203. *The Preparation, Properties, and Chlorination Products of Carbon Diselenide.*

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The action of methylene chloride vapour on heated selenium readily provides a good yield of carbon diselenide, which thus becomes accessible in considerable quantities for the first time. The vapour pressure of pure carbon diselenide has been measured over a range of temperatures and its behaviour with various reagents and solvents has been given preliminary study. It reacts vigorously with chlorine, giving a variety of products, of which selenium tetrachloride, *perchloromethylselenol, hexachlorodimethyl selenide* and *diselenide* have been isolated and characterised. Attempts to prepare selenocarbonyl chloride have not been successful.

THE only practical method hitherto available for the preparation of carbon diselenide depends on the interaction of hydrogen selenide with carbon tetrachloride in a hot tube (Grimm and Metzger, *Ber.*, 1936, **69**, 1356), but, contrary to the statement of these authors, this has been found to give an exceedingly poor yield of diselenide dissolved in excess of carbon tetrachloride, with which it forms an azeotrope. It has been found that methylene chloride vapour reacts with molten selenium with copious production of carbon diselenide, which has thus been prepared in the pure state in considerable quantities. It possesses interesting physical and chemical properties and presents a number of chemical problems which call for further investigation.

Methylene chloride vapour, carried in a stream of nitrogen, begins to react with molten selenium at 500° and produces carbon diselenide smoothly and rapidly at 550—600°. The deposition of carbon in the reaction zone tends to slow down and eventually stop the reaction, but this can be avoided by arranging for the supply of selenium in small quantities at a time to the reaction system. Copious evolution of hydrogen chloride occurs and some selenium is lost as a red, particulate cloud carried over in the gas stream : this difficulty may be partly obviated by the use of a fractionating column kept at about 200°. In a laboratory apparatus designed to meet these difficulties, the best yield of pure diselenide was 52% of the selenium used, without allowance for the considerable amounts of the element which should be easily recoverable from the reaction residues. In the routine preparation, however, a simpler apparatus giving a rather lower yield was found to be advantageous. Attempts to carry out the reaction solely in the vapour phase were unsuccessful, and the impression was gained that it occurs on the surface of liquid selenium.

Other hot-tube experiments of similar type gave no significant results. Methylene chloride gave no carbon disulphide with sulphur at 420° : carbonisation occurred and small amounts of hydrogen sulphide and hydrogen chloride were produced. No carbon sulphoselenide was formed by the interaction of methylene chloride with a mixture of selenium and ferrous sulphide at 425—560°, or by the action of methylene chloride and sulphur vapours on selenium at 500° : small amounts of carbon diselenide were produced in each case. Carbon ditelluride was not produced by the action of methylene chloride on tellurium at 450—680°. Methyl chloride with selenium at 400—550°, in addition to hydrogen selenide and hydrogen chloride, gave traces of a foul-smelling, lachrymatory, yellow liquid, which appeared to be different from carbon diselenide, but was not obtained in amount sufficient for characterisation.

Crude carbon diselenide was readily purified by distillation in steam, followed by distillation under either atmospheric or reduced pressure. It is a bright yellow, non-inflammable, highly refractive liquid (Grimm and Metzger, *loc. cit.*, report $n_D^{20°}$ 1·845) which does not wet glass. It has an intolerable odour, causes nose and lung irritation and lachrymation, and has a slight irritant action on the skin. On standing, it darkens, becoming brown, then black and deposits dark polymerisation products : loss of material due to this amounts to about 1% per month. The following physical properties were determined, values in parentheses being those previously recorded by Grimm and Metzger (*loc. cit.*) : b. p. 125—126°/760 mm. (124°/760 mm.), m. p. (pentane thermometer) — 40° to — 45° (— 45·5°), $d_{4°}^{20°}$ 2·6824 (2·679), $d_{4°}^{25°}$ 2·6626. Vapour pressures of the pure diselenide were determined, using a " spoon guage " incorporated in a high-vacuum apparatus, care being taken to ensure the complete " outgassing " of the sample used and to avoid any possibility of decomposition of vapour during the usual sealing-off procedure. Manometric readings were corrected to 0°, sea-level, and latitude 45°. The results are shown in the table, together with vapour pressures calculated from the equation $\log_{10} P$ (mm.) = 7·9153 — 1987·4/T, where T is the absolute temperature.

Temp.	0·00°	5·07°	10·07°	15·07°	20·07°	25·06°	30·04°	35·04°	40·02°	50·01°
$P_{\text{obs.}}$, mm.	4·7	5·7	7·7	10·4	13·6	17·9	23·3	29·6	37·0	58·2
$P_{\text{calc.}}$, mm.	4·4	5·9	7·9	10·4	13·7	17·8	22·9	29·3	37·1	58·3

It will be seen that the vapour-pressure equation fits the experimental points with a mean deviation of ± 0·2 mm. and leads to an average latent heat of evaporation over this temperature range of 9092 cals./mole. Comparison with carbon disulphide has been made by Othmer's method (*Ind. Eng. Chem.*, 1940, **32**, 841), leading to an approximate latent heat of evaporation at the b. p. of 7855 cals./mole and an entropy of evaporation of 19·7 cals./deg./mole. Hildebrand's constant has been calculated as 28·5 (cf. carbon disulphide, 27·1).

Various observations have been made of the behaviour of carbon diselenide with solvents and reagents, in addition to those already recorded by Grimm and Metzger (*loc. cit.*). It is completely miscible with carbon tetrachloride, with which it forms a constant-boiling mixture containing about 40% of the latter; it is also miscible in all proportions with carbon disulphide and toluene. These solvents appear to retard the polymerisation of the selenide. It is readily soluble in light petroleum (b. p. 60—80°), but in this case the polymerisation does not appear to be retarded. Medicinal paraffin dissolves carbon diselenide to about 25% by volume and the components show an upper critical solution temperature. The diselenide is very sparingly soluble in glacial acetic acid and also in ethanol, which appears to promote decomposition. It is insoluble in water and appears to suffer loss of stability under moist conditions: the upper aqueous layer rapidly becomes turbid. White phosphorus dissolves to a very large extent. Selenium oxychloride reacts violently with carbon diselenide, much elementary selenium being deposited with liberation of unidentified volatile products. Selenium monochloride reacts briskly after a period of induction, giving selenium and a volatile product of intolerable odour. Bromine reacts with a " quenching " sound, giving a clear red liquid which deposits a dark brown solid on standing. Dry hydrogen chloride has no apparent reaction and neither has the concentrated aqueous acid, from which the diselenide steam-distils on boiling. Concentrated nitric acid has little action in the cold, but destroys the diselenide on boiling, although the compound distils in the vapour of the boiling acid for a considerable time. Concentrated sulphuric acid has a more rapid action, but again unchanged selenide can be distilled from admixture for some time. Oleum produces rapid decomposition. Concentrated aqueous sodium hydroxide has little action in the cold, but dissolves carbon diselenide on heating, giving an orange solution. Alcoholic potash dissolves and destroys the diselenide rapidly and affords the best means of decontaminating apparatus which has contained it. Dry bleaching powder produces a vigorous exothermic reaction accompanied by the evolution of most aggressive vapours. It is apparent that there is a wide field of investigation still open in the chemistry of carbon diselenide, but the only reaction which opportunity has allowed us to study is that with chorine.

Chlorine is absorbed rapidly in large amounts by carbon diselenide, with evolution of much heat. A great variety of interesting products appears to be formed: bright red and yellow solids, white red and black sublimates, red, yellow, and green liquids. Some of these are very unstable; a yellow solid deliquescing rapidly in air, with evolution of pink fumes, provides a striking example. Simplification of this complex reaction was achieved by carrying out chlorination in carbon tetrachloride, in which selenium tetrachloride is sparingly soluble, removal of the latter product by filtration, removal of carbon tetrachloride by distillation, rapid washing of the residue with water, and high-vacuum distillation. Four products were thus characterised with reasonable certainty, the chief of which was selenium tetrachloride. The others were *perchloromethylselenol*, $CCl_3{\cdot}SeCl$, a deep red liquid, b. p. 62°/23 mm., with a biting odour, fuming in air and hydrolysing fairly rapidly with water. *Hexachlorodimethyl selenide*, $(CCl_3)_2Se$, was obtained in small amount. It is a white, crystalline solid, m. p. 37°, with an odour resembling that of hexachloroethane. It is soluble in benzene and carbon tetrachloride, and is intermediate in volatility between the above selenol and *hexachlorodimethyl diselenide*, which was obtained in very small yield as a yellow oil, b. p. 126°/0·5 mm., with a camphoraceous odour and an irritant action on the skin. Further treatment with chlorine appears to convert the diselenide into the selenol and selenium tetrachloride.

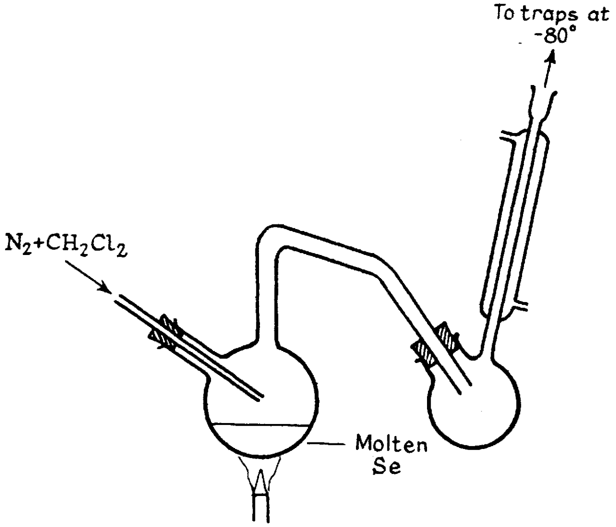
It is remarkable that no success was achieved in obtaining selenocarbonyl chloride as a product of this chlorination reaction, and although high volatility would not be expected in this compound, it is noteworthy that a volatile selenium compound with a most aggressive and quite intolerable odour has been produced in a number of ways which might conceivably lead to this compound. Such a substance was present in the carbon tetrachloride distilled from the carbon diselenide chlorination mixture, was produced by the interaction of selenium monochloride with carbon diselenide and by the reaction of the latter with dry bleaching powder, and also by the reduction of perchloromethylselenol with anhydrous stannous chloride in carbon tetrachloride solution. The chlorination of selenoformaldehyde was also attempted as a source of selenocarbonyl chloride, but other products, not yet investigated, were produced in this reaction.

It is clear that much work remains to be done in this interesting field of selenium chemistry, but it is attended by the disadvantage of the rather toxic and highly disgusting nature of the products obtained.

EXPERIMENTAL.

Carbon Diselenide.—Various experimental conditions and types of apparatus indicated the desirability of removing the reaction products as rapidly as possible from the zone of reaction between methylene chloride and molten selenium in order to minimise the deposition of carbon. Too high a temperature and too extensive a heated zone were also to be avoided from this point of view. These requirements, and the desirability of a reasonable production rate, made unavoidable the loss of considerable amounts of selenium in the form of red smoke, which could ultimately, however, be recovered. The simplest satisfactory apparatus consisted of a Pyrex retort, delivering into a receiver, as indicated in the figure. Methylene chloride vapour, provided by a vessel containing the liquid maintained at a suitable fixed temperature, was delivered above the surface of molten selenium in a stream of dry nitrogen. The crude product was steam-distilled directly from the receiver, separated from the aqueous layer, dried ($CaCl_2$), and, for purposes of the physical measurements, fractionated through a 30-cm. vacuum-jacketed Dufton column under reduced pressure (b. p. 46°/50 mm.) (Found: Se, by combustion, 92·77; by Kjeldahl, 92·96. Calc. for CSe_2: Se, 92·93%).

Chlorination of Carbon Diselenide.—Preliminary attempts at separation of the products of reaction indicated the importance of analyses for selenium and chlorine at frequent intervals. The most rapid and satisfactory methods were found to be as follows: for selenium, digestion with oleum and perhydrol (Kjeldahl), followed by dilution, reduction with sulphur dioxide and then with hydroxylamine hydrochloride, and gravimetric estimation as elementary selenium; for chlorine, treatment with sodium in liquid ammonia, followed, after evaporation of ammonia, by treatment with alcohol, boiling with dilute sulphuric acid, treatment with sulphur dioxide, further boiling, filtration, and precipitation with silver nitrate in the usual way.



The course of a chlorination experiment was as follows. Carbon diselenide (50 g.), dissolved in carbon tetrachloride (300 c.c.) in a 1-l. flask fitted with a mechanical stirrer and reflux condenser, was treated with dry chlorine until an increase in weight of 81 g. was reached (approx. 4 moles of Cl_2). A large precipitate of whitish solid was produced, together with red and yellow sublimates. The reaction mixture was set aside for two days, and darkening occurred. The solid was removed by filtration, washed at the pump with carbon tetrachloride, and proved to be selenium tetrachloride (Found: Se, 35·9; Cl, 64·0. Calc. for $SeCl_4$: Se, 35·8; Cl, 64·2%). The filtrate was carefully fractionated, a vacuum-jacketed Dufton column being used with controlled reflux-ratio head. The first distillate, consisting mainly of carbon tetrachloride, was yellow-brown, contained considerable amounts of selenium, and had an intolerable odour reminiscent of carbonyl chloride, but no definite compound could be isolated from it. The residue from this fraction was completely distilled at 200 mm. The second distillate was shaken with water, separated, dried ($CaCl_2$), and redistilled in vacuum. The first fraction consisted of *perchloromethylselenol* (17 g.), b. p. 62°/23 mm. (Found: Se, 33·75; Cl, 60·7; *M*, cryoscopic, in C_6H_6, 247. $CCl_3{\cdot}SeCl$ requires Se, 33·9; Cl, 60·9%; *M*, 233). Further distillation yielded a pale yellow oil which solidified in the condenser. This and the residue in the distillation flask were removed and examined separately. The liquid residue was removed to a smaller apparatus and redistilled (b. p. 124—129°/2 mm.). Admission of air to the apparatus caused oxidation, with production of green and red substances. In view of this difficulty and the low volatility of the substance, redistillation was effected in a high vacuum. A small homogeneous fraction consisting of *hexachlorodimethyl diselenide* was obtained (Found: Se, 40·2; Cl, 53·8; *M*, cryoscopic in C_6H_6, 392. $C_2Cl_6Se_2$ requires Se, 40·0; Cl, 53·9%; *M*, 395). The solid condensate from the previous distillation was recovered by dissolving in carbon tetrachloride. The solvent was removed, and the residue sublimed in a high vacuum, giving a small yield of *hexachlorodimethyl selenide* (Found: Se, 25·3; Cl, 67·4; *M*, cryoscopic in C_6H_6, 317. C_2Cl_6Se requires Se, 25·0; Cl, 67·4%; *M*, 316).

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