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Capture of SO_3 Isomers in the Oxidation of Sulfur Monoxide with Molecular Oxygen

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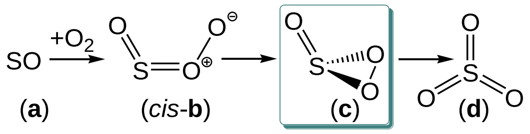
When mixing SO with O_2 in N_2, Ne, or Ar, an end-on complex OS–OO forms in the gas phase and can subsequently be trapped at cryogenic temperatures (2.8–15.0 K). Upon infrared light irradiation, OS–OO converts to SO_3 and SO_2 + O with concomitant formation of a rare 1,2,3-dioxathiirane 2-oxide, i.e., cyclic OS(=O)O. Unexpectedly, the ring-closure of $^{16}OS–^{18}O^{18}O$ yields a ca. 2:1 mixture of cyclic $^{18}OS(=^{16}O)^{18}O$ and $^{16}OS(=^{18}O)^{18}O$. The characterization of OS–OO and OS(=O)O with IR and UV/Vis spectroscopy is supported by high-level *ab initio* computations.

Sulfur is the fourteenth most abundant element in Earth's crust and it plays important roles in the chemical functioning of Earth.[1] For example, fully oxidized sulfate has been identified as the major component in "acid rain" and the cloud condensation nuclei (CCN), and is thus of vital importance for the global sulfur cycle.[2] In addition to anthropogenic and biological emissions, eruptions of volcanoes are an important sulfur source in the atmosphere, in which the most abundant sulfur gases are SO_2 and H_2S.[3] Subsequent photochemistry of both gases yields sulfur clusters, sulfur oxides, and eventually various sulfate-containing aerosols in the atmosphere.[4]

As the initial oxidation product of sulfur, diatomic sulfur monoxide (SO) can further be oxidized to SO_2 and SO_3.[5] In the stratosphere, highly reactive SO can reversibly be regenerated from UV photolysis (190–220 nm) of SO_2 (→ SO + O), a reaction believed to be responsible for the sulfur isotope mass-independent fractionation (S-MIF) in Earth's atmosphere.[5,6] The photo-induced reversible interconversion of SO, SO_2 and SO_3 has also been proposed to occur in the atmosphere of both Io (the innermost moon of Jupiter)[7] and Venus.[8] However, models developed from studies on Io's volcano Pele suggested that recombination of SO with O_2 would not happen in Io's low-temperature atmosphere, despite an activation barrier of merely 4.8 kcal mol^{-1}.[9]

Although the reaction of SO with O_2 to SO_3 appears simple, a stepwise pathway has been proposed in a recent theoretical study (Scheme 1).[10] The oxidation is suggested to occur by first forming an end-on complex OSOO (**b**), followed by ring-closure to 1,2,3-dioxathiirane 2-oxide (cyclic OS(=O)O, **c**). Singlet cyclic OS(=O)O (**c**) should be kinetically stable due to large activation barriers for ring-opening to either *trans*-OSOO (34 kcal mol^{-1}, UCCSD(T)-F12//B3LYP/aug-cc-pVTZ) or C_{3v}-SO_3 (51 kcal mol^{-1}). Metastable cyclic OS(=O)O (**c**) has a singlet ground state with a rather small singlet-triplet energy gap (ΔE_{ST} = –1 kcal mol^{-1}), hence, its isomerization to SO_3 (**d**) might be facilitated by spin state crossing.



Scheme 1 Proposed pathway for the oxidation of SO.[10]

As an intriguing intermediate, cyclic OS(=O)O has been also proposed as the link in the photo-oxidation of SO_2 with O_3.[11] Despite being unobserved in solid Ar-matrix at 11 K, its involvement in the reaction was rationalized by the observation of the unexpected ^{18}O-isotopic effects (Scheme 2). Moreover, it was suggested that quantum mechanical tunneling (QMT) should be responsible for its absence in the cryogenic matrix due to fast ring-opening to SO_3 (route **A**).

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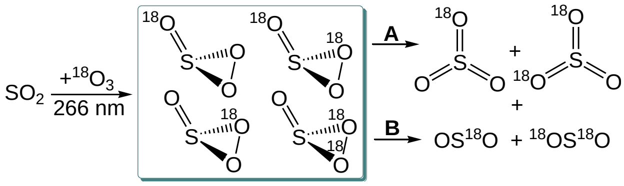

Scheme 2 Proposed pathway for the oxidation of SO_2.[11]

Experimentally, dioxathiiranes including cyclic SO_2 remain unreported, although this class of species has been frequently proposed as intermediates in the oxidation of sulfides.[12] Attempts to generate cyclic SO_2 through laser (193 nm) photolysis of sulfur dioxide in a solid Ar-matrix at 13 K led to the formation of SOO.[13] The same laser photolysis of SO_3 in an Ar-matrix at 12 K furnishes SO_2 and an O atom, followed by recombination to *cis*-OSOO, which was identified by IR spectroscopy.[14] Continuing our interest in reactive sulfur and oxygen intermediates (e.g., CH_3SO_3,[15] OSN,[16] $HNSO_2$,[17] and CF_3SO/CF_3OS[18]), herein, we now report the first time gas-phase generation of *cis*-OSOO and the observation of its photoisomerization to a rare dioxathiirane cyclic OS(=O)O.

As an important building block in synthetic organic sulfur chemistry, SO can readily be generated through pyrolysis of episulfoxides.[19] A typical IR spectrum of the matrix-isolated high vacuum flash pyrolysis (HVFP) products of ethylene episulfoxide (**e**) at *ca.* 1000 K is shown in Fig. 1A. The decomposition of **e** (*ca.* 80%) is evident from the formation of SO (**a**, 1139.3 cm^{-1})[20] and ethylene (**f**, 3106.6, 3076.8, 2989.4, 1438.4, 947.6, and 829.7 cm^{-1}).[21] Additionally, a species with a prominent IR band at 1103.1 cm^{-1} (**h**) also forms, which is tentatively assigned to the SO dimer OSSO based on comparison with the computed strongest IR band at 1120 cm^{-1} at the fc-CCSD(T)/cc-pV(Q+d)Z level.[22]

When performing the HVFP of the episulfoxide (e) in the presence of O_2 (**e**/O_2/N_2= 1:50:1000), the resulting IR spectrum of the matrix-isolated pyrolysate (Fig. 1B) suggests the disappearance of SO (**a**) and OSSO (**h**) but the formation of SO_2 (**g**, 1347.5, 1153.1, and 522.9 cm^{-1}) and SO_3 (**d**, 1396.9 cm^{-1}).[15] In addition, a new species with strong IR bands at 1235.8, 1037.4, and 605.3 cm^{-1} appears, its assignment to *cis*-OSOO (**b**) is assured by the good agreement with the previously reported IR frequencies of 1229.6, 1041.3, and 597.6 cm^{-1} found in an Ar-matrix.[14] Due to weak interactions with surrounding molecules, the band positions observed in different solid matrices are slightly shifted (Ar-matrix: 1231.2, 1044.6, and 597.9 cm^{-1}; Ne-matrix: 1233.4, 1043.3, and 601.5 cm^{-1}). Therefore, it is clear that the initially generated SO quantitatively reacted with O_2 in the gas phase. The presence of SO_2 and SO_3 among the products indicates fragmentation and isomerization of OSOO under the pyrolysis conditions.

Given the theoretically predicted very weak vertical transition at 699 nm (oscillator strength f = 0.0001, TD-B3LYP/6-311+G(3df)) for OSOO, the matrix was first irradiated with various light sources with wavelengths in the range of 600–850 nm, we found that the 830 nm light-emitting diode (LED) is most effective in depleting OSOO. The corresponding IR difference spectrum (Fig. 1C) reveals the complete depletion of *cis*-OSOO (**b**) within 20 minutes and formation of SO_3 (**d**), SO_2 (**g**), O_3 (**i**, 1041.9 and 704.3 cm^{-1}),[23] and a new species (**c**) with IR bands at 1299.8, 927.3, 660.9, 629.7, and 459.9 cm^{-1}. When the irradiation changes to UV light (365 or 266 nm), consumption of OSOO also happens (Fig. 1D), after which SO_2 and SO_3 form.

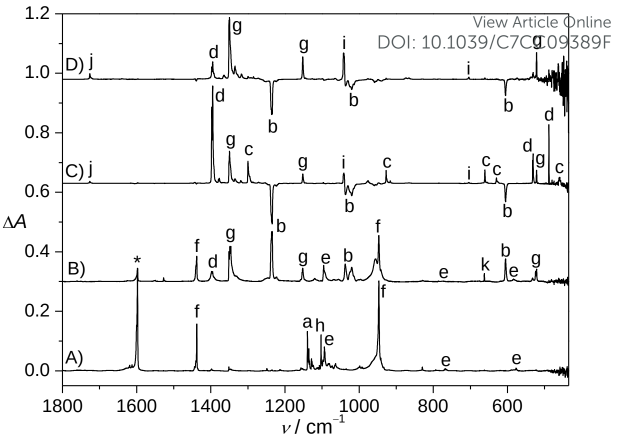

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Fig.1 A) IR spectrum of matrix isolated HVFP (1000 K) products of ethylene episulfoxide (**e**) in N_2 (1:1000) at 15 K. B) IR spectrum of matrix isolated HVFP (1000 K) products of a mixture of **e**/O_2/N_2 (1:50:1000) at 15 K. C) IR difference spectrum showing the change of the matrix upon 830 nm LED irradiation (20 min). D) IR difference spectrum showing the change of the HVFP (1000 K) products of a mixture of **e**/O_2/N_2 (1:50:1000) upon 365 nm UV-light irradiation (1 min). IR bands of SO (**a**), *cis*-OSOO (**b**), cyclic OS(=O)O (**c**), SO_3 (**d**), CH_2CH_2 (**f**), SO_2 (**g**), OSSO (**h**), O_3 (**i**), $CH_3C(O)H$ (**j**), CO_2 (**k**), and H_2O (*) are marked.

For the spectral assignments, we computed the IR spectrum of the most likely candidate species cyclic OS(=O)O (**c**, Table 1). The good agreement of the observed IR spectrum with the computational results, particularly with the anharmonic CCSD(T)/cc-pVTZ IR frequencies, supports the assignment. The strongest IR band at 1299.8 cm^{-1} belongs to the S=O stretching vibration with an isotopic shift of 13.0 cm^{-1} (13.8 cm^{-1}, calc.) for the naturally abundant ^{34}S. The band at 927.3 cm^{-1} is assigned to the O–O stretching vibration that mixes with the symmetric O–S–O stretch as evident from a ^{34}S-isotopic shift of 5.2 cm^{-1} (5.0 cm^{-1}, calc.). The asymmetric O–S–O stretch appears at 629.7 cm^{-1}, and the corresponding deformation mode locates at 660.9 cm^{-1} with a ^{34}S-isotopic shift of 6.4 cm^{-1} (6.8 cm^{-1}, calc.). Note that traces of cyclic OS(=O)O (**c**) can also be identified among the HVFP products of the **e**/O_2/N_2 mixture, indicating the occurrence of a thermal conversion from OSOO.

To further verify the assignment and probe the mechanism for the conversion of various sulfur oxides (SO, SO_2, OSOO, cyclic OS(=O)O, and SO_3), isotopic labeling experiments using $^{18}O_2$ (97 atom %) for the oxidation of SO were performed. As expected, OS–$^{18}O^{18}O$ (**b'**, Fig. 2A) forms via combination of SO with $^{18}O_2$. The concomitant generation

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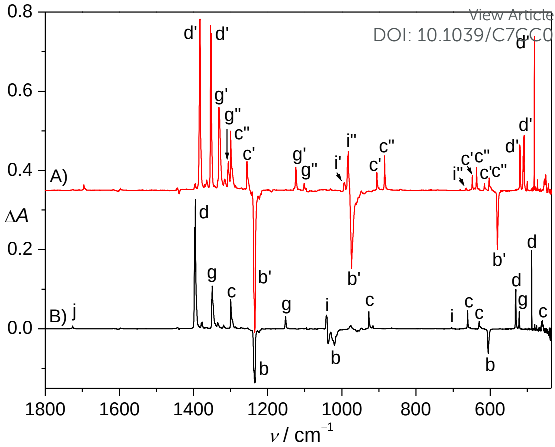

Fig.2 A) IR difference spectrum showing the change of the N_2-matrix isolated HVFP (1000 K) products of a mixture of **e**/$^{18}O_2/N_2$ (1:50:1000) upon 830nm LED irradiation (20 min). For comparison, the corresponding IR difference spectrum with $^{16}O_2$ is shown as Fig.2B.The bands of ^{16}OS-^{18}O^{18}O (**b'**), ^{16}OS(=^{18}O)^{18}O (**c'**), ^{18}OS(=^{16}O)^{18}O (**c''**), doubly ^{18}O-labeled SO_3 (**d'**), ^{16}OS^{18}O (**g'**), and ^{18}OS^{18}O (**g''**), ^{16}O^{18}O^{18}O (**i'**), and ^{18}O^{18}O^{18}O (**i''**) are marked.

of singly ^{18}O-labeled SO_2 and traces of doubly ^{18}O-labeled SO_3 clearly demonstrates unimolecular dissociation and isomerization of OS-^{18}O^{18}O in the gas phase.

Unexpectedly, subsequent 830 nm LED irradiation (Fig. 2A) leads to the formation of a mixture of^{16}OS(=^{18}O)^{18}O (**c'**) and^{18}OS(=^{16}O)^{18}O (**c''**). Given the almost equal intensities for each IR band computed at the CCSD(T)/cc-pVTZ level for **c'** and **c''** (see the details in the ESI†), a ratio of 2:1 for the two isotopomers can be estimated. In sharp contrast to the sole observation of singly ^{18}O-labeled SO_2 during the gas-phase oxidation of SO with $^{18}O_2$, a mixture of isotopologues ^{16}OS^{18}O (**g'**) and ^{18}OS^{18}O (**g''**) is observed among the photolysis products of OS-^{18}O^{18}O with an estimated ratio of about 4:1 based on the intensities of the two well-resolved IR bands at 1124.2 and 1101.5 cm^{-1}, respectively. The mixture of ^{16}O^{18}O^{18}O (**i'**) and ^{18}O^{18}O^{18}O (**i''**) in a ratio of 1:4 ensues (Fig. 2A), which means that the photodissociation (830 nm) of O=S–OO to OSO and O (immediately trapped by O_2 in 5% O_2-doped matrices) occurs likely through the formal cleavage of either the terminal O–O bond or the O=S bond. The absence of the SOO intermediate[12] in the latter case is probably due to isomerization to OSO under the irradiation conditions. Nevertheless, only the doubly ^{18}O-labeled SO_3 (**d'**) was obtained as the final oxidation product in the reaction of SO with $^{18}O_2$. The abnormal ^{18}O isotopic distributions in the ring-closure of OS–OO (**b**) to cyclic OS(=O)O (**c**) and subsequent dissociation to SO_2 and O suggest that the mechanism might be more complex than the previously proposed (Scheme 1).

The oxidation of SO and subsequent photochemistry can be followed by UV/Vis spectroscopy at 12 K (Fig. 3). Consistent with the observation of an intense red color for the matrix-isolated HVFP products of the **e**/O_2/N_2 mixture, a strong and structured broad absorption band centered at 410 nm (λ_{max}) is observed. It is very close to the most characteristic absorptions found for zwitterionic carbonyl oxides $R_2C=O^+–O^-$ ranging from300 to 500 nm.[24] This is also consistent with a predicted very strong vertical transition at 349 nm (f = 0.0962, TD-B3LYP/6-311+G(3df)) for OSOO. In line with the IR spectroscopic observation, irradiation of the matrix with 850 nm LED causes depletion of this and another band at 230 nm. As a result, a band at 255 nm appears but subsequently vanishes completely upon low-pressure mercury lamp irradiation (254 nm). By referring to a computed transition at 290 nm (f = 0.0015), it is assigned to the cyclic OS(=O)O (**c**). A weak band at 280 nm becomes apparent after 254 nm irradiation, which is likely associated with the remaining species in the matrix such as O_3, SO_3, and the undecomposed ethylene episulfoxide.

Table 1. Computed and observed IR spectra (cm^{-1}) of cyclic OS(=O)O (**c**).

IR fundamentals						^{18}O isotopic shifts^d				assignment^g
CCSD(T)-F12^a	CCSD(T)/cc-pVTZ^b		Observed^c			^{16}OS(=^{18}O)^{18}O		^{18}OS(=^{16}O)^{18}O		
anharmonic	harmonic	anharmonic	Ar-matrix	N_2-matrix	Ne-matrix	calc.^{e}	obs.^{f}	calc.^{e}	obs.^{f}	
1311.7 (243)	1308.5	1291.9 (138)	1296.6	1299.8	1294.8	47.1	43.8	0.5	0.5	A', ν(SO')
940.1 (72)	947.1	925.3 (38)	923.9 (52)	927.3 (34)	925.2 (49)	21.9	21.6	42.1	42.5	A', ν(OO)
669.9 (62)	672.8	658.1 (40)	659.5 (27)	660.9 (30)	659.3 (35)	13.1	12.7	24.9	24.0	A', δ(OSO)
635.3 (14)	630.9	618.4 (18)	624.3 (16)	629.7 (21)	626.5 (22)	14.7	14.3	27.4	26.9	A'',
459.1 (27)	449.7	444.9 (17)	460.0 (35)	459.9 (40)	n.o.^{h}	16.0		8.6		A', δ(O'SO)
344.9 (8)	342.0 (5)	337.6 (5)				11.6		10.9		A'', ω(O'SO)

[a] With the VTZ-F12 basis set. [b] Computed IR intensities (km mol^{-1}) in parentheses. [c] Band positions for the most intense matrix sites. [d] ^{18}O-isotopic shifts relative to the IR bands of ^{16}OS(=^{16}O)^{16}O. [e] At the CCSD(T)/cc-pVTZ level. [f] Observed in N_2-matrix. [g] Tentative assignment based on the computed vibrational displacement vectors. [h] Not observed.

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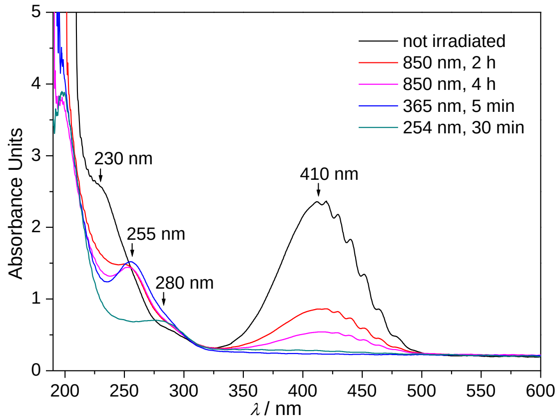

Fig.3 UV/Vis spectra of the HVFP products of a mixture of **e**/O_2/N_2 (1:50:1000) at 12 K.

In summary, two SO_3 isomers *cis*-OSOO and dioxathiirane cyclic OS(=O)O have been identified in the oxidation reaction of SO with O_2 by matrix-isolation IR and UV/Vis spectroscopy. This dioxathiirane is the first experimentally reported cyclic SO_3 isomer. A stepwise reaction process of OS + O_2→ OSOO → cyclic OS(=O)O → SO_3 has been experimentally unraveled. The unexpected ^{18}O isotopic distributions observed in the photo-induced ring-closure of OSOO to cyclic OS(=O)O and the dissociation of OSOO to SO_2 and O requires further experimental and theoretical studies. The facile generation of OSOO and cyclic OS(=O)O in the gas phase will stimulate further studies on their structures and reactivities.

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Conflicts of interest

There are no conflicts to declare.

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