native-like binding geometries represents an important first step towards this goal.

Finally, we have shown that the LeadQuest Database provides an ideal source for the discovery of novel lead compounds,[31] in terms of both structural diversity[8] and chemical purity.[30]

Received: June 14, 2000 [Z 15270]

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[30] The LeadQuest product description guarantees $>85\%$ purity for every compound as determined by analytical HPLC (HP110 system) using a universal water/acetonitrile gradient and a UV detector at 254 nm.

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Thioformaldehyde *S*-sulfide (Thiosulfine)**

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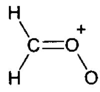
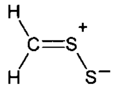
Hans Peter Reisenauer, and Günther Maier*

The elucidation of the course of events in the ozonolysis of olefins by Criegee[1] was a milestone in the effort to understand the mechanism of organic reactions. As early as in 1949 it was recognized that carbonyl oxides are the decisive intermediates in this process.[2] However, to date it has not been possible to observe these species directly during the transformation of "primary" into "secondary" ozonides. In contrast, an entry into carbonyl oxides exists in the trapping of carbenes with oxygen under matrix conditions;[3] however, the unsubstituted formaldehyde *O*-oxide **1** cannot be isolated even upon using this procedure. In the reaction of methylene with oxygen in an argon matrix only formic acid was detected.[4]



1



2

The idea that it might be possible to generate formaldehyde together with its oxide by cycloreversion of 1,2,4-trioxolane has not yet been realized, presumably due to the fact that the required ozonide of ethene is difficult to handle.[5] As is shown herein,[6] the situation is completely different in the sulfur series. 1,2,4-Trithiolane (**3**) is a stable, easily accessible

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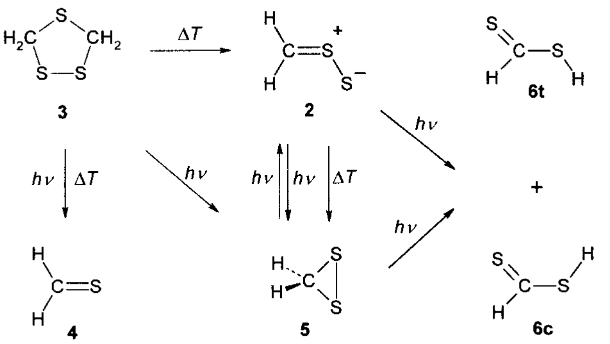
[**] This work was supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the Polish State Committee for Scientific Research (KBN Grant 3T09A00716).

substance.[7] There are additional reasons to try the thermal fragmentation of **3** into the title molecule **2**, the analogue of Criegee's "zwitterion", and thioformaldehyde (**4**). On the one hand such a cycloreversion was successfully used by Huisgen and Rapp[8] for the preparation of substituted derivatives of **2**, on the other hand Bock et al.[9] identified **4** by photoelectron spectroscopy upon the pyrolysis of **3**.



Indeed, the gas-phase pyrolysis of **3** in combination with matrix isolation of the formed products opens an ideal route for the system thiosulfine (**2**)/dithiirane (**5**)/dithioformic acid (**6**),[10] which is of importance from the preparative and the theoretical point of view.

We pyrolyzed 1,2,4-trithiolane (**3**) in high vacuum (quartz tube: diameter 8 mm, heating zone 5 cm, ca. 10^{-5} mbar, 950 °C) and condensed the reaction products together with argon on a CsI window at 10 K. In the IR spectrum of the formed matrix besides the known bands of **3** and **4** (**4** generated independently by pyrolysis of allylmethyl sulfide gave an identical IR spectrum) only the absorptions shown in Tables 1 and 2 and in Figure 1 were registered.

Fabian and Senning[10] calculated the energy and geometry of thioformaldehyde *S*-sulfide (**2**) on the B3LYP/6-311+G(3df,3pd) level, but its IR spectrum on the B3LYP/6-31G* level. Since especially the position of the S–S stretching vibration strongly depends on the used basis set (6-31G*: 586, 6-311+G(3df,3pd): 612, exp: 623 cm^{-1}) we additionally calculated the IR spectra with the first mentioned method. As the comparison shows the theoretical IR spectrum obtained in this manner fits quite well with the experimental one of **2** (Table 1).

Table 1. Calculated (B3LYP/6-311+G(3df,3pd), harmonic approximation; intensities [km mol^{-1}] in parentheses) and experimental (argon matrix, 10 K) IR spectrum of thioformaldehyde *S*-sulfide (**2**).

	Mode[a]	$\tilde{\nu}_{calcd}$ [cm^{-1}]	$\tilde{\nu}_{exp}$ [cm^{-1}]
ν_1 a'	CH$_2$ str.	3264 (2)	3126.3 (vw)
ν_2 a'	CH$_2$ str.	3140 (3)	3010.4 (w)
ν_3 a'	CH$_2$ sciss.	1416 (12)	1366.4 (m)
ν_4 a'	CS str.	1019 (23)	970.9 (m)
ν_5 a'	CH$_2$ rock.	934 (13)	910.2 (m)
ν_8 a''	CH$_2$ wag.	809 (59)	756.8 (s)
ν_6 a'	SS str.	612 (47)	622.8 (s)
ν_9 a''	CH$_2$ twist.	575 (3)	–
ν_7 a'	def.	310 (1)	–

[a] str. = stretching vibration, sciss. = scissoring vibration, rock. = rocking vibration, wag. = wagging vibration, twist. = twisting vibration, def. = deformation vibration.

Table 2. Calculated (B3LYP/6-311+G(3df,3pd), harmonic approximation; intensities [km mol^{-1}] in parentheses) and experimental (argon matrix, 10 K) IR spectrum of dithiirane (**5**).

	Mode[a]	$\tilde{\nu}_{calcd}$ [cm^{-1}]	$\tilde{\nu}_{exp}$ [cm^{-1}]
ν_6 b$_1$	CH$_2$ str.	3215 (0)	–
ν_1 a$_1$	CH$_2$ str.	3118 (9)	2986.7 (m)
ν_2 a$_1$	CH$_2$ sciss.	1461 (2)	1412.0 (w)
ν_7 b$_2$	CH$_2$ wag.	1072 (2)	1053.0 (m)
ν_5 a$_2$	CH$_2$ twist.	952 (0)	–
ν_8 b$_1$	CH$_2$ rock.	944 (3)	928.3 (m)
ν_3 a$_1$	ring str.	856 (1)	–
ν_9 b$_2$	ring str.	588 (9)	581.0 (s)
ν_4 a$_1$	SS str.	501 (1)	–

[a] See footnote [a] in Table 1.

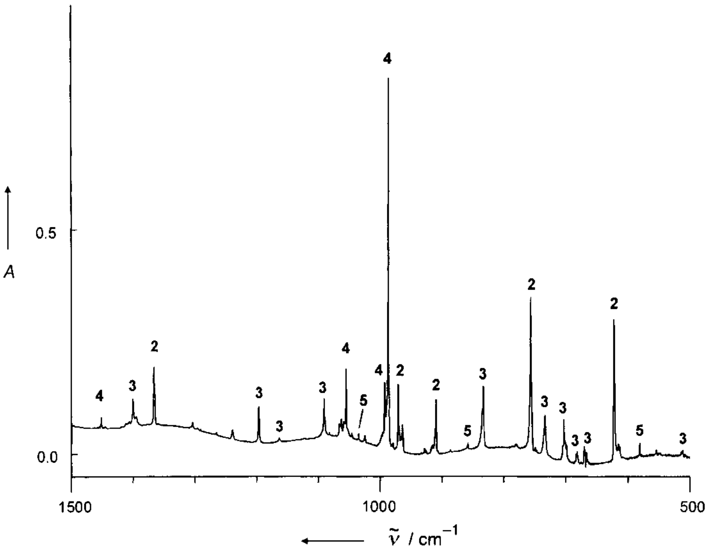


Figure 1. Selected region of the experimental IR spectrum (Ar, 10 K) of the products of the pyrolysis of 1,2,4-trithiolane (**3**).

As the calculation indicates, the IR bands of dithiirane (**5**) should be much less intense than those of **2**. In accordance with this prediction the experimental spectrum of **5** shows a very weak but clearly visible band at 581 cm^{-1}. On the basis of the calculated band intensities it can be estimated that the cycloreversion of **3** at 950 °C leads to a ratio **2**:**5** of about 2:1. At 850 °C a minor amount of dithiirane **5** (ratio **2**:**5** ca. 3.5:1) is found. At even lower temperatures (650 °C) the starting molecule **3** remains intact. That means, in the thermal fragmentation of **3** a considerable barrier must be passed. If a fragmentation occurs, a thermal ring closure of **2** to **5** partly takes place already during the pyrolysis.

In the UV spectrum **2** shows an intense band at 356 nm. Since a photoisomerization of **2** is even possible with light of very long wavelengths ($\lambda > 570$ nm; see below), the compound has to have a second, bathochromically shifted absorption; however, its intensity is too low for a direct observation under the applied experimental conditions. This finding fits to the calculations of Fabian and Senning,[10] which predict an intense $\pi \rightarrow \pi^*$ transition at 300 nm and a very weak $n \rightarrow \pi^*$ absorption at 373 nm for **2**. For dithiirane (**5**) no distinct absorption maximum could be found. The photochemical behavior of **5** dicussed below demands, however, also an absorption in the long-wavelength region (at ca. 500 nm) for this molecule.

Depending on the applied wavelength the products of the pyrolysis of **3** undergo various photoreactions. Light of wavelength >385 nm leads to s-*cis*- and s-*trans*-dithioformic acid **6c** and **6t**, respectively, as indicated by the comparison with the known[11] matrix IR spectra and with the theoretical spectra calculated on the B3LYP/6-311 + G(3df,3pd) level (Figure 2). If the pyrolysis products are irradiated with light of even longer wavelengths ($\lambda > 570$ nm), the IR spectra show initially a selective rearrangement of *S*-sulfide **2** into dithiirane **5**. If the irradiation is continued with light of wavelength $\lambda > 570$ nm the bands of **2** decrease further and one registers besides absorptions of **5** those of **6c** and **6t** (Figure 2). If the secondary irradiation is carried out with monochromatic light ($\lambda = 500 \pm 10$ nm) the reaction starts with a partial back reaction **5**→**2**. A photoequilibrium **5**⇄**2** is established, from which the final conversion into **6c** and **6t** originates.

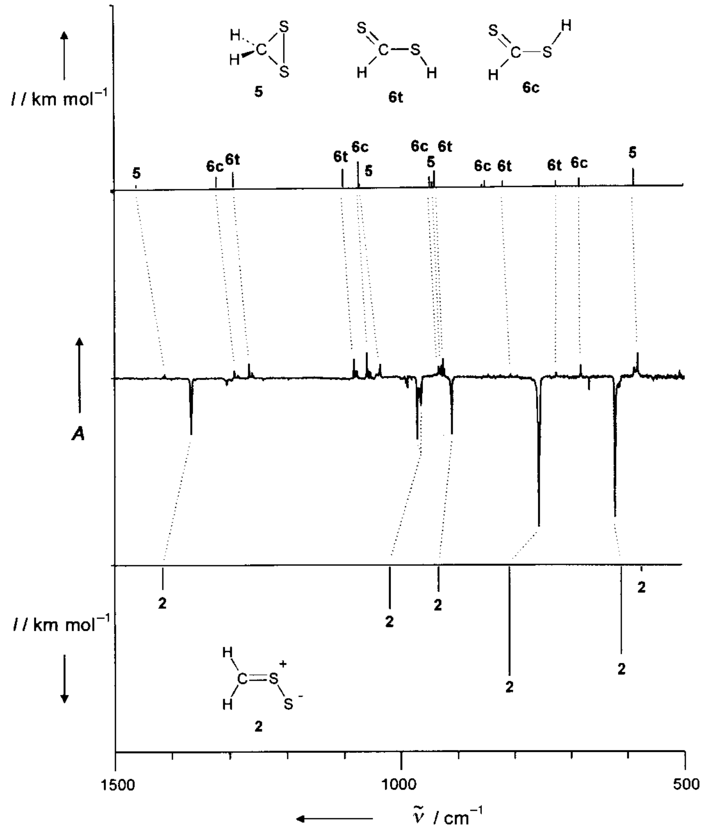


Figure 2. Selected region of the experimental (Ar, 10 K) and calculated (B3LYP/6-311 + G(3df,3dp)) IR spectra of the CH_2S_2 isomers thioformaldehyde *S*-sulfide (**2**), dithiirane (**5**), s-*cis*- and s-*trans*-dithioformic acid (**6c**/**6t**). Middle: Experimental difference spectrum before and after irradiation of the matrix isolated pyrolysis products of **3** with light of the wavelength >570 nm (the positive bands grow, the negative ones disappear during irradiation). Top: Calculated spectrum of a 10:1:1 mixture of **5**, **6c**, and **6t**. Bottom: Calculated spectrum of **2**, related to the same scale.

If the mixture of the dithioformic acids **6c** and **6t** is irradiated in the matrix with light of wavelength 313 nm CS and H_2S are generated. Changing the wavelength to 254 nm induces a partial recapture within the matrix cage and **6** is reformed. After longer irradiation only CS_2 can be detected, probably under elimination of H_2.

$$\mathbf{6c,t} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} CS + H_2S \xrightarrow{h\nu} CS_2 + H_2$$

Remarkably, upon direct irradiation ($\lambda = 313$ nm) of trithiolane **3** no IR bands of thioformaldehyde *S*-sulfide (**2**) but only those of thioformaldehyde (**4**), dithiirane (**5**), and dithioformic acid (**6**) can be observed. It has to be assumed that thiosulfine **2**, which is generated photochemically from **3**, is photoisomerized immediately to the isomers **5** and **6**.

Conclusion: a) The expectation by Fabian and Senning[10] that the calculated spectroscopic data of **2** may lead to its detection under matrix conditions has been fulfilled. Herewith, a thiosulfine—and even better, the unsubstituted parent compound—has been directly identified. The existence of thiosulfines had been illustrated using trapping reactions by Huisgen and Rapp[8] already in 1987. b) The good agreement between the experimental and calculated IR spectra is an indication that the geometry (planar, bent) and the electronic structure of **2** is correctly expressed by the calculations. Consequently, thioformaldehyde *S*-sulfide (**2**) should be regarded more as a dipole (ylide form) and less as a singlet diradical.[10] c) After the isolation of sterically hindered dithiiranes, which has been achieved recently,[12] now the existence of the unsubstituted parent molecule **5** is also proven. d) The calculated[10] high barrier of 28.6 kcal mol^{-1} for the isomerization of **2** into more stable dithiirane **5** (by 5.9 kcal mol^{-1}; the global minimum is represented by **6**) explains why the ring closure **2**→**5** needs a relatively high temperature (kinetic control; the higher the temperature of pyrolysis, the more **5**) or photoexcitation. The thermal threshold for the transformation **2**/**5**→**6** is evidently too high to be passed under the applied pyrolysis conditions. e) This observation provides new insight on the question whether substituted thiosulfines can be isomerized in solution into esters of dithiocarbonic acid via the corresponding dithiiranes, which is controversially discussed in the literature.[8, 13]

Received: August 25, 2000 [Z15699]

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