## Carbon Monosulfide: A Review<sup>1</sup>

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Carbon monosulfide, CS, is a short-lived, highly reactive gaseous species that has been known for almost a century. In spite of the unstable nature of CS it has been subjected to numerous investigations in various fields, and especially in recent years where improved techniques for the study of transient molecules have become available, the interest in CS has been considerable.

The potential importance of CS becomes obvious when one considers that CS is isoelectronic with widely used compounds such as, e.g., carbon monoxide and isocyanides. Our main interest is to elucidate the chemical reactivity of CS. Therefore, complete coverage of the literature on this subject including studies on polymeric CS is included. Also included are data from various dissertations that are not easily accessible and a few of our own unpublished results.

The majority of the published literature on CS is in the spectroscopic and theoretical fields, and the reaction of CS with oxygen has also attracted a great deal of interest due to the importance of this reaction in chemical CO lasers. These fields are covered for the period 1976–July 1986 except where more recent, specialized reviews have appeared. For earlier literature the reader is referred to previous reviews.<sup>2-4</sup>

Finally, numerous reports on observations of interstellar CS have appeared, and a list of these reports registered in *Chemical Abstracts* during the period 1976–July 1986 is included.

#### 1. Generation of CS

CS has been produced by a variety of different methods, but the most common source of CS is dissociation of CS<sub>2</sub>. This dissociation is accomplished by photolysis, thermolysis, or various types of discharges. These methods are well established and are not the main subject of the investigations in which they are applied. Therefore, these investigations are treated under the headings corresponding to their main subjects. The reader is referred to previous reviews<sup>2-4</sup> for a listing of these methods.

The best method for the production of large amounts of CS in relatively pure form is dissociation of  $CS_2$  in a high-voltage ac discharge.<sup>5,6</sup> Matrix isolation studies have shown<sup>7,8</sup> that the gas mixture produced by this method consists mainly of CS and  $CS_2$  together with minor amounts of  $S_8$  and  $C_3S_2$ . When the gas mixture is passed through a -112 °C trap, synthetic amounts of CS in up to 85% purity can be obtained.<sup>5</sup> The remaining 15% is  $CS_2$ . Other types of discharges are also useful, and Cossart<sup>9</sup> has published a useful comparative study of various discharges through  $CS_2$ .

Other studies in which CS has been observed include thermolysis of 5,5-dimethyl-1-phenyl- $\Delta^3$ -1,2,3-triazoline-2-thione, <sup>10</sup> dissociation of thiophene in a glow discharge, <sup>11,12</sup> decomposition of CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S, CH<sub>3</sub>SCN, and CH<sub>3</sub>NCS, respectively, in a radio frequency pulse discharge, <sup>13,14</sup> photolysis of diethyl methylphosphonothioate <sup>15a</sup> and diphenylcyclopropenethione, <sup>15b</sup> and electron-impact dissociation of HNCS. <sup>16</sup>

Finally, CS has been observed as a pollutant from combustion processes<sup>17,18</sup> and might play a role in the production of atmospheric COS.<sup>19</sup>

#### 2. Spectroscopic Studies of CS

The spectroscopic properties of CS have been intensively investigated. Since the discovery of the main transition, A<sup>1</sup>Π-X<sup>1</sup>Σ<sup>+</sup>, of CS in 1934 by Crawford and Shurecliff,<sup>20</sup> numerous studies have been published and the electronic, vibronic, and rotational states of CS are now known in much detail. The short-lived nature of CS has, of course, complicated these investigations, but the development of new spectroscopic techniques has made detailed studies of transient species as, e.g., CS possible. Especially, applications of laser techniques<sup>21</sup> have become a widely used tool during the last decade. The high spectral intensity of laser light permits processes that employ the simultaneous or successive absorption of more than one quantum per molecule, thus giving access to highly excited states, and the concentration of the laser intensity in a small-wavelength range allows the excitation of molecules to specific well-defined states. The narrow bandwidth of lasers is illus-

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Kenneth J. Klabunde was born in Madison, WI, in 1943 and grew up in the Madison area and later Davenport, IA. He is married and has three children. Dr. Klabunde graduated from Augustana College in 1965 and attended graduate school at the University of Iowa, obtaining a Ph.D. in 1969. He has always enjoyed research in nontraditional areas and was attracted to Donald Burton's fluorocarbon research group at Iowa; he later did postdoctoral work at Penn State in Phil Skell's carbon vapor program. His first position was at the University of North Dakota where he established research programs in metal atom chemistry, surface chemistry, and studies of reactive intermediates. In 1979 he moved to Kansas State University, where his research efforts are continuing in catalysis, vapor synthesis, reactive intermediates, and material science. He has been active in the enhancement of industrialacademic relations and serves on the governing board of the Council for Chemical Research.

trated by the work by Loree et al.22 who were able to separate carbon and sulfur isotopes of CS<sub>2</sub> by irradiation with an ArF laser (such separation requires a resolution better than 0.5 Å).

The spectroscopic properties of CS are in some respects unique. The vibronic levels of the first excited electronic configuration  $\pi^4 \sigma \pi^*$  (a<sup>3</sup> $\Pi$ , A<sup>1</sup> $\Pi$  states; see Figures 1 and 2) are interspersed among the vibronic levels of the second excited configuration  $\pi^3 \sigma^2 \pi^*$  (a' $^3\Sigma^+$ ,  $d^3\Delta$ ,  $e^3\Sigma^-$ ,  $A'^1\Sigma^+$ ) states (Figures 1 and 2), resulting in extensive spin-orbit perturbations. Such perturbations



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are well-known in diatomic molecules consisting of group IVA-VIA or group VA-VA atoms; however, as pointed out by Cossart,23 the particular situation is more pronounced for CS as compared with isoconfigurational species because of the following: (a) The homonuclear molecules such as N2, P2, As2, etc., do not present the corresponding spin-orbit perturbations in their spectra, since the states arising from the two first excited configurations have different symmetry relative to the exchange of nuclei. (b) In the heavier species such as e.g. CSe, SiS, and AsN the relative magnitudes of rotation-orbit compared to spin-orbit interactions are so small that the rotational perturbation parameters can be neglected. (c) In the isoelectronic SiO the polarization gives rise to a large spatial separation of  $\pi$  and  $\sigma$ , leading to small spin-orbit interactions so that forbidden transitions are not observed. (d) The molecule most similar to CS is carbon monoxide;24 however, in the heavier CS the spin-orbit interactions are larger and the vibronic levels are more closely spaced so that perturbation effects are more extensive and severe than

In most cases the determination of the interaction elements accounting for spin-orbit perturbations, such as singlet-triplet mixing, perturbation level shifts, and off-diagonal spin-orbit contributions, spin-spin, and other fine-structure parameters, is made purely by theoretical methods. In diatomic molecules like CS, however, these spin-orbit perturbations are evident in the optical spectrum, and a number of the interaction elements can be obtained experimentally, thus allowing a far more extensive comparison between experimental data and theoretical calculations.

Very extensive studies of the  $A^1\Pi$ ,  $e^3\Sigma^-$ ,  $d^3\Delta$ ,  $a'^3\Sigma^+$ , and a<sup>3</sup>Π states, based on UV emission and absorption transitions to the  $X^1\Sigma^+$  ground state of CS, have been published by Cossart and Bergeman et al.<sup>23,25-27</sup> These

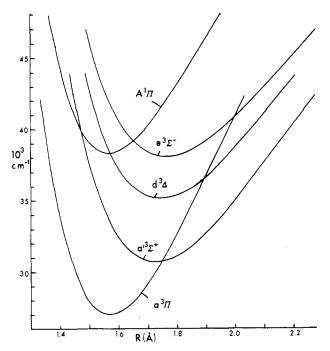


Figure 1. RKR potential curves for the lower excited states of CS. Energies are relative to  $X^1\Sigma^+_{\nu=0,J=0}$ . From ref 25.

reports also include the near-infrared spectrum of the  $d^3\Delta-a^3II$  transition.  $^{23,27}$  The bulk of the data corresponds to the  $^{12}C^{32}S$  isotope, but several bands for  $^{12}C^{34}S$  and  $^{13}C^{32}S$  are presented. Analyses of the obtained data have yielded a wealth of new information on these lower excited states including rotational data for a large number of vibrational states, diagonal and off-diagonal spin-orbit parameters, and spin-spin and Coriolis parameters. A complete listing of the obtained data is too extensive in this context, and the reader is referred to the original work. The derived deperturbed molecular constants are listed in Table I.

Information on the vibrational and rotational states of the electronic ground state has been obtained by high-resolution infrared spectroscopy. These studies include both the most abundant isotope, 12C32S, and the  $^{12}\mathrm{C}^{33}\mathrm{S},\,^{12}\mathrm{C}^{34}\mathrm{S},$  and  $^{13}\mathrm{C}^{32}\mathrm{S}$  isotopes. The 2–0 vibration–rotation bands of  $^{12}\mathrm{C}^{32}\mathrm{S}$  and  $^{12}\mathrm{C}^{34}\mathrm{S}$  near 2530 cm<sup>-1</sup> were measured by Todd,28 and spectroscopic constants for these bands were derived. Also a set of Dunham coefficients for the  $X^1\Sigma^+$  state of  $^{12}C^{32}S$  were determined. Yamada and Hirota<sup>29</sup> applied diode laser spectroscopy<sup>30</sup> to CS, and the 1-0 bands of the electronic ground states of <sup>12</sup>C<sup>32</sup>S, <sup>12</sup>C<sup>34</sup>S, <sup>12</sup>C<sup>33</sup>S, and <sup>13</sup>C<sup>32</sup>S together with the 2-1 band of 12C32S were observed. Todd and Olsen<sup>31</sup> also applied a tunable diode laser spectrometer and measured the vibration-rotation transitions between 1180.5 and 1266.1 cm<sup>-1</sup>, which were assigned to the 1-0, 2-1, 3-2, and 4-3 bands of <sup>12</sup>C<sup>32</sup>S, the 0-1 and 2-1 bands of  $^{12}C^{34}S$  and  $^{13}C^{32}S$ , and the 1-0 band of <sup>12</sup>C<sup>33</sup>S. An improved set of Dunham coefficients together with the Dunham potential expansion constants were determined.

Winkel et al.  $^{32}$  recorded the  $\Delta v=2$  infrared emission bands of  $^{12}\mathrm{C}^{32}\mathrm{S}$  and  $^{12}\mathrm{C}^{34}\mathrm{S}$  by using a Fourier transform IR spectrometer. For  $^{12}\mathrm{C}^{32}\mathrm{S}$  the 2–0 to 8–6 vibrational band sequence was observed in detail, and the band heads and a few rotational lines for the 9–7 and 10–8 bands were also observed. R-Branch lines were iden-

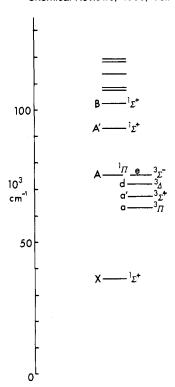


Figure 2. Energy level diagram of CS. From ref 50.

tified up to J=126; P-branch lines, up to J=82. For  $^{12}\text{C}^{34}\text{S}$  the band sequence 2–0 through 6–4 was recorded and analyzed.

The microwave spectrum of CS was first measured by Mockler and Bird<sup>33</sup> and later reviewed by Lovas and Krupenie.<sup>34</sup> More recently Bustreel et al.<sup>35</sup> recorded the microwave spectrum of CS produced by dissociation of CS<sub>2</sub> in an rf discharge. The J=0-1 lines of the electronic ground state up to v=14 for  $^{12}\text{C}^{32}\text{S}$ , v=5 for  $^{12}\text{C}^{34}\text{S}$ , and v=3 for  $^{13}\text{C}^{32}\text{S}$  were measured. From the observed spectra Dunham coefficients were derived.

Bogy et al.<sup>36,37</sup> have investigated the millimeter and submillimeter spectra of CS. The  $\Delta J=1$  transitions  $(J \leq 11)$  for a number of vibrational states have been measured for  $^{12}\text{C}^{32}\text{S}$ ,  $^{12}\text{C}^{34}\text{S}$ , and  $^{13}\text{C}^{32}\text{S}$ , and several molecular parameters were derived from the observed spectra. The results obtained by Bogey et al. are in good agreement with similar studies performed by Tiemann et al.<sup>38</sup>

Finally, it is mentioned that calculated absorption coefficients and rotational transition frequencies have been given in graphical form for microwave frequencies up to 1400 GHz<sup>39</sup> and that millimeter wave detection of CS has been performed to demonstrate the effectiveness of microwave spectrometers for the detection of short-lived species.<sup>40</sup>

## 2.1. Dynamics of CS

A large number of studies have been devoted to the elucidation of the dynamics of CS. The main subjects of interest are (a) the exact mechanism for the formation of CS, (b) the populations of the various energy levels of CS in status nascendi, (c) the lifetimes of excited CS, and (d) quenching rates of excited CS with various quenchers. The first two subjects, (a) and (b), depend not only on the choice of precursor for CS but

TABLE I. Spectroscopic Constants for Electronic States of CS (All Data in cm-1 Except Re; from Ref 27)

state	$T_e{}^a$	$\omega_{ m e}$	$\omega_{ m e} x_{ m e}$	$B_{e}$	$lpha_{e}$	$R_{ m e}$ , Å
$X^1\Sigma^+$	0.00	1285.154 (3)	6.502 (2)	0.8200449 (7)	0.005921 (2)	1.53496
$a^3\Pi$	27030.37 (18)	1135.41 (12)	7.747 (10)	0.78478 (16)	0.00692 (12)	1.5691
$\mathbf{a}'^3\Sigma^+$	30695.90 (110)	829.24 (34)	4.943 (37)	0.64727 (166)	0.00570 (32)	1.728
$\mathrm{d}^3\Delta$	35041.28 (36)	796.17 (12)	4.966 (7)	0.63685 (42)	0.00614 (6)	1.742
$e^3\Sigma^-$	38040.75 (26)	752.93 (24)	4.955 (19)	0.62251 (58)	0.00627 (16)	1.762
$A^1\Pi$	38255.13 (26)	1077.23 (7)	10.639 (9)	0.78760 (62)	0.0083 (35)	1.566
$A'^1\Sigma^+$	55864.00	462.42	7.458	0.5114	0.109	1.944

TABLE II. Threshold Energies for Dissociation of  $CS_2$  (from Ref 42 and 66)

`					
products	electronic state	energy, eV	products	electronic state	energy, eV
CS + S	$X^1\Sigma^+$ , $^3P$	4.46	$CS + S^+$	$X^1\Sigma^+$ , $^4S^\circ$	14.852
	$X^1\Sigma^+$ , $^1D$	5.60		a³Π, ⁴S°	18.272
	$X^1\Sigma^+$ , $^1S$	7.21		a <sup>3</sup> Π, <sup>2</sup> D°	20.113
	$a^3\pi$ , $^3P$	7.85		a³Π, ² <b>P°</b>	21.313
	$a^3\pi$ , $^1D$	8.99		А <sup>1</sup> П, <sup>4</sup> S°	19.662
	$A^1\pi$ , $^3P$	9.305		$A^1\Pi$ , $^2D^{\circ}$	21.503
$S_2 + C$	$X^3\Sigma^-$ , $^3P$	7.86		$A^1\Pi$ , $^2P^{\circ}$	22,703
-	$a^1\Delta$ , $^3P$	8.44	$CS^+ + S$		15.83
$\mathrm{CS_2}^+$	$\mathrm{X}^2\Pi_{3/2}$	10.077		$A^2\Pi$ , $^3P$	17.29
-	$X^2\Pi_{1/2}$	10.133		$A^2\Pi$ , $^1D$	18.43
	$A^2\Pi_{3/2}$	12.696		$A^2\Pi$ , <sup>1</sup> S	20.14
$CS_2^+$	$A_{1/2}^{2}$	12.719		$A^2\Pi$ , $^5S^\circ$	23.81
-	$\mathrm{B}^2\Sigma^+$	14.479		$A^2\Pi$ , $^3S^{\circ}$	24.15
	$\mathrm{C}^2\Sigma^+$	16.192		$\mathrm{B}^2\Sigma^+$ , $^3\mathrm{P}$	20.32
	$\mathrm{D}^2\Sigma^+$	16.85		$B^2\Sigma^+$ , $^1D$	21.47
	E	19.52		$B^2\Sigma^+$ , <sup>1</sup> S	23.07
				E, 3P	22.50
				E. <sup>1</sup> D	23.64

also on the method applied for the dissociation of the precursor. The determination of (c) and (d) is complicated by the transient nature of excited CS, and it is especially in these fields that laser-induced fluoresence (LIF) spectroscopy has become a very useful tool. These subjects cover a large and very complex area, which still is under investigation.

#### 2.1.1. Photolytic Dissociation of CS2

One of the most commonly used routes to CS is photolytical dissociation of CS<sub>2</sub>. This apparently simple system turns out to be quite complex. The ultraviolet spectrum of CS<sub>2</sub> is very complex and is not yet fully understood;<sup>41</sup> as shown in Table II, a number of different pathways for the dissociation of CS<sub>2</sub> have to be considered, the pathway depending on the energy of the applied photons.

Fournier et al.<sup>42</sup> irradiated  $CS_2$  trapped in an Ar matrix at 6 K with VUV photons (147 nm). The only emission observed was the CS ( $a^3\Pi-X^1\Sigma^+$ ) emission. Three asymmetric bands were assigned to  $v'=0 \rightarrow v''=0-2$  vibrational transitions. The energy of the light source corresponds to 8.4 eV so other dissociative processes are possible. However, no excited atomic sulfur was detected. This might be explained either by the reaction (1) or by rapid quenching of initially formed

$$CS_2 \xrightarrow{h\nu} CS (a^3\Pi) + S (^3P_2)$$
 (1)

excited S. Black et al.<sup>43</sup> performed gas-phase VUV photolysis of  $CS_2$ . For photodissociation below 135 nm the strong CS (A<sup>1</sup> $\Pi$ -X<sup>1</sup> $\Sigma$ <sup>+</sup>) transition was observed. However, below 160 nm the same transition as reported by Fournier et al.; namely the a<sup>3</sup> $\Pi$ -X<sup>1</sup> $\Sigma$ <sup>+</sup> transition, was

observed. The threshold for producing this emission was found to be  $158 \pm 2$  nm, and by using the assumption that the process occurring is (1), they estimated the bond dissociation energy  $D_0^{\circ}(SC - S)$  to be  $102 \pm 2$  kcal/mol. The quantum yield in the region 125-140 nm was estimated to be close to unity.

In 1980 Ashfold et al.<sup>44</sup> studied the VUV photodissociation of CS<sub>2</sub> at 121.6, 129.5, and 130.4 nm, respectively. The majority of the fluorescence could be attributed to the  $\Delta v = \pm 2, \pm 1, 0$  sequence bands of the  $A^1\Pi - X^1\Sigma^+$  system. From the relative intensities of the recorded bands, the relative vibrational populations,  $N_v$ , of CS ( $A^1\Pi$ ) $_v$  were estimated; all energetically accessible vibrational states (v = 0–6) were populated, with the v = 0 state having the highest population. The overall transition moments,  $R_{v'v'}$ , together with Franck–Condon factors for the A–X system were also estimated.

Finally, the fragmentation of  $CS_2$  by VUV photons (60–125 nm) has also been studied by mass spectrometry. The ions observed were  $CS_2^+$ ,  $CS^+$ ,  $S^+$ , and  $S_2^+$ , and from the threshold energies for the formation of these fragment ions various thermodynamic data for CS were obtained (see Table VI).

Ebata et al.<sup>47</sup> investigated the vibrational distribution of CS ( $X^1\Sigma^+$ ) formed in the UV flash photolysis of gaseous CS<sub>2</sub> ( $\sim$ 200 nm). Levels up to v=5 were populated, and the vibrational distribution was represented by a sum of two modified Poisson distributions with different mean values. This distribution is explained by assuming two photodissociation processes of CS<sub>2</sub> (eq 2). One is direct dissociation; the other is

$$CS_{2} \xrightarrow{\hbar\nu} \left( \begin{array}{c} CS(X^{1}\Sigma^{+}) + S(^{1}D) \\ \\ CS_{2} (\overline{A}^{1}B_{2}) \longrightarrow CS_{2}(T) \longrightarrow CS(X^{1}\Sigma^{+}) + S(^{3}P) \end{array} \right)$$

predissociation through a triplet state. The  $CS_2$  absorption band near 200 nm corresponding to the bent  $\bar{A}^1B_2$  state was observed, and the formation of singlet sulfur was confirmed by Addison et al.<sup>48</sup> who observed S ( $^1D$ ) directly by photolysis of  $CS_2$  at 200 nm.

A number of studies on the dissociation of CS<sub>2</sub> at 193 nm (ArF excimer laser) have been published. <sup>49–54</sup> The dissociation products were mainly analyzed by time of flight (TOF) experiments <sup>51,52,54</sup> and by LIF spectroscopy. <sup>49,50,51,53,54</sup> The energy of the photons from the ArF laser (6.42 eV) allows the two processes in (2) to occur (cf. Table II). The initially formed ground-state CS might then be excited CS to the A' $^{1}\Sigma^{+}$  state by a further photon, thus accounting for the observed A' $^{1}\Sigma^{+}$ -X $^{1}\Sigma^{+}$  transition. The A $^{1}\Pi$ -X $^{1}\Sigma^{+}$  transition is also observed, and the CS (A $^{1}\Pi$ ) is formed mainly by collisionally induced excitation of CS (X $^{1}\Sigma^{+}$ ). <sup>53</sup>

A controversy has arisen concerning the S (<sup>3</sup>P) to S (<sup>1</sup>D) branching ratio in (2). Yang et al.<sup>51</sup> found by TOF

and LIF experiments that 80% of the sulfur atoms formed was S (<sup>1</sup>D). This result was confirmed recently by McCrary et al.<sup>54</sup> who found 60% S (<sup>1</sup>D). Addison et al.,<sup>49</sup> however, estimated that 85% of the sulfur atoms formed was S (<sup>3</sup>P), according to LIF studies, while Dornhoefer et al.<sup>53</sup> found 75% S (<sup>3</sup>P).

In addition Hynes and Brophy<sup>55</sup> have reported the observation of the  $d^3\Delta - X^1\Sigma^+$  transition by excitation of CS  $(X^1\Sigma^+)$  with a tunable dye laser.

Seaver et al.  $^{56}$  investigated the mechanism underlying the multiphoton ionization and fragmentation of  $\mathrm{CS}_2$  at 193 and 266 nm. At both wavelengths the mass spectrometric ion signal intensity as a function of reagent pressure and laser intensity, respectively, was recorded. The results of the 193-nm dissociation support the existence of a predissociative  $\tilde{\mathrm{A}}^1\mathrm{B}_2$  state of  $\mathrm{CS}_2$ , which dissociates into the neutral fragments  $\mathrm{CS}$  and  $\mathrm{S}$ . At 266 nm the experiments indicate that ionization and fragmentation occur via absorption of four photons.

Further studies of the photolysis of CS<sub>2</sub> at 248 nm have been published by Donovan and Fotakis et al.57-60 CS<sub>2</sub> is transparent at this wavelength, and the dissociation involves the simultaneous absorption of at least two photons. The main species formed are CS  $(A^1\Pi)$  and CS  $(X^1\Sigma^+)$ . In the first studies<sup>57,58</sup> the dominant emission came from CS  $(A^1\Pi)_{v=4}$  with weaker fluorescence from the v = 2, 3, and 5 levels. The high population of the  $A^1\Pi_{\nu=4}$  level was concluded to be due to excitation of initially formed  $CS(X^1\Sigma^+)_{\nu=2}$ , which can be pumped to the  $A^{1}\Pi_{n=4}$  level by the laser light. In a recent study<sup>59</sup> this experiment was repeated while a frequency of narrowed laser was applied, and the obtained results differed markedly. The main emission observed was still associated with the  $A^1\Pi - X^1\Sigma^+$  transition; however, the  $\Delta v = 0-2$  sequence bands were observed without any peak at the v' = 4 level. No evidence of laser-induced fluorescence was found, and it is concluded that CS  $(A^1\Pi)$  is formed by two-photon dissociation of CS<sub>2</sub>. The relative vibrational populations in CS  $(A^1\Pi)$  were obtained from the relative intensities of the observed sequence bands, and as a result it is estimated that approximately 40% of the available energy appears as vibrational excitation in CS  $(A^1\Pi)$ . Weak emissions due to the spin-forbidden  $d^3\Delta - X^1\Sigma^+$ transition were also observed.

## 2.1.2. Dissociation of CS<sub>2</sub> and Ionization of CS by Impact with Metastable Atoms and Rare-Gas Ions

The application of metastable rare-gas atoms such as, e.g., He (2  $^3$ S), Ne ( $^3$ P<sub>0,2</sub>) and Ar ( $^3$ P<sub>2,0</sub>) as energy sources for the dissociation of molecules allows the transfer of much higher energies to the target molecule than in the photolytic dissociation of molecules. This is illustrated by the available energy from He (2  $^3$ S), which is 19.8 eV corresponding to radiation in the X-ray region. The dissociation of CS<sub>2</sub> by these energetic species produces not only neutral fragments but also ionic fragments (Penning ionization); cf. Table II.

Coxon et al.<sup>61</sup> let  $CS_2$  interact with He (2 <sup>3</sup>S) and obtained rather complex emission spectra. The observed transitions could be assigned to S\*, C\*,  $CS_2^+$  (B<sup>2</sup> $\Sigma^+$ -X<sup>2</sup> $\Pi$ ), CS (A<sup>1</sup> $\Pi$ -X<sup>1</sup> $\Sigma^+$ ), CS (a<sup>3</sup> $\Pi$ -X<sup>1</sup> $\Sigma^+$ ), CS<sub>2</sub><sup>+</sup> (A<sup>2</sup> $\Pi$ -X<sup>2</sup> $\Pi$ ), and CS (A<sup>2</sup> $\Pi$ -X<sup>2</sup> $\Sigma^+$ ). A group of bands in the 390-420-nm range could not be assigned. For the

CS<sup>+</sup> (A) and CS<sup>+</sup> (X) states, spectroscopic constants are deduced and a vibrational analysis of the CS<sup>+</sup> (A–X) system is performed. The formation of the neutral CS fragments, CS ( $a^3\Pi$ ) and CS ( $A^1\Pi$ ), is due to secondary CS<sub>2</sub><sup>+</sup>-electron recombination processes. This was shown by performing the experiment in the presence of SF<sub>6</sub>, which is an effective electron scavenger, causing a strong intensity reduction of the CS ( $A^1\Pi$ – $X^1\Sigma$ <sup>+</sup>) and CS ( $a^3\Pi$ – $X^1\Sigma$ <sup>+</sup>) transitions. CS<sup>+</sup> ( $A^2\Pi$ ) is reported to be formed via predissociation of some excited state of CS<sub>2</sub><sup>+</sup> which, in turn, is formed by Penning ionization of CS<sub>2</sub>.

Later Yencha and Wu<sup>62</sup> reported similar experiments where they applied both He (2 3S) and Ne (3P<sub>0,2</sub>), respectively. The results for the He (2 3S) experiments are in general agreement with Coxon et al.'s, and the previously unidentified emissions in the 390-420-nm range were assigned to a superposition of the CS  $(B^1\Sigma^+-A^1\Pi)$  and  $CS^+$   $(B^2\Sigma^+-A^2\Pi)$  transitions. These emissions could be completely suppressed by "filtering" the stream of metastable helium with a 20-V dc potential, thus showing that the production of these emissions is due to the presence of small amounts of He<sup>+</sup>. Application of Ne (<sup>3</sup>P<sub>0,2</sub>) produced a very similar emission spectrum, the major differences being the absence of the CS  $(B^1\Sigma^+-A^1\Pi)$ , CS<sup>+</sup>  $(B^2\Sigma^+-A^2\Pi)$ , and  $CS^+$  (A<sup>2</sup> $\Pi$ -X<sup>2</sup> $\Sigma^+$ ) emissions due partly to the lower energy of Ne (<sup>3</sup>P<sub>0.2</sub>) compared to He (2 <sup>3</sup>S) and partly to the absence of Ne<sup>+</sup> ions.

In a recent report Wu<sup>63</sup> investigated the dissociative excitation of CS2 by Ar (3P0.2), which has an excitation energy of 11.55 eV. The most prominent emission originated from the CS ( $A^1\Pi - X^1\Sigma^+$ ) transition, and contrary to the He (2 3S) experiment, this emission was not suppressed by adding SF<sub>6</sub>, thus excluding the CS<sub>2</sub><sup>+</sup>electron recombination formation mechanism. Instead, it is concluded that CS (A¹II) is formed via a predissociative CS<sub>2</sub>\* state as in the photodissociation of CS<sub>2</sub>. Estimates of the rotational, vibrational, and translational energy disposal in CS (A<sup>1</sup>II) are given and compared to results from VUV photolysis of CS2. It was found that the translational energy disposal is consistent with the result predicted from the simple impulsive model, while the vibrational energy distributions are influenced principally by the Franck-Condon effects.

A study of the collisional energy dependence of Penning ionization of  $CS_2$  and of the dissociative fluorescence producing CS ( $A^1\Pi$ ) by Ar ( $^3P_{0,2}$ ) showed<sup>64</sup> that the cross sections for the two competing processes had nearly the same functional velocity dependence.

Two reports by Tsuji et al. on the dissociative charge-transfer reactions of He<sup>+</sup> or Ar<sup>+</sup> with CS<sub>2</sub> have appeared. The obtained emission spectra are in good agreement with electron-impact spectra (see section 2.1.3). The observed emissions could be assigned to CS<sub>2</sub><sup>+</sup> ( $\bar{B}^2\Sigma^+-\bar{X}^2\Pi$ ) and CS ( $A^1\Pi-X^1\Sigma^+$ ) transitions. In the more thorough study, the CS<sup>+</sup> ( $B^2\Sigma^+-A^2\Pi$ ) band was observed together with the bands reported by Coxon et al. A vibrational analysis of the CS<sup>+</sup> ( $B^2\Sigma^+-A^2\Pi$ ) system is given. Tsuji et al. do, however, not agree with Coxon et al. on the mechanism of formation of CS<sup>+</sup> ( $B^2\Sigma^+$ ) but suggest the mechanism (3).

TABLE III. Spectroscopic Constants for Electronic States of CS<sup>+</sup> (from Ref 68)

state	$T_{\rm e},~{ m cm}^{-1}$	$\omega_{\rm e},~{ m cm}^{-1}$	$\omega_{\rm e} {\rm x_e},~{\rm cm}^{-1}$	R <sub>e</sub> , Å
$X^2\Sigma^+$	0	1376.6	7.8	1.493
${ m A}^2\Pi$	11984.9	1013.7	6.7	1.640
$\mathrm{B}^2\Sigma^+$	36509.0	$911 \pm 3$	$6.5 \pm 1.0$	1.665

In a series of papers the reactions of metastable rare-gas atoms with preformed CS have been reported. The reaction of He (2  $^3$ S) with CS produced in a hollow cathode discharge was studied by Wu and Yencha. The same CS transitions as those obtained in the corresponding reaction with CS<sub>2</sub> were observed. However, the CS<sup>+</sup> (B<sup>2</sup>S<sup>+</sup>-A<sup>2</sup>\Pi) emission in the 406–415-nm region could be unambiguously identified, and, furthermore, an emission around 276 nm was tentatively assigned to the CS<sup>+</sup> (B<sup>2</sup>S<sup>+</sup>-X<sup>2</sup>S<sup>+</sup>) transition. Tsuji et al. 8 confirmed that finding and obtained a detailed vibrational assignment of this system together with some molecular constants of CS<sup>+</sup> (see Table III).

In a comparison study<sup>69</sup> of the He (2  $^3$ S)/CS and Ne ( $^3$ P<sub>0,2</sub>)/CS reactions similar emission spectra were obtained, clearly showing that Penning ionization of CS is the major route to CS<sup>+</sup> (A<sup>2</sup>Π) and CS<sup>+</sup> (B<sup>2</sup>Σ<sup>+</sup>) since the energy provided by Ne ( $^3$ P<sub>0,2</sub>) is insufficient for the production of these species from CS<sub>2</sub> (see Table II). Recently the argon afterglow reactions of CS were investigated,<sup>70</sup> and the observed CS<sup>+</sup> (B<sup>2</sup>Σ<sup>+</sup>–A<sup>2</sup>Π) emission could be shown to originate from the interaction between Ar<sup>+</sup> and CS. The vibrational populations of the CS<sup>+</sup> (B<sup>2</sup>Σ<sup>+</sup>) state were determined.

## 2.1.3. Dissociation of CS2 by Electron Impact

The dissociative ionization of CS<sub>2</sub> by electron impact has been studied by mass spectrometry.<sup>71-73</sup> The main ions observed were S<sup>+</sup>, CS<sup>+</sup>, and CS<sub>2</sub><sup>+</sup>, and by measurement of the appearance potentials and kinetic energies of these ions, the heat of formation and the electron affinity of CS were calculated (see Table VI). The possible fragmentation mechanisms are discussed.

Gauyago and Horani<sup>74</sup> have published an extensive study of the  $CS^+$  ( $A^2\Pi - X^2\Sigma^+$ ) transition. The CS ( $A^2\Pi$ ) was obtained by dissociation of  $CS_2$  by electrons in a low-pressure hot cathode discharge. A rotational analysis was performed, and the derived molecular constants of the A and X states of  $CS^+$  are reported.

A single report on the photoelectron spectrum of the CS<sup>-</sup> ion, produced by electron bombardment of CS<sub>2</sub>, has appeared.<sup>75</sup> The observed spectrum could be assigned to the CS<sup>-</sup> (X<sup>2</sup> $\Pi$ )–CS (X<sup>1</sup> $\Sigma$ <sup>+</sup>) transition, and the equilibrium bond length of CS<sup>-</sup> was determined ( $R_e$ (CS<sup>-</sup>) = 1.627  $\pm$  0.02 Å).

## 2.1.4. Dissociation of CS<sub>2</sub> in Discharges

The formation of CS in various types of discharges is a widely applied source of  $CS.^{2-4}$  A useful spectroscopic study of the composition of the mixture obtained by various types of discharges through  $CS_2$  has been published.<sup>9</sup>

#### 2.1.5. Dissociation of COS

The dissociation of COS<sup>76</sup> yields both CO and CS, and CO seems to be the major product.

TABLE IV. Lifetimes of Excited CS

state	τ, ns	ref	state	τ, ns	ref
$\overline{\mathbf{a}^3\Pi_0, v = 0^a}$	$3.4 \times 10^{6}$	91	$\mathrm{d}^3\Delta,v=4,J=21$	2300	55
$a^3\Pi_1, v = 0^a$	$6.4 \times 10^{6}$	91	$\mathrm{d}^3\Delta,v=4,J=25$	2980	55
$a^{3}\Pi_{2}, v = 0^{a}$ $a^{3}\Pi$ $a^{3}\Pi$ $a^{3}\Pi$ $a^{3}\Pi$ $d^{3}\Delta, v = 4, J = 2$	$\geq 10^9$ >10 <sup>6</sup> 16 × 10 <sup>6</sup> 7.5 × 10 <sup>6</sup> 1760	91 90 43 86 55	$A^{1}\Pi, v = 0$ $A^{1}\Pi, v = 0$ $A^{1}\Pi, v = 1$ $A^{1}\Pi, v = 2$	$185 \pm 10$ $171 \pm 10$ $225 \pm 20$ $220 \pm 20$	85 88b 85 85
$d^3\Delta$ , $v = 4$ , $J = 6$ $d^3\Delta$ , $v = 4$ , $J = 12$	1980 1950	55 55	$\mathbf{A}^{1}\mathbf{\Pi},\upsilon=3$	$230 \pm 20$	85 85
$d^3\Delta$ , $v = 4$ , $J = 12$ $d^3\Delta$ , $v = 4$ , $J = 16$	2010	55	$A^{1}\Pi, v = 4$ $A^{1}\Pi, v = 5$	$235 \pm 20$ $225 \pm 20$	85
$d^{3}\Delta, v = 4, J = 18$	2050	55	$A^{-11}, v = 5$ $A^{\prime 1}\Sigma^{+}, v = 5$	$15 \pm 2$	53

<sup>a</sup>In matrix. All other values in gas phase.

In a recent work<sup>77</sup> the fluorescence following dissociation of COS by VUV photons (67–112 nm) was analyzed. The CS ( $A^1\Pi-X^1\Sigma^+$ ) transition could be identified together with several bands originating from CO. In similar experiments, involving photons in the 106–124-nm range,<sup>78</sup> CS in the lower lying triplet states were observed. Laser photolysis of COS at 157 nm<sup>79</sup> also yielded excited CS.

Tsuji et al.<sup>66,80</sup> have investigated the reactions of COS in a helium afterglow, and the CS ( $A^1\Pi-X^1\Sigma^+$ ), CS ( $a^3\Pi-X^1\Sigma^+$ ), and CS<sup>+</sup> ( $B^2\Sigma^+-A^2\Pi$ ) transitions could be identified together with several CO and COS bands. As in the case CS<sub>2</sub>, the formation of CS ( $A^1\Pi$ ) is due to ion–electron recombination processes.

The main product from the dissociation of COS in a radio-frequency discharge (13.6 MHz) is CO.  $^{81}$  CS is, however, also formed as shown both by mass spectroscopy and by the emission spectrum where an intense CS ( $A^1\Pi$ - $X^1\Sigma$ +) band could be observed, and it is suggested that the excited CS is formed via ionelectron dissociative recombination. Investigation of a high-voltage discharge through COS by millimeter and submillimeter rotational spectroscopy  $^{82}$  also showed CO to be the main product, with small amounts of CS being produced via secondary reactions.

A mass spectroscopic study of the dissociation of COS by electron impact has been performed<sup>72</sup> and, finally, the reaction of atomic carbon with COS<sup>83</sup> produced CS ( $a^3\Pi$ ) as shown by observation of the CS ( $a^3\Pi$ - $x^1\Sigma$ <sup>+</sup>) transition.

#### 2.1.6. Lifetime of Excited CS

The radiative lifetimes of excited CS have been of major interest, and a number of reports on both vibrational and electronical relaxation times have appeared together with estimates of quenching rates by various quenching gases. Data published prior to 1978 have been reviewed, 84,85a and more recently a summary of Slanger 85b has appeared. The quenching rates and lifetimes published after 1978 are summarized in Tables IV and V. While a number of these data have appeared in the reports reviewed in the preceding sections, a few studies have been devoted entirely to this subject.

The vibrational to translational energy transfer of nonequilibrium vibrational distributions of CS ( $A^1\Pi$ ) prepared by dissociation of  $CS_2$  in a helium afterglow has been investigated by Marcoux et al.,<sup>86</sup> and it was found that CS ( $A^1\Pi$ ) relaxes readily in helium. Electronic quenching was also observed. In argon it was

TABLE V. Quenching Rates at 300 K

state	rate	mult factor $(X = cm^3 mol^{-1} s^{-1})$	ref
$\mathrm{d}^3\Delta$	$k_{\rm CS_2} = 2.64^a$	1014	55
$\mathbf{A}^1\Pi$	$k_{O_2} = 1.3^a$	1014	88b
	$k_{\rm CO} = 2.17,^a 1.1^b$	1014	88b
	,	$10^{10}$	87
	$k_{CO_2} = 1.1^b$	$10^{10}$	87
	$k_{\text{CO}_2} = 1.1^b$ $k_{\text{CS}_2} = 16^b$	$10^{10}$	87
	$k_{N_2}^{002} < 0.25$	$10^{10}$	87
	$k_{\rm Ar}^{N_2} < 0.15$	$10^{10}$	87
	$k_{\mathbf{Xe}}^{\mathbf{A}\mathbf{a}} = 1.4^{b}$	$10^{10}$	87
	$k_{\rm He}^{\rm Re} = 78$	1010	89
$A'^1\Sigma^+, v = 5$	$k_{\rm CS_2} = 50 \pm 15$	$10^{13}$	53
= , • •	$k_{N_2} = 9 \pm 3$	$10^{13}$	53
	$k_{\rm Ar}^{\rm N_2} = 6 \pm 2$	1013	53

<sup>a</sup> Averaged over several rotation levels. <sup>b</sup> Averaged over several vibrational levels.

found that electronic quenching dominated over vibrational relaxation.

Carlson et al.<sup>85</sup> investigated the lifetimes of the v = 0–5 levels of CS (A<sup>1</sup> $\Pi$ ). Besides the known increase of the lifetime by singlet–triplet perturbations, long-lived components ( $\tau > 6~\mu s$ ) were observed. Higher CS<sub>2</sub> pressure or addition of catalyzer gases such as He, Ne, Ar, Kr, N<sub>2</sub>, or CO<sub>2</sub> greatly enhanced the intensity of these long-lived components. This phenomenon is ascribed to collisionally induced intersystem crossings.

The collisional quenching of CS  $(A^1\Pi)_{v=0-5}$  by CS<sub>2</sub>, CO<sub>2</sub>, CO, N<sub>2</sub>, Xe, and Ar was studied by Ashfold et al.<sup>87</sup> They found that the rate of electronic quenching by CS<sub>2</sub> and Xe is too fast to allow competition from rotational or vibrational relaxation, while rotational relaxation does compete in the remaining systems. The quenching rate of the CS  $(d^3\Delta)_{v=4}$  state by CS<sub>2</sub> is also estimated (see Table V).

Hynes and Brophy<sup>88</sup> measured the radiative lifetime and quenching rates for rotational levels of CS  $(A^1\Pi)_{v=0}$ . O<sub>2</sub>, CO, and O (<sup>3</sup>P) were used as quenchers. Their results reflect the perturbation of the  $A^1\Pi$  state of CS by the  $a'^3\Sigma^+$  and  $d^3\Delta$  states.

Recently Black et al.<sup>89</sup> found by LIF studies that vibrationally excited CS rapidly relaxes to  $CS_{v=0}$ , and they also estimated the quenching rate of CS (A<sup>1</sup>II) by He and the rate coefficients for reactions of  $CS_{v=0}$  with  $O_0$ ,  $O_0$  and  $NO_0$ , respectively

 $O_2$ ,  $O_3$ , and  $NO_2$ , respectively. Finally,  $Wang^{90}$  and Fournier et al.  $^{91}$  estimated the lifetime of CS ( $a^3\Pi$ ). (see Table IV). They found that CS ( $a^3\Pi$ ) decays nonexponentially to the CS ( $X^1\Sigma^+$ ) ground state. The decay could be decomposed into three components that decay independently. The lifetimes of the  $a^3\Pi_0$  and  $a^3\Pi_1$  states are of similar magnitude due to spin-orbit coupling to the  $A^1\Pi$  state that makes the transition to the singlet ground state partially allowed. The lifetime of the  $a^3\Pi_2$  state is several magnitudes larger since the only perturber is the  $X^1\Sigma^+$  ground state itself, thus making this transition strictly forbidden.

#### 3. Thermodynamic Data of CS

Thermodynamic data of CS have been estimated by a variety of different methods, both experimentally and theoretically. Data reported prior to 1978 have been reviewed, and more recent data are summarized in Table VI.

#### 4. Theoretical Studies on CS

For the same reasons as those mentioned in the introduction of section 2, several theoretical studies of the CS molecule have been carried out. The majority of the references mentioned in section 2 also include theoretical calculations.

The ground state of CS has been studied by diagrammatic perturbation theory<sup>93</sup> and MNDO calculations.<sup>94</sup> Bozhenko and Charkin<sup>95</sup> calculated the electronic structure of the  $X^1\Sigma^+$  and  $a^3\Pi$  states of CS by using the Hartree–Fock–Roothaan method including estimates of the energy of the  $a^3\Pi-X^1\Sigma^+$  transition and dipole moment. These calculated results, however, differed markedly from the experimental values.<sup>3</sup>

The incorporation of the valence-electron-only model potential (VEOMP) method in the GAUSSIAN 70 program was tested by calculations of orbital energies, equilibrium bond length, and dipole moment of ground-state CS.<sup>96</sup> Good agreement with known data<sup>3</sup> was obtained. Berthier et al.<sup>97</sup> calculated some one-electron properties of CS by means of configuration interaction (CI) calculations and obtained good agreement with experimental data.<sup>3</sup>

Robbe and Schamps<sup>98</sup> calculated wave functions, SCF-CI energies, dipole moment, and spectroscopic constants of low-lying electronic states of CS and obtained from these data the perturbation parameters between valence states of CS by ab initio calculations. Rhee et al.<sup>99</sup> obtained atom in molecule polarizability sensors, atom in molecule partial charges, and hybrid dipole moments of CS by CNDO/2-FPP calculations.

Two studies on the contribution of triply excited and quadruply excited states to the valence correlation energy of CS using diagrammatic many-body perturbation theory have appeared. Sannigrahi et al. Compared the calculations of the transition energy and geometry of the lowest excited singlet and triplet states of CS by the CNDO/S and CNDO/2- $V_{N-1}$  potential methods.

Recently<sup>102</sup> several spectroscopic properties of ground-state CS including potential energy functions, vibrational term energies, electric dipole moment functions, vibrationally averaged dipole moments, transition dipole moments, and IR intensities have been calculated by ab initio methods. The proton affinity of CS (see Table VI) and enthalpies of various reactions of CS leading to HCS<sup>+</sup> are also calculated.

Band intensity parameters, Franck–Condon factors, and r centroids for the systems CS ( $a^3\Pi-X^1\Pi^+$ ), CS ( $A^1\Pi-X^1\Sigma^+$ ), and CS ( $A'^1\Sigma^+-X^1\Sigma^+$ ) have been evaluated from calculated potentials,  $^{103}$  and an analysis of experimental data showed regular changes of the electronic transition probabilities in a wide range of diatomic molecules.  $^{104}$ 

The energies and relative intensities of the inner and outer valence electrons of CS have been calculated both by CI calculations <sup>105</sup> and by the 2pH–TDA method. <sup>106</sup> Both calculations showed a breakdown of the one-particle model.

Two reports on calculations of the vibrational structure of CS following core ionization have appeared, <sup>107</sup> and the photoelectron spectrum of CS has been calculated. <sup>108,109</sup>

Finally, several theoretical studies of collision processes with CS have been published. These include calculations of collision-induced relaxation of rotation-

TABLE VI. Thermodynamic Data for CS (All Values in kcal/mol)

$\Delta H_{\mathrm{f}}^{\circ}(\mathrm{CS})$	ref	$D_0^{\circ}(\mathrm{CS})$	ref	EA (CS)	ref	proton affinity	ref
$34 \pm 6^{b}$	71	171 ± 1	45	$25.4 \pm 2^{a}$	72	189.5ª	102
$67.5 \pm 2^{b}$	72	$170.2 \pm 0.5^a$	46	$4.7 \pm 0.5$	75	174	114
$64.57 \pm 1.85^a$	73	167.5	113			188	116
$65.2 \pm 0.5$	46	168	115				

ally excited CS,  $^{110}$  use of the quantum theory of scattering in a three-body system for the calculation of vibrational excitation of the products from the O/CS reaction,  $^{111}$  and several reports  $^{112}$  on theoretical calculations of the CS/H<sub>2</sub> reaction, which is of astrophysical interest.

## 5. Chemistry of CS

#### 5.1. Polymerization of CS

The most striking feature of CS is perhaps its ability to polymerize spontaneously. This property was reported for the first time by Loew in  $1868^{117}$  and by Sidot in  $1872^{118}$  who observed the formation of a brown precipitate when  $CS_2$  was exposed to sunlight.

The first thorough investigation of the polymer was performed by Dewar and Jones. 119 Treatment of Ni-(CO)<sub>4</sub> with thiophosgene gave a nonconductive, brown-black powder that was insoluble in alcohol, ether, benzene, petroleum ether, and dilute H<sub>2</sub>SO<sub>4</sub>, slightly soluble in CS<sub>2</sub>, ethylene dibromide, nitrobenzene, naphthalene, and phenol, giving highly colored, redbrown solutions, and readily soluble in concentrated H<sub>2</sub>SO<sub>4</sub>, concentrated HNO<sub>3</sub>, and aqueous or alcoholic solutions of NaOH or NH<sub>3</sub>. Addition of water to the acidic solutions and of acids to the basic solutions precipitated the polymer in almost unchanged form.

When the polymer was heated up to 360 °C only a very slight evolution of  $H_2S$  could be observed, and no HgS was formed when Hg was added during the warmup. Above 360 °C  $CS_2$  was evolved, leaving mainly carbon with a sulfur content of less than 10%. Heating in the presence of  $H_2$  gave  $H_2S$  and carbon, while heating with  $Cl_2$  gave sulfur chlorides, thiophosgene, and carbon. Elemental analysis showed a C to S molar ratio of 1:1.

When Dewar and Jones<sup>119</sup> dissociated  $CS_2$  in an electrical discharge, they were able to trap monomeric CS at -190 °C, either as a crystalline, colorless solid or as a glassy, amorphous, colorless condensate. At low temperature (even at -220 °C) the condensate slowly turned brown, forming a brown-black polymer. When the condensate was heated above -160 °C, a violent polymerization took place with emission of light and heat. The polymerization reaction is able to shatter glass. If the CS was condensed on charcoal, the polymerization took place immediately without explosions.

The polymer obtained by this method had somewhat different physical properties than the polymer obtained from the Ni(CO)<sub>4</sub>/Cl<sub>2</sub>CS reaction. It was only soluble in hot (>100 °C) concentrated H<sub>2</sub>SO<sub>4</sub>, slightly soluble in warm alcohol/NaOH, and insoluble in all organic solvents. <sup>120</sup> Elemental analysis showed a C to S molar ratio of 1:0.93. The difference between the two polymers was explained to be due to different degrees of polymerization.

The melting point of polymeric CS has been reported to exceed 300 °C, $^{122}$  and more recent pyrolysis experiments $^{2.7}$  up to 600 °C gave  $H_2O$ ,  $SO_2$ ,  $CS_2$ , COS, CO,  $S_2$ , and  $C_2S$ , leaving carbon as the only nonvolatile product.

The reported lifetimes of gaseous CS range from less than 1 s to many minutes, depending primarily on the surface to volume ratio of the container but also on the pressure and temperature.  $^{2,123-131}$  CS trapped in a CS<sub>2</sub> matrix at -190 °C could be observed for several hours.  $^7$ 

It has been shown that the decay of CS is first order in CS<sup>129</sup> and that the polymerization is not diffusion controlled. <sup>128,129</sup> It is well established that the polymerization is a wall reaction. <sup>128,129</sup> In an older work <sup>132</sup> it is suggested that the decay of CS follows the expression

[CS] = [CS]<sub>0</sub> exp(
$$-2.3 \times 10^{-3}$$
)

and Hogg and Spice<sup>133</sup> estimated the heat of formation of polymeric CS from gaseous CS to be

$$\Delta H_{\rm polym} \sim -47 \pm 23 \text{ kcal/mol of CS}$$

This estimation was based on the assumption that polymeric CS consists of carbon chains cross-linked by sulfur atoms.

The polymerization of CS can be catalyzed by Pt, Ni, and Ag powders, <sup>119</sup> metal carbonyls, <sup>134</sup> and Cu(I) compounds. <sup>5</sup>

Much effort has been devoted to the elucidation of the mechanism for the polymerization of CS and the determination of the structure of the polymer, but no clear answers to these problems have been found yet.

In early reports a simple polymerization according to (4) is suggested. This result is mainly based on elemental analysis of the polymer. However, numerous

$$nCS \xrightarrow{\text{wall}} (CS)_n$$
 (4)

elemental analyses have been reported and the C to S molar ratios range from 1:2 to 5:1,7,119,121,122,130,134,135 depending on the method of preparation of the polymer.

Steudel<sup>2,7</sup> trapped the gaseous products formed in a high-frequency discharge through CS<sub>2</sub> in a CS<sub>2</sub> matrix at -190 °C and recorded the change of the matrix in time by IR spectroscopy. The initially formed products were identified as CS, CS<sub>2</sub>, and C<sub>3</sub>S<sub>2</sub>, and while the concentration of CS decreased with time, the C<sub>3</sub>S<sub>2</sub> concentration increased. On the basis of these observations the reaction sequence (5)-(8) was proposed.

$$2CS \to C_2S + S \tag{5}$$

$$C_2S + CS \rightarrow C_3S_2$$
 (6)

$$nS \to s_n$$
 (7)

$$C_2S + S_n$$

$$C_xS_y \qquad (8)$$

$$C_3S_2 + S_n$$

Richardson et al.  $^{130}$  prepared CS by dissociation of CS<sub>2</sub> in a microwave discharge, and after passing the gas stream through a -117 °C trap almost pure CS gas was obtained. A glass container was filled with CS gas, and the polymerization was recorded by mass spectroscopy and by a vacuum gauge. Disappearance of CS was observed simultaneously with an increase in CS<sub>2</sub> concentration. The rates of these two changes were the same. This result led the authors to propose the reaction (9)

$$2CS + C_n(solid) \xrightarrow{\text{wall}} CS_2 + C_{n+1}(solid)$$
 (9)

to be responsible for the decay of CS. The experiments did not reveal the nature of the induction processes by which the first carbon layer is deposited on a clean surface. The presence of sulfur in the resulting solid, as evidenced by elemental analysis, was explained by adsorption of  $CS_2$  on the carbon formed. Breckenridge et al.<sup>131</sup> have later supported this suggestion.

There is, however, no conclusive evidence for any of these proposed mechanisms. The fact that Richardson et al. 130 and Breckenridge et al. 131 did not observe any carbon sub-sulfide formation is at variance with Steudel's<sup>2,7</sup> suggestion. Finally, the idea that the polymer should be a mixture of carbon and CS2 is contradicted by ESCA spectroscopy of the polymer. Recently two reports on the formation of polymeric CS by irradiation of  $CS_2$  vapor with lasers 136,137 ("laser snow effect") have appeared, and an ESCA spectrum of the obtained polymer gave a C to S molar ratio of 1:1. An ESCA spectrum recorded by us138 showed one C (1s) peak at 285.6 eV and one 2 (2p) peak at 164.8 eV. The polarization could be calculated to be  $q_{\rm C}$  = -0.18 and  $q_{\rm S}$  = +0.18. By comparison with ESCA spectra of various compounds, 139-142 these peaks could be assigned to divalent, single-bonded sulfur and to carbon bonded in a benzene-like structure. These results are not compatible with Richardson et al.'s suggestion.

X-ray analysis of the polymer indicated an amorphous structure, <sup>138</sup> and the IR spectrum<sup>2</sup> shows very weak and broad absorptions at 805, 1075, 1260, 1730, and 1980 cm<sup>-1</sup> assigned to C—S, C—S, and C—C bonds. No signals were observed in <sup>13</sup>C solid-state NMR at 300 MHz. <sup>138</sup>

Obviously, the formation and structure of polymeric CS is far from being completely understood. A recent theoretical study<sup>143</sup> on dimeric CS, S—C—C—S, indicates that this species might be of importance as an intermediate in the polymerization process.

# 5.2. Reactions of CS with O and ${\rm O_2}$ . Chemical CO laser

The reactions of  ${\rm O/O_2}$  with  ${\rm CS/CS_2}$  have been of much interest. In these reactions vibrationally excited CO is formed that relaxes with emission of light. This IR emission can be used for a CO laser. The reaction responsible for the formation of CO\* (eq 10) is the reaction of CS with atomic oxygen. The kinetic data of the reactions involved in this system (vide infra) published prior to 1979 have been reviewed, and recently investigations using LIF spectroscopy have appeared.  $^{89,146-148}$ 

$$CS + O \rightarrow CO^* + S \tag{10}$$

Black et al.<sup>89</sup> found the rate coefficients for the reactions of CS (X, v = 0) with  $O_2$ ,  $O_3$ , and  $NO_2$  to be (2.9  $\pm$  0.4)  $\times$  10<sup>-19</sup>, (3.0  $\pm$  0.4)  $\times$  10<sup>-16</sup>, and (7.6  $\pm$  1.1)  $\times$  10<sup>-17</sup> cm<sup>3</sup>·molecule<sup>-1</sup>·s<sup>-1</sup>, respectively.

Clough and Johnston<sup>146</sup> determined the vibrational distribution of CS formed in the reaction (11), while Hsu et al.<sup>147</sup> investigated the reactions of O with CS, CS<sub>2</sub>, and OCS, respectively, and determined the resulting vibrational distribution of CO together with branching ratios for the various reactions. Hancock and Zacharias<sup>148</sup> studied the vibrational distribution of CO (A<sup>1</sup> $\Pi$ ) formed by UV laser excitation of high vibrational levels of ground electronic state CO, which was produced in the reaction between O and CS.

Two main types of CO lasers have been described. One type is based on the reaction sequence (11)–(13). Atomic oxygen, which is necessary to initiate this chain reaction, can be produced by discharges through  $O_2$ . The power of lasers based on this chain reaction, however, is limited since (11) is consuming atomic oxygen, thus limiting (12).

$$O + CS_2 \rightarrow CS + SO \tag{11}$$

$$O + CS \rightarrow CO^* + S \tag{12}$$

$$S + O_2 \rightarrow SO + O \tag{13}$$

A more powerful laser is obtained by fueling the laser directly with CS and  $O_2$  according to (14)–(16). In this

$$CS_2 \xrightarrow{h\nu} CS + S \tag{14}$$

$$S + O_2 \rightarrow SO + O \tag{15}$$

$$CS + O \rightarrow CO^* + S \tag{16}$$

sequence all the atomic oxygen produced is available for the reaction with CS. These lasers operate as supersonic flow and mixing systems where CS is produced by thermal dissociation of  $\mathrm{CS_2}^{151-153}$  or by photolytic dissociation of  $\mathrm{Cl_2CS.^{154}}$  The  $\mathrm{CS/S/CS_2}$  mixture is supersonically pumped into the laser cavity where it is mixed with  $\mathrm{O_2.^{155-161}}$  A computed model of this system has appeared,  $^{162}$  and calculations of the energy characteristics have been performed.  $^{163}$ 

Attempts to utilize overtone transitions of the CO molecule for lasers gave only a low-power laser. The potential application of CS ( $a^3\Pi$ ) as lasing species has been discussed.  $^{165}$ 

## 5.3. Reactivity of CS

Except for the above-mentioned reactions of CS with  $O/O_2$ , only a few reports on the reactivity of CS have appeared until recently. This fact is due to the short lifetime of CS because of the competitive polymerization reaction.

Dewar and Jones<sup>119</sup> were the first to attempt reactions with gaseous CS. Reactions with Fe<sub>2</sub>O<sub>3</sub>, HgO, and AgO resulted in the formation of the corresponding metal sulfides. Also BaO reacted with CS to give BaS. Gaseous CS was completely decomposed by concentrated HNO<sub>3</sub>, while a violent reaction with concentrated H<sub>2</sub>SO<sub>4</sub> took place, giving SO<sub>2</sub>, CO<sub>2</sub>, CO, and N<sub>2</sub> as gaseous products. CS was inert toward NaOH, AgNO<sub>3</sub>, Pb(OAc)<sub>4</sub>, and sodium peroxide.

Norman and Porter<sup>166</sup> photolyzed CS<sub>2</sub> in a matrix consisting of a mixture of 3-methylpentane and isopentane but observed only polymer formation upon warming. De Sorgo et al. 167 photolyzed gaseous mixtures of CS<sub>2</sub> in the presence of hydrogen, ethylene, butane, and propane, respectively, but could not observe any product formation except polymer formation. Hogg and Spice<sup>133</sup> cocondensed CS with BCl<sub>3</sub> or NH<sub>3</sub>, but no products except polymer were formed. Cocondensation with ethylene 133 delayed the polymerization, which only occurred after removal of the ethylene matrix. Cocondensation with benzene or acetylene gave only polymeric CS.<sup>168</sup>

The first successful reactions with monomeric CS were reported by Steudel.<sup>2,169</sup> He obtained CSSe and CSTe by treatment of elemental Se and Te with CS. The reaction of CS with Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> yielded Cl<sub>2</sub>CS, Br<sub>2</sub>CS, and I<sub>2</sub>CS, respectively. In the reaction with Cl<sub>2</sub> the initially formed thiophosgene was partially chlorinated to Cl<sub>3</sub>CSCl.

Klabunde and Skell<sup>170</sup> prepared CS by treatment of CS<sub>2</sub> with carbon atoms. Treatment of the so-prepared CS with propylene oxide resulted in deoxygenation, giving propylene and COS. It was shown later 122 that CS also was able to abstract oxygen from cyclohexene oxide. In 1974 Klabunde et al. 171 reported cocondensation experiments and low-temperature solution-phase experiments of CS with halogens and hydrogen halides. This report constitutes the first synthetic-scale application of CS. Contrary to Steudel's results, the reactions with Cl<sub>2</sub> and Br<sub>2</sub> only gave secondary products according to (17). With BrCl a mixture of products

$$CS + X_2 \rightarrow [X_2CS] \xrightarrow{X_2} X_3CSX \qquad X = Cl, Br (17)$$

$$CS \xrightarrow{BrCl} Cl_3CSCl + Br_3CSBr + BrCl_2CSCl$$

$$38\%$$

$$15\%$$

$$27\%$$

$$(18)$$

according to (18) was obtained. Reaction with I<sub>2</sub> gave no stable products. With HBr and HCl trithianes were obtained according to (19).

$$CS + HX \longrightarrow [HCX] \xrightarrow{trim.} X \longrightarrow S \qquad (X = CI, Br) \quad (19)$$

Fjeldstad et al.<sup>11</sup> and Skramstad et al.<sup>12</sup> obtained small amounts of CS by dissociation of thiophene in a glow discharge and were able to trap the CS with morpholine as N-(thioformyl)morpholine. Recently the synthetic-scale reactions of amines with CS formed in an electric discharge through CS2 have been investigated systematically.<sup>5</sup> The main products with both primary and secondary amines were the corresponding thioformamides according to (20). The product yields

$$RR'NH + CS \rightarrow RR'NC(S)H$$
 (20)

in these reactions depended highly on the substituents R and R' and the most basic yet least sterically hindered amines as, e.g. morpholine, gave an almost quantitative yield, while less basic amines as, e.g. primary amines, gave low yields of thioformamide. With aniline only the secondary product N,N'-diphenylformamidine was obtained. Tertiary amines were inert toward CS.

This report<sup>5</sup> also includes a study on the reactivity of CS toward thiols. Insertion of CS into the S-H bond occurs, and the unstable dithioformate reacts with excess thiol to form mainly bis(alkylthio)methanes according to (21). With aliphatic thiols the corresponding orthotrithioformates, (RS)<sub>3</sub>CH, were formed as minor byproducts. Methanol was inert to CS.

$$RSH + CS \rightarrow [RSC(S)H] \xrightarrow{+RSH} RSCH_2SR \qquad (21)$$

CS reacts readily with sulfenyl chlorides according to (22).  $^{135,172-175,177}$  While stable chlorodithioformates could be isolated with R = Ph<sup>172</sup> and CCl<sub>3</sub>, <sup>173</sup> the

$$RSCl + CS \rightarrow RSC(S)Cl$$
 (22)

R = Ph, CCl<sub>3</sub>, CH<sub>3</sub>CO, PhCO, Cl<sub>3</sub>CSCCl<sub>2</sub>, morpholino

products obtained with  $R = CH_3CO^{174}$  and  $PhCO^{174}$ were unstable and decomposed into CS2 and the corresponding acyl chloride. The morpholine derivative 135 could only be obtained in low yield and was only stable for a few days. Treatment of S<sub>2</sub>Cl<sub>2</sub> with CS gave<sup>172</sup> the corresponding unstable diinsertion product, bis(chlorothiocarbonyl) disulfide.

Also thiosulfenyl chlorides reacted quantitatively with CS according to (23).6 This is so far the only route to perthiochloroperformates.

$$RSSC1 + CS \rightarrow RSSC(S)C1 \tag{23}$$

$$R = Cl_3C$$
,  $C_9Cl_5$ ,  $CH_3CO$ ,  $ClCO$ 

A few successful cycloaddition reactions with CS have been reported.<sup>176</sup> These include reactions of aminoacetylenes with CS, giving cyclopropenethiones according to (24). This reaction is highly restricted to very electron-rich acetylenes, and a variety of other acetylenes failed to react with CS (see Table VI).

$$RC = CR' + CS - RC = CR'$$
 $R.R' = Me_2N, Me_2N; Et_2N, Et_2N; Me, Et_2N$ 

(24)

Finally, it has been reported that CS easily displaces nitrogen in diazo compounds, giving thioketenes according to (25).

$$R_2CN_2 + CS \rightarrow R_2C = C = S$$
 (25)  
 $R = 7 - Bu, ^{135}CF_3, ^{122}S$ 

A variety of compound types are reported 122,135,171,177 to be inert toward CS, and since these reports are not easily available, these attempts are summarized in Table VII.

Some general trends can be concluded from the presently reported chemistry of CS. A remarkable selectivity is observed, which is quite surprising considering the fact that CS is very reactive. The explanation for this must be that the polymerization reaction is highly competitive and only relatively few substrate types are sufficiently reactive toward CS to make the polymerization less favored. CS is isoelectronic with CO and isocyanides, and it is interesting to note that

TABLE VII. Organic Compounds Inert to CSa

compound	ref	compound	ref
PhCH <sub>2</sub> Cl <sup>c</sup>	177	PhC≡CPh <sup>c</sup>	135
PhCH <sub>2</sub> Br <sup>c</sup>	177	cyclooctyne <sup>c</sup>	135
$C_6F_6^b$	122	3,3,8,8-tetramethylcyclooctyne <sup>c</sup>	135
CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>3</sub> <sup>b</sup>	122	3,3,7,7-tetramethyl-5-thiacycloheptyne <sup>c</sup>	135
PhOH <sup>c</sup>	177	bis(N,N-dimethylamino)acetylene <sup>c</sup>	135
CH₃COOH <sup>b</sup>	122	$PhC \equiv CNa^h$	135
CF <sub>3</sub> COOH <sup>b</sup>	122	$\text{Et}_2\text{NC} = \text{CSEt}^{c,e}$	135
$[C\tilde{F}_3C(O)]_2O^b$	122	$Et_2NC = CSPh$	135
$CH_3C(O)Cl^b$	122	$t$ -BuOC $\equiv$ CO- $t$ -Bu $^c$	135
PhČHO <sup>c</sup>	177	$(CH_3)_3SiC = CSi(CH_3)_3^c$	177
$PhCOOH^c$	177	$\text{EtS}\mathring{\mathbf{C}} = \mathbb{C}\mathbf{S}\mathbf{E}\mathbf{t}^c$	135
PhC(O)Cl <sup>c</sup>	177	$CH_3SeC \equiv CSeCH_3^c$	135
benzoyl peroxide <sup>c</sup>	177	$CH_3^cSSSCH_3^c$	177, 13
$CF_2 = CFCF_3^b$	122	Cl <sub>3</sub> ČSSSCCľ <sub>3</sub> <sup>c</sup>	135, 17
anthracene <sup>g</sup>	177, 135	$PhSO_2Cl^c$	177
cyclooctatetrenec	177, 135	$\mathrm{Cl_3CS}(\mathrm{O})\mathrm{Cl}^c$	135, 17
azulene <sup>c</sup>	135, 177	$SO_2Cl_2^c$	135, 17
N-morpholino-1-cyclohexene <sup>c</sup>	135	$SOCl_2^{\tilde{c}}$	135, 17
N,N'-dimethylpiperazine-2,3-dithione <sup>c,e</sup>	135	$PhN(CH_3)_2^c$	177
tetrachloro-1,2-benzoquinonec	177	$\operatorname{BrCN}^b$	122
PhNHCHS <sup>e</sup>	135	$\mathrm{B}(\mathrm{OCH_3})_3{}^c$	177
Ph <sub>2</sub> CSO <sup>c</sup>	135	$BF_{3} \cdot O(\ddot{CH}_{3})_{2}^{d}$	177
cyclohexyl isocyanide <sup>c</sup>	135	$\operatorname{SiCl}_{\lambda^c}$	177
$Ph_3PS^c$	177	$Cl_{2}SiH(CH_{3})^{c}$	177
CH <sub>3</sub> OOCC≡CCOOCH <sub>3</sub> <sup>c</sup>	177	• • •	

<sup>&</sup>lt;sup>a</sup>The table contains material from ref 122, 135, and 177. <sup>b</sup>Codeposition at −196 °C followed by warmup. <sup>c</sup>In toluene solution at −70 °C. <sup>d</sup>In THF solution at −100 °C. <sup>e</sup>Neat at 0 °C. <sup>f</sup>Neat at 45 °C. <sup>g</sup>In chlorobenzene at −45 °C. <sup>h</sup>In DMF at −35 °C.

TABLE VIII. Attempted Preparations of Thiocarbonyl Metal Complexes with CS

starting compound	ref	starting compound	ref
Ni powder <sup>a</sup>	122	(bpy) <sub>2</sub> Ni <sup>g</sup>	177
Fe atoms <sup>b</sup>	177	$Pt(PPh_3)_3^h$	196
Mn/cyclopentadiene <sup>b</sup>	177	$(C_6F_5)_2Co(PEt_3)_2^g$	196
LiPdCl <sub>3</sub> <sup>c</sup>	122	$(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)\text{Ni}(\text{SiCl}_3)_2^{g,i,j}$	196, 177
$ClRh(PPh_3)_3^d$	122	$(\eta^6\text{-CH}_3^{\circ}\text{C}_6^{\circ}\text{H}_5)\text{Ni}(\text{C}_6\text{F}_5)_2^{\mathscr{S}}$	196
Ni(CO) <sub>4</sub> <sup>b</sup>	122	$(\eta^6 - \text{CH}_3\text{C}_6\text{H}_5)\text{Co}(\text{C}_6\text{F}_5)_2^g$	196
Fe(CO) <sub>5</sub> <sup>e</sup>	134	$(diphos)_2Mo(N_2)_2^g$	196
$Cr(CO)_5^e$	134	$(diphos)_2 PtMe_2^{g,\bar{j}}$	196
$W(CO)_{6}^{e}$	134	$(PPh_3)(CO)_3CoMe^g$	196
$\text{Fe}_2(\text{CO})_9^f$	177	9./	196
MeCpMn(CO) <sub>3</sub> g	177	Pt(diphos)	100

<sup>a</sup> Neat, room temperature. <sup>b</sup> Codeposition at -196 °C. <sup>c</sup> In acetonitrile at -45 °C. <sup>d</sup> In methanol at -78 °C. <sup>e</sup> Gas-phase reaction. <sup>f</sup> In THF at -114 °C. <sup>g</sup> In toluene at -70 °C. <sup>h</sup> In chlorobenzene at -40 °C. <sup>i</sup> In C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> at -40 °C. <sup>j</sup> Reaction resulted in decomposition.

all known CS reactions have an isocyanide counterpart. The Apparently the reactivity of isocyanides to some extent can be used as guideline for the reactivity of CS.

#### 6. Transition-Metal Thiocarbonyl Complexes

The chemistry of transition-metal complexes containing CS ligands has evolved very slowly. The first thiocarbonyl complex, trans-RhCl(PPh<sub>3</sub>)<sub>2</sub>(CS), was prepared by Wilkinson et al.<sup>179</sup> in 1966, and since then a few hundred CS complexes have been prepared (an excellent review has been published recently by Broadhurst<sup>180</sup>). This is a surprisingly low number compared to the thousands of known CO complexes when one considers that CS is isoelectronic with CO.

There is good evidence that this scarcity of thiocarbonyl complexes is not due to any inherent instability. In 1967 Richards<sup>181</sup> predicted by ab initio calculations that CS is both a better  $\sigma$  donor and a better  $\pi$  acceptor than CO. This result has been verified both by more recent theoretical studies  $^{182-186}$  and by spectroscopic studies.  $^{185-188}$  The superior properties of CS as a metal ligand compared to CO is also reflected in the chemistry of thiocarbonyl complexes. A variety of reactions can be carried out without influencing the CS ligand.  $^{180}$ 

The main reason for the relatively low number of known thiocarbonyl complexes in spite of the good ligand properties of CS is the lack of general synthetic pathways. Virtually all known CS complexes have been prepared by indirect routes mainly using CS<sub>2</sub> as the source of CS, <sup>180</sup> and these procedures are usually complicated by complex reaction mixtures and formation of unexpected byproducts.

The most direct route would be application of neat CS gas analogous to the use of CO gas in the preparation of CO complexes. The efforts made in this area so far have, however, met with very little success. The attempted preparation of Ni(CS)<sub>4</sub> by cocondensation of argon, Ni atoms, and CS at 10 K followed by warm-up<sup>189</sup> is the only report on direct use of CS gas. IR and MS indicated the formation of Ni(CS)<sub>4</sub>, but the evidence is far from conclusive. Other similar attempts have been unsuccessful (see Table VIII). The main problem seems to be the competitive, apparently favored polymerization reaction.

Since the appearance of Broadhurst's review a number of reports on new thiocarbonylmetal complexes have appeared. Burgmayer and Templeton<sup>190</sup> prepared the dinuclear complex  $Mo_2(S_2CNEt_2)_3(\mu\text{-CSC}(S)S)(\mu\text{-}S_3C_2NEt_2)$  by treating  $Mo(CO)_2(S_2NEt_2)_2$  with  $CS_2$  in the presence of triphenylphosphine. This reaction can be considered as a net addition of two CS fragments and one  $CS_2$  molecule to two  $Mo_2(CO)_2(S_2NEt_2)$  with dimerization and loss of all CO ligands. One CS moiety inserts into a coordinated dithiocarbamate, forming the  $S_2C_2NEt_2$  unit, while the other CS moiety has coupled with  $CS_2$  to form the  $C_2S_3$  group. Triphenylphosphine acts as sulfur abstractor.

Ebner et al. 191 observed the fragmentation and recombination of CS2 and CSSe in the coordination sphere of platinum or palladium. Thus, treatment of the complex 1 with a platinum complex gave insertion into the C-E bond with metal-metal bond formation according to (26). Attempts to substitute the PPh<sub>2</sub> and

M = Pd, Pt; E = S, Se;  $L = (PPh_3)_2$ ,  $C_2H_4$ ; P = diphos, dpmp

CS ligands by diphos or dpmb resulted in a recombination of CS and E according to (27).

$$2 \xrightarrow{PPh_3} P \times E - C \longrightarrow P t \longrightarrow P$$
 (27)

Touchard et al. 192 reported the Fe(0) thiocarbonyl complex, 3, by reduction of  $Fe(\eta^2-CS_2R)^+$  cations with sodium amalgam according to (28). This method can be applied to metal cations when donor groups are bonded to the metal center, and the method is complementary to desulfurization of  $M(\eta^2-CS_2)$  precursors by phosphines that readily occurs with nonbasic ligands.

$$(CO)_{2}L_{2}Fe(\eta^{2}\text{-}CS_{2}Me)^{+}PF_{6}^{-} \xrightarrow{Na/Hg} (CO)_{2}L_{2}Fe(CS)$$

$$(28)$$

## $L = PMe_3, PMe_2Ph, P-n-Bu_3$

The preparation of the end-to-end bridging thiocarbonyl complex  $(\eta^6-C_6H_5R)(CO)_2CrCSCr(CO)_5$  (4: R = Me, OMe) was reported by Lotz et al. 193 Only a few reports on this type of CS complex have appeared, 180 and the single-crystal X-ray structure of 4 presented by Lotz is the first for this complex type. The preparation of 4 was accomplished in good yields by treatment of  $\pi$ -arene thiocarbonyl complexes with  $Cr(CO)_5$ -THF. The S-Cr linkage is weak and can easily be broken in polar solvents with coordinating properties.

The conversion of coordinated CS<sub>2</sub> into CS ligands can be accomplished by various methods, 180 and recently Herberhold et al. 194 have described two new procedures. The CS<sub>2</sub> ligand in OsCl(NO)(CS<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> could easily be methylated to give cationic complexes, MC(S)SMe+. Reduction with NaTeH gave OsX- $(NO)(CS)(PPh_3)_2$  (5: X = Cl, I), while reduction with NaBH<sub>4</sub> gave OsH<sub>2</sub>(CS<sub>2</sub>Me)(NO)(PPh<sub>3</sub>)<sub>2</sub> which could be converted to 5 by treatment with electrophilic reagents (HCl, HI, I<sub>2</sub>). The halide in 5 is labile and can easily be substituted by neutral ligands, thus providing various cationic complexes.

The first example of a semibridging CS ligand has been reported recently by Angelici et al. 195 who treated  $[HB(pz)_3](CO)_2W(CS)^-$  with  $ClAu(PR_3)$  and obtained the bimetallic complex 6. The semibridging nature of the CS ligand could be confirmed by X-ray diffraction studies.

#### 7. Interstellar CS

Carbon monosulfide was discovered in interstellar clouds in 1971,<sup>197</sup> and since then numerous reports on observations of CS in space have appeared. A review of those reports is outside the scope of this paper, but for the benefit of the interested reader a list of the reports on interstellar CS including titles of each paper cited in Chemical Abstracts in the period 1976-1986 is available as Supplementary Data.

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