Matrix Isolation of Chalcogeno Heterocumulenes

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The application of matrix isolation techniques connected with quantum mechanical calculations on generation and structural elucidation of cumulenic compounds containing sulfur or oxygen has been reviewed. Experimental matrix IR and UV/VIS data for all known species of this class of substances have been summarized together with some matrix electron spin resonance (ESR) studies.

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1. INTRODUCTION

Matrix isolation is a very suitable technique for the synthesis and detection of chalcogeno heterocumulenes $X=(C)_n=Y$ ($n \geq 2$; X, Y: O, S), since many of them are not stable under usual conditions. This method allows spectroscopic studies of highly reactive radicals and other species with short lifetimes without making use of fast time-resolved techniques. As postulated by Porter[1] and Pimentel[2] in 1954, the reactive species are prevented from any chemical reaction by embedding them in a solid, if three conditions are fulfilled: (a) The solid has to be chemically inert, (b) isolation of the single molecules must be achieved by choosing concentrations which are sufficiently low, and (c) diffusion in the solid has to be suppressed by applying low temperatures

during the experiments. In this way the kinetic instability inherent to all heterocumulenes is counteracted. In general, there are two possibilities to create a solid with the desired properties, the so-called *matrix*. The molecules of interest can be generated from suitable precursors by pyrolytic or discharge reactions in the gas phase and codeposited with an excess of host material on the cooled matrix holder. The second way is to produce the reactive species *in situ* by photolysis after trapping and isolating the precursor molecules in the matrix material. For detailed information on the development of matrix isolation methods and their application range the reader is referred to several monographies[3-8] and reviews.[9-14]

The properties of the matrix material determine the spectroscopic methods that can be applied. The use of solid rare gases like argon and xenon or solid nitrogen is well established, since they are optically transparent in the commonly observed spectral ranges. The fact that there is nearly no interaction between the host lattice and the enclosed guest species and that the rotational movements are frozen has an important effect on the IR spectra: under ideal conditions the recorded infrared spectra are reduced to line spectra. These can easily be compared with the theoretically predicted spectra. UV/VIS spectra are also obtained easily and are useful for the structural elucidation of unknown species as well. What is even more important: The UV absorptions allow the selection of the appropriate wavelengths for the induction of photochemical reactions, which under matrix conditions are often reversible.

The expected electronic ground state of the heterocumulenes $X=(C)_n=Y$ can be derived from simple MO considerations. Supposing a linear structure, all heterocumulenes possess doubly degenerated π orbitals as HOMOs. For even n these orbitals are half-filled, resulting in a triplet ground state due to Hund's rule, analogous to the O_2 molecule. In the case of odd n the HOMOs are fully occupied, with a singlet ground state as the consequence. Thus, with growing chain length the multiplicity of the electronic ground state of the chalcogeno heterocumulenes alternates between singlet and triplet. Experimental evidence for the latter is accessible by recording the electron spin resonance (ESR) spectrum of the matrix isolated species.

The large number of heterocumulenes identified by matrix isolation illustrates the strength of this method, as demonstrated in this review on

studies of di- and monosulfides and sulfide oxides of carbon. Syntheses and properties of the analogous di- and monoxides follow very similar principles. Hence they are included here and for chronological reasons we start with matrix isolation studies on carbon monoxides.

2. MONOXIDES $(C)_n{=}O$

2.1. Oxoethenylidene C_2O

The history of matrix isolation of heterocumulenes goes back to the year 1965: Jacox et al.[15] generated oxoethenylidene C_2O (2) by reaction of carbon atoms obtained from cyanogen azide 1 with carbon monoxide and by vacuum UV photolysis of matrix isolated C_3O_2 (3).

$$N{\equiv}C{-}N_3 \xrightarrow[+\,CO,\,-\,2\,N_2]{h\nu} O{=}C{=}C: \xleftarrow[-\,CO]{h\nu} O{=}C{=}C{=}C{=}O$$

$$\qquad 1 \qquad\qquad\qquad 2 \qquad\qquad\qquad 3$$
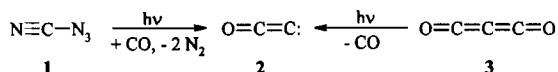
The linear structure of 2 was derived from experiments with isotopically substituted precursor molecules and by correlation of vibrational frequencies calculated from estimated force constants with the recorded IR absorptions. All three fundamentals were observed as well as the UV/VIS spectrum,[16] which has been resolved and analyzed by gas phase measurements.[17] The predicted triplet ground state was confirmed by recording the ESR spectrum of 2 isolated in various matrices.[16]

2.2. Oxopropadienylidene C_3O

In 1971 DeKock and Weltner thermolyzed tantalum carbide and codeposited the resulting beam of carbon with a mixture of Ar and CO at 4 K.[18] Together with the known IR bands of 2 they observed a new absorption and ascribed it to oxopropadienylidene C_3O (5). Starting materials with varying isotopic substitution were used and the structural elucidation again was based on a force field analysis.
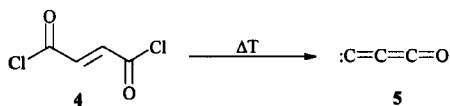
Further spectral information on the molecule was not available, until in 1985 Brown et al.[19] found several other pathways to **5**, e.g. pyrolysis of fumaric acid dichloride **4**. They observed two more IR absorptions (a stretching and a bending mode) of C_3O in an Ar matrix.

In this publication for the first time vibrational frequencies calculated by *ab initio* theory were used to identify a heterocumulene. Today this method is well established and turns out to be very successful (see the accompanying review by Janoschek).
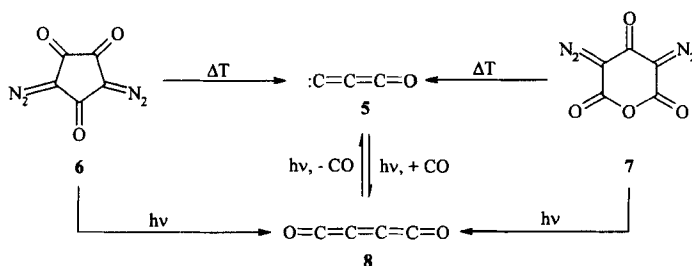
Finally, in experiments aimed at the synthesis of the homologous dioxide C_4O_2 (**8**),[20] the preparation of **5** was achieved by pyrolysis of the cyclic diazoketones **6** and **7** or by photolysis of **8**, which was generated by matrix irradiation of both precursors (see Section 3.3). Based on these results, the detailed matrix IR spectrum of **5** was reported in 1991 in a comprehensive theoretical study by Botschwina and Reisenauer.[21] Several combination modes and overtones were described as well as an additional fundamental, which shows an overtone of remarkably high intensity. Fermi resonance with the most intense stretching vibration is responsible for this observation.

In the same year a high-resolution FTIR study of C_3O was published by McNaughton et al.[22]

2.3. Oxobutatrienylidene C_4O

According to the same synthetic principle (splitting off of CO), the next member in the series of carbon monoxides, C_4O (**10**), could be prepared in 1988 by matrix photolysis of C_5O_2 (**9**) by Maier et al.[23] Five bands were observed in the matrix IR spectrum corresponding to four stretching modes and one bending vibration, as was calculated by semiempirical and *ab initio* methods[24] based on a linear triplet molecule.

$$O=C=C=C=C=C=O \xrightarrow[-CO]{h\nu} O=C=C=C=C=C: \xleftarrow[+CO]{h\nu} :C=C=C:$$

<div align="center">

9   **10**   **11**

</div>
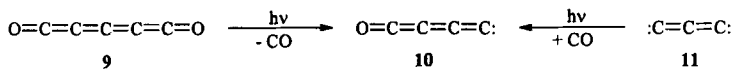
C_4O is also formed by photochemical reaction of carbon monoxide with matrix isolated graphite vapor[25] by selective excitation of C_3 (**11**). In these experiments, carried out in Ne and Ar matrices, Weltner *et al.* showed the triplet character of **10** by ESR spectroscopy as well as the linear structure with cumulene-like bonding by use of ^{13}C and ^{17}O isotopomers of the starting material.

2.4. Oxopentatetraenylidene C_5O

C_5O could be generated in 1995 by an electric discharge in a mixture of C_3O_2 and Ar.[26] The reaction products were analyzed by rotational spectra, from which the linear cumulenic structure and the bond lengths were derived. Matrix studies on this molecule have not been carried out so far.

2.5. Oxohexapentaenylidene C_6O

During the experiment concerning C_4O, Weltner *et al.*[25] observed another triplet ESR signal which they ascribed to C_6O (**13**), a linear cumulenic species as well. The mechanism of its formation under the chosen conditions is not clear, speculations tend to the reactions $C_3 + C_3O$ or $C_5 + CO$.

$$O=C=C=C=C=C=C=O \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} O=C=C=C=C=C=C: + CO$$

<div align="center">

12   **13**

</div>
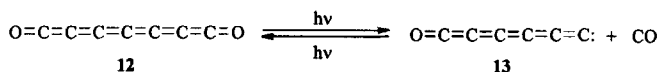
A matrix IR spectrum, which probably corresponds to C_6O, was recorded in 1991, again by Maier and co-workers.[27] This spectrum correlates well with scaled *ab initio* vibrational frequencies calculated again on the basis of a linear molecule.[24] The generation of this reactive molecule was achieved in an analogous manner to C_4O by photo-chemical cleavage of C_7O_2 (**12**), which can be reversed by change of the excitation wavelength.

2.6. The Carbon Monoxides C_7O, C_8O and C_9O

No matrix isolation studies on the also known carbon monoxides C_7O, C_8O and C_9O[26,28] have been published so far. They were

prepared in the same way as C_5O and studied by microwave spectro-scopy as well.

3. DIOXIDES $O=(C)_n=O$

3.1. Ethenedione C_2O_2

Many attempts to generate or matrix isolate ethenedione C_2O_2 (**15**) were not successful so far. Neutralization of the radical cation in the gas phase also failed.[29] Theoretical considerations are in accordance with these experimental findings: triplet C_2O_2, computationally a minimum, can be transformed into singlet C_2O_2 by passing over a small energy barrier. This singlet molecule is predicted to dissociate spontaneously into two CO molecules.[30]
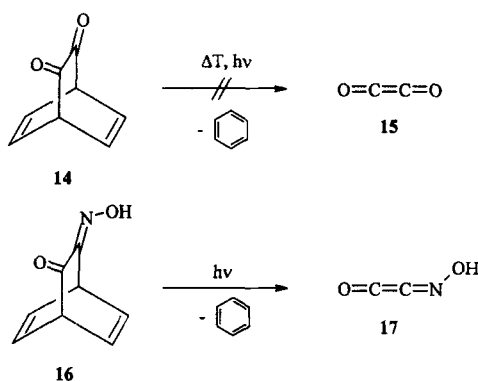
The bridged diketone **14**, a very promising precursor for **15** because of a pre-formed C_2O_2 moiety, fragments into benzene and carbon monoxide instead of the desired heterocumulene,[31] even under matrix conditions.[32] A molecule very closely related to C_2O_2 was studied by matrix isolation spectroscopy in 1996. The bicyclic precursor **16** yields ethenedione monoxime **17** upon matrix irradiation.[32] In contrast to ethenedione, **17** is calculated to be a bent singlet species.

As will be discussed below, it is possible to generate $O=C=C=S$ by photoaddition of CS to CO. This method works well, since CS and C_2OS absorb at different wavelengths. As a result the photoequilibrium can be shifted to one side or the other.

$$
\begin{array}{c}
N=C=O \\
| \\
N=C=O
\end{array}
\quad \xrightarrow{\;h\nu\;} \quad
\left(
\begin{array}{cc}
O=C & C=O \\
& N_2
\end{array}
\right)_{Ar}
\quad \xrightarrow{\;h\nu\;}\!\!\!/\!\!\!/ \quad
O=C=C=O
$$

$$\textbf{18} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{15}$$
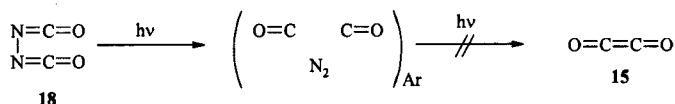
It is tempting to try the same with CO alone. An ideally suited precursor for this purpose is the diisocyanate **18**.[33] Upon irradiation, N_2 is eliminated and CO is formed. It is obvious that the matrix cage contains one molecule of N_2 and two molecules of CO, an ideal situation for the photodimerization of CO. If one of the CO molecules could be excited to the triplet state, the reaction could directly lead to triplet C_2O_2. According to the calculations this molecule should be thermally stable enough to survive under matrix conditions. In reality, upon irradiation of **18** with 185 and 193 nm only CO is detected. Thus, either no dimerization of CO occurs or C_2O_2 is formed but is apparently non-existent, since this molecule may absorb at a similar wavelength as CO and is therefore split immediately by the irradiating light.

3.2. Propadienedione C_3O_2

Carbon suboxide C_3O_2 (**3**) is a well-known substance, which was prepared in 1906 for the first time.[34] It is stable under normal conditions; hence, no matrix isolation studies are reported here. For detailed information on this compound see Ref. [35] or [36].

3.3. Butatrienedione C_4O_2

As mentioned above, photolysis of matrix isolated 3,5-bisdiazo-1,2,4-cyclopentanetrione **6** or 3,5-bisdiazo-2,4,6-tetrahydropyranetrione **7** with light of the appropriate wavelength leads mainly to C_4O_2 (**8**).[20] This first dioxide with an even number of carbon atoms was characterized by both, its two IR active stretching modes and one bending vibration. A large number of observed combination bands allowed the indirect determination of three IR inactive fundamentals.

Like all heterocumulenes with an even-numbered carbon chain, **8** is expected to be a linear molecule with a triplet ground state. Semiempirical analysis as well as *ab initio* calculations[37] resulted in a small energy gap between a linear triplet molecule and a slightly bent singlet species with C_{2h} symmetry, the most elaborate methods favoring the latter. Infrared spectra derived from both structures corresponded with

the observed absorptions. Hence, no conclusion concerning the ground state of **8** is possible by matrix IR spectroscopy. The matrix ESR spectrum of **8** showed no triplet signal; however, the observation range of the spectrometer used was not sufficient for a conclusive statement. The UV/VIS spectrum was measured as well and compared with calculated electronic transitions for both states. Yet, also in this case no significant difference between the singlet and the triplet state was obtained. As a consequence, the question concerning the ground state of **8** remains unanswered.

3.4. Pentatetraenedione C_5O_2

The third dioxide of carbon besides the well-known and stable compounds CO_2 and C_3O_2 was synthesized in 1988 by Maier's group. They used 2,4,6-trisdiazo-1,3,5-cyclohexanetrione **19** as a precursor molecule, which forms the surprisingly stable C_5O_2 (**9**)[23] in good yields on irradiation or thermal decomposition with C_3O_2 as a by-product. This heterocumulene represents a stable, yellow solid at temperatures below $-90\,°C$. Dioxide **9** can even be kept in solution at room temperature for some time. Hence, it was possible to convert **9** to propadienedicarboxylic acid dimethyl ester by reaction with methanol, a first structural proof for **9**. The infrared spectrum of matrix isolated C_5O_2 exhibits three stretching modes and two bending vibrations, which were compared with the semiempirically calculated IR spectrum (linear molecule, singlet ground state). Probably, the three-membered ring compound **20**, which could have been formed after splitting off three molecules N_2, followed by a three-fold Wolff rearrangement, is an intermediate of the photocleavage of **19**.
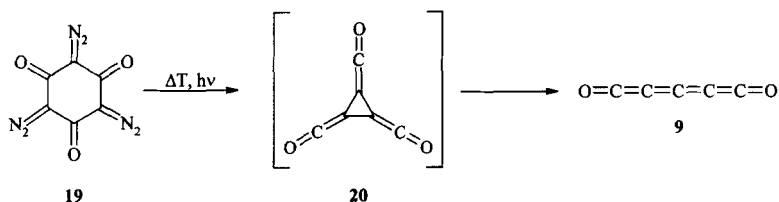
Three of the Raman active stretching modes of **9** were observed in a CCl_4 matrix and a high resolution FTIR spectrum of the most intense fundamental was recorded as well.[38]

3.5. Hexapentaenedione C_6O_2

No experimental evidence on C_6O_2 has been published so far.

3.6. Heptahexaenedione C_7O_2

In 1991 pyrolysis and matrix photolysis of mellithic acid trianhydride **21** was investigated.[27] In these experiments several IR bands were observed, which were ascribed to C_7O_2 (**12**), representing the longest heterocumulene studied by matrix isolation spectroscopy so far. All four IR active stretching vibrations were detected. Combination bands indicated a centrosymmetric molecule and gave a hint to two additional fundamentals. The correlation of the recorded IR spectrum with semi-empirical calculations and the reversible photochemical cleavage into C_6O and CO (see Section 2.5) supported structure **12**.
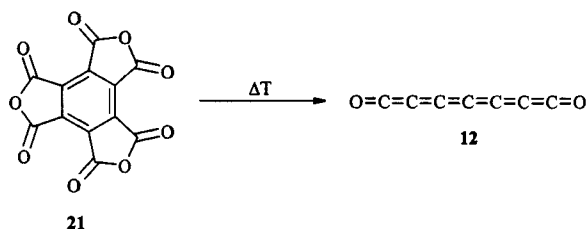
The observed intense absorption in the UV/VIS spectrum of **12** fits well into the series of the spectra of the so far known carbon dioxides (see Table II). The mechanism for the formation of **12** in these experiments is not fully understood, by-products are C_5O_2 and C_3O.

4. SULFIDE OXIDES $O=(C)_n=S$

4.1. Thioxoethenone C_2OS

Access to matrix isolated thioxoethenone C_2OS (**22**) was gained in 1997.[39] The photochemical addition of carbon monosulfide CS, generated by a microwave discharge in CS_2, to CO was achieved by selective excitation of CS. This reaction could be reversed completely by changing the excitation wavelength.

$$O=C \; + \; C=S \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} \quad O=C=C=S$$

<div align="center">22</div>
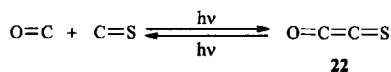
Density functional theory calculations were carried out for the identification of **22**, resulting in a very good agreement of theoretical prediction and observed IR spectra. The experimental bands represent two of three expected stretching modes, the third was calculated from combination vibrations, one of which has a remarkably high intensity due to anharmonic resonance. One bending vibration was recorded as well, the second being predicted as too low-lying and of too weak intensity to be detected. Experiments using [13]CO together with calculated isotopic frequency shifts demonstrated the linear geometry of the molecule. Thus, C_2OS very likely possesses a triplet ground state, since the lowest computed singlet state is a transoidally bent species.

The matrix UV/VIS spectrum was recorded as well and the observed absorption ($\lambda_{max} = 306$ nm) correlates with the photochemical cleavage of **22** into CO and CS on excitation with 313 nm light.

4.2. Thioxopropadienone C_3OS

The first heterocumulene containing sulfur and oxygen was prepared in 1976 by single O/S exchange in C_3O_2 (**3**) in very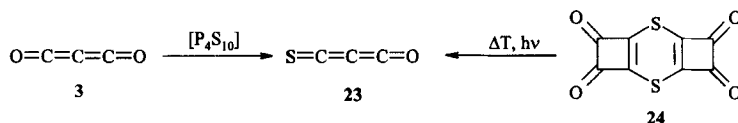 poor yields.[40] A much better source for C_3OS (**23**) is the squaric acid derivative **24**, which yields **23** as the main product on pyrolysis[41] or photolysis.[42]

$$O=C=C=C=O \xrightarrow{[P_4S_{10}]} S=C=C=C=O \xleftarrow{\Delta T, h\nu}$$

<div align="center">3   23   24</div>

Matrix isolation is not necessary for this compound, since it is fairly stable under normal conditions, in analogy to C_3O_2 and C_3S_2.

4.3. Thioxobutatrienone C_4OS

In 1991 preparation and matrix isolation of two additional sulfide oxides, C_5OS (**29**) and C_4OS (**26**), was achieved. C_4OS (**26**) is indirectly formed by matrix photolysis of 7-diazo-2-thia-3,4-diazabicyclo[3.3.0]hepta-1,3-diene-6,8-dione **25**,[43] which was prepared from
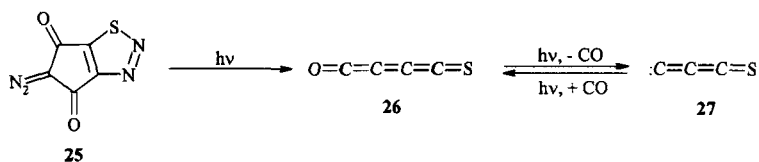
the C_4O_2 precursor **6** by single O/S exchange. In a first step after photochemical loss of N_2 and CO, **25** yields thioxopropadienylidene C_3S (**27**) (see Section 5.2). After changing the excitation wavelength, all of the five IR active stretching vibrations and a bending vibration of **26** were detectable. The UV/VIS spectrum of **26** (two absorption maxima) was accessible in the same way and was used for selective induction of the splitting off of CO.

There is no experimental evidence on the multiplicity of the ground state of **26**, an ESR spectrum has not been recorded so far. Semi-empirical and *ab initio* calculations are inconclusive concerning the singlet–triplet gap and the linear structure of the molecule.

4.4. *Thioxopentatetraenone C_5OS*

C_5OS (**29**) is generated by pyrolysis of benzo[1,2-*d*:4,5-*d'*]bis[1,2,3]-thiadiazole-4,7-dione **28** or by pyrolysis or matrix photolysis of thiophenetetracarboxylic acid bisthioanhydride **30**.[44] The structural identification and correlation of the observed IR bands was carried out on the basis of semiempirical computations. Five stretching vibrations were detected directly, the remaining one was calculated from combination modes. The matrix UV/VIS spectrum of **29** shows an absorption which exhibits a bathochromic shift with respect to the transition obtained for C_5O_2. This behaviour is similar to that observed in the system C_3O_2/C_3OS. The relative stability of **29** allowed to record a UV/VIS spectrum in solution. In this way a second, weaker absorption could be detected.
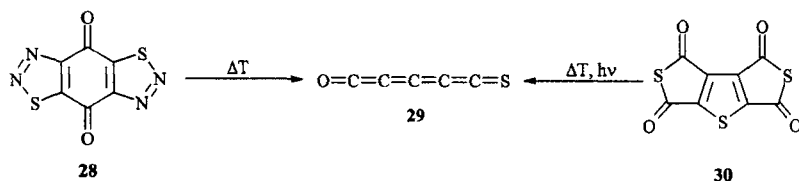
As partially mentioned above, the observed IR absorptions of C_3OS (23), C_4OS (26) and C_5OS (29) have been compared with vibrational frequencies obtained by semiempirical calculations. These correlations are strongly supported by a density functional theory study by Lee et al.,[45] in which all calculations were based on linear molecules.
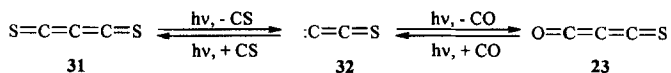
5. MONOSULFIDES $(C)_n$=S

5.1. Thioxoethenylidene C_2S

Ten years after its detection in interstellar space by microwave spectroscopy,[46] thioxoethenylidene C_2S (32) was studied by matrix isolation spetroscopy.[47] It was generated by laser-induced photolysis of matrix isolated C_3S_2 (31) or C_3OS (23). In both cases the photoreaction is fully reversible.

$$S{=}C{=}C{=}C{=}S \xrightleftharpoons[hv, +CS]{hv, -CS} \;:C{=}C{=}S \xrightleftharpoons[hv, +CO]{hv, -CO} O{=}C{=}C{=}C{=}S$$

$$\textbf{31} \qquad\qquad\qquad \textbf{32} \qquad\qquad\qquad \textbf{23}$$

Two of three expected fundamentals of 32 are observed directly at 1666.6 and $862.7\,cm^{-1}$ and from an overtone and a combination vibration, the position of the missing bending mode in the far infrared region can be derived (ca. $234\,cm^{-1}$). The correlation was carried out on the basis of density functional theory calculations, which predict a linear molecule with a triplet ground state. The agreement of experiment and theory is excellent. The matrix UV/VIS spectrum of 32 shows an intense absorption with a vibrational progression ($\lambda_{max} = 319\,nm$) and several broad, weaker absorptions in the range between 730 and 880 nm, depending on the precursor molecule used.

5.2. Thioxopropadienylidene C_3S

After the first synthesis of carbon monosulfide CS[48] at the beginning of the twentieth century, it was not until 1991 that two other monosulfides of carbon were studied by matrix isolation spectroscopy. As shown above, the initial reaction product of the photolysis of 25 in the course of the preparation of C_4OS is thioxopropadienylidene C_3S (27).[43] It was identified by three vibrational bands corresponding to stretching modes on the basis of semiempirical calculations. Reversible photochemical addition of CO embedded in the same matrix cage can be

achieved by selective irradiation with 366 nm light into the observed UV maximum ($\lambda_{max} = 378$ nm). In an analogous way, 25 is also accessible by matrix photolysis of C_4S_2 (41) (see Section 6.3).

Similar to the case of C_3O, Botschwina *et al.* published comprehensive theoretical calculations on C_3S and compared their results with experimental values, including a detailed matrix spectrum of 25.[49]

5.3. Thioxobutatrienylidene C_4S

The next member in the series of carbon monosulfides, C_4S (33), can be synthesized by analogous photochemical cleavage of matrix isolated C_5OS (29).[44]

$$O=C=C=C=C=C=S \quad \xrightleftharpoons[\text{hv, + CO}]{\text{hv, - CO}} \quad :C=C=C=C=S$$
$$\qquad\quad \textbf{29} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{33}$$
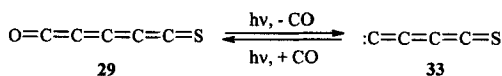
The characterization of this molecule remained rather incomplete, since only one of four expected stretching modes could be observed and ascribed to 33 by semiempirical computations. The matrix UV/ VIS spectrum exhibits two absorptions, one at short wavelengths ($\lambda_{max} = 240$ nm) and another one with vibrational fine structure at $\lambda_{max} = 450$ nm.

5.4. Thioxopentatetraenylidene C_5S

C_5S has been observed by its rotational spectrum,[50] yet no matrix isolation studies have been carried out so far. It has been prepared by electric discharge in a mixture of CS_2, C_2H_2 and Ar.

Similar to the computational study on sulfide oxides, Lee published density functional theory calculations concerning carbon monosulfides,[51] strongly supporting the above mentioned correlation of the observed IR bands to linear singlet C_3S and triplet C_4S.

6. DISULFIDES $S=(C)_n=S$

6.1. Ethenedithione C_2S_2

In 1990 it was shown that ethenedithione C_2S_2 (38) is a stable molecule under matrix conditions.[52] It can be prepared by photolysis of the

matrix isolated precursors **34–36** or by thermolysis of **36**. Cleavage of **38** into two molecules CS is achieved by irradiation with light of the appropriate wavelength. In analogy to C_2OS this reaction is completely reversible. Different pathways to **38** have been found, e.g. pyrolysis of the dithiacyclopentylidene derivatives **37** and **39**.[53]

The matrix IR spectrum of **38** shows one absorption corresponding to the only IR active stretching mode. The IR active bending vibration is expected to appear in the unobserved far infrared region. The positions of both IR inactive stretching vibrations were derived from two observed combination bands. Like all carbon disulfides, the UV/VIS spectrum of **38** exhibits two absorptions, one intense ($\lambda_{max} < 220$ nm) and one weaker electronic transition ($\lambda_{max} = 384$ nm), the latter showing a vibrational progression.
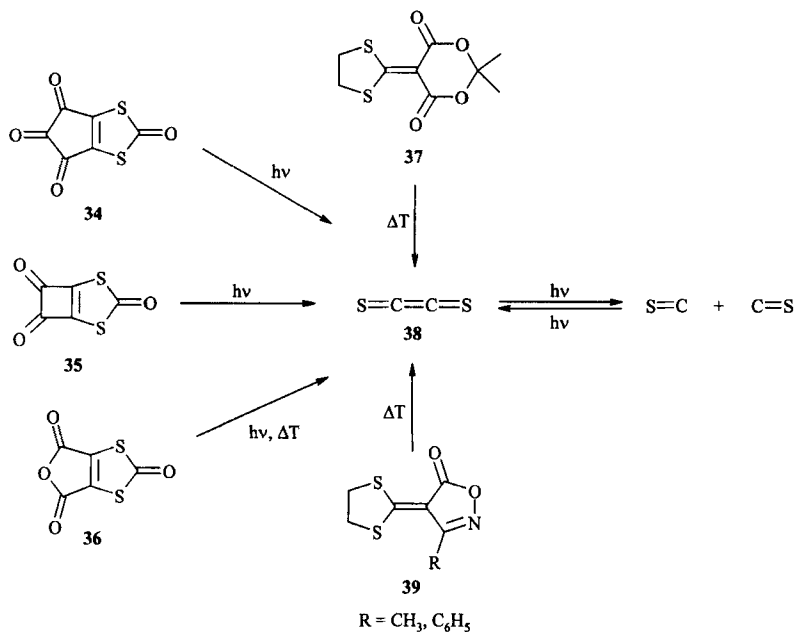
The multiplicity of the ground state of **38** is still subject to considerable discussion. After irradiation of **36** in the Ar matrix an extremely weak signal was recognizable in the ESR spectrum, which could arise from a triplet species. Its assignment to **38**, however, is doubtful. As in the case of C_4O_2, the experimental findings were inconclusive, since

the expected signal may lie beyond the range of the spectrometer used. The theoretical prediction of the infrared spectrum allowed no distinction, since the equilibrium geometries of both states are almost identical (linear molecule). Hence, the isotopic frequency shifts observed for the most intense fundamental were almost identical with the calculated values for both singlet and triplet. Extended *ab initio* calculations, in contrast to the earlier report,[52] favor the triplet state.[54]

In another matrix study, **38** was prepared by an electric discharge in a mixture of CS_2 and Ar.[55] The reaction of triplet CS with CS was made responsible for the generation of the heterocumulene. This procedure is similar to the photochemical pathway shown above. In addition to the known IR bands the most intense fundamentals of two more isotopomers of **38** were observed. As far as the UV/VIS spectrum is concerned, the authors described a second vibrational progression in the weaker absorption band.

6.2. Propadienedithione C_3S_2

Similar to the corresponding dioxide, carbon subsulfide C_3S_2 (**31**) has been known for a long time,[56] a sign for its considerable stability. The synthesis of **31** is based mainly on a discharge reaction in CS_2, yet it is often found as a by-product in many matrix studies cited in this review. For detailed information on this compound see Ref. [57].

6.3. Butatrienedithione C_4S_2

The last carbon disulfide investigated by matrix isolation spectroscopy so far was C_4S_2 (**41**) in 1991.[43] This molecule is formed by matrix photolysis of the polycyclic compounds **28** and **24**, and as a by-product upon irradiation of **30**. As mentioned above, **41** can be cleaved reversibly into C_3S and CS by use of light of the appropriate wavelength. The formation of C_4S_2 from **28** and **24** was surprising at first glance, since these compounds, on the other hand, proved to be very good photochemical or pyrolytic precursors of C_3OS (**23**). However, because two molecules of **23** embedded in the same matrix cage are formed during the photolysis of **28** or **24**, the generation of C_2S (**32**) by splitting off

of CO is believed to be the crucial step. The intermediate **32** should dimerize very fast or react with remaining **23** to CO and C_4S_2, since it was not detected in these experiments.

The matrix IR spectrum of **41** exhibits both IR active stretching modes. The great number of observable combination bands allowed the location of the three inactive stretching vibrations. Again, the two absorption bands in the UV/VIS spectrum of **41** show bathochromic shifts with respect to C_4OS and C_4O_2, in analogy to the other systems discussed.

The question concerning the ground state of **41** was conclusively answered by *ab initio* theory: the molecule is calculated to be a linear triplet species, yet, there is no experimental evidence for this prediction so far.
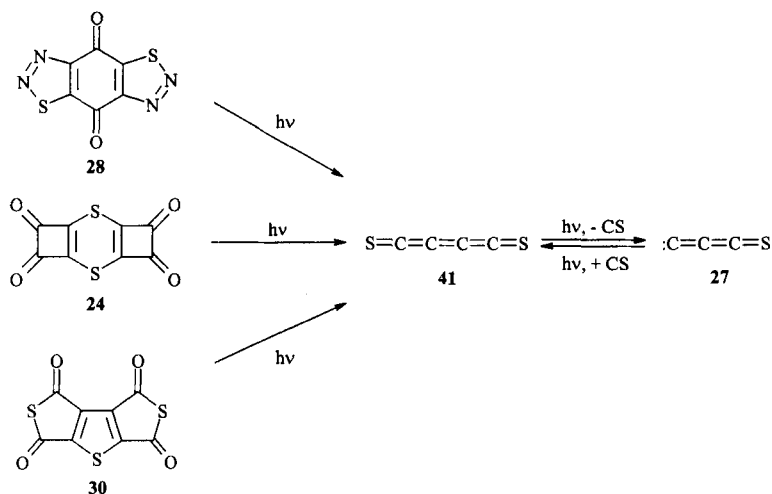
6.4. Pentatetraenedithione C_5S_2

In 1990 the first carbon disulfide beyond CS_2 and C_3S_2 was synthesized and studied by Maier *et al.*[58] Matrix photolysis or pyrolysis of the benzotristhiadiazole **42** leads to pentatetraenedithione C_5S_2 (**43**). Compound **42** was prepared by triple O/S exchange in the C_5O_2 precursor **19**. Similar to C_5O_2 and C_5OS, **43** can be kept in a solution at room temperature for some time without polymerization.

42   →   (ΔT, hν)   → $S=C=C=C=C=C=S$

43
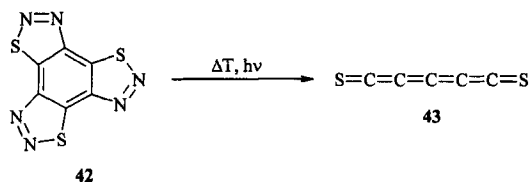
The infrared spectrum of the photolysis products exhibits all of the three IR active stretching vibrations of **43**, whereas the deformation modes are not observable, being very weak in intensity as predicted by semiempirical calculations based on a linear singlet molecule. Again, in the Ar matrix one UV/VIS maximum of **43** was observed, which shows a bathochromic shift with respect to the corresponding sulfide oxide and dioxide, as is the case with the chalcogeno cumulenes containing three carbon atoms. Because of the considerable stability of **43** a second UV transition could be detected in solution. However, irradiation of matrix isolated **43** with light of wavelengths of the two UV absorptions causes no reaction, thus preventing a different route to the poorly characterized C_4S molecule.

6.5. Hexapentaenedithione C_6S_2

The longest known carbon disulfide C_6S_2 has been detected in the gas phase.[59] However, no matrix isolation studies have been published so far.

7. SUMMARY OF EXPERIMENTAL DATA

Table I summarizes all known IR active fundamentals of chalcogeno heterocumulenes which have been observed in an Ar matrix so far. The identification of many of these compounds on the basis of infrared spectra would have been almost impossible without the help of theoretically calculated vibrations. Thus, the interplay between theory (see the accompanying review by Janoschek) and experiment is necessary for a successful use of the matrix isolation technique.

In Table II all known UV/VIS absorptions of the same compounds are given. Obviously, substitution of an oxygen atom by a sulfur atom results in a bathochromic shift. In a similar way, lengthening of the carbon chain leads to red-shifted UV/VIS transitions.

TABLE I Experimentally observed IR bands of fundamental vibrations of chalcogeno heterocumulenes in Ar matrices (symmetry in parentheses)

Compound	Wavenumbers (cm^{-1})	Reference
C_2O	1978 (σ), 1074 (σ), 381 (π)	[15]
C_3O	2242.9 (σ), 1907.0 (σ), 939.1 (σ), 580.0 (π)	[21]
C_4O	2221.7 (σ), 1922.7 (σ), 1431.5 (σ), 774.8 (σ), 484.0 (π)	[23]
C_6O	2163.8 (σ), 1447.8 (σ)	[27]
C_3O_2	2282 (σ), 1594 (σ), 536 (π)	[60]
C_4O_2	2130.3 (σ) 1276.9 (σ), 457.1 (π)	[20]
C_5O_2	2213.0 (σ), 2058.7 (σ), 1144.1 (σ), 539.0 (π), 470.0 (π)	[23]
C_7O_2	2187.4 (σ), 2118.5 (σ), 1696.1 (σ), 856.3 (σ)	[27]
C_2OS	2156.0 (σ), 1505.2 (σ), 452.2 (π)	[39]
C_3OS	2244.3 (σ), 1963.5 (σ), 1281.0 (σ), 601.0 (σ), 539.7 (π)	[42]
C_4OS	2209.6 (σ), 1998.5 (σ), 1625.3 (σ), 1055.9 (σ), 486.0 (σ), 428.1 (π)	[43]
C_5OS	2227.0 (σ), 2137.8 (σ), 1880.8 (σ), 1448.3 (σ), 945.5 (σ)	[44]
C_2S	1666.6 (σ), 862.7 (σ)	[47]
C_3S	2046.2 (σ), 1533.2 (σ), 725.5 (σ)	[49]
C_4S	1757.4 (σ)	[44]
C_2S_2	1179.3 (σ)	[52]
C_3S_2	2078.4 (σ), 1024.6 (σ)	[58]
C_4S_2	1872.1 (σ), 897.7 (σ)	[43]
C_5S_2	2105.0 (σ), 1687.9 (σ), 783.5 (σ)	[58]

TABLE II Experimentally observed UV/VIS bands (λ_{max}) of chalcogeno heterocumulenes in Ar matrices

Compound	Wavelength (nm)	Reference
C_2O	500, 630–845	[15,16]
C_3O	295	[21]
C_4O	—	—
C_6O	—	—
C_3O_2	178, 265[a]	[35]
C_4O_2	212, 340	[20]
C_5O_2	231, 436[b]	[23]
C_7O_2	276/288	[27]
C_2OS	306	[39]
C_3OS	220, 376[b]	[42]
C_4OS	238, 426	[43]
C_5OS	262, 546[b]	[44]
C_2S	319, 730/810/840	[47]
C_3S	378	[49]
C_4S	240, 450	[44]
C_2S_2	< 220, 384	[52]
C_3S_2	264, 482[b]	[58]
C_4S_2	272, 514	[43]
C_5S_2	320, 662[b]	[58]

[a]Gas phase value. [b]Recorded in solution at room temperature.

8. CONCLUSION

Ten years ago only a few carbon oxides and sulfides had been identified and many white spots on the map of chalcogeno heterocumulenes had to be noticed. Matrix isolation turned out to be the method of choice for the preparation and identification of this kind of elusive molecules. With the exception of C_2O_2, today all the missing candidates with $n = 2$–5 (and even some with $n > 5$) are known.

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