The calculated vapor pressures were obtained using

$$\log P_{\text{mm}} = (-1903.2/T) + 7.1490$$

The normal boiling point extrapolated from these data is 170.4°. The reported atmospheric distillation temperature is 162–163°.

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Contribution from the Division of Applied Chemistry,
National Research Council, Ottawa, Ontario, Canada

Poly(carbon diselenide)[1a]

By A. J. Brown[1b] and E. Whalley

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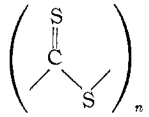
Carbon disulfide can be polymerized to a black solid at high pressures which has the structure[2]



Carbon diselenide[3] spontaneously precipitates a black solid at the rate of about 1%/month at room temperature whose structure has not been investigated. It is probably similar to that of poly(carbon disulfide), and its structure has therefore been investigated by infrared spectroscopy.

Experimental Methods and Results

The carbon diselenide was kindly supplied by Noranda Research Centre, Pointe Claire, Quebec. It was allowed to polymerize spontaneously for several months. The monomer was removed by vacuum distillation, and the solid was evacuated at 100°. Like poly(carbon disulfide) it is amorphous to X-ray diffraction.

The infrared spectra were taken as mulls in Nujol and, less satisfactorily, as dispersions in potassium bromide or polyethylene wax pellets. The frequency range 4000–50 cm^{-1} was covered with a Perkin-Elmer 301 spectrophotometer. The spectrum, with allowance for the scattering, is shown in Figure 1. There is a strong band at 885 cm^{-1} and there are weak bands at 940 and 775 cm^{-1}, all due to the polymer. In addition there is a band near 1260 cm^{-1} of variable intensity relative to the other bands, presumably caused by the ν_3 vibration of the residual monomer,[4] and weaker bands near 1460, 1355, and 1316 cm^{-1} of unknown origin. The 885-cm^{-1} band is too strong relative to the 1260-cm^{-1} band for it to be associated with the 925-cm^{-1} band[4] of the monomer.

The thermodynamics of polymerization of carbon disulfide and diselenide are of some interest. It has been reported[5] that carbon and sulfur will react at 37 kbars and 800° to give poly(carbon disulfide). This seems unlikely to be correct on thermodynamic grounds (see Discussion) and several attempts to repeat this observation have failed, in agreement with observations reported by Butcher, Weston, and Gebbie.[6]

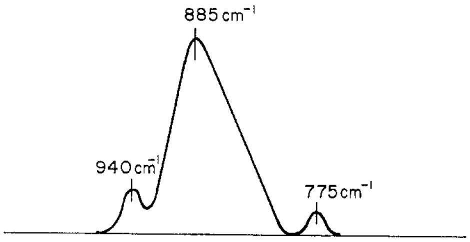
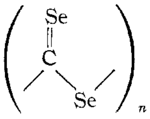


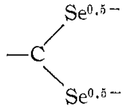
Figure 1. Infrared spectrum of poly(carbon diselenide).

Discussion

Poly(carbon disulfide) has a strong absorption at 1062 cm^{-1},[2] which is due to the C=S stretching vibration. If black carbon diselenide has an analogous structure, a strong infrared band due to the C=Se stretching vibration would be expected in the region 800–900 cm^{-1}. The 885-cm^{-1} band can probably be associated with this vibration. It seems very likely therefore that black carbon diselenide has essentially the structure



and is thus poly(carbon diselenide). Diselenocarboxylate ions, which contain the unit



have strong bands in this region.[7] Furthermore, the frequency ratio of the asymmetric stretching band of the monomer (1270 cm^{-1})[4] to the strong band of the polymer is 1.44 for carbon diselenide and 1.437 for carbon disulfide,[2] which provides further evidence for the assignment. The 775-cm^{-1} band can perhaps be associated with the C–Se stretching motion. Minor departures from the proposed structure would of course not be detectable by the techniques used and could cause some of the unassigned bands. Since the polymerization proceeds spontaneously at room temperature, the stable form of carbon diselenide is not the triatomic molecule but the polymer.

The thermodynamic relations between the monomer, the polymer, and the elements of both carbon disulfide and carbon diselenide are of some interest. Liquid carbon disulfide at room temperature is unstable relative to the elements by 15 kcal mol^{-1} in the Gibbs energy.[8] Carbon disulfide can be polymerized at pressures as

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[1] (a) NRC No. 10160; (b) NRC Postdoctoral Fellow, 1963–1965.

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low as 30 kbars,[9,10] and consequently at this pressure the polymer is stable relative to the monomer; that is, the pressure is above the polymerization pressure[11] for the monomer–polymer equilibrium. The volume of polymerization of carbon disulfide at 1 bar is about -20 cm^3 mol^{-1} according to the reported densities of the polymer.[9,12] In the range 0–30,000 kg cm^{-2} carbon disulfide compresses[11,13] over 20 cm^3 mol^{-1}, most of which occurs[13] in the first 5000 kg cm^{-2}, and the compressibility of the polymer is undoubtedly much less. If it is assumed that the volume of polymerization averages -10 cm^3 mol^{-1} in the range 0–30 kbars, which seems an upper limit to the decrease, then the polymer is not more than 7 kcal mol^{-1} of Gibbs energy unstable relative to the monomer of 1 atm. The difference in volume between the elements and the polymer is small,[9,12] so the pressure should have little effect on the Gibbs energy change between the elements and the polymer. It follows from this that the polymer must be unstable relative to the elements by well over 15 kcal mol^{-1} in the Gibbs energy over a wide pressure range. The failure of carbon and sulfur to react to give the polymer is therefore not unexpected.

Somewhat similar arguments apply to carbon diselenide. As carbon diselenide is less stable relative to the elements than carbon disulfide,[8] it is even less likely that the reaction of carbon and selenium will yield the polymer. Carbon ditelluride will be even less stable relative to the elements, and this is probably a partial explanation of why it has never been prepared. In addition, it should polymerize readily.

The polymerization of carbon disulfide is irreversible in the sense that once the polymer is formed it is not reported to depolymerize. In principle, the monomer–polymer equilibrium is undoubtedly mobile. It appears that an appreciable rate is obtained only well above the polymerization pressure.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
AND CHEMICAL ENGINEERING,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Bismuth Iodide Complexes in Aqueous Solution of High Iodide Concentration

BY G. P. HAIGHT, JR., AND L. JOHANSSON

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The bismuth iodide system has been investigated earlier using potentiometric and solubility measurements by Ahrland and Grenthe.[1] They established a maximum coordination number $N = 6$ for $[I^-] \leq 0.5\ M$. Eve and Hume[2] studied the system spectrophotometrically and found, at $0.4\ M \leq [I^-] \leq 1.4\ M$, a change in the ultraviolet and visible spectra, which they attributed to the partial formation of BiI_7^{4-}.

Dyrssen[3] has performed a study of the solubility of BiI_3 and BiOI and suggests that $Bi_2I_9^{3-}$ is formed besides the mononuclear complexes. The arguments for $Bi_2I_9^{3-}$ are not very strong, however,[4] and this complex is probably only formed (if at all) at bismuth concentrations higher than those employed in this study and in that of Eve and Hume.[2]

Recent studies[5] have indicated the formation of $BiBr_8^{5-}$ in solutions of bismuth bromide in HBr[5e] and of SnI_8^{6-} in tin(II) iodide[5g] systems, in both cases without the intermediate formation of any MX_7^{n-7} complex. This prompted us to consider the possibility that the results of Eve and Hume could be interpreted as a formation of BiI_8^{5-} instead of BiI_7^{4-}.

Our primary aim was, however, to investigate the usefulness of a new kind of solubility technique on this system. Previously, we have used salts with three different ions to study various complex systems,[5] *e.g.*, $[(CH_3)_4N]_2SnI_4$(s) on the tin(II) iodide system.[5g] It was then noted that if the solutions were simultaneously saturated also with the ligand salt of the third ion, the results would be particularly easy to interpret.

For the bismuth iodide system, $Co(NH_3)_6BiI_6$(s) was chosen as the three-ion salt.[6] The second salt, $Co(NH_3)_6I_3$(s), has a very low solubility at high $[I^-]$. Therefore, at high $[I^-]$, $Co(NH_3)_6BiI_6$(s) is partly converted to $Co(NH_3)_6I_3$(s) and solutions become saturated with both salts. This establishes the equilibrium

$$Co(NH_3)_6BiI_6 + nI^- \rightleftarrows Co(NH_3)_6I_3 + BiI_{3+n}{}^{n-} \qquad (I)$$

The method works even if the solubility of the second salt is higher than that of the first one, provided enough of the second salt is added initially. It will be shown below that the mixture acts, in part, as if BiI_3(s) were present alone. We shall designate [Bi(III)] as the "solubility" of the solid phase. Thus, the slope of a logarithmic plot of the solubility (the total bismuth concentration) *vs.* $[I^-]$ is simply $\bar{n} - 3$. However, for any $[I^-]$ the solubility over the mixture is necessarily lower than that of BiI_3(s); otherwise the double salt would not be formed. While the actual solubility of BiI_3(s) is far too high[1] at $[I^-] \geq 1\ M$, the solubility over the mixture is low enough for convenient mea-

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