concentration were obtained by least-squares fits[16] to eq 2. The values are $b = 6900 \pm 200$, 1420 ± 40, and $540 \pm 70\ M^{-1}\ \text{sec}^{-1}$, at 0.0010, 0.010, and 0.10 *M* free chloride, respectively. These *b* values were fitted to eq 5, where f_n represents the fraction of total

$$b = (k_1 + k_{-1}[\text{R}])f_1 + (k_2 + k_{-2}[\text{R}])f_2 \qquad (5)$$

mercury that is $HgCl_n^{2-n}$. These calculated[14] fractions are listed with Table I. Using the above *b* values and $Q_1 = 4.4\ M^{-1}$, the values $k_1 = 1.7 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, $k_{-1} = 7.4 \times 10^7\ M^{-2}\ \text{sec}^{-1}$, $k_2 = 8.5 \times 10^2\ M^{-1}\ \text{sec}^{-1}$, and $k_{-2} = 3.7 \times 10^3\ M^{-2}\ \text{sec}^{-1}$ were obtained. These values for the rate constants were used in the calculated constants given in Table I.

Terms involving Hg^{2+} and $HgCl_3^-$ were omitted from eq 5 because this two-term expression provides an adequate fit. Further, even at 0.001 *M* chloride, the value of f_0 is so small (6×10^{-8})[14] that postulation of a diffusion-controlled process would not permit k_0 to make more than a few per cent contribution to the observed *b* value. A two-term expression involving $HgCl_2$ and $HgCl_3^-$ gives an extremely poor fit. Preliminary experiments indicated that Hg^{2+} does provide catalysis when it is present at significant concentrations; it is likely that $HgCl_3^-$ also provides catalysis at very high chloride concentration, but eq 5 describes the catalysis in the region 0.0010–0.10 *M* chloride.

Though it was not the purpose of this study to search for stable binuclear $FeClHgCl_{n-1}^{5-n}$ complexes, a few absorbance measurements were done on equilibrium iron(III)–mercury(II)–chloride mixtures. These measurements provided no evidence for binuclear complex formation, even in solutions containing up to 0.02 *M* $HgCl_4^{2-}$.

The mercury(II)-catalyzed pathways for aquation and formation probably involve chloride bridging,[2,3] leading to elementary reactions 6 and 7, consistent with the transition-state compositions specified by eq 5. The primed rate constants in eq 6 and 7 are related to

$$Fe^{3+} + HgCl_2 \underset{k_1}{\overset{k_1'}{\rightleftharpoons}} FeCl^{2+} + HgCl^+ \quad Q(2,1) \qquad (6)$$

$$Fe^{3+} + HgCl_3^- \underset{k_2}{\overset{k_2'}{\rightleftharpoons}} FeCl^{2+} + HgCl_2 \quad Q(3,2) \qquad (7)$$

parameters in eq 5 as follows: $k_1' = k_{-1}/Q_{2\text{Cl}} = 7.4 \times 10^7/3.02 \times 10^6 = 25\ M^{-1}\ \text{sec}^{-1}$ and $k_2' = k_2/Q_{3\text{Cl}} = 3.7 \times 10^3/7.08 = 520\ M^{-1}\ \text{sec}^{-1}$.

It has been pointed out[11] that second-order rate constants for substitution of $Fe(H_2O)_6^{3+}$ fall in a rather narrow range, 2–127 sec^{-1},[9] and, similarly,[11] rate constants for substitution of $Fe(H_2O)_5OH^{2+}$ fall in another rather narrow range, 2×10^3 to $3 \times 10^5\ M^{-1}\ \text{sec}^{-1}$.[9] It is proposed[11] that the rate-determining step is elimination of water from the inner coordination shell of Fe(III), accounting for the lack of rate dependence on identity of the entering ligand. Since the rate constants k_1' and k_2' are presumably composites, containing contributions from both acid-independent and -dependent pathways, their magnitudes should not necessarily fit into either of the ranges listed above.[17] However, if it is assumed that 20% of k_1' and k_2' arise from reaction with $Fe(H_2O)_6^{3+}$ and 80% from reaction with $Fe(H_2O)_5OH^{2+}$, as is true when chloride ion is the ligand,[5] at 0.45 *M* H^+, then all the formation rate constants fall in the previously observed ranges. Thus, our data appear consistent with the tentative conclusion that the metal complexes $HgCl_2$ and $HgCl_3^-$ coordinate to iron(III) by mechanisms similar to those for simpler ligands.

The ratio k_2/k_1 is 5.0×10^{-5}. The analogous ratio for the mercury(II)-catalyzed aquation of $Cr(H_2O)_5Cl^{2+}$ is about 2×10^{-5} at 25°, 0.3 *M* H^+, and 1.00 *M* ionic strength.[10] The similarity of these ratios, together with the fact that the equilibrium quotient ratios, $Q(3,2)/Q(2,1)$, are identical (except for ionic strength effects) for the two systems is consistent with other evidence that chromium(III) complex formation rates are also approximately independent of the nature of the entering ligand.[18]

[16] The calculations were done using a computer program based on reports from Los Alamos Scientific Laboratory, LASL-2367 + Addenda.

[17] At hydrogen ion concentrations as low as 0.2 *M*, the rate of the uncatalyzed reaction alone is near the upper limit of our ability to measure.

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CONTRIBUTION FROM BELL LABORATORIES,
MURRAY HILL, NEW JERSEY 07974

Pressure-Induced Polymerization and Decomposition of Carbon Subsulfide

BY A. P. GINSBERG,* J. L. LUNDBERG, AND W. E. SILVERTHORN

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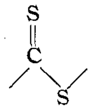
At pressures of about 45 kbars and temperatures in the range 165–235° or at 27 kbars and 220–280°, carbon disulfide slowly transforms into a black polymer $(CS_2)_x$ which gives a broad, diffuse X-ray diffraction pattern.[1,2] The infrared spectrum of the black solid is consistent with the presence of the repeating unit



A black polymeric solid is also slowly formed by carbon subsulfide at atmospheric pressure and room temperature.[3] This has the stoichiometry $(C_3S_2)_x$, and an infrared investigation[4] has shown the presence of $\nu(C{=}C)$ bands at almost the same frequencies as in the carbon suboxide polymer $(C_3O_2)_x$. Bands due to $\nu(C{=}S)$ and $\nu(C{-}S)$ are also reported to be present. Since we had available considerable quantities of liquid carbon subsulfide from our study of its use as a ligand for transition metals,[5] it appeared to be of interest to examine the effect of pressure on its polymerization and decomposition.

Experimental Section

Infrared spectra were measured with a Perkin-Elmer Model

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[1] P. W. Bridgman, *Proc. Amer. Acad. Arts. Sci.*, **74**, 399 (1941).

[2] E. G. Butcher, M. Alsop, J. A. Weston, and H. A. Gebbie, *Nature (London)*, **199**, 756 (1963).

[3] B. V. Lengyel, *Ber.*, **26**, 2960 (1893).

[4] A. O. Diallo and J. H. Dixmier, *C. R. Acad. Sci., Ser. C*, **263**, 375 (1966).

[5] A. P. Ginsberg and W. E. Silverthorn, *Chem. Commun.*, 823 (1969).

457 spectrophotometer over the range 4000–400 cm^{-1} with samples in KBr or TlBr disks.

Carbon subsulfide was prepared by striking a dc carbon arc in a CS_2 atmosphere as described by Lengyel.[3] The product was purified by trap to trap distillation on a vacuum line and showed no appreciable impurity bands in its ir spectrum. Polymerized C_3S_2 was prepared either by allowing a sample of C_3S_2 to stand at room temperature until it was completely transformed to a black solid (several days) or by warming a sample of C_3S_2 on a steam bath until it was mostly converted to a black solid (0.5–1 hr). The black solid was washed with methylene chloride and dried at 25° (10^{-3} mm). Either method of preparation gave samples with essentially the same ir spectrum. *Anal.* Calcd for $(C_3S_2)_x$: C, 35.97; S, 64.03. Found: C, 34.63; S, 65.20 (microanalyses by Galbraith Laboratories, Knoxville, Tenn.).

Effect of Pressure on C_3S_2.—The pressure experiment was carried out with a Teflon cell container in a conventional piston–cylinder device using the technique described by Jayaraman, *et al.*[6] About 1.5 g of C_3S_2 was placed in the Teflon cell (0.494-in. o.d., 0.050-in. wall) which was fitted with a chromel–alumel thermocouple and platinum leads for conductivity measurement. Pressure was applied slowly and the temperature and conductivity were recorded. Pressure values quoted in the Results and Discussion are indicated pressures, uncorrected for friction and other effects.[6]

Results and Discussion

As pressure was slowly applied to C_3S_2, the temperature of the sample gradually increased, reaching 29° at ~1.2 kbars. There was then a slight decrease in temperature, to 28° at ~1.5 kbars, followed by an increase to 50° as the pressure increased to ~2.4 kbars. This temperature rise was accompanied by a very slight decrease in the resistance of the sample (from $R \approx 1.70 \times 10^6$ ohms before pressure was applied to $R \approx 1.69 \times 10^6$ ohms at ~2.4 kbars). As the pressure was increased further, the temperature decreased, reaching 29° at ~8.4 kbars. The temperature then slowly increased with increasing pressure, reaching 32° at ~12.0 kbars. Further increase in pressure caused a rapid rise in temperature to something greater than 362° when the pressure had reached ~14.0 kbars. At this point there was a minor explosion accompanied by ejection of C_3S_2 fumes and black solid through the thermocouple and conductivity lead holes. After the explosion the resistance of the sample had decreased to ~0.90 ohm. On opening the sample cell it was found to contain a black metallic appearing solid molded to the cylindrical shape of the container. *Anal.* Calcd for C_3S_2: C, 35.97; S, 64.03. Found: C, 35.73; S, 64.01.

The black solid is not ordinary $(C_3S_2)_x$ polymer because ir absorption in the 4000–400-cm^{-1} range is absent. The sample scattered the ir beam badly and only very dilute disks could be measured. When a portion of the black solid was boiled with 6 *N* sodium hydroxide, a yellow solution and a black residue were obtained. Acidification of the yellow solution with 8 *N* sulfuric acid gave a milk of sulfur from which elementary sulfur settled out on standing. A powder pattern (Cu Kα) of the NaOH-insoluble residue was very poor (broad, weak lines) but suggests that it is graphite. Sulfur is also extracted from the black product on shaking it with carbon disulfide. By contrast, the $(C_3S_2)_x$ polymer dissolves completely in boiling 6 *N* sodium hydroxide to give a red-brown solution from which a brown-black solid precipitates on acidification.

Its behavior with sodium hydroxide and carbon disulfide indicates that the product from the application of ~14-kbar pressure to C_3S_2 is simply a mixture of graphite and elementary sulfur; this is confirmed by the X-ray powder pattern (Table I). There are a total of 22 lines, all but one of which can be accounted for as being due to orthorhombic sulfur or graphite. All of the strong lines of orthorhombic sulfur (ASTM No. 8-247) and graphite (ASTM No. 12-213) are present. The single anomaly is the line at 1.92 Å; although orthorhombic sulfur has a line at 1.926 Å, its intensity is too low to account for the observed line.

TABLE I

THE d_{obsd} SPACINGS (Å) AND RELATIVE INTENSITIES (Cu Kα) FOR THE BLACK SOLID FORMED BY APPLICATION OF ~14-KBAR PRESSURE TO C_3S_2[a]

7.7 vvvw	3.21 m	2.28 vvvw	1.78 vvvw
5.75 vvw	3.05–3.1 w	2.09–2.13 w	1.72 vvvw
4.05 vvvw	2.84 vw	2.03 vvvw	1.69 vvvw
3.85 vs	2.61 vvw	1.92 vvvw	1.23 vvvw
3.55 vvvw	2.50 vvvw	1.9 vvvw	
3.31–3.45 vs, b	2.42 vvvw	1.82 vvvw	

[a] Abbreviations: b, broad; m, medium; s, strong; v, very; w, weak.

In order to identify the product of the exothermic transformation which takes place between ~1.5 and ~2.4 kbars, a second sample of C_3S_2 (~0.1 g) was subjected to ~1.6 kbars for 5 min; it was largely transformed to a black solid. The latter was washed with methylene chloride to remove unchanged C_3S_2, and the solid was then dried at 25° (10^{-3} mm). The ir spectrum is essentially the same as the spectrum of $(C_3S_2)_x$ polymer formed on standing or warming at atmospheric pressure. We note here that the spectrum which we obtained for $(C_3S_2)_x$ polymer differs from the results reported by Diallo and Dixmier.[4] We observe the following bands (KBr disk, cm^{-1}): 1645 (s), 1500 (sh), 1400 (s), 1250 (m), 480 (w). The first three frequencies may be assigned as ν(C=C) by analogy with the corresponding bands in the $(C_3O_2)_x$ polymer.[7] The 1250-cm^{-1} frequency is reasonable for ν(C=S). Similar bands were observed by Diallo and Dixmier, but the latter also reported strong absorptions at 1070 (doublet) and 807 cm^{-1} and weak or medium bands at 870 and 705 cm^{-1} which we do not observe. This discrepancy has not been investigated.

In summary, application of pressure (~1.2 kbars) to liquid C_3S_2 causes an initial slight temperature rise which we attribute to pressure–volume work. This is followed at ~1.5 to ~2.4 kbars by an exothermic transformation to $(C_3S_2)_x$ polymer of the same type formed at room temperature and atmospheric pressure. Finally, as the pressure is increased to ~14 kbars, there is a rapid exothermic decomposition of the $(C_3S_2)_x$ polymer to a mixture of graphite and orthorhombic sulfur.

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