The following contains the comments of the referee (black) and our replies (blue) indicating changes made to the revised document (red).

Referee #2

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 publishable in ACP after these comments are addressed.

We thank the referee for this positive assessment of our manuscript.

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).

A total of 4-experiments were evaluated to obtain the cross-sections of MSAM. We now indicate this in the manuscript and modify a figure in the supplementary information (Fig. S3) to include data from all 4 experiments. The text now reads:

Figure S3 of the supplementary information illustrates the strict proportionality between the relative change of the SO_2 concentration and the MSAM absorption feature at 1384 cm^{-1} in 4 different experiments. From these 4 experiments we derive an absorption cross-sections for MSAM at this wavenumber of $(4.06 \pm 0.17) \times 10^{-19}$ cm^2 $molecule^{-1}$. This value was used to scale the spectrum of MSAM (Fig. 1) and was used to calculate initial concentrations in all other experiments.

We also noticed that the Figure 1 had the wrong exponent (20 instead of 19) on the y-axis. This has been rectified.

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?).

We now state:

The quartz reactor was at room temperature (296 ± 2 K) and for most experiments at 700 Torr total pressure (1 Torr = 1.333 hPa) using synthetic air bath gas.

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

Correction made

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

This was a typo. We now write:

In a typical experiment, the starting concentrations of O_3 and H_2 were ≈ 5 × 10^{14} and ≈ 5-7 × 10^{15} molecule cm^{-3}.

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.

The text in the experimental section has been modified to mention the dimer:

Owing to its low vapour pressure, MSAM was eluted into the reaction chamber by flowing synthetic air (450 cm^3 STP min^{-1}, sccm) through a finger containing crystalline MSAM warmed to 333 K, and subsequently through a cold trap at 298 K (to prevent condensation downstream). This way we could ensure that the saturation vapour pressure of MSAM at 298 K was achieved. In initial experiments without the trap we observed extra absorption features, which could be assigned to a dimer of MSAM (see below).

Line 164 – 'different' spelled incorrectly.

Correction made.

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?

We do not give a vapour pressure of MSAM (only an upper limit) as we were not able to directly measure the pressure of the vapour above MSAM crystals at 298 K. We always operated under conditions of maximum MSAM eluting from the trap at 298 K. WE now write:

Crystalline MSAM melts at 363 K, has a boiling point of approximately 453 K and an unknown vapour pressure (< 0.02 Torr) at room temperature.

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

This is true. We now write:

Figure 5 plots the concentration of SO_2 (the only sulphur containing product observed), the sum of HNO_3 + 2 N_2O (the total reactive nitrogen observed as product)

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.

We no longer list the yield of CO and mention that the yields are derived for 80% MSAM depletion.

In contrast, the CO yield is initially larger than unity (indicative of extra sources from the chamber walls) and then decreases with time as it is removed (via reaction with OH) to form CO_2.

The molar yields (after 6000 seconds of photolysis when MSAM has depleted to ~20% of its original concentration) of the products obtained at 298 K and 700 Torr of synthetic air are:

$\Phi(SO_2) = 0.96 \pm 0.15$, $\Phi(HNO_3) = 0.62 \pm 0.09$, $\Phi(N_2O) = 0.09 \pm 0.02$, $\Phi(CO_2) = 0.73 \pm 0.11$, $\Phi(HC(O)OH) = 0.03 \pm 0.01$.

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

We now explain why we did not detect NO, NO_2 or HCHO:

The simulations indicate that the maximum concentrations of NO (7×10^9 molecule cm^{-3}) and NO_2 (~10^{12} molecule cm^{-3}) are below the detection limit of the instrument, and were therefore not observed. The strongest absorption features of HCHO (1700-1800 cm^{-1}) overlap with those of H_2O and HNO_3 so that the predicted concentrations of HCHO (< 10^{12} molecule cm^{-3}) are also below the detection limit.

Line 376 – s should be s^-1.

Correction made.

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

Correction made.

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

This was a mistake; the yield-line for CO_2 had not been re-drawn after scaling the plot.

This has been corrected as shown below

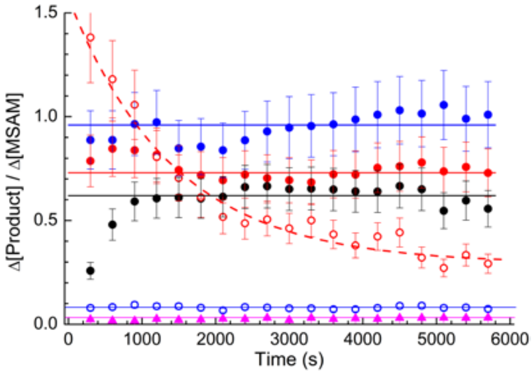


Figure 7: Is there any chance that the radical down at the bottom of the scheme, O=CS(O)(O)NH2, adds O2 rather than decomposing? This would probably lead to a CO2 rather than a CO?

This may also happen, though it probably also ends up as SO_2NH_2 and does not change anything as far as the sulphur and nitrogen containing products are concerned. Nonetheless, we have added this reaction to the scheme in Figure 7 and added some text.

$C(O)SO_2NH_2$ may either decompose to SO_2NH_2 and CO (R17) or react with O_2 to form a α-carbonyl peroxy radical (R18).

$$C(O)SO_2NH_2 \rightarrow SO_2NH_2 + CO \quad (R17)$$

$$C(O)SO_2NH_2 + O_2 + M \rightarrow O_2C(O)SO_2NH_2 + M \quad (R18)$$

The fate of $O_2C(O)SO_2NH_2$ is likely to be dominated by reaction with HO_2 which, by analogy to $CH_3C(O)O_2$ (another α-carbonyl peroxy radical) is expected to lead to the reformation of OH (Dillon and Crowley, 2008; Groß et al., 2014).

$O_2C(O)SO_2NH_2 + HO_2 \rightarrow OH + O_2 + CO_2 + SO_2NH_2$ (R19)

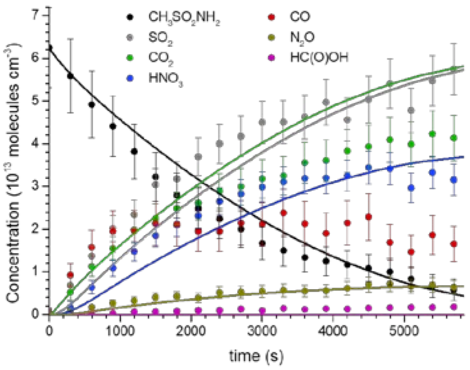
In both scenarios, SO_2NH_2 is the sulphur containing product, whereas formation of the peroxy radical will result in prompt CO_2 formation and OH-recycling.

We also included this reaction in the numerical simulations. It results in the production of prompt CO_2 (which better matches the observations) but CO is no longer formed (contrary to the observations). We now write:

The simulation also captures the CO profile well, but fails to predict the early formation of CO_2. The match between simulation and experiment could be improved to some extent for CO_2 by amending the fate of the $C(O)SO_2NH_2$ radical as described above (R17-R18) so that CO_2 rather than CO is formed. The results (Fig S5 of the supplementary information) indicate that the improved simulation of CO_2 is accompanied by complete loss of agreement with CO (which is no longer formed in measurable amounts) and poorer agreement with e.g. SO_2 and HNO_3. However, given that CO_2 is generated from the cell walls during irradiation and cannot be used quantitatively (Section 3.5), the fate of the $C(O)SO_2NH_2$ radical remains obscure. We emphasise that the reproduction of the profiles of the observed end products does not constitute quantitative understanding of the fate of several radical and non-radical intermediates formed.

We have added an extra plot the SI to exemplify this.

Fig S5



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

We cannot rule out that $NH_2SO_2CH_2O_2$ can self-react to make an alcohol and aldehyde (as well as the alkoxy channel listed). Simulations showed that this reaction had little effect, presumably because the high levels of HO_2 mean that most RO_2 react with HO_2 and not with themselves.

Table S2: It doesn’t matter to the final result, but a decomposition of 10ˆ25 s-1 for the alkoxy species doesn’t seem possible to me.

As indicated in the footnotes this is a theoretical value and not expected to be accurate. For simplicity we now write > 1 × 9 s^{-1} and note that any value above a few s^{-1} would have the same effect.

[f]Calculated with G4MP2 level of theory. As this is the only reaction of $OCH_2SO_2NH_2$ that we consider, any lifetime shorter than a few seconds would give the same simulation result.

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

The self-reaction of HO_2 was included in the simulations, but we did not list it in Table S2 as its inclusion had no significant impact on the results.

To make the reaction scheme more complete, we now list the HO_2 self-reaction (and several other reactions that we had previously neglected to include) in Table S2.

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??

The Referee is correct. The reaction of NHOH with O2 was considered (along with OH) in the reaction mechanism and, with a rate constant = 9.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, it is the dominant loss process.

Table S2 has been modified accordingly.