

Oxathiirane

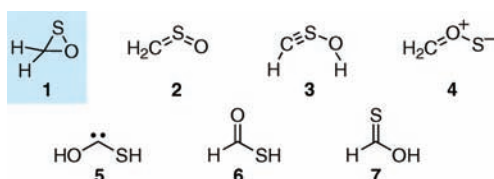
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The parent molecule oxathiirane (**1**, Scheme 1) and its derivatives have been implicated as the key intermediates in the photolytically initiated sulfur transfer reactions¹ of thiocarbonyl *S*-oxides (sulfines),² but **1** has never been directly observed experimentally. The diphenyl derivative was suggested as a transient species with a UV absorption at $\lambda = 390$ nm in the photochemical decomposition ($\lambda = 330$ nm) of thiobenzophenone *S*-oxide.³ The only firm spectroscopic evidence for the formation of an oxathiirane derivative (6,7-dimethyl-1,5-dioxia-2-thiaspiro[2.4]heptan-4-one) comes from the photolytic rearrangement of the corresponding sulfine precursor (4,5-dimethyl-3-thioxodihydrofuran-2(3*H*)-one *S*-oxide).⁴ Here we report the first preparation and matrix isolation of **1** and its IR-spectroscopic and high-level computational characterization.

Scheme 1. H₂CSO Isomers



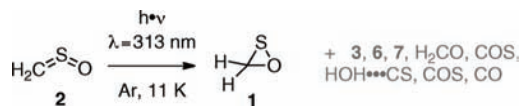
The lack of information on **1** is surprising in view of the important role sulfines [whose parent, thioformaldehyde *S*-oxide (**2**), is shown in Scheme 1] play as synthetic intermediates^{5,6} and biologically active compounds⁷ (e.g., as the lachrymatory factor in onions⁸). There are a few theoretical studies on **1**, and they all predict, at a variety of levels of theory, that this molecule should be experimentally observable.^{9,10} Some experimental evidence has been provided for aryl-substituted carbonyl sulfides,¹⁰ for which formaldehyde *O*-sulfide **4** is the parent.

The challenge in the preparation of **1** lies in the unexpectedly rich unimolecular (photo)chemistry observed for **2**.¹¹ For instance, we recently showed that irradiation of **2** at $\lambda = 254$ nm (Ar, 11 K) gives **3**, a very surprising structure with a formal carbon–sulfur triple bond.^{12,13} The anticipated carbene HO–C–SH (**5**)¹⁴ has not been observed, although it lies only ca. 15 kcal mol⁻¹ above **2** [at the CCSD(T)/cc-pVTZ + ZPVE level], while **3** is ca. 28 kcal mol⁻¹ less stable than the sulfine (see below). Hence, irradiation indeed may provide access to high-lying isomers of **2**, and we envisaged that irradiation with an appropriate wavelength would provide access to **1**.

Preparation of **2**^{6,11} from its dimer (1,3-dithietane 1,3-dioxide) through flash vacuum pyrolysis¹² and subsequent irradiation at $\lambda = 313 \pm 10$ nm in an Ar matrix at 11 K led to a slow photoreaction. After 1 h, all of the characteristic IR and UV bands of **2** disappeared, and quite a number of new IR bands were recorded [for the spectrum, see Figure S1 in the Supporting Information (SI)],

corresponding to a total of nine different species (Scheme 2). The most intense bands belonged to an *E/Z* mixture of methanethioic *S*-acid (**6**),¹⁵ CO, and COS; there was also a small amount of unconverted **2**.¹² Some formaldehyde was also detected, and its carbonyl absorption was slightly bathochromically shifted from 1742 to 1736.0 cm⁻¹, most likely because of a sulfur atom in its vicinity in the matrix cage. The assignment of the remaining bands to **1**, methanethioic *O*-acid (**7**), and a hitherto unknown HOH...CS complex was accomplished through irradiation at other wavelengths (see the SI for assignments of the IR spectra): At $\lambda > 360$ nm, only the conversion of **1** to **6** took place, while the HOH...CS complex rearranged to **6** at $\lambda = 254$ nm.

Scheme 2. Photochemical Generation of **1** Along with Other H₂CSO Isomers or Fragments



The excellent agreement of the IR difference spectra and the CCSD(T)/cc-pVTZ computed IR absorptions¹⁶ for **1** underline its successful preparation (Figure 1).

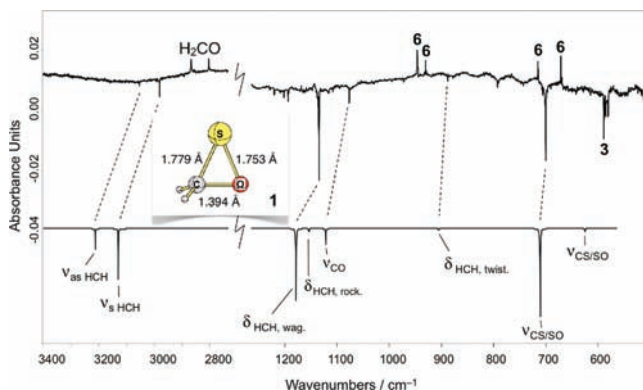


Figure 1. (top) IR difference spectrum of the photolysis of **1** with $\lambda > 360$ nm (positive bands, products; negative bands, **1**) in Ar at 11 K. (bottom) Computed CCSD(T)/cc-pVTZ IR spectrum of **1** (unscaled). Inset: the computed CCSD(T)/cc-pVTZ structure.

For confirmation of these assignments, we also prepared *d*₂-**1** from *d*₂-**2**, and the matching of experimental with unscaled computed IR absorptions as well as frequency shifts was also very good (Figure 2).

The relative energy ordering of the H₂CSO isomers (Figure 3) shows that **1** lies ca. 10 kcal mol⁻¹ above the starting material and reference point **2**. This is in marked contrast to the corresponding structures on the CH₂O₂ potential energy hypersurface (PES), where the dioxirane structure is much more stable [24.2 kcal mol⁻¹ at the CCSD(T)/6-311+G(2d,2p)/B3LYP/6-311+G(2d,2p) level¹⁷ and 24.7 kcal mol⁻¹

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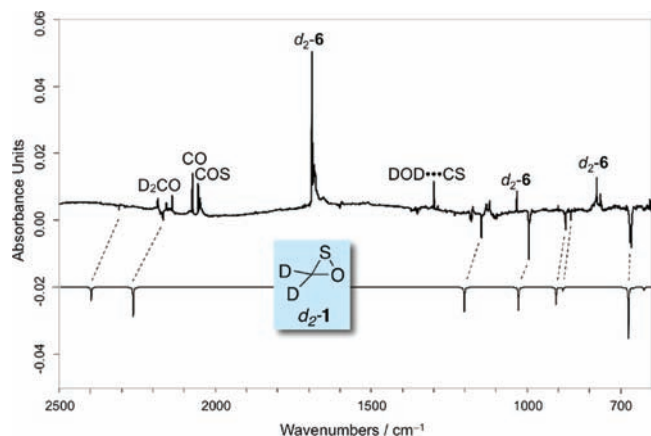


Figure 2. (top) IR difference spectrum of the photolysis of d_2-1 with $\lambda > 360$ nm (positive bands, products; negative bands, d_2-1) in Ar at 11 K. (bottom) computed CCSD(T)/cc-pVTZ IR spectrum of d_2-1 (unscaled). Inset: structure of d_2-1 .

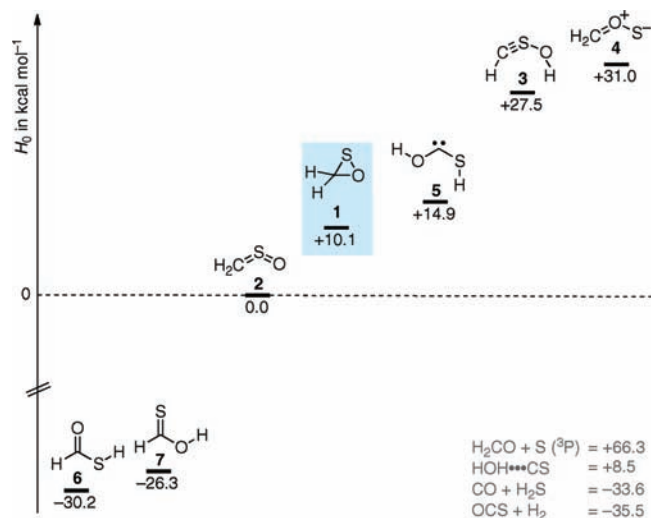
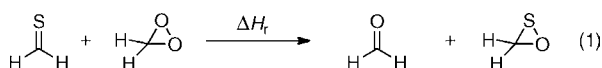


Figure 3. Energies of CH_2SO species [at the CCSD(T)/cc-pVTZ + ZPVE level] relative to sulfine **2**, the starting material for the preparation of **1** and **4** (energies not drawn to scale).

at the CCSD(T)/cc-pVTZ + ZPVE level] than the carbonyl oxide form. This may be due to the much higher polarizability of sulfur and its electropositivity relative to oxygen and carbon (see the table of contents graphic, which shows the electrostatic potential around **1**, indicating the high positive polarization of the sulfur atom). This is in part supported by the large reaction enthalpy of the homodesmotic reaction shown in eq 1 [$\Delta H_r = -44.8$ kcal mol $^{-1}$ at the CCSD(T)/cc-pVTZ + ZPVE level], which is also in line with the expectation that **1** should be an excellent sulfur atom donor.¹ In addition, this is also due to the much higher C=O versus C=S bond energy in formaldehyde versus thioformaldehyde.¹⁸



As there is now evidence for the existence of **1–3** and even **4**, we are hopeful that the last low-lying isomer on this PES, carbene **5**, can also be prepared. In view of the remarkable tunneling behavior of the parent hydroxycarbene HCOH,¹⁹ this is a worthwhile scientific goal that is currently being pursued in our laboratories.

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Supporting Information Available: IR spectra, computational details, and additional references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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