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<sub>2</sub> concentration and the MSAM absorption feature at 1384 cm<sup>-1</sup> 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<sup>2</sup> molecule<sup>-1</sup>. 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  $(296 \pm 2 \text{ K})$  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 cm<sup>-3</sup> value given here.

This was a typo. We now write: In a typical experiment, the starting concentrations of O<sub>3</sub> and H<sub>2</sub> were  $\approx 5 \times 10^{14}$  and  $\approx 5-7 \times 10^{15}$  molecule cm<sup>-3</sup>.

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<sup>3</sup> STP min<sup>-1</sup>, 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<sub>2</sub>.

The molar yields (after 6000 seconds of photolysis when MSAM has depleted to  $\sim$ 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<sub>2</sub> or HCHO:

The simulations indicate that the maximum concentrations of NO (7 × 10<sup>9</sup> molecule cm<sup>-3</sup>) and NO<sub>2</sub> (~10<sup>12</sup> molecule cm<sup>-3</sup>) are below the detection limit of the instrument, and were therefore not observed. The strongest absorption features of HCHO (1700-1800 cm<sup>-1</sup>) overlap with those of H<sub>2</sub>O and HNO<sub>3</sub> so that the predicted concentrations of HCHO (< 10<sup>12</sup> molecule cm<sup>-3</sup>) 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  $\alpha$ -carbonyl peroxy radical (R18).

 $\begin{array}{ccc} C(O)SO_2NH_2 & \rightarrow & SO_2NH_2 + CO & (R17) \\ C(O)SO_2NH_2 + O_2 + M & \rightarrow & O_2C(O)SO_2NH_2 + M & (R18) \end{array}$ 

The fate of  $O_2C(O)SO_2NH_2$  is likely to be dominated by reaction with HO<sub>2</sub> which, by analogy to  $CH_3C(O)O_2$  (another  $\alpha$ -carbonyl peroxy radical) is expected to lead to the reformation of OH (Dillon and Crowley, 2008; Groß et al., 2014).  $O_2C(O)SO_2NH_2 + HO_2$  $OH + O_2 + CO_2 + SO_2NH_2$ (R19)  $\rightarrow$ 

In both scenarios, SO<sub>2</sub>NH<sub>2</sub> is the sulphur containing product, whereas formation of the peroxy radical will result in prompt CO<sub>2</sub> formation and OH-recycling.

We also included this reaction in the numerical simulations. It results in the production of prompt CO<sub>2</sub> (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<sub>2</sub>. The match between simulation and experiment could be improved to some extent for CO<sub>2</sub> by amending the fate of the C(O)SO<sub>2</sub>NH<sub>2</sub> radical as described above (R17-R18) so that CO<sub>2</sub> rather than CO is formed. The results (Fig S5 of the supplementary information) indicate that the improved simulation of CO<sub>2</sub> is accompanied by complete loss of agreement with CO (which is no longer formed in measurable amounts) and poorer agreement with e.g. SO<sub>2</sub> and HNO<sub>3</sub>. However, given that CO<sub>2</sub> 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<sub>2</sub>SO<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> mean that most RO<sub>2</sub> react with HO<sub>2</sub> and not with themselves.

Table S2: It doesn't matter to the final result, but a decomposition of 10<sup>25</sup> 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  $> 1 \times 9$  s<sup>-1</sup> and note that any value above a few s<sup>-1</sup> would have the same effect.

<sup>f</sup>Calculated with G4MP2 level of theory. As this is the only reaction of OCH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub> 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 =  $9.6 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, it is the dominant loss process.

Table S2 has been modified accordingly.

## Kinetic and mechanistic study of the reaction between methane sulphonamide (CH<sub>3</sub>S(O)<sub>2</sub>NH<sub>2</sub>) and OH

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Abstract. Methane sulphonamide (MSAM), CH<sub>3</sub>S(O)<sub>2</sub>NH<sub>2</sub>, was recently detected for the first time in ambient air over the Red Sea and the Gulf of Aden where peak mixing ratios of  $\approx 60$  pptv were recorded. Prior to this study the rate constant for its reaction with the OH radical and the products thereby formed were unknown, precluding assessment of its role in the atmosphere. We have studied the OH-initiated photo-oxidation of MSAM in air (298 K, 700 Torr total pressure) in a photochemical reactor using in situ detection of MSAM and its products by FTIR absorption spectroscopy. The relative rate technique, using three different reference compounds, was used to derive a rate coefficient of (1.4 ± 0.3) × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The main end products of the photo-oxidation observed by FTIR were CO<sub>2</sub>, CO, SO<sub>2</sub> and HNO<sub>3</sub> with molar vields of (0.73 ± 0.11), (0.28 ± 0.04), (0.96 ± 0.15) and (0.62 ± 0.09), respectively. N<sub>2</sub>O and HC(O)OH were also observed

15 in smaller yields (0.09  $\pm$  0.02), (0.03  $\pm$  0.01). Both the low rate coefficient and the products formed are consistent with hydrogen abstraction from the -CH<sub>3</sub> group as the dominant initial step. Based on our results MSAM has an atmospheric lifetime with respect to loss by reaction with OH of about 80 days.

#### **1** Introduction

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Natural emissions of organosulphur compounds from phytoplankton comprise up to 60% of the total sulphur flux into the 20 marine boundary layer (Andreae, 1990; Bates et al., 1992; Spiro et al., 1992) and in remote oceanic areas are the main source

- of climatically active sulphate aerosols, which can influence the radiation balance at the earth's surface (Charlson et al., 1987; Andreae and Crutzen, 1997). The main organo-sulphur trace gases in the marine boundary layer are dimethyl sulphide (CH<sub>3</sub>SCH<sub>3</sub>, DMS) and its oxidation products dimethyl sulphoxide (DMSO), dimethyl sulphone (DMSO<sub>2</sub>), methyl sulphonic acid (MSA) and methyl sulphinic acid (MSI) for which atmospheric lifetimes with respect to their degradation by the OH
- 25 radical vary between hours (DMS) and several weeks (DMSO<sub>2</sub>).

Recently, the first detection of methane sulphonamide (CH<sub>3</sub>S(O)<sub>2</sub>NH<sub>2</sub>, MSAM) in ambient air was made during the Air Quality and Climate Change in the Arabian Basin campaign (AQABA-2017). Mixing ratios of MSAM approached 60 pptv over the Arabian Sea; details of these measurements and a discussion of the likely sources of MSAM in these regions are given in a companion paper (Edtbauer et al., 2019). As MSAM had not been considered to be an atmospheric trace gas prior

- 30 to the observations of Edtbauer et al. (2019), there have been no laboratory studies to investigate either its spectroscopy or the kinetics of its reactions with atmospheric radicals, such as OH, so that its atmospheric lifetime and the products formed during its degradation in air were unknown. Combining carbon, nitrogen, sulphur and oxygen in a single, small molecule, MSAM is an intriguing species not only as an atmospheric trace gas but also from a spectroscopic and kinetic perspective. Unlike basic alkyl amines such as e.g. CH<sub>3</sub>NH<sub>2</sub>, MSAM contains an acidic –NH<sub>2</sub> group (Remko, 2003).
- 35 This work presents the first kinetic and mechanistic study of the OH induced oxidation of MSAM in air. A reaction mechanism is proposed that, through numerical simulation, describes the time dependent formation of the end-products we observed. From these results, we calculate the lifetime and the likely role of MSAM in the atmosphere.

#### 2 Methods

#### 2.1 Experimental set-up

- 40 The experimental set-up used to study the reaction of OH with MSAM has been described in detail previously (Crowley et al., 1999; Bunkan et al., 2018). Briefly, the reaction vessel was a 44.39 L cylindrical quartz-wall chamber equipped with a White-type multiple reflection mirror system resulting in an 86.3 m optical path length for absorption spectroscopy in the infra-red. The quartz reactor was at room temperature ( $296 \pm 2$  K) and for most experiments at 700 Torr total pressure (1 Torr = 1.333 hPa) using synthetic air bath gas. Six external, radially mounted, low pressure Hg-lamps emitting mainly at
- 45 253.65 nm provided a homogeneous light flux within the reactor for radical generation. A 1000 Torr capacitance manometer was used to measure the pressure inside the reactor.

MSAM and other gases used to generate OH (see below) were mixed in a glass vacuum-line which was connected directly to the reaction chamber by a PTFE piping. Two capacitance manometers (10 Torr and 100 Torr ranges) were used to accurately measure pressures in the vacuum-line. Crystalline MSAM melts at 363 K, has a boiling point of approximately 453 K and an

- 50 unknown vapour pressure (< 0.02 Torr) at room temperature. Owing to its low vapour pressure, MSAM was eluted into the reaction chamber by flowing synthetic air (450 cm<sup>3</sup> STP min<sup>-1</sup>, 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).
- 55 Gas-phase infrared spectra in the range of 4000–600 cm<sup>-1</sup> were recorded with a resolution of 2 cm<sup>-1</sup> from 16 co-added interferograms (128 scans for the background) using a Fourier Transform Infra-Red (FTIR) spectrometer (Bruker Vector 22) equipped with an external photoconductive mercury-cadmium-telluride (MCT) detector cooled to liquid nitrogen temperature. OPUS-software was used to analyze and manipulate the IR spectra. Interferograms were phase-corrected (Mertz) and Boxcar apodized with a zero-filling-factor of 4. Most of the products obtained (CO<sub>2</sub>, CO, HC(O)OH, HNO<sub>3</sub> and
- 60 SO<sub>2</sub>) were identified and quantified from the IR reference spectra of pure samples under similar experimental conditions (700 Torr and 298.2 K, Figure S1).

The low vapour pressure of MSAM precluded accurate dosing into the chamber and thus generation of a calibration spectrum. In order to calibrate the infra-red absorption features of MSAM we oxidized it in air and then conducted a sulphur and nitrogen balance of the products. As discussed below, the only sulphur-containing product detected from MSAM

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degradation was SO<sub>2</sub> (which can easily be calibrated) and the only nitrogen contained products were HNO<sub>3</sub> and N<sub>2</sub>O, which can also be calibrated. Experiments in which MSAM was almost completely converted to known amounts of SO<sub>2</sub>, HNO<sub>3</sub> and N<sub>2</sub>O thus provided an indirect calibration (via assumption of 100% sulphur or nitrogen balance) of its concentration and thus IR-cross-sections.

#### 2.2 Generation of OH

70 OH was generated by the 254 nm photolysis of  $O_3$  in the presence of  $H_2$ .

$O_3 + hv$ (254 nm)	$\rightarrow$	$O(^{1}D) + O_{2}$	(R1)
$O(^{1}D) + H_{2}$	$\rightarrow$	OH + H	(R2)
$H + O_2 + M$	$\rightarrow$	$HO_2 + M$	(R3)

Further reactions that cycle OH and HO<sub>2</sub> (e.g. OH +  $H_2$ , H + O<sub>3</sub>, HO<sub>2</sub> + O<sub>3</sub>) are listed in Table S1 of the supplementary information.

In a typical experiment, the starting concentrations of  $O_3$  and  $H_2$  were  $\approx 5 \times 10^{14}$  and  $\approx 5.7 \times 10^{15}$  molecule cm<sup>-3</sup>. As described previously (Bunkan et al., 2018), this scheme generates not only OH radicals but (via e.g. (R3) also HO<sub>2</sub>. HO<sub>2</sub> is not expected to react with MSAM but will influence the course of secondary reactions in this system (e.g. by reacting with organic peroxy radicals) and thus the end-product distribution, as described in detail in section 3.5. Simulations of the radical concentrations when generating OH in this manner indicate that the HO<sub>2</sub> / OH ratio is approximately 30, with individual

so concentrations when generating OH in this manner indicate that the HO<sub>2</sub> / OH ratio is approximately 30, with individual concentrations of  $\approx 1 \times 10^{11}$  molecule cm<sup>-3</sup> HO<sub>2</sub> and  $3 \times 10^{9}$  molecule cm<sup>-3</sup> OH.

As OH source, the photolysis of  $O_3$  in the presence of  $H_2$  has the advantage over other photochemical sources (e.g. photolysis of  $H_2O_2$ , HONO or CH<sub>3</sub>ONO) that neither  $H_2$  nor  $O_3$  have strong absorption features in the infra-red, resulting in a less cluttered spectrum which simplifies retrieval of concentration-time profiles of reactants and products.

#### 85 2.3 Chemicals

A commercially available sample of methane sulphonamide (Alfa Aesar, > 98%) was used. O<sub>3</sub> was generated by flowing synthetic air (Westfalen) through a stainless steel tube that housed a low-pressure Hg-lamp (PenRay) emitting at 184.95 nm. Synthetic air (Westfalen, 99.999%), H<sub>2</sub> (Westfalen, 99.999%), CO<sub>2</sub> (Westfalen 99.995%), CO (Westfalen, 99.997%), SO<sub>2</sub> (Air Liquide, 1 ppmv in air) and HC(O)OH (Sigma Aldrich) were obtained commercially. Anhydrous nitric acid was

90 prepared by mixing KNO<sub>3</sub> (Sigma Aldrich, 99%) and H<sub>2</sub>SO<sub>4</sub> (Roth, 98%), and condensing HNO<sub>3</sub> vapour into a liquid nitrogen trap.

#### 2.4 Relative rate constant determination

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The rate constant ( $k_4$ ) of the reaction between OH and CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (Reaction R4) was measured using the relative rate method using (in different experiments) formic acid (HC(O)OH), acetone (CH<sub>3</sub>C(O)CH<sub>3</sub>) and methanol (CH<sub>3</sub>OH) as reference compounds.

$CH_3S(O)_2NH_2 + OH$	$\rightarrow$	Products	(R4)
$CH_3C(O)CH_3 + OH$	$\rightarrow$	Products	(R5)
HC(O)OH + OH	$\rightarrow$	Products	(R6)
$CH_{3}OH + OH$	$\rightarrow$	Products	(R7)

100 Relative rate constants were derived by monitoring the depletion of one or more IR-features of MSAM relative to those of the reference compounds. The following expression links the depletion factors (e.g. ln([MSAM]<sub>0</sub>/[MSAM]<sub>t</sub>) to the relative rate coefficient:

$$\ln\left(\frac{[\text{MSAM}]_0}{[\text{MSAM}]_t}\right) = \frac{k_4}{k_{\text{ref}}} \ln\left(\frac{[\text{ref}]_0}{[\text{ref}]_t}\right) \tag{1}$$

- where [MSAM]<sub>0</sub>, [MSAM]<sub>t</sub>, [ref]<sub>0</sub>, and [ref]<sub>t</sub> are the concentrations of MSAM and reference compound at times 0 and t; *k*<sub>4</sub>
  and *k*<sub>ref</sub> are the rate constants for reactions of OH with the MSAM and reference, respectively. As only relative changes in the IR-signal are used in the analysis, absolute concentrations are not required as long as the absorption features used display a linear relation with concentration. Plots of ln([MSAM]<sub>0</sub>/ [MSAM]<sub>t</sub>) versus ln([ref]<sub>0</sub> / [ref]<sub>t</sub>) should therefore be linear, pass through the origin, and have a slope of *k*<sub>4</sub> / *k*<sub>ref</sub>. The experimental procedure consisted of filling the cell with a mixture of MSAM / reference / O<sub>3</sub> / H<sub>2</sub> / N<sub>2</sub> and allowing it to mix (5-10 min) prior to subjecting the mixture to 253.65 nm radiation whilst monitoring IR features at 3-5 min intervals.
- This analysis inherently assumes that the only loss process for MSAM and the reference molecules is reaction with OH. Experiments in which the starting gas-mixture was allowed to stand for several hours with no discernible loss of MSAM, formic acid, methanol or acetone confirmed that none of these gases are lost to the wall or react with  $O_3$  to a significant extent. From observation of MSAM and  $O_3$  mixtures we were able to derive an upper limit for the reaction of MSAM with  $O_3$  of  $1 \times 10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

#### **3** Results and Discussion

#### 3.1 Vibrational characterisation of CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>

The experimental, infra-red absorption spectrum of MSAM (Fig. 1) shows characteristic bands corresponding to  $SO_2$  stretching vibrations at 1385 and 1172 cm<sup>-1</sup>, the NH<sub>2</sub> wagging vibration at 857 cm<sup>-1</sup>, stretching vibrations at 3476 and 3380

120 cm<sup>-1</sup>, bending at 1551 cm<sup>-1</sup>, and the CH<sub>3</sub> wagging band at 976 cm<sup>-1</sup>. Assignment of the infra-red features (Table 1) was made by comparison with a theoretical spectrum calculated using density functional theory (DFT) at the B3LYP/6-311++G(3d,2p) and B3LYP/aug-cc-pVTZ-pp levels of theory for the vibrational characterization of MSAM in gas phase. These basis sets should be sufficient to describe the relative energies for the isomers. Harmonic vibrational frequencies and zero-point energies (ZPE) were calculated at these levels of theory to check whether the stationary points obtained were either isomers

- 125 or first-order transition states (all calculated conformers had only real frequencies). The high accuracy energy method Gaussian-4 with Møller-Plesset expansion truncated at second order (G4MP2) was also used for the calculation of the barrier energies. The determination of the Hessian matrix also enabled the calculation of the thermochemical quantities for the conformers at 298.15 K. All symmetry restrictions were turned off in the calculations. All calculations were run with the Gaussian 09 program package (Frisch, 2010). Assuming that the point group for the molecule is Cs, all 24 fundamental
- 130 modes should be both IR and Raman active, fourteen of them belonging to A' representation and ten to A". All the vibrational frequencies are real and positive. The assignments in Table 1 were made from an evaluation of the normal modes displacement vectors; as many of the modes are strongly coupled, this information is rather subjective. The frequencies of the absorption bands of the theoretical spectrum displayed in Fig.1 were adjusted by a scaling factor of 0.968  $\pm$  0.019 recommended for the B3LYP/aug-cc-pVTZ level of theory (column "ratio" in Table 1) (Halls et al., 2001).
- 135 If the "cold trap" is removed, extra absorption bands originating from the MSAM-dimer are observed. These slowly disappear with time as the condensation of the low-volatility dimer to the reactor surfaces takes place. Fig. S1 of the supplementary information shows the IR spectra of the dimer after the subtraction of the monomer. A complete characterization of the vibrational modes is presented in Table S1 of the supplementary information. According to our calculations, two hydrogen-bond interactions between the -HNH…OSO- are formed in the dimer which produce a
- 140 bathochromic shift of the absorption bands. For each kinetic experiment we ensure that no dimer band is present in the initial spectrum.

#### 3.2 Relative rate measurements: Determination of k<sub>4</sub>

Once the concentrations of MSAM and the reference compound were stable (i.e. mixing in the chamber was complete) the Hg-lamps were switched on for a period of typically one hour during which FTIR spectra (duration of ~20 seconds) were obtained every few minutes. The concentrations of the reactants in each individual experiment can be found in Table 2. Figure 2 shows the loss of absorption features due to MSAM and the reference compound (in this case acetone) at different times during the experiment.

The depletion of MSAM was quantified by integrating the Q-branch of the 857, 1172, 1383 cm<sup>-1</sup> absorption bands, and the complete absorption band at 3380 cm<sup>-1</sup>. The relative depletion of the MSAM absorption-features agreed to within ~ 5%.

150 Depletion of the reference gases were quantified by integrating their absorption bands at 1221-1249 cm<sup>-1</sup> (acetone), 2788-3070 cm<sup>-1</sup> (methanol) and 1073-1133 cm<sup>-1</sup> (formic acid). An alternative analysis procedure, in which the relative depletion of MSAM was derived by scaling a reference spectrum of MSAM (e.g. that obtained prior to photolysis) to match those at various times after photolysis was also used. The depletion factors thus obtained were indistinguishable from those using individual absorption features.

- Figure 3 shows plots of the depletion factors for MSAM versus those of the three reference compounds following exposure to OH radicals in 700 Torr of synthetic air at 296 K. A linear least-squares analysis of the data gives rate constant ratios  $k_4/k_5 = (0.778 \pm 0.008)$ ,  $k_4/k_6 = (0.307 \pm 0.004)$  and  $k_4/k_7 = (0.158 \pm 0.002)$  where the quoted errors are two standard deviations. Table 2 summarizes the experimental conditions and the rate coefficient ratios obtained when using each MSAM absorption band. The difference between the rate coefficient ratios obtained for the three absorption bands experiments is
- always less than 5%. The rate constant ratios were placed on an absolute basis using evaluated rate coefficients (Atkinson et al., 2006; IUPAC, 2019) whereby  $k_5 = (1.8 \pm 0.36) \times 10^{-13}$ ,  $k_6 = (4.5 \pm 1.8) \times 10^{-13}$ , and  $k_7 = (9.0 \pm 1.8) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. We derive values of  $k_4$  (relative to acetone) =  $(1.40 \pm 0.28) \times 10^{-13}$ ,  $k_4$  (relative to formic acid) =  $(1.38 \pm 0.55) \times 10^{-13}$ , and  $k_4$  (relative to methanol) =  $(1.42 \pm 0.28) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (where the uncertainties include uncertainty associated with the evaluated rate coefficients for  $k_5$ ,  $k_6$  and  $k_7$ ). The values of  $k_4$  obtained using the three different reference compounds
- 165 are, within experimental uncertainties, identical, indicating the absence of significant systematic errors associated with the use of the reference reactants. We prefer the value of  $k_4$  from the experiment using acetone as reference. For acetone, the relative rate constant is close to unity and the rate coefficient for OH has been extensively studied and is associated with low uncertainty. The preferred value of the rate coefficient,  $k_4$ , is  $(1.4 \pm 0.3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> where the uncertainty is  $2\sigma$ .

#### 170 **3.3 Product yields**

In order to identify and quantify the end-products of the title reaction in air, approximately  $(6.25 \pm 0.75) \times 10^{13}$  molecule cm<sup>-3</sup> of MSAM,  $4.04 \times 10^{14}$  molecule cm<sup>-3</sup> of O<sub>3</sub> and  $1.00 \times 10^{15}$  molecule cm<sup>-3</sup> of H<sub>2</sub> were loaded into the chamber at a total pressure of 700 Torr of synthetic air and 298 K. Subsequent to initiation of the reaction between OH and MSAM by switching the Hg-lamps on, IR-spectra (700 – 4000 cm<sup>-1</sup>) were taken at 300 seconds intervals.

- Figure 4 shows the initial spectrum of the gas mixture with  $O_3$  bands at 903-1068 and 2064-2134 cm<sup>-1</sup> (A), the spectrum after 3000 s (B) showing depletion of MSAM and formation of products and the final products after the disappearance of the Qbranches (at 1172 and 1385 cm<sup>-1</sup>) of MSAM after 5700 s (C). The IR-absorption bands of water vapour have been subtracted from the spectra. Both CO<sub>2</sub> (2387-2300 cm<sup>-1</sup>) and CO (2226-2050 cm<sup>-1</sup>) are observed from the photolysis of compounds adsorbed on the walls and surfaces of the cell, and do not result solely from MSAM degradation.
- 180 Figure 4 also displays reference spectra (measured at the same temperature and pressure) of the compounds we identified as reaction products. Other than CO<sub>2</sub> and CO, nitric acid (HNO<sub>3</sub>) and sulphur dioxide (SO<sub>2</sub>) are easily identified, with weak features from N<sub>2</sub>O, NO<sub>2</sub> and formic acid (HC(O)OH) also apparent. The absorption of each product was converted to a concentration using calibration curves that were obtained at the same pressure and temperature (see Fig. S2 of the supplementary information).
- Figure 5 plots the concentration of SO<sub>2</sub> (the only sulphur containing product observed), the sum of  $HNO_3 + 2 N_2O$  (the total reactive nitrogen observed as product) and the sum of  $CO_2 + CO + HC(O)OH$  (total carbon containing products observed)

versus the fractional depletion of MSAM. The concentrations after 6000 seconds (when ~90% of the MSAM had reacted) were:  $[SO_2] = 5.74 \times 10^{13}$ ,  $[HNO_3] = 3.15 \times 10^{13}$ ,  $[N_2O] = 4.17 \times 10^{12}$ ,  $[CO_2] = 4.13 \times 10^{13}$ ,  $[CO] = 1.65 \times 10^{13}$  and  $[HC(O)OH] = 1.77 \times 10^{12}$  molecules cm<sup>-3</sup>. MSAM contains one atom each of sulphur, nitrogen and carbon. If SO<sub>2</sub>, reactive

- 190 nitrogen and carbon are conserved, we can derive initial concentrations of MSAM (from the slope) of  $6.12 \pm 0.08 \times 10^{12}$ molecule cm<sup>-3</sup> (based on the sulphur balance),  $5.10 \pm 0.05 \times 10^{12}$  molecule cm<sup>-3</sup> (based on the nitrogen balance) and  $7.4 \pm 0.2$  $\times 10^{12}$  molecule cm<sup>-3</sup> (based on the carbon balance at the maximum fractional depletion of MSAM). As already mentioned, total carbon is very likely to be overestimated due to its formation and desorption at/from the walls of the chamber. As the main nitrogen product is HNO<sub>3</sub>, which has a large affinity for surfaces and which is likely to be lost to the walls, we also
- 195 expect that use of reactive nitrogen will result in an underestimation of the initial MSAM concentration. For these reasons we consider that the best method to estimate the initial concentration of MSAM is via the formation of SO<sub>2</sub>. Figure S3 of the supplementary information illustrates the strict proportionality between the relative change of the SO<sub>2</sub> concentration and the MSAM absorption feature at 1384 cm<sup>-1</sup> in 4 different experiments. From these 4 experiments we derive an absorption crosssections for MSAM at this wavenumber of  $(4.06 \pm 0.17) \times 10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup>. This value was used to scale the spectrum of
- 200 MSAM (Fig. 1) and was used to calculate initial concentrations in all other experiments. Figure 6a presents a plot of  $\Delta$ [product] versus - $\Delta$ [MSAM] from one experiment. Apart from CO, we observe a roughly linear relationship for all products. Time dependent yields of each product are displayed in Fig. 6b. Whereas the yields of SO<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O and HC(O)OH are, within experimental scatter roughly constant, that of HNO<sub>3</sub> (black line) reaches a constant value only after 800 seconds, indicating that it is not formed directly, but in a secondary reaction. In contrast, the CO yield is initially slightly
- 205 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<sub>2</sub>. 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:  $\Phi(SO_2) = 0.96 \pm 0.15$ ,  $\Phi(HNO_3) = 0.62 \pm 0.09$ ,  $\Phi(N_2O) = 0.09 \pm 0.02$ ,  $\Phi(CO_2) = 0.73 \pm 0.11$ ,  $\Phi(HC(O)OH) = 0.03 \pm 0.01$ . The slight deviation of  $\Phi(SO_2)$  from unity stems from the fact that the quoted yield is at a fixed time, whereas the initial MSAM concentration was derived using all the SO<sub>2</sub> data in this experiment as described above. As N<sub>2</sub>O contains two N-atoms, the nitrogen balance is thus 0.80
- $\pm$  0.13. It is likely that some HNO<sub>3</sub> is lost to reactor surfaces, explaining the deviation from unity. Note that if we had used the nitrogen balance to derive the MSAM IR-cross-sections, the SO<sub>2</sub> yield would have exceeded unity.

#### 3.4 Reaction mechanism

The time dependent formation of HNO<sub>3</sub>, SO<sub>2</sub>, N<sub>2</sub>O and CO provide important clues to the reaction mechanism. Addition to 215 the S-atom is not possible so that the initial step will be abstraction of hydrogen by the OH radical, either from the -CH<sub>3</sub> group (Reaction R8a) or from the -NH<sub>2</sub> group (Reaction R8b):

$$CH_{3}SO_{2}NH_{2} + OH \longrightarrow CH_{2}SO_{2}NH_{2} + H_{2}O$$

$$(R8a)$$

$$CH_{3}SO_{2}NH_{2} + OH \longrightarrow CH_{3}SO_{2}NH_{2} + H_{2}O$$

$$(R8b)$$

$$H_3SO_2NH_2 + OH \longrightarrow CH_3SO_2NH + H_2O$$
(R8b)

Based on results of previous studies of the reactions of OH with trace-gases containing both CH<sub>3</sub> and -NH<sub>2</sub> entities (e.g.

220 CH<sub>3</sub>NH<sub>2</sub> or CH<sub>3</sub>C(O)NH<sub>2</sub>) we expect abstraction at the –CH<sub>3</sub> group (Reaction R8a) to dominate (Onel et al., 2014; Borduas et al., 2015; Butkovskaya and Setser, 2016). H-abstraction at the methyl-group is also consistent with a rate coefficient for R4 that is very similar to that for OH + acetone.

#### **3.4.1** Abstraction from the -CH<sub>3</sub> group

In section 3.4.1 we focus on the fate of the peroxy radical, OOCH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub>, formed by reaction of initially formed 225 CH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub> with O<sub>2</sub> (R9). The most important reactions of organic peroxy radicals are self-reactions (R10) or reactions with NO (R11), NO<sub>2</sub> (R12), or HO<sub>2</sub> (R13).

$CH_2SO_2NH_2+O_2\\$	$\rightarrow$	OOCH <sub>2</sub> SO <sub>2</sub> NH <sub>2</sub>	(R9)
2 OOCH <sub>2</sub> SO <sub>2</sub> NH <sub>2</sub>	$\rightarrow$	$OCH_2SO_2NH_2 + O_2$	(R10)
$OOCH_2SO_2NH_2 + NO$	$\rightarrow$	$OCH_2SO_2NH_2 + NO_2$	(R11)

 $\begin{array}{rcl} 230 & OOCH_2SO_2NH_2 + NO_2 & \rightarrow & O_2NOOCH_2SO_2NH_2 \\ & OOCH_2SO_2NH_2 + HO_2 & \rightarrow & HOOCH_2SO_2NH_2 + O_2 \end{array} \tag{R12}$ 

Peroxy nitrates such as the one formed in Reaction (R12) are thermally unstable with respect to dissociation back to reactants at room temperature and given the very low concentrations of  $NO_2$  in our system, Reaction (R12) will not play a significant role in this study.

The oxy-radical, OCH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub> formed in Reactions (R10) and (R11) will react with O<sub>2</sub> to produce an aldehyde (Reaction R14). Alternatively, it could undergo C-S bond cleavage (Reaction R15) to form formaldehyde (CH<sub>2</sub>O) and the SO<sub>2</sub>NH<sub>2</sub> radical:

 $OCH_2SO_2NH_2 + O_2 \longrightarrow HC(O)SO_2NH_2 + HO_2$ (R14)

 $OCH_2SO_2NH_2 \longrightarrow CH_2O + SO_2NH_2$ (R15)

240 The fate of HC(O)SO<sub>2</sub>NH<sub>2</sub> will be reaction with OH to form C(O)SO<sub>2</sub>NH<sub>2</sub> (R16) which may dissociate to form CO + SO<sub>2</sub>NH<sub>2</sub> (R17). The rate coefficient for reaction (R16) is expected to be  $\approx 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> as for many similar reactions of OH with aldehydes (e.g. CH<sub>3</sub>CHO).

$$HC(O)SO_2NH_2 + OH \rightarrow C(O)SO_2NH_2 + H_2O$$
(R16)

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

245  $C(O)SO_2NH_2 \rightarrow SO_2NH_2 + CO$  (R17)  $C(O)SO_2NH_2 + O_2 + M \rightarrow O_2C(O)SO_2NH_2 + M$  (R18)

The fate of  $O_2C(O)SO_2NH_2$  is likely to be dominated by reaction with HO<sub>2</sub> which, by analogy to  $CH_3C(O)O_2$  (another  $\alpha$ 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) 250 In both scenarios, SO<sub>2</sub>NH<sub>2</sub> is the sulphur containing product, whereas formation of the peroxy radical in R18 will result in early CO<sub>2</sub> formation and OH-recycling.

Formaldehyde formed in R15 will react with OH to form CO and subsequently CO<sub>2</sub>:

265

	$CH_2O + OH$	$\rightarrow$	$HCO + H_2O$	(R20)
	$HCO + O_2$	$\rightarrow$	$HO_2 + CO$	(R21)
255	$CO + OH (+O_2)$	$\rightarrow$	$CO_2 + HO_2$	(R22)
	But it may also react with	$HO_2$ to f	form formic acid:	
	$CH_2O+HO_2+M\\$	$\rightarrow$	$HOCH_2OO + M$	(R23)

$2 \text{ HOCH}_2\text{OO} \rightarrow$	$HOCH_2O + O_2$	(R24)
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 $HOCH_2O + O_2 \rightarrow HC(O)OH + HO_2$  (R25)

260 The above reactions explain, at least qualitatively, the observed formation of CO, CO<sub>2</sub> and HC(O)OH. Note that the room temperature rate coefficient for reaction of OH with HCHO is large ( $8.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, Atkinson et al. (2006)) compared to that for reaction with CO ( $2.2 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> Atkinson et al. (2006)), which explains why CO was observed as an intermediate product at high concentrations whereas HCHO was not.

The likely fate of the  $SO_2NH_2$  radical formed in Reaction (R15) is either reaction with  $O_2$  to generate  $SO_2NH$  or dissociation by S-N bond-scission to produce  $SO_2$  and the  $NH_2$  radical.

$$SO_2NH_2 + O_2 \longrightarrow SO_2NH + HO_2$$
(R26)  
$$SO_2NH_2 \longrightarrow SO_2 + NH_2$$
(R27)

We did not observe features in the IR- spectrum that that could be assigned to  $SO_2NH$  based on the spectrum reported by Deng et al. (2016) and propose that reaction (R27) is the source of  $SO_2$  as a major reaction product. By analogy with the

270 thermal decomposition of the similar CH<sub>3</sub>SO<sub>2</sub> radical, which dissociates to CH<sub>3</sub> and SO<sub>2</sub> on a millisecond time scale (Ray et al., 1996), we expect SO<sub>2</sub>NH<sub>2</sub> to decompose stoichiometrically to SO<sub>2</sub> and NH<sub>2</sub> on the time scale of our experiments. The NH<sub>2</sub> radical, is known to react with O<sub>3</sub>, HO<sub>2</sub> and NO<sub>2</sub> (IUPAC, 2019):

$$NH_2 + O_3 \qquad \rightarrow \qquad NH_2O + O_2 \tag{R28}$$

$$NH_2 + HO_2 \rightarrow NH_2O + OH$$
 (R29a)

$$275 \quad NH_2 + HO_2 \qquad \rightarrow \qquad HNO + H_2O \tag{R29b}$$

$$NH_2 + NO_2 \rightarrow N_2O + H_2O$$
 (R30)

NH<sub>2</sub>O rearranges within ~1 ms to NHOH (Kohlmann and Poppe, 1999), which then reacts with OH or O<sub>2</sub> to generate HNO:

$$NHOH + OH \longrightarrow HNO + H_2O$$
(R31)

$$NHOH + O_2 \longrightarrow HNO + HO_2$$
(R32)

280 The fate of HNO is the reaction with OH or  $O_2$  to generate NO (reactions R33 and R34):

 $HNO + O_2 \rightarrow NO + HO_2$  (R33)

$$HNO + OH \rightarrow NO + H_2O$$
 (R34)

High concentrations of  $O_3 \approx 10^{14}$  molecule cm<sup>-3</sup>) and HO<sub>2</sub> ( $\approx 10^{11}$  molecule cm<sup>-3</sup>) in our system ensure that NO is converted to NO<sub>2</sub> in less than 1s, explaining the non-observation of the IR absorption features of NO.

Finally, NO2 in this system will react with OH to form the main reactive nitrogen compound we observed, HNO3.

$$NO_2 + OH + M \rightarrow HNO_3 + M$$
 (R37)

Thus far we have not considered the reaction of the peroxy radical, OOCH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub> with HO<sub>2</sub> (Reaction R13), which is expected to result in the formation of a peroxide, HOOCH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub>. The most likely fate of HOOCH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub> is reaction with OH for which (via comparison with CH<sub>3</sub>OOH) a rate coefficient close to  $1-5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> may be expected with H-abstraction from both the peroxide group (Reaction R38) or the adjacent carbon (Reaction R39).

$$HOOCH_2SO_2NH_2 + OH \rightarrow OOCH_2SO_2NH_2 + H_2O$$
(R38)

 $HOOCH_2SO_2NH_2 + OH \rightarrow HOOCHSO_2NH_2 + H_2O$ (R39)

295 Reaction (R38) regenerates the peroxy radical, whereas the HOOCHSO<sub>2</sub>NH<sub>2</sub> radical may decompose (Reaction R40) to form formic acid HC(O)OH or via Reaction (R41) to form the same aldehyde that is generated in Reaction (R14), whilst regenerating OH:

$$HOOCHSO_2NH_2 \rightarrow HC(O)OH + SO_2NH_2$$
(R40)

$$HOOCHSO_2NH_2 \rightarrow OH + HC(O)SO_2NH_2$$
(R41)

300 The final products are thus the same as those resulting from the self-reaction of the peroxy radical. The path from MSAM to the observed end-products including the reactive intermediates that were not observed is illustrated in Fig. 7.

#### 3.4.2 Abstraction from the -NH<sub>2</sub> group

In analogy to the reaction between  $CH_3C(O)NH_2$  and OH (Barnes et al., 2010), H- abstraction from the - $NH_2$  group is expected to result in decomposition of the initially formed  $CH_3SO_2NH$  radical via C-S bond fission.

 $305 \quad CH_3SO_2NH \qquad \rightarrow \qquad CH_3 + SO_2NH \qquad (R42)$ 

The methyl radical would react with  $O_2$  to form the methyl-peroxy radical and in subsequent reactions (via CH<sub>3</sub>O) would result in CH<sub>2</sub>O formation. As discussed above CH<sub>2</sub>O will be efficiently oxidized to CO and CO<sub>2</sub> in this system. However, the characteristic IR-absorption bands (Deng et al., 2016) of the SO<sub>2</sub>NH product were not observed in our experiments and calculations at the G4MP2 level of theory indicate that Reaction (R40) is endothermic (by 137 kJ mol<sup>-1</sup>). We conclude that

310 H-abstraction from the –NH<sub>2</sub> group is a minor channel.

### **3.5 Kinetic Simulation**

The proposed reaction mechanism (considering initial reaction by H-abstraction from the  $-CH_3$  group only) was tested by kinetic simulation using the KINTECUS program package (Ianni, 2015). The reactions used in the chemical scheme and the

associated rate coefficients are presented in Table S2. Where experimental rate coefficients were not available, we used rate

- 315 parameters from similar reactions, and rationalize these choices in the text associated with Table S2. Figure 8 shows the variation of the concentrations of the reagent, intermediates and products observed as a function of time in an experiment conducted at 298 K and 700 Torr of synthetic air. The error bars consider uncertainty associated with the absorption cross-sections (5 - 12%) and uncertainty in deriving the areas of the absorption bands areas (less than 3% in all cases). For MSAM, an uncertainty of ≈ 25% is expected, based on the indirect method of calibration (see Section 3.2). The
- 320 simulation results are depicted as solid lines. The good agreement with the N<sub>2</sub>O (formed from NH<sub>2</sub> in Reaction R28) and HNO<sub>3</sub> experimental data suggests that the fate of NH<sub>2</sub> (the only source of reactive nitrogen in this system) is accurately described in the model. Note that the wall loss rate of HNO<sub>3</sub> ( $1 \times 10^{-5}$  s<sup>-1</sup>) in the simulation was adjusted to match the HNO<sub>3</sub> profile. The simulated amount of HNO<sub>3</sub> lost to the wall at the end of the experiment was  $\approx 14\%$  of that formed, which helps to explain the non-unity yield of gas-phase nitrogen
- 325 compounds. The simulations indicate that the maximum concentrations of NO (7 × 10<sup>9</sup> molecule cm<sup>-3</sup>) and NO<sub>2</sub> (~10<sup>12</sup> molecule cm<sup>-3</sup>) are below the detection limit of the instrument, and explain why they were not observed. The strongest absorption features of HCHO (1700-1800 cm<sup>-1</sup>) overlap with those of H<sub>2</sub>O and HNO<sub>3</sub> so that the predicted concentrations of HCHO (< 10<sup>12</sup> molecule cm<sup>-3</sup>) are also below the detection limit.

The grey line in Fig. 8 represents the sum of  $SO_2 + SO_3 + H_2SO_4$ , i.e. all model trace gases containing sulphur, which, in the 330 absence of IR absorption features of  $SO_3$  or  $H_2SO_4$ , we equate to  $SO_2$ . We now draw attention to the fact that  $SO_2$  (the yield

of which is constant with time, see Fig. 6) is only well simulated if we neglect its removal by OH (Reaction R41).

$$OH + SO_2 + M \longrightarrow HOSO_2 + M$$
 (R43)

Otherwise, using the preferred rate constant (IUPAC, 2019) at 700 Torr and 298 K of  $9.0 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> we find that the simulated SO<sub>2</sub> concentration is significantly reduced and its yield is time dependent. At one bar of air, collisionally

335 stabilized HOSO<sub>2</sub> is converted within 1  $\mu$ s to HO<sub>2</sub> and SO<sub>3</sub>. In the atmosphere, SO<sub>3</sub> reacts with H<sub>2</sub>O to form H<sub>2</sub>SO<sub>4</sub> (R45). The conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> may be suppressed under our "dry" conditions.

SO<sub>2</sub> should therefore not behave like a stable end-product in our experiments, but be converted to more oxidized forms. In order to confirm that SO<sub>2</sub> is indeed stable in our experiments, we measured the relative rate of loss of SO<sub>2</sub> and acetone under the same experimental conditions (Fig. S4 of the supplementary information). The apparent, relative rate constant  $k_{43} / k_5$  was 0.46, which converts to an effective rate constant for SO<sub>2</sub> loss of 8.2 x 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This is more than a factor of ten lower than the preferred value, indicating that the net rate of the OH-induced SO<sub>2</sub> loss in our system is much lower than expected and not simply governed by the rate constant for the forward reaction to form HOSO<sub>2</sub>. The reformation of SO<sub>2</sub>

345 under our experimental conditions is subject of ongoing experiments in this laboratory, which are beyond the scope of the

present study. We note that the unexpected behaviour of SO<sub>2</sub> does not significantly impact on the conclusions drawn in this work.

The simulation also captures the CO profile well, but fails to predict the early formation of CO<sub>2</sub>. The match between simulation and experiment could be improved to some extent for CO<sub>2</sub> by amending the fate of the C(O)SO<sub>2</sub>NH<sub>2</sub> radical as

350 described above (R17-R18) so that CO<sub>2</sub> rather than CO is formed. The results (Fig S5 of the supplementary information) indicate that the improved simulation of CO<sub>2</sub> is accompanied by complete loss of agreement with CO (which is no longer formed in measureable amounts) and poorer agreement with e.g. SO<sub>2</sub> and HNO<sub>3</sub>. However, given that CO<sub>2</sub> is generated from the cell walls during irradiation and cannot be used quantitatively (Section 3.5), the true fate of the  $C(O)SO_2NH_2$  radical remains obscure.

#### 355 **3.6 Atmospheric Implications**

370

The rate coefficient for a number of tropospheric, organo-sulphur trace gases are listed in Table 3. The rate coefficient for the title reaction is significantly lower than those for CH<sub>3</sub>SCH<sub>3</sub> (CH<sub>3</sub>SCH<sub>3</sub>) and CH<sub>3</sub>S(O)CH<sub>3</sub>, (DMSO) for which reaction with OH is the major atmospheric loss process (lifetimes of hours), but comparable to CH<sub>3</sub>S(O)<sub>2</sub>CH<sub>3</sub> which also has two S=O double bonds. However, as for most tropospheric trace gases, the lifetime of MSAM will be controlled by a number of

processes including photolysis, reactions with the three major oxidants, OH, NO<sub>3</sub> and O<sub>3</sub> as well as dry deposition ( $k_{dd}$ ) and 360 heterogeneous uptake to particles  $(k_{het})$ , followed by wet deposition.

The lack of C=C double-bonds in MSAM suggest that the reaction with  $O_3$  will be a negligible sink, which is confirmed by the low upper limit to the rate constant of  $1 \times 10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> described in section 2.4. Whereas the reaction with NO<sub>3</sub> represents an important loss mechanism for DMS, we do not expect this to be important for MSAM. CH<sub>3</sub>SCH<sub>3</sub> reacts

365 with NO<sub>3</sub> (despite lack of a C=C double bond) as the high-electron density around the sulphur atom enables a pre-reaction complex to form prior to H-abstraction. This mechanism is not available for MSAM because the electron density around the sulphur atom is reduced by the two oxygen atoms attached to it, which also provide steric-hindrance.

Owing to its low vapour pressure, we were unable to measure the UV-absorption spectrum of MSAM, but note that it was not photolysed at a measureable rate by the 254 nm radiation in our study. We conclude that photolysis in the troposphere, where actinic flux only at wavelengths above  $\geq 320$  nm is available is a negligible sink of MSAM.

Therefore, the lifetime of MSAM can be approximated by:

$$\tau_{\rm MSAM} = \frac{1}{k_4 [\rm OH] + k_{\rm dd} + k_{\rm het}} \tag{2}$$

Using our overall rate coefficient,  $k_4 = 1.4 \times 10^{-13} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> for the title reaction and taking a diel-averaged OH concentration of 1 x 10<sup>6</sup> molecules cm<sup>-3</sup>, we can use equation (2) to calculate a first-order loss rate constant of  $k_4$ [OH] = 1.4  $\times 10^{-7}$  s<sup>-1</sup>. Which is equivalent to a lifetime of  $\approx 80$  days.

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MSAM is highly soluble and a dry deposition velocity of  $\approx 1 \text{ cm s}^{-1}$  to the ocean has been estimated (Edtbauer et al., 2019). Combined with a marine boundary height of  $\approx 750 \pm 250$  m, this results in a loss rate coefficient of  $1.3 \times 10^{-5}$  s<sup>-1</sup> or a lifetime with respect to uptake to the ocean of less than one day. Wet deposition is also likely to play a role, which may limit the MSAM lifetime to days under rainy conditions and to weeks in dry regions.

380 To a first approximation the heterogeneous loss rate of a trace gas to a particle is given by:

$$k_{het} = 0.25 \, \gamma \bar{c} A \tag{3}$$

where  $\gamma$  is the uptake coefficient which represents the net efficiency (on a per collision basis) of transfer of MSAM from the gas-phase to the particle phase),  $\bar{c}$  is the mean molecular velocity of MSAM (~26000 cm s<sup>-1</sup>) and A is the surface area density of particles (in cm<sup>2</sup> cm<sup>-3</sup>) for which a typical value in low to moderately polluted regions would be 1 × 10<sup>-6</sup> cm<sup>2</sup> cm<sup>-3</sup>.

385 A rather low uptake coefficient of  $\sim 2 \times 10^{-5}$  would then be sufficient to compete with MSAM loss due to reaction with OH, but a value of  $2 \times 10^{-3}$  would be necessary to compete with dry-deposition.

#### **4** Conclusions

The rate coefficient for reaction of methane sulphonamide (MSAM) with OH was determined using the relative rate method as  $(1.4 \pm 0.3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The major, stable, quantifiable sulphur and nitrogen containing end-products of the reaction are SO<sub>2</sub> and HNO<sub>3</sub> with molar yields of (0.96 ± 0.15) and (0.62 ± 0.09), respectively. CO and CO<sub>2</sub> are the dominant carbon-containing products. N<sub>2</sub>O and HC(O)OH were also observed at lower yields of (0.09 ± 0.02) and (0.03 ± 0.01), respectively. The end-products (and the low rate coefficient) are consistent with an initial abstraction by OH from the CH<sub>3</sub> group. Based on our results MSAM has an atmospheric lifetime with respect to loss by reaction with OH of about 80 days,

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Data availability. The rate coefficients measured during this experimental study are listed in Table 2.

*Author contributions*. The experiments and data analysis were carried out by MB and DA. The preparation of the paper was by MB and JNC, with contributions from DA, JL, JW and AE.

400 *Competing interests.* The authors declare that they have no conflict of interest.

indicating that other processes (e.g. deposition) will likely dominate.

Financial support. The article processing charges for this open access publication were covered by the Max Planck Society.

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Mode-	mode		Mode description			
symm.		Experiment <sup>a</sup>	$6-31++(d,p)^{a,b}$	Aug-CC-pVTZ <sup><i>a,b</i></sup>	ratio	
A''	v <sub>1</sub>	3476 (18.8)	3627 (18.8)	3612 (19.6)	0.958	NH <sub>2</sub> asym. stretch
	v <sub>3</sub>		3193 (<0.1)	3169 (0.2)		CH <sub>3</sub> deformation
	ν <sub>7</sub>		1461 (1.1)	1457 (0.4)		CH <sub>3</sub> rocking
	$v_{10}$	1383 (100)	1322 (100)	1342 (100)	1.048	SO <sub>2</sub> asym. stretch
	v <sub>12</sub>		1085 (2.2)	1087 (1.5)		NH <sub>2</sub> rocking
	$v_{14}$		981 (0.3)	972 (0.3)		CH <sub>3</sub> twisting
	v <sub>20</sub>		385 (<0.1)	392 (<0.1)		C-S-N twist
	v <sub>21</sub>		321 (1.1)	328 (1.2)		C-S-N twist
	v <sub>23</sub>		218 (0.2)	216 (1.5)		CH <sub>3</sub> twist
	$v_{24}$		170(14.9)	179(11.2)		NH <sub>2</sub> twist
A'	v <sub>2</sub>	3380 (17.2)	3512 (13.0)	3508 (13.8)	0.962	NH <sub>2</sub> sym. stretch
	$\nu_4$		3184 (<0.1)	3161 (<0.1)		CH <sub>3</sub> asym. stretch
	ν <sub>5</sub>		3079 (0.1)	3065 (<0.1)		CH <sub>3</sub> sym. stretch
	$\nu_6$	1551 (15.6)	1591 (15.2)	1582 (13.5)	0.975	NH <sub>2</sub> bend
	ν <sub>8</sub>		1460 (2.5)	1456 (1.9)		CH <sub>3</sub> asym. bend
	v <sub>9</sub>	1428 (3.7)	1363 (3.3)	1350 (4.2)	1.048	CH <sub>3</sub> umbrella
	v <sub>11</sub>	1172 (72.8)	1115 (69.6)	1135 (64.2)	1.051	SO <sub>2</sub> sym. stretch
	v <sub>13</sub>	976 (17.8)	994 (7.6)	987 (8.9)	0.982	CH <sub>3</sub> wagging
	v <sub>15</sub>	857 (43.1)	867 (42.4)	864 (40.8)	0.988	NH <sub>2</sub> wagging
	$v_{16}$		704 (7.2)	704 (4.2)		C-S stretch
	v <sub>17</sub>		663 (81.9)	649 (81.5)		S-N stretch
	v <sub>18</sub>		480 (14.9)	490 (15.8)		SO <sub>2</sub> wagging
	v <sub>19</sub>		457 (5.1)	468 (3.5)		SO <sub>2</sub> bend
	v <sub>22</sub>		285 (1.8)	290 (1.9)		C-S-N bend

**Table 1.** Experimental and Calculated Vibrational Wavenumbers for MSAM.

a) Relative absorbance at band maximum in parentheses. b) Calculated using the B3LYP method.

Table 2. Rate coefficients ratios and experimental condition	ns for the relative rat	te experiments.
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Reference reactant <sup>a</sup>	Concentration (10 <sup>14</sup> molecule cm <sup>-3</sup> )				$\operatorname{Band}^{e}$	k4 / kref	$k_4$ (10 <sup>-13</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	
reactant	[MSAM] <sup>b</sup>	[Ref] <sup>c</sup>	$[O_3]^d$	$[H_2]^c$	(em )			cule 5)
					857	$0.792\pm0.012$	$1.43\pm0.10$	
Apatona	0.21	0.24	7.71	71.8	1172	$0.771 \pm 0.005$	$1.39\pm0.09$	$1.40 \pm 0.09^{f}$
Acetone 0.31	0.51	0.34			1383	$0.779 \pm 0.006$	$1.40\pm0.09$	
					3380	$0.770\pm0.010$	$1.39\pm0.10$	
<b>.</b> .					857	$0.312\pm0.004$	$1.41\pm0.11$	
Formic	0.56	0.55	5.74	65.2	1172	$0.311 \pm 0.002$	$1.40\pm0.10$	$1.38\pm0.09^{f}$
Aciu					1383	$0.302\pm0.002$	$1.36\pm0.10$	
					1172	$0.159 \pm 0.001$	$1.43\pm0.17$	
Methanol	0.88	0.25	4.58	46.6	1383	$0.153 \pm 0.001$	$1.38\pm0.17$	$1.42 \pm 0.16^{f}$
					3380	$0.161 \pm 0.003$	$1.45 \pm 0.19$	

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a) Depletion of reference reactants monitored at 1221-1249, 1073-1133 and 2788-3070 cm<sup>-1</sup> for acetone, formic acid and methanol, respectively.

b) Concentration estimated from the absorption cross section reported in Figure 1.

c) Concentration calculated from the measured pressures,

d) Concentration derived from the absorption cross section of O<sub>3</sub>

e) IR absorption bands of MSAM used for the determination of the concentration change over time,

f) Relative rate constant obtained from the linear fitting of all the data and using  $k_4 = (1.8 \pm 0.1) \times 10^{-13}$ ,  $k_5 = (4.5 \pm 0.36) \times 10^{-13}$ , and  $k_6 = (9.0 \pm 1.3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> rate constants respectively (IUPAC, 2019).

Table 3. Lifetimes of atmospheric organo-sulphur trace gases with respect to reaction with OH

	k(OH) <sup>a</sup>	Lifetime <sup>b</sup>	Reference
CH <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub>	$1.4 \times 10^{-13}$	80 days	This work
CH <sub>3</sub> SO <sub>2</sub> CH <sub>3</sub>	$< 3 \times 10^{-13}$	> 40 days	(Falbe-Hansen et al., 2000)
CH <sub>3</sub> S(O)CH <sub>3</sub>	$5.9 \times 10^{-11}$	5 hours	(Falbe-Hansen et al., 2000)
CH <sub>3</sub> SO <sub>2</sub> H	9.0×10 <sup>-11</sup>	2.8 hours	(Burkholder et al., 2015)
CH <sub>3</sub> SCH <sub>3</sub>	$2.2 \times 10^{-12}$	1.6 days	(Atkinson et al., 2004)

<sup>a</sup> Units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup>Assumes a diel average OH concentration of  $1 \times 10^6$  molecule cm<sup>-3</sup>.



**Figure 1.** Comparison of the experimental infra-red absorption spectrum (black line) of MSAM (~1 × 10<sup>14</sup> molecule cm<sup>-3</sup>) and the calculated spectrum at B3LYP/aug-cc-pVTZ-pp levels of theory (red line). The cross-sections ( $\sigma$ ) are in base e.



**Figure 2.** Raw data from a relative rate experiments (using acetone as reference reactant) showing the gradual depletion of reactants and formation of products. The lower two spectra are reference spectra, indicating (red arrows and red min-max lines) which absorption features were used for the relative rate analysis. The strong absorption close to 2100 cm<sup>-1</sup> at t = 0 s is due to O<sub>3</sub>. CO<sub>2</sub> and CO absorption bands are centered at  $\approx$  2350 and 2140 cm<sup>-1</sup>, respectively.



**Figure 3.** Relative depletion factors for MSAM and the reference compounds  $CH_3C(O)CH_3$ , HC(O)OH, and  $CH_3OH$  obtained at room temperature and a total pressure of 700 Torr of air. The different absorption bands of MSAM used in the analysis are indicated. The slopes are equal to the ratio of rate coefficients  $k_4 / k_{ref}$  as defined in Eqn. 1).



**Figure 4.** Infrared spectrum acquired prior to (A) and after (B and C) photolysis of a mixture of MSAM, O<sub>3</sub>, H<sub>2</sub> and air. During irradiation, OH concentrations were  $\approx 3 \times 10^9$  molecule cm<sup>-3</sup>. H<sub>2</sub>O-absorption features have been subtracted from the spectra. Reference spectrum of HNO<sub>3</sub>, NO<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, CO, SO<sub>2</sub>, and HC(O)OH recorded under the same experimental conditions (700 Torr and 298 K) are also shown.



**Figure 5.** Summed concentration of carbon containing products (CO<sub>2</sub>, CO and HC(O)OH), sulphur containing products (SO<sub>2</sub>) and nitrogen containing products (N<sub>2</sub>O and HNO<sub>3</sub>) plotted versus the relative depletion of MSAM. The slope gives the initial concentration of MSAM assuming stoichiometric conversion to the products listed.



**Figure 6.** a) Formation of products versus depletion of MSAM. The slopes of the linear fits are the yields of SO<sub>2</sub>, HNO<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>O and HC(O)OH from this particular experiment. The polynomial fit to the CO data (red dash line) is added to guide the eye. b) Time dependence of the product yields from the same experiment. The solid, horizontal lines represent the



**Figure 7.** Mechanism for the formation of carbon containing (HC(O)OH, CO, CO<sub>2</sub>), nitrogen containing (HNO<sub>3</sub> and N<sub>2</sub>O) and sulphur containing (SO<sub>2</sub>) end products (in red circles) observed in the OH-initiated photo-oxidation of MSAM.



**Figure 8.** Concentration–time profiles of MSAM and reaction products formed in an experiment at 298 K and 700 Torr air. The error bars represent uncertainty in infra-red cross sections. The uncertainty associated with the MSAM concentration is estimated to be  $\approx 25\%$ . Solid lines are simulated profiles.

# Kinetic and mechanistic study of the reaction between methane sulphonamide $(CH_3S(O)_2NH_2)$ and OH

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## **Supplementary Information**

mode	IR Gas <sup>a</sup>	Frequ	uencies $(\text{cm}^{-1})^{a,b}$		Mode description
		6-31++G(d,p)	Aug-CC-pVTZ	ratio	
$v_1, v_2$	3362 (18.1)	3599 (21.3)	3531 (17.8)	0.952	NH <sub>2</sub> asym. stretch
<b>v</b> <sub>3</sub>	3266 (100)	3393 (100.0)	3326 (100.0)	0.982	NH <sub>2</sub> sym. stretch
$\nu_4$		3373 (<0.1)	3304 (0.2)		NH <sub>2</sub> sym. stretch
$\nu_5, \nu_6$		3192 (<0.1)	3131 (<0.1)		CH <sub>3</sub> deformation
$\nu_7, \nu_8$	3030 (1.3)	3185 (0.1)	3124 (<0.1)	0.970	CH <sub>3</sub> asym. stretch
V9, V10	2940 (0.7)	3079 (0.1)	3029 (<0.1)	0.971	CH <sub>3</sub> sym. stretch
$\nu_{11}$		1619 (1.0)	1610 (0.5)		NH <sub>2</sub> bend
V <sub>12</sub>	1557 (4.2)	1610 (4.1)	1604 (2.8)	0.971	NH <sub>2</sub> bend
$v_{13}, v_{14}$		1461 (0.7)	1461 (0.8)		CH <sub>3</sub> rocking
$v_{15}, v_{16}$	1419 (0.7)	1460 (1.0)	1461 (0.6)	0.971	CH <sub>3</sub> asym. bend
$v_{17}, v_{18}$		1364 (1.6)	1358 (1.4)		CH <sub>3</sub> umbrella
<b>v</b> <sub>19</sub>		1306 (16.7)	1273 (13.9)		SO <sub>2</sub> asym. stretch
V20	1326 (36.9)	1299 (41.1)	1267 (34.4)	1.047	SO <sub>2</sub> asym. stretch
$v_{21}$	1216 (2.0)	1135 (3.3)	1128 (3.6)	1.078	NH <sub>2</sub> rocking
$v_{22}$		1125 (2.0)	1122 (4.0)		NH <sub>2</sub> rocking
<b>V</b> 23	1157 (22.9)	1114 (26.2)	1084 (22.5)	1.065	SO <sub>2</sub> sym. stretch
<b>V</b> 24	1105 (3.4)	1092 (5.3)	1061 (4.5)	1.041	SO <sub>2</sub> sym. stretch
V <sub>25</sub>		1000 (2.0)	997 (2.0)		CH <sub>3</sub> wagging
V <sub>26</sub>	989 (4.1)	998 (4.1)	994 (4.0)	0.995	CH <sub>3</sub> wagging
$v_{27}, v_{28}$		985 (0.3)	985 (0.2)		CH <sub>3</sub> twisting
V29		916 (9.0)	906 (7.1)		C-S stretch
<b>V</b> 30	885 (1.4)	894 (12.3)	888 (10.6)	0.997	C-S stretch
$v_{31}$	773 (3.8)	738 (19.5)	736 (20.7)	1.050	NH <sub>2</sub> wagging

Table S1. Experimental and calculated vibrational wavenumbers for the dimer of  $CH_3SO_2NH_2$ .

736 (<0.1),  $v_{32}$ ; 705 (2.0),  $v_{33}$ ; 695 (12.1),  $v_{34}$ ; 491 (4.3),  $v_{35}$ ; 489 (3.4),  $v_{36}$ ; 465 (3.7),  $v_{37}$ ; 464 (<0.1),  $v_{38}$ ; 424 (<0.1),  $v_{39}$ ; 420 (1.2),  $v_{40}$ ; 358 (0.4),  $v_{41}$ ; 355 (2.3),  $v_{42}$ ; 302 (0.5),  $v_{43}$ ; 302 (2.4),  $v_{44}$ ; 291 (0.1),  $v_{45}$ ; 289 (0.1),  $v_{46}$ ; 225 (0.3),  $v_{47}$ ; 224 (<0.1),  $v_{48}$ ; 139 (2.0),  $v_{49}$ ; 117 (0.1),  $v_{50}$ ; 98 (<0.1),  $v_{51}$ ; 41 (0.4),  $v_{52}$ ; 32 (1.2),  $v_{53}$ ; 25 (<0.1),  $v_{54}$ .<sup>*b*</sup>

a) Relative absorbance at band maximum in parentheses.

b) Calculated using the B3LYP method.

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**Figure S1.** Comparison of the experimental spectrum of the MSAM-dimer (black line, after the subtraction of the monomer) and the simulated spectrum at the same level of theory as used for the monomer (red line).

ka	Reaction	References /
n 0.5 105 1		notes
$8.5 \times 10^{-5}  \mathrm{s}^{-1}$	$O_3 \rightarrow O_2 + O(^1D)$	0
$1.2 \times 10^{-10}$	$O(^{1}D) + H_{2} \rightarrow OH + H$	IUPAC
$6.7 \times 10^{-15}$	$OH + H_2 \rightarrow H_2O + H$	IUPAC
1 × 10 <sup>-12</sup>	$H + O_2 \rightarrow HO_2$	IUPAC
$2.8 \times 10^{-11}$	$H + O_3 \rightarrow OH + O_2$	IUPAC
$1.6 \times 10^{-12}$	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	IUPAC
$2.0 \times 10^{-15}$	$HO_2 + O_3 \rightarrow OH + 2 O_2$	IUPAC
$1.4 \times 10^{-13}$	$CH_3SO_2NH_2 + OH \rightarrow CH_2SO_2NH_2 + H_2O$	This work
8.3 × 10 <sup>-12</sup>	$CH_2SO_2NH_2 + O_2 \rightarrow O_2CH_2SO_2NH_2$	с
6 × 10 <sup>-12</sup>	$2 \text{ O}_2\text{CH}_2\text{SO}_2\text{NH}_2 \rightarrow \text{O}_2 + 2 \text{ OCH}_2\text{SO}_2\text{NH}_2$	d
8 × 10 <sup>-12</sup>	$O_2CH_2SO_2NH_2 + NO \rightarrow NO_2 + OCH_2SO_2NH_2$	e
$> 1 \times 10^9 \text{ s}^{-1}$	$OCH_2SO_2NH_2 \rightarrow CH_2O + SO_2NH_2$	f
8.5 × 10 <sup>-12</sup>	$CH_2O + OH \rightarrow HCO + H_2O$	IUPAC
6.5 × 10 <sup>-12</sup>	$O_2CH_2SO_2NH_2 + HO_2 \rightarrow HOOCH_2SO_2NH_2 + O_2$	g
6 × 10 <sup>-12</sup>	$HOOCH_2SO_2NH_2 + OH \rightarrow HOOCHSO_2NH_2 + H_2O$	h
$\alpha \times 1 \times 10^{15}$	$HOOCHSO_2NH_2 \rightarrow HC(O)OH + SO_2NH_2$	i
$(1-\alpha) \times 1 \times 10^{15}$	$HOOCHSO_2NH_2 \rightarrow OH + HC(O)SO_2NH_2$	i
$1.5 \times 10^{-11}$	$HC(O)SO_2NH_2 + OH \rightarrow C(O)SO_2NH_2 + H_2O$	j
1 × 10 <sup>-11</sup>	$C(O)SO_2NH_2 + O_2 + M \rightarrow O_2C(O)SO_2NH_2 + M$	k
0 or $1 \times 10^{10}$	$C(O)SO_2NH_2 \rightarrow CO + SO_2NH_2$	1
$1.4 \times 10^{-11}$	$O_2C(O)SO_2NH_2 + HO_2 \rightarrow OH + CO_2 + O_2 + SO_2NH_2$	m
$2.01 \times 10^{-13}$	$CH_2O + OH \rightarrow HCOOH + H$	IUPAC
$5.6 \times 10^{-12}$	$HCO + O_2 \rightarrow HO_2 + CO$	IUPAC
$1.5 \times 10^{-13}$	$CO + OH (+O_2) \rightarrow CO_2 + HO_2$	IUPAC
500 s <sup>-1</sup>	$SO_2NH_2 \rightarrow SO_2 + NH_2$	n
1.9 × 10 <sup>-13</sup>	$NH_2 + O_3 \rightarrow NH_2O + H_2O$	KP 1999
3.2 × 10 <sup>-11</sup>	$NH_2 + HO_2 \rightarrow NH_2O + OH$	KP 1999
4.8 × 10 <sup>-12</sup>	$NH_2 + HO_2 \rightarrow HNO + H_2O$	KP 1999
1.9 × 10 <sup>-12</sup>	$NH_2 + NO \rightarrow HO_2 + OH + N_2$	KP 1999
1.41 × 10 <sup>-11</sup>	$NH_2 + NO \rightarrow H_2O + N_2$	KP 1999
1.2 × 10 <sup>-11</sup>	$NH_2 + NO_2 \rightarrow N_2O + H_2O$	KP 1999
8 × 10 <sup>-12</sup>	$NH_2 + NO_2 \rightarrow NH_2O + NO$	KP 1999
$1.2 \times 10^{-14}$	$NH_2O + O_3 \rightarrow NH_2 + O_2$	KP 1999
1300 s <sup>-1</sup>	$\rm NH_2O \rightarrow \rm NHOH$	KP 1999
9.3 × 10 <sup>-15</sup>	$NH + O_2 \rightarrow NO + OH$	KP 1999
4.9 × 10 <sup>-11</sup>	$\rm NH + \rm NO \rightarrow \rm OH + \rm N_2$	KP 1999

**Table S2.** Reaction mechanism used for the kinetic simulation.

1.49 × 10 <sup>-11</sup>	$HNO + OH \rightarrow NO + H_2O$	KP 1999
$1.04 \times 10^{-14}$	$HNO + NHOH \rightarrow NH_2OH + NO$	KP 1999
9.6 × 10 <sup>-12</sup>	$\rm NHOH + O_2 \rightarrow \rm HNO + \rm HO_2$	KP 1999
$4.86 \times 10^{-12}$	$HONO + OH \rightarrow NO_2 + H_2O$	KP 1999
3.16 × 10 <sup>-14</sup>	$\rm NH_2OH + OH \rightarrow NHOH + H_2O$	KP 1999
$7.2 \times 10^{-21}$	$HNO + O_2 \rightarrow HO_2 + NO$	KP 1999
8.5 × 10 <sup>-12</sup>	$NO + HO_2 \rightarrow NO_2 + OH$	KP 1999
$1.20 \times 10^{-11}$	$NO_2 + OH \rightarrow HNO_3$	KP 1999
$5 \times 10^{-5} \text{ s}^{-1}$	$HNO_3 \rightarrow wall$	р

<sup>a</sup> Units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unless otherwise stated. Calculated for 1 bar and 298 K.

<sup>b</sup> Adjusted to match the observed loss rate of a hydrocarbon e.g. acetone during photolysis.

<sup>c</sup> Set equal to the rate constant for the reaction  $CH_3CH_2 + O_2 \rightarrow CH_3CH_2O_2$  at 1 bar.

<sup>d</sup> Set equal to the rate constant for the reaction 2 CH<sub>3</sub>C(O)CH<sub>2</sub>OO  $\rightarrow$  O<sub>2</sub> + 2 CH<sub>3</sub>C(O)CH<sub>2</sub>O.

<sup>e</sup> Set equal to the rate constant for the reaction  $CH_3C(O)CH_2O_2 + NO \rightarrow NO_2 + CH_3C(O)CH_2O$ .

 $^{\rm f}$  Calculated with G4MP2 level of theory. As this is the only reaction of OCH<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub> that we consider, any lifetime shorter than a few seconds would give the same simulation result.

 $^{\rm g}$  Set equal to the rate constant for the reaction  $C_2H_5O_2+HO_2$ 

<sup>h</sup> Set equal to the rate constant for the reaction  $C_2H_5OOH + OH$ 

<sup>i</sup> As these are the only reactions of HOOCHSO<sub>2</sub>NH<sub>2</sub> that we consider, any lifetime shorter than a few seconds would give the same simulation result.  $\alpha$  was varied to match the observed HC(O)OH concentration.

 $^{\rm j}$  Set equal to the rate constant for the reaction OH + CH<sub>3</sub>CHO

<sup>k</sup> Set equal to the rate constant for the reaction  $CH_3C(O) + O_2$ 

<sup>1</sup> set to zero when considering reaction of C(O)SO<sub>2</sub>NH<sub>2</sub> with O<sub>2</sub>. At  $1 \times 10^{10}$  s<sup>-1</sup>, the reaction with O<sub>2</sub> is insignificant.

<sup>m</sup> Set equal to the rate constant for the reaction  $CH_3CO3 + HO_2$ 

<sup>n</sup> Set to the thermal decomposition rate coefficient for  $CH_3SO_2$  (see manuscript for details). Note that any value greater than  $10^{-3}$  s<sup>-1</sup> yields in the same simulation result.

<sup>p</sup> Adjusted to obtain best agreement with the observed HNO<sub>3</sub> profile.

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KP 1999: Kohlmann, J.-P., and Poppe, D.: The tropospheric gas-phase degradation of  $NH_3$  and its impact on the formation of  $N_2O$  and  $NO_x$ , J. Atmos. Chem., 32, 397-415, 1999.



**Figure S2.** Calibration curves for the main products of the reaction  $CH_3SO_2NH_2 + OH$ . Experimental conditions were 298 K and 700 Torr synthetic air. Abs = Absorbance  $[log_{10}(I_0/I)]$ .



Figure S3. Comparison of the absorbance of  $SO_2$  product with respect to the depletion in absorbance of MSAM during oxidation.



**Figure S4.** Relative rate study of  $OH + SO_2$  relative to  $OH + CH_3C(O)CH_3$ . The experiment was conducted at a total pressure of 700 Torr air and at room temperature.



**Figure S5.** As Fig. 8 of the manuscript but with the fate of the  $C(O)SO_2NH_2$  radical modified in the simulation so that  $CO_2$  rather than CO is formed (i.e. R18-R19 are used instead of R17). Note that CO is no longer formed in measurable amounts.