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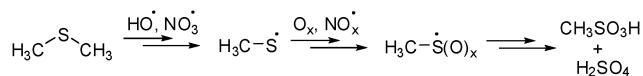
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## Reactions of the methylsulfinyl radical [CH<sub>3</sub>(O)S<sup>•</sup>] with oxygen (<sup>3</sup>O<sub>2</sub>) in solid argon†

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The atmospherically highly relevant methylsulfinyl radical (CH<sub>3</sub>(O)S<sup>•</sup>) readily reacts with molecular triplet oxygen in cryogenic argon matrices containing small amounts of <sup>3</sup>O<sub>2</sub>. Comparison of experimental and computed IR- and UV/Vis spectra, including isotope exchange, show that the initially formed <sup>3</sup>O<sub>2</sub> adduct has the structure of a peroxy radical (CH<sub>3</sub>(O)SOO<sup>•</sup>), which upon irradiation with UV light isomerizes to the methylsulfonyl radical (CH<sub>3</sub>SO<sub>2</sub><sup>•</sup>). The latter transforms into the methansulfonic acid radical (<sup>•</sup>CH<sub>2</sub>SO<sub>3</sub>H) by irradiation with visible light. During the matrix photolysis small amounts of SO<sub>3</sub> and the methyl radical were detected indicating competitive direct photodissociation.

Volatile sulfur compounds such as hydrogen sulfide and dimethylsulfide (Me<sub>2</sub>S and DMS) produced from natural plankton are emitted into the atmosphere and are converted into a plethora of sulfur products *via* radical processes. As part of the so-called 'sulfur cycle' they are of great importance for the atmospheric sulfur balance<sup>1</sup> with DMS as the major component of biogenic emissions.<sup>2</sup> The impact of sulfur compounds on the climate is explained based on the 'CLAW' hypothesis.<sup>3</sup> DMS and other volatile sulfur compounds undergo cascade conversions in the atmosphere eventually leading to sulfuric acid and methanesulfonic acid (Scheme 1).<sup>3c</sup> The methylsulfinyl radical (1) and the methylsulfonyl radical (2) are recognized as important intermediates involved in these processes.<sup>4</sup>

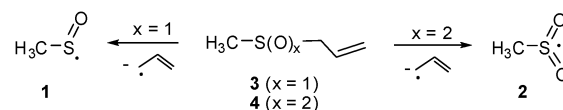


Scheme 1 Postulated reaction cascade for dimethyl sulfide oxidation to sulfuric acid and methanesulfonic acid in the atmosphere.

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† Electronic supplementary information (ESI) available: Table, experimental, additional IR spectra and computational details. See DOI: 10.1039/c5cc02168e



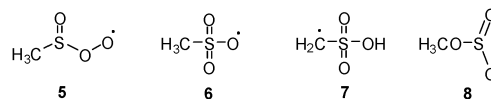
Scheme 2 Generation of 1 and 2 starting with allylmethylsulfoxide (3) and allylmethylsulfone (4), respectively.

A recent study reports the high vacuum flash pyrolysis (HVFP) of allylmethylsulfoxide (3) generating the highly stabilized  $\pi$ -radical 1 isolated in an Ar matrix at 10 K.<sup>5</sup> Similarly, 2 was trapped starting with allylmethylsulfone (4) (Scheme 2).<sup>6</sup>

The study showed that 2 in comparison with 1 is significantly less stable and easily undergoes partial decomposition in the gas phase leading to the formation of SO<sub>2</sub> and the methyl radical. To date little is known about the reactions of 1 and there are only a few kinetic studies of its reactions with O<sub>2</sub>, O<sub>3</sub>, and NO<sub>2</sub>.<sup>7</sup> In the case of the reaction with <sup>3</sup>O<sub>2</sub>, the formation of an adduct with the structure of the methylsulfinylperoxy radical (5) as the key intermediate was postulated (Scheme 3).<sup>8</sup> However, to the best of our knowledge, no spectroscopic data for 5 have been presented to date.

The fundamental question whether the formation of 5 by addition of 1 to molecular oxygen is an exo- or an endothermic process has not yet been unambiguously answered by theory. The  $\Delta H^\circ$  values computed at *ab initio* and density functional theory (DFT) levels with large basis sets vary considerably; G2(MP2) computations indicate slightly exothermic ( $-2.5 \text{ kcal mol}^{-1}$ ) formation of 5.<sup>9</sup>

The main goal of the present work was to determine if this reaction takes place at all and to examine the structure of the product formed. Equally important for the understanding of atmospheric chemistry is an investigation of the photochemistry of the initially formed oxygen adduct. The matrix isolation technique currently is the best method to provide reliable answers to both questions.



Scheme 3 Most relevant [CH<sub>3</sub>SO<sub>3</sub>]<sup>•</sup> radical species 5–8.





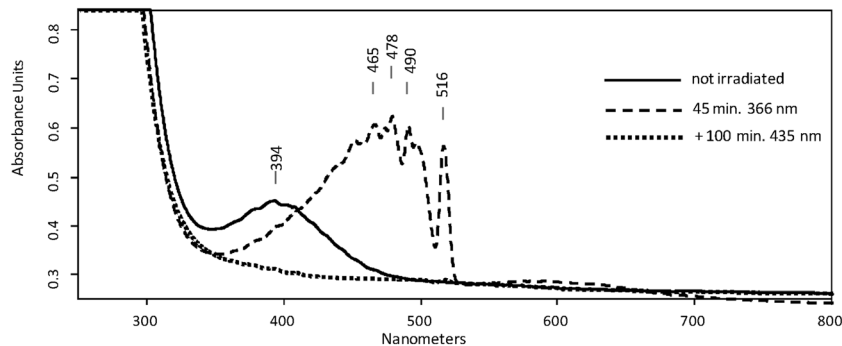


Fig. 2 UV/Vis spectra of pyrolysis of precursor **2** isolated in an Ar matrix containing 5.0 vol%  $^3\text{O}_2$ .

The electronic situation of **6** is similar to that of the highly symmetric  $\text{NO}_3$  radical for which it was shown that standard DFT and *ab initio* methods completely fail in predicting the vibrational frequencies due to vibronic coupling and highly anharmonic potentials.<sup>15</sup>

Prolonged irradiation of the matrix with light at  $\lambda = 435$  nm showed the disappearance of **6**, and no absorption maximum could be found in the UV/Vis spectrum above 300 nm. The IR spectra of the new product can be assigned to C-centered radical **7**. The absorption band located at  $3569\text{ cm}^{-1}$  unambiguously proves the formation of the  $-\text{S}(\text{O})_2\text{OH}$  group. This position is very close to OH-stretching vibration of argon matrix isolated  $\text{H}_2\text{SO}_4$  at  $3567\text{ cm}^{-1}$  and  $\text{CH}_3\text{SO}_3\text{H}$  at  $3579\text{ cm}^{-1}$ , respectively.<sup>16</sup> In addition, absorptions at 1403, 1391, 1383, 1189, 1184, 842, 827,  $784\text{ cm}^{-1}$ , partially split by matrix effects, can also be attributed to **7** (ESI,† Fig. S3). Upon labelling two of the three oxygen atoms of **7** by  $^{18}\text{O}$ , two distinct OH stretching bands at  $3570.0$  and  $3559.0\text{ cm}^{-1}$  with an intensity ratio of 1:2 were observed (ESI,† Fig. S4) as expected for the postulated structure. Apparently, the thermodynamically most stable isomeric radical **8** does not form in the matrix under photolysis. Neither **8** nor

the expected decomposition products such as the methoxy radical and  $\text{SO}_2$  could be detected.

Structure **5** is expected to exist as a mixture of rotamers by rotation around the S–O single bond. The results of DFT and *ab initio* computations show that they differ by  $0.5\text{ kcal mol}^{-1}$  (see data for **5** in ESI†). The computed IR spectrum of equal amounts of two representative rotamers fits well to the experimental spectrum (Fig. 3). The most intense band observed at  $1191\text{ cm}^{-1}$  is attributed to the S=O double bond stretch. Apparently, within the applied experimental spectral resolution the positions of the  $\nu(\text{S=O})$  absorption bands are identical for both rotamers.

The formation of **5** as the initial product in the reaction of **1** with  $^3\text{O}_2$  is strongly supported by additional isotopic labelling experiments. In particular, the observed spectral shifts in the IR spectrum of the  $^{18}\text{O}$ -labelled product were key for the spectral assignments (Fig. 4; in ESI,† Tables S1 and S2).

The most intense IR band of **5** displayed only a very small isotopic band shift ( $+0.2\text{ cm}^{-1}$ ) when triplet  $^{18}\text{O}_2$  was used instead of triplet  $^{16}\text{O}_2$ . This IR band could be attributed unambiguously to a pure S=O stretching vibration. Furthermore, the labelling

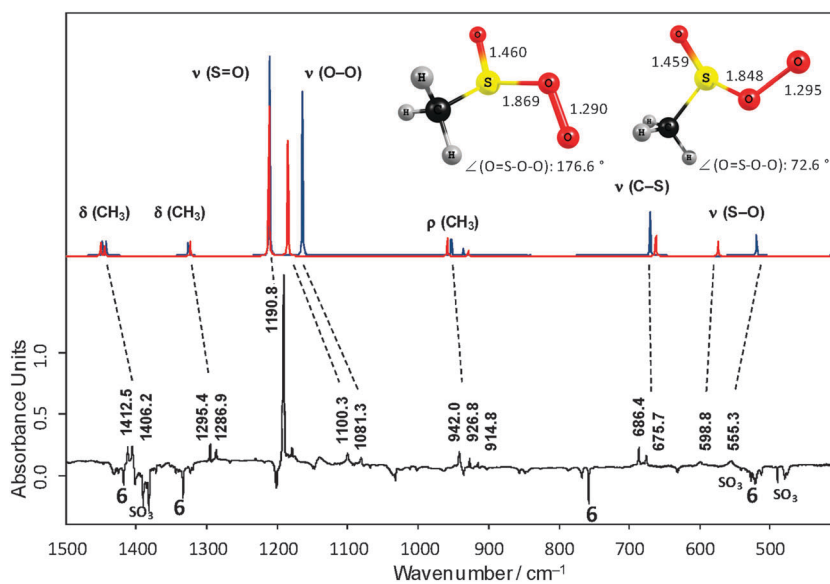


Fig. 3 Comparison of the computed IR spectra of two conformers of **5** (UB3LYP/6-311+G(3df,3pd) unscaled, above) and the experimental difference spectrum of the 366 nm photolysis of the  $^3\text{O}_2$  adduct **5** (below); positive bands vanish, negative bands appear upon irradiation.



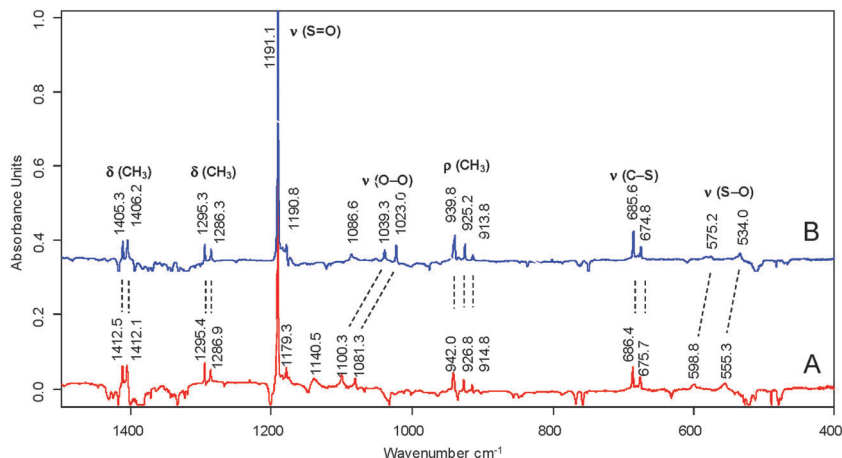


Fig. 4 Isotopic band shifts of the  $^{18}\text{O}_2$ -methylsulfinyldioxy radical ( $^{18}\text{O}_2$ -**5**); radicals **5** were obtained by reaction of methylsulfinyl radical (**1**) with triplet  $^{16}\text{O}_2$  (A) and triplet  $^{18}\text{O}_2$  (B).

experiment provides evidence that a pair of weak bands at 1100 and  $1082\text{ cm}^{-1}$  has to be assigned to the O–O stretching vibrations of two rotamers of **5**. The experimental band shifts of  $-61.0$  and  $-58.0$  correspond well to the isotopic shifts (ESI,† Tables S1 and S2). Moreover, the expected band shifts were also observed for the S–O stretching vibration ( $600\text{ cm}^{-1}$  and  $555\text{ cm}^{-1}$  versus  $575\text{ cm}^{-1}$  and  $534\text{ cm}^{-1}$ , respectively). The observed IR band shifts after deuteration of the methyl group (ESI,† Fig. S5) also agree very well with these band assignments. Whereas, in accordance with DFT computation (ESI,† Fig. S6), the positions of the  $\nu(\text{S}=\text{O})$  and the  $\nu(\text{O}-\text{O})$  remain almost unchanged, and large bathochromic shifts were observed for the  $\delta(\text{CH}_3)$  and  $\rho(\text{CH}_3)$  vibrations.

The present study shows that atmospherically highly relevant radical **1** generated in the gas phase by high-vacuum flash pyrolysis reacts spontaneously with molecular oxygen in a solid argon matrix under cryogenic conditions. Obviously, the formation of the oxygen adduct is a nearly barrierless, exothermic process. The structure of initially formed peroxy radical **5** was proven by comparison of computed with experimental IR and UV spectra as well as through extensive isotopic labelling experiments. Upon irradiation with near UV light, adduct **5** undergoes photochemical dissociation into  $\text{SO}_3$  and a methyl radical or isomerization to **6**. The latter is also not stable against irradiation with visible light and eventually transforms to **7**. These results underscore earlier postulates regarding the existence of a reactive oxygen adduct of the methylsulfinyl radical. Furthermore, our results demonstrate the importance of photochemical transformations in atmospheric oxidation processes of volatile organic sulfur compounds. These photochemical pathways have not yet been considered in the discussions related to the atmospheric sulfur cycle.

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