X.—*Carbon Sulphidoselenide.*

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IN the course of attempts to prepare carbon diselenide, carbon disulphide was passed over heated ferrous selenide, in the hope that a complete replacement of sulphur by selenium would occur. Although this has not been realised, a partial replacement occurs whereby some of the carbon disulphide is converted into carbon sulphidoselenide, CSSe.

Our knowledge of this interesting compound has rested hitherto entirely on the work of Stock and Willfroth (*Ber.*, 1914, **47**, 144), who prepared it by striking an arc under liquid carbon disulphide between poles of carbon containing selenium. We have, therefore, prepared a quantity of this substance by the new method here described, purified it carefully, and investigated further both its physical properties and some of its chemical reactions. Besides redetermining some of the physical constants given by Stock and Willfroth, whose data we are able generally to confirm, we have determined for the first time the coefficient of expansion, the vapour density, and the surface tension.

Little was known of the chemical properties of carbon sulphidoselenide. The data here recorded afford evidence that, though it is markedly less stable than carbon disulphide, it is similarly constituted. Attempts to prepare analogues of the thiocarbonates have failed, but *compounds* of carbon sulphidoselenide with phenylhydrazine and with aniline have been obtained. Under certain conditions the reaction of the sulphidoselenide with ammonia yields compounds which appear to be highly polymerised and are difficult to characterise.

Other attempts to prepare carbon diselenide by striking arcs between carbon rods both in hydrogen selenide and in selenium vapour or between a compressed mixture of carbon and selenium were unsuccessful.

EXPERIMENTAL.

Preparation.—Ferrous selenide, prepared by heating the elements together, was packed into an inclined silica tube 22″ long and 2″ in diameter, electrically heated to 650°. The upper end of the tube carried a tap funnel with drop indicator, from which carbon disulphide was delivered at the rate of about 1 litre in 12 hours : the lower end of the tube was connected to a condenser. The condensate, on fractionation through a 50-inch, bead-filled, glass column, left about 0·5% of a deep yellow liquid as residue. This, when sufficient had been collected, was again repeatedly fractionated through the same column and thus yielded a middle fraction of pure carbon sulphidoselenide (Found : C, 9·7 ; S, 26·8 ; Se, 63·4. Calc. : C, 9·8 ; S, 26·0 ; Se, 64·2%).

Physical Properties.—Carbon sulphidoselenide is a deep yellow liquid, b. p. 83·90—83·95°/749·2 mm. ; it is oily and moderately viscous and only partly wets glass. By the use of glass Ostwald–Sprengel pyknometers of about 10 c.c. capacity, the following values of the density at various temperatures were obtained : $d_{4°}^{20°}$ =

1·9874; $d_{4^\circ}^{25^\circ} = 1{\cdot}9777$; $d_{4^\circ}^{30^\circ} = 1{\cdot}9678$; $d_{4^\circ}^{40^\circ} = 1{\cdot}9484$ (compare $d_{4^\circ}^{20^\circ} = 1{\cdot}979$, recorded by Stock and Willfroth, *loc. cit.*); hence the mean coefficient of cubical expansion over the range 20—40° is $3\alpha = 0{\cdot}000996$.

The vapour density, determined by Dumas's method in glass bulbs of about 150 c.c. capacity, was 129·2, 129·3, and 126·1, at 100°, 150°, and 200°, respectively (Calc. : 123·2).

These results were confirmed by cryoscopic determinations of the molecular weight, which gave 128·7 in benzene and 135·7 in bromoform solutions.

Owing to the reluctance of carbon sulphidoselenide to wet glass, attempts to determine its surface tension by the method of capillary rise were quite inconclusive. With the same sample at the same temperature (20°), the difference in height of the liquid in the same two capillary tubes at different settings varied between 5·84 mm. and 8·02 mm., and the maximum value given by this method was $\gamma = 39{\cdot}70$ dynes per cm., which must be regarded as low. On the other hand, the method of maximum bubble pressure gave constant and reproducible results : $\gamma = 40{\cdot}44$ dynes per cm. at 20°, whence the molecular parachor $M\gamma^{\frac{1}{4}}/D = 156{\cdot}4$. Deducting from this value the parachors of carbon (4·8), sulphur (46·5), and of two double bonds ($2 \times 23{\cdot}2$), we obtain 58·7 as the parachor of selenium. This value is rather lower than that found for the element in selenophen (Briscoe and Peel, J., 1928, 1741) but clearly indicates that carbon sulphidoselenide has the constitution Se=C=S.

Chemical Properties.—The vapour of carbon sulphidoselenide is lachrymatory and causes violent irritation of the nasal mucous membrane; when largely diluted with air it has a disgusting odour. Stock and Willfroth reported that the liquid decomposed on exposure to sunlight and on keeping, but we have found that, although it appears to be slightly affected by sunlight, it remains entirely unchanged on being kept in the dark. This difference in stability suggests that our product may be rather purer than that obtained by Stock and Willfroth, and this may explain the slight difference in density (*vide supra*).

Carbon sulphidoselenide is immiscible with water, but freely soluble without decomposition in ethyl alcohol, benzene, bromoform, acetone, and other organic solvents. Sulphur is very sparingly soluble and selenium is insoluble in the liquid. In marked contrast with carbon disulphide, the liquid sulphidoselenide is non-inflammable, but when warmed its vapour burns with the intense blue flame typical of selenium compounds. At the ordinary temperature it does not react with hydrogen sulphide or hydrogen selenide, but it is readily reduced by zinc and hydrochloric acid to yield these gases.

In contact with saturated aqueous ammonia, after several hours at 15° or in a few minutes at 80°, carbon sulphidoselenide yields a yellow solid which, being insoluble in all solvents and decomposing on heating, could not be purified. Various preparations, washed with water, alcohol, and ether, and dried on a porous plate, gave S from 5·5—10·7% and Se from 52—70%, and on boiling with caustic soda, dissolved completely with evolution of ammonia. The material was slowly but wholly soluble in boiling aqueous ammonia, yielding a blood-red solution, which, when poured into hydrochloric acid, evolved hydrogen sulphide and deposited an orange-red gelatinous precipitate. This precipitate, after being washed with water, alcohol, and ether, and dried, gave Se from 61·4—91·1%, contained no sulphur, easily decomposed on heating, and was insoluble. Attempts to prepare compounds analogous to the thiocarbonates by interaction of the sulphidoselenide with aqueous sodium sulphide, ammonium polysulphides, or caustic soda gave only blood-red solutions from which no crystalline product could be obtained; these solutions when acidified gave similar gelatinous precipitates.

The action of gaseous ammonia on a solution of carbon sulphidoselenide in absolute alcohol produced a considerable rise of temperature and yielded a blood-red solution from which a red amorphous solid was later suddenly precipitated. After being washed with alcohol and ether and dried on porous tile, this product was obtained as a fine brick-red powder containing neither sulphur nor nitrogen; it decomposed on heating, was insoluble in all solvents, and was not attacked by caustic soda solution (Found : Se, 86·9, 88·9, 88·0, 90·0 in various samples; C, 5·6; H, 1·9% in one sample).

In absolute alcohol carbon sulphidoselenide and phenylhydrazine react with evolution of heat, and after about an hour light greenish-yellow, tabular crystals separate. After being washed with alcohol and ether and dried on porous tile, these melt at 98° on rapid heating, but are unstable and on keeping become first brown and later black, with separation of selenium [Found : S, 8·8; C, 41·4; H, 4·25; N, 15·1; Se, 23·7. $(C_6H_5\cdot NH\cdot NH_2)_2,CSSe$ requires S, 9·4; C, 46·0; H, 4·7; N, 16·5; Se, 23·3%]. This *compound*, therefore, appears to be analogous to that formed by phenylhydrazine and carbon disulphide (Fischer, *Annalen*, 1877, **190**, 114).

Carbon sulphidoselenide, dissolved in alcohol, was treated with aniline in the same solvent and kept for 2 days, during which period there was a continuous evolution of the hydrides of sulphur and selenium. The precipitate of fine, white, crystalline plates, mixed with a little grey selenium, was filtered off, washed with alcohol and ether, and extracted with cold acetone. The extract on evaporation under reduced pressure yielded fine white plates, m. p. 164° [Found : C, 61·1 ; H, 4·8 ; N, 11·2 ; S, 6·75. $(C_6H_5{\cdot}NH)_4CSSe$ requires C, 61·1; H, 4·9; N, 11·4; S, 6·5%]. The *compound*, which is more stable in air than the phenylhydrazine derivative, is not analogous to the product formed by aniline and carbon disulphide, *viz*., $(NHPh)_2CS$ (Losanitsch, *Ber*., 1891, **24**, 3021).

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