CCXXIV.—*The Preparation and Properties of Selenophen and Certain Halogen Derivatives of Selenophen.*

By HENRY VINCENT AIRD BRISCOE and JOHN BUTTERY PEEL.

ALTHOUGH the analogy between sulphur and selenium is well defined and thiophen is an interesting and important compound, its selenium analogue, *selenophen*, has hitherto been unknown to chemists. Relatively complex derivatives of selenophen, such as dimethylselenophen (Paal, *Ber.*, 1885, **18**, 2255), have been described and one investigator (Foa, *Gazzetta*, 1909, **39**, ii, 527) has stated that selenophen is obtained in small yield by heating together sodium succinate and phosphorus triselenide; but the product of this reaction, described as an unstable yellow liquid, b. p. 147—149°/250 mm., and but slightly soluble in alcohol, differs so seriously from the substance we have prepared (*vide infra*) as to lead us to believe that Foa's observations are untrustworthy.

During attempts to prepare certain simple selenium compounds we found that the action of acetylene upon selenium at moderately high temperatures produced a mixture of substances, liquid at the ordinary temperature, from which selenophen could be isolated. The present communication describes the preparation of selenophen and records data for its b. p., m. p., density, thermal expansion, vapour density, molecular weight, surface tension, and refractive index, its salient chemical properties, and the preparation and properties of tetrabromoselenophen and tetrachloroselenophen.

The Preparation and Identification of Selenophen.—Although the action of acetylene on selenium has not previously been investigated, there are references in the literature to the analogous action of acetylene on sulphur. Meyer and Sandmeyer (*Ber.*, 1883, **16**, 2176) have reported that thiophen is thus produced, and Capelle (*Bull. Soc. chim.*, 1908, **4**, 150) states that the product is thiophten. Work now in progress in these laboratories, however, affords conclusive proof that appreciable quantities of thiophen can be produced from acetylene and sulphur.

The reaction between acetylene and selenium was carried out in a silica tube 22″ long and of 1½″ bore, heated over a length of 9″ by a suitable winding of nichrome wire lagged with alundum cement and asbestos millboard. The tube was slightly inclined and a glass adapter at the lower end led the volatile products into a vertical test-tube immersed in a cooling bath, whence uncondensed gases were led by a tube to the flue. Selenium, in lots of about 10 g., contained in a large porcelain boat, was placed in the heated portion of the tube, the temperature being held at about 400° by adjustment of a rheostat in series with the furnace winding. Acetylene, taken from a cylinder of dissolved acetylene, was led through concentrated sulphuric acid in a bubbler and a drying-tube charged with phosphoric oxide, into the upper end of the furnace tube. At first no evidence of reaction was perceived, but after several hours hydrogen selenide was evolved and a dark brown oil began to condense in the receiver : in 24 hours about 15 c.c. of the oil were obtained. The tube, when opened, contained a black solid deposit at the lower end and, as in subsequent experiments the production of the brown oil began as soon as the tube attained the proper temperature, it seems probable that its formation is catalytically assisted by the black deposit. This point, however, is obscure.

A quantity of the brown oil, collected in a series of experiments, was fractionally distilled at a pressure of about 30—40 mm. and yielded the following fractions :

(i) A yellow liquid, collected up to 90°.
(ii) A yellow solid, collected at 95—135°.
(iii) A yellow-brown liquid, collected at 135—200°.
(iv) A dark brown residue.

Fraction (ii), after several recrystallisations from hot methyl alcohol, was white and proved to be naphthalene, m. p. 79·5°, mixed m. p. with naphthalene 80°. By a series of fractional distillations and crystallisations other solid products were obtained from the residues of fraction (ii) and fractions (iii) and (iv), among them anthracene, phenanthrene, and a bright yellow crystalline solid, m. p. 124°, which was probably either stilbene or distyrene. None of the higher fractions contained more than traces of selenium.

The low-boiling liquid, fraction (i), burned in an open dish with a bluish-white flame, a considerable amount of selenium being deposited. It was therefore submitted to a systematic fractional distillation at atmospheric pressure. In the first distillation, using an 18″ glass spiral column, the first fraction, collected between 79—90°, contained only a trace of selenium and consisted largely of benzene, but the greater part distilled between 104—110° and was evidently a selenium compound. This was twice fractionated, a well-lagged 48″ column packed with 4 mm. cylindrical glass beads being used, and yielded a final main fraction, b. p. 109·9—110·1°/752·1 mm. The liquid was finally purified by fractional solidification; it was thrice frozen partially in a bath of alcohol cooled with solid carbon dioxide, and the liquid portions were rejected. About 15% of the original oil was thus obtained as a pale lemon-yellow liquid, f. p. —38°, mobile, dense, and highly refractive, and having a slight odour, not unpleasant, resembling both that of carbon disulphide and that of benzene: it burned in air with a bright blue flame, from which selenium was deposited on a cold surface. Subsequent experiments showed that the yellow colour was due to a minute trace of impurity, and that the liquid was really colourless.

To estimate selenium in the product, it was oxidised with concentrated nitric acid in a sealed tube at 200°, the contents of the tube were evaporated with excess of concentrated hydrochloric acid, the solution was boiled with sulphurous acid, and the precipitated elementary selenium was collected and weighed in the usual way. This method gives poor results but is the only one available. Carbon and hydrogen were determined by combustion in the usual way in a tube packed with copper oxide and lead chromate (Found: Se, 59·4, 58·2; C, 37·1, 37·5; H, 3·3, 3·3. C_4H_4Se requires Se, 60·3; C, 36·6; H, 3·05%).

The vapour density of the substance was determined by the Dumas method with a glass bulb heated in liquid paraffin or glycerol:

Temperature	140°	150°	200°
Barometric pressure (mm. Hg)	737·6	760·0	760·1
Volume of bulb (c.c.)	139·28	174·04	135·84
Weight of selenophen (g.)	0·5341	0·6710	0·4659
Molecular weight	133·9	134·0	133·0

The calculated value for C_4H_4Se is 131·2. The V.D. determinations were confirmed by two cryoscopic determinations of the molecular weight in benzene and bromoform. The former value is a little high, probably because a solid solution of selenophen in benzene crystallises out.

	Benzene as solvent.	Bromoform as solvent.
Weight of selenophen (g.)	0·4948	0·8282
Weight of solvent (g.)	17·91	56·80
Depression of freezing point	0·900°	1·580°
Molecular weight	156·0	132·2

The Physical Properties of Selenophen.—Using the Hofmann apparatus, with water in the jacket, determinations of the vapour pressure of selenophen were made over the range 25—85° and are recorded in Table I.

TABLE I.

Temp.	25°	30°	35°	38°	40°	43°	45°
Vap. press. (mm. Hg. at 0°)	46·5	55	66	74	78·5	87	94
Temp.	48°	50°	55°	58°	60°	65°	68°
Vap. press. (mm. Hg. at 0°)	104	112	131	146	156·5	185·5	206
Temp.	70°	73°	75°	77°	80°	83°	85°
Vap. press. (mm. Hg. at 0°)	221	243	259	277	305·5	335·5	356

Fig. 1 gives the vapour-pressure curve derived from these data and also the relationship of log P–T^{-1}, which is substantially linear.

The latter curve, extrapolated to 760 mm. pressure, gives a value (108°) for the boiling point in reasonable agreement with that observed in the distillation of selenophen.

Determinations of density were made over the range 15—50° in glass Sprengel pyknometers of 10 c.c. capacity, fitted with ground glass stoppers and weighed against a tare. At each temperature of observation the pyknometer was filled with water and weighed and then filled with selenophen and weighed, the densities of selenophen and water at each of the six selected temperatures thus being directly compared. The data, recorded in Table II, show that the coefficient of expansion of the liquid is 3α (15—30°) = 0·001040, 3α (30—50°) = 0·001040, and 3α (15—50°) = 0·001045.

FIG. 1.

Vapour pressure of selenophen.

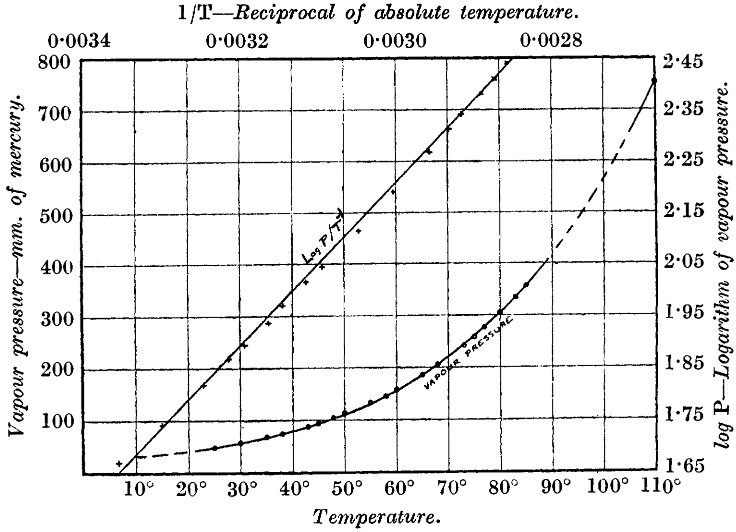

TABLE II.

Temp.	15·00°	20·00°	25·00°	30·00°	40·00°	50·00°
Density (g./c.c.)	1·5307	1·5232	1·5156	1·5078	1·4943	1·4763

The refractive index ($n_D^{15°}$) determined with a Pulfrich refractometer was 1·568.

The surface tension of selenophen was determined by Sugden's method, two especially good capillaries, calibrated by Dr. Robinson and Mr. Mills and kindly lent by them for this purpose, being used.

The radii of the tubes being respectively 0·25287 mm. and 0·49920 mm., the following data were obtained :

Temperature	15°	20°	25°
Difference in capillary rise (mm.)	9·56	9·44	9·30
Surface tension (dynes/cm.)	36·49	35·83	35·14
Parachor ($\gamma^{\frac{1}{4}}M/D$)	210·6	210·8	210·5

Dr. Sugden has very kindly made check determinations of the parachor, with the following results :

Temperature	17·5°	28·5°	33·5°	42°
D (g./c.c.)	1·501	1·485	1·476	1·464
γ (dynes/cm.)	35·63	34·28	33·31	32·32
Parachor	213·8	213·9	213·7	213·8

Unfortunately the sample of selenophen available for his measurements was less highly purified than that we had used : nevertheless his data serve to confirm the general nature of our results.

In the Eötvös–Ramsay–Shields' equation $(M/d)^{2/3}\gamma = K(T_c - T_0)$ the value of K is about 2·1, which may be held either to confirm the molecular weight deduced above or to show that selenophen is a " normal " liquid.

Assuming selenophen to have the constitution  $\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}\!>\!\mathrm{Se}$, by deducting from its observed parachor (210·5), 4·8 for 4C, 17·1 for 4H, 23·2 for two double bonds, and 8·5 for one five-membered ring (total 142·5), we obtain for selenium the parachor 68·0. This value is in fair agreement with the value 64 obtained by Dr. Sugden (private communication) in a study of several other selenium compounds.

Chemical Properties of Selenophen.—Selenophen is insoluble in water, but is miscible in all proportions with a number of non-aqueous liquids, including acetone, benzene, and carbon disulphide. At its boiling point it dissolves sulphur quite readily. It closely resembles thiophen in its remarkable stability and chemical inactivity. It is unaffected by boiling with water, caustic soda solution or concentrated hydrochloric acid. It does not form a picrate and yields no methiodide even when treated with methyl iodide in a sealed tube at 160° for 24 hours. It has but a very slight reducing action on potassium permanganate in acetone solution and when distilled from the unchanged permanganate and fractionated to remove acetone, practically the whole of the selenophen taken is recovered, but as a *colourless* liquid. Evidently the only effect of the permanganate is to oxidise the small trace of impurity, probably a hydrocarbon, responsible for the slight yellow colour of the distilled and crystallised selenophen.

Selenophen is not reduced by the ordinary agents, such as zinc and hydrochloric acid, and it is recovered practically unchanged after thrice being passed together with hydrogen at 250° over nickel (on pumice; obtained by heating the sulphate in a current of hydrogen at 400° for 24 hours).

Selenophen reacts with concentrated sulphuric acid with the production of a greenish-black mass; when warmed with concentrated sulphuric acid and isatin, it gives an indophenin reaction characterised by a greenish-blue colour, becoming purple when the product is poured into water. When concentrated sulphuric acid was added cautiously to a solution of selenophen in acetic anhydride well cooled in ice and the product was poured into water, a brown, semi-solid substance was obtained which may possibly have been a sulphonic derivative. It was, however, insoluble in water and the common organic solvents and decomposed on heating. Further attempts are being made to investigate the product.

Difficulties also attended attempts to prepare nitro-derivatives of selenophen. It was vigorously oxidised by concentrated nitric acid, but when solutions of selenophen and of concentrated nitric acid in acetic anhydride were slowly mixed in the cold, and the product was poured into ice-cold water, a dark brown oil separated which slowly set to a brown tar. This tar had the characteristic smell of nitro-compounds and dissolved readily in aqueous caustic soda to give a red solution, but it was insoluble in water, ether, light petroleum, benzene, alcohol, carbon tetrachloride, ethyl acetate, or acetic acid and so its investigation was deferred.

Tetrabromoselenophen.—A vigorous reaction occurred and hydrogen bromide was evolved when a solution of bromine in carbon disulphide, slightly in excess of the calculated amount, was added to a well-cooled solution of selenophen (10 g.) in the same solvent. After 24 hours, the solution was washed with dilute caustic soda solution and with water and evaporated on the water-bath. The brown residue, on recrystallisation from alcohol, gave *tetrabromoselenophen* as a white, finely crystalline substance, m. p. 102° (yield, about 70%). Tetrabromoselenophen is stable at its m. p., and does not reduce permanganate in acetone solution, but on boiling with water it slowly decomposes and deposits selenium.

Bromine and selenium were estimated in the compound by oxidising it with nitric acid and silver nitrate in a sealed tube at 200°, and boiling the silver bromide with dilute nitric acid to dissolve any silver selenite present. The silver bromide was dried, and weighed, and selenium was estimated in the filtrate by precipitation as the element in the usual way after the excess of silver had been removed as silver chloride (Found: C, 11·2, 11·1; Br, 71·5, 71·3; Se, 15·7, 17·7; M, cryoscopic in benzene, 565, 541. C_4Br_4Se requires C, 10·7;

Br, 71·4; Se, 17·9%; *M*, 447·2). Hence the compound appears to have the simple molecular formula, but probably forms solid solutions with benzene.

Attempts to isolate a corresponding iodine derivative by similar methods have failed.

Tetrachloroselenophen.—On adding a slight excess of a saturated solution of chlorine in carbon disulphide to a solution of selenophen (10 g.) in the same solvent, reaction occurred and hydrogen chloride was evolved. After 2 days the solution deposited a pale yellow, crystalline solid, which appeared to be insoluble in most solvents and steadily evolved hydrogen chloride on keeping. A similar product, prepared by bubbling gaseous chlorine slowly through a carbon disulphide solution of selenophen (10 g.), when washed well with water and dried on a porous plate, was sufficiently soluble in toluene to be recrystallised from that solvent and the product was a finely crystalline, white solid (Found: C, 16·9; Cl, 53·5; Se, 30·5. C_4Cl_4Se requires C, 17·7; Cl, 52·6; Se, 29·6%).

The yield in this case was only about 25%, and the mother-liquor contained other selenium compounds, which are being investigated. When heated to 87°, the solid decomposes, evolving an acid gas, and fuses to a yellow liquid that does not resolidify. A similar decomposition appears to occur in toluene or alcohol solutions, which, if overheated, become yellow and thereafter do not, on cooling, deposit crystals.

The compound was not soluble in a solvent of convenient freezing point, and so its molecular weight was not determined.

Although the analysis given appears to show that the compound is tetrachloroselenophen, it differs from tetrabromoselenophen to a rather remarkable extent. Unlike the latter, it is easily decomposed, with deposition of selenium, on warming with water or with acids, and slowly decomposes at the ordinary temperature, in air in a closed tube or in a vacuum, evolving acid fumes and turning brown. These differences suggest some difference in chemical character between the two halogen derivatives, and this is the subject of further inquiry.

Acknowledgment is made of a grant from the Research Fund Committee of Armstrong College, which enabled one of us (J. B. P.) to take part in this investigation.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.
[*Received, March* 29*th*, 1928.]