75 – Initial H₂ concentrations shown in Table 1 are lower than the 5e16 molecule cm⁻³ value given here.

Line 135 - The existence of an MSAM dimer hits the reader rather abruptly. I suggest discussing the existence of the dimer in more detail in the experimental setup section – how the dimer was identified, its elimination with the cold-trap, etc.

Line 164 – ‘different’ spelled incorrectly.

Line 170 – product yield studies: concentrations of MSAM employed are quite a bit lower than the vapour pressure upper limit given earlier. Could higher [MSAM] have been used to limit the extent of 2ry chemistry, and get a better handle on the initial products formed?

Line 185 – I think this should be HNO₃ + 2*N₂O?

Line 209 – I would argue that, given the complex time profile for CO, giving a yield for this species is not meaningful, and potentially misleading. It might be also worth reiterating somehow that HNO₃ and CO₂ are secondary products, and so the yields really only apply after significant loss of MSAM has occurred.

Section 3.4.1 – I am assuming that NO is not seen in any of the IR spectra? Is this

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consistent with the mechanism, and the NO detection limit? Also, can more be said about whether the NO₂ temporal profile observed matches the mechanistic predictions? Can the authors be more quantitative about the CH₂O steady-state seen in the model, compared with its IR detection limit?

Line 376 – s should be s⁻¹.

Table 1 – Footnote b should only refer to the theoretical headers, not the experimental one?

Figure 6, lower trace: All the CO₂ measurements fall below the average line. Please clarify.

Figure 7: Is there any chance that the radical down at the bottom of the scheme, O=CS(O)(O)NH₂, adds O₂ rather than decomposing? This would probably lead to a CO₂ rather than a CO?

Also, it may end up not changing anything, but there could also be a ‘molecular channel’ to the peroxy radical self-reaction?

Table S2: It doesn’t matter to the final result, but a decomposition of 10²⁵ s⁻¹ for the alkoxy species doesn’t seem possible to me.

Maybe not critical, but the HO₂ self-reaction is not included in the mechanism.

NHOH seems likely to be a fairly reactive radical – are there other possible losses for this species that are not included in the mechanism? Reaction with O₂ to make HNO and HO₂??

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