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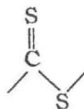
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Pressure-Induced Polymerization and Decomposition of Carbon Subulfide

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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 subulfide at atmospheric pressure and room temperature.³ This has the stoichiometry $(C_3S_2)_x$, and an infrared investigation⁴ 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 subulfide 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

- (1) P. W. Bridgman, *Proc. Amer. Acad. Arts. Sci.*, **74**, 399 (1941).
- (2) E. C. 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 $(\text{C}_3\text{S}_2)_x$: 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 $(\text{C}_3\text{S}_2)_x$ 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 $K\alpha$) 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 $(\text{C}_3\text{S}_2)_x$ 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

TABLE I
THE d_{obsd} SPACINGS (Å) AND RELATIVE INTENSITIES (Cu $K\alpha$)
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.

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.

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 $(\text{C}_3\text{S}_2)_x$ polymer formed on standing or warming at atmospheric pressure. We note here that the spectrum which we obtained for $(\text{C}_3\text{S}_2)_x$ 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 $\nu(\text{C}=\text{C})$ by analogy with the corresponding bands in the $(\text{C}_3\text{O}_2)_x$ polymer.⁷ The 1250- cm^{-1} frequency is reasonable for $\nu(\text{C}=\text{S})$. 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 $(\text{C}_3\text{S}_2)_x$ 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 $(\text{C}_3\text{S}_2)_x$ polymer to a mixture of graphite and orthorhombic sulfur.

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(6) A. Jayaraman, A. R. Hutson, J. H. McFee, A. S. Coriell, and R. G. Maines, *Rev. Sci. Instrum.*, **38**, 44 (1967).

(7) A. R. Blake, W. T. Eeles, and P. P. Jennings, *Trans. Faraday Soc.*, **60**, 691 (1964).