LIV.—*Volatile Platinum Compounds.*

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THE object of this work was to determine, if possible, the vapour density of some compound of platinum. In order to obtain a suitable substance for this purpose, and to find the best conditions under which the trials could be made, some miscellaneous phenomena were observed, worthy of note, but apparently unconnected with the subject.

The only volatile compounds of platinum hitherto known are those described by Schützenberger (*Ann. Chim. Phys.* [4], **21**, 350; *Annalen*, Suppl. **8**, 242) in the year 1872. They were obtained by passing alternately streams of chlorine and carbon monoxide over platinum sponge heated at 250° in a combustion tube by means of a gas-furnace. The volatilised substance was collected in a suitable receiver. In this manner, Schützenberger obtained a mixture of three volatile compounds, namely, carbonyl chloroplatinite, $CO,PtCl_2$, dicarbonyl chloroplatinite, $C_2O_2,PtCl_2$, and sesquicarbonyl chloroplatinite, C_3O_3,Pt_2Cl_4.

Now if we follow out the instructions given by Schützenberger, substituting a small furnace for the oil-bath in which he heated the tube, we obtain another yellow substance, which remains behind after the volatile compounds have been driven from the heated part of the tube. This compound occupies the same position as the platinum originally did, nor can any amount of heating volatilise it. When hot, it is brick-red, and, on cooling, changes to a bright canary-yellow. It was obtained in two different experiments, but was only homogeneous in the first. From the method of formation, it seemed probable that the product was a combination of platinum, chlorine, and carbon monoxide, since it was not formed till the latter gas had been passed over the platinum chloride for a considerable time. It absorbed water from the air very slowly. An analysis of the substance was made in the following manner.

The *water* absorbed from the air was determined by heating the substance in an air-bath to successively rising temperatures till its weight was constant. It proved to be anhydrous at 105°.

The *platinum and chlorine* were determined by reducing the compound by pure magnesium and acetic acid.

The reduced platinum was collected and weighed. The chlorine was precipitated by silver nitrate in large excess of nitric acid, and the precipitate treated and weighed in the usual manner.

The carbon monoxide was found by difference. The percentage composition thus obtained was :—

Platinum	40·36
Chlorine	44·71
Water	4·19
Carbon monoxide	10·74

Now the water present bears no molecular ratio to the other constituents. Calculating, therefore, the percentage composition of the anhydrous substance, we obtain the values :—

Platinum	42·12	against the theoretical	42·01
Chlorine	46·66		45·89
Carbon monoxide	11·32		12·08
	100·00		100·00

which are the values calculated for a compound having the formula $PtCl_2,2COCl_2$ or $PtCl_6,C_2O_2$. The compound would, therefore, appear to be a combination of platinum dichloride with phosgene.

It was thought possible that this substance had resulted from the action of a small amount of phosgene on the platinum dichloride. An attempt was, therefore, made to obtain it by passing a stream of phosgene over the heated chloride, but without success.

Properties of the New Compound.

It is a yellow, crystalline solid, stable in air, but slightly deliquescent. It dissolves easily in water without blackening, and, on evaporation, separates from its solution in yellow crystals apparently unaltered. In alcohol it is only slightly soluble, and carbon tetrachloride dissolves scarcely any. When strongly heated, it is decomposed with evolution of chlorine and phosgene. Thus it has none of the properties characteristic of Schützenberger's compounds. It may perhaps be called phosgeneplatinum dichloride.

Specimens of carbonyl chloroplatinite, $CO,PtCl_2$, and dicarbonyl chloroplatinite, C_2O_2,Pt_2Cl_4, were next prepared in the pure state. The former was obtained by bubbling carbon monoxide for over an hour through the melted crude product; the latter, by a similar method, substituting carbon dioxide for the monoxide.

Schützenberger says that the action of water on these compounds is very complex (*loc. cit.*). This perhaps results from a secondary action which takes place between the hydrogen chloride and the undecomposed substance.

The equations given for the action of water are:—

(1.) $CO,PtCl_2 + OH_2 = CO_2 + Pt + 2HCl,$
(2.) $C_2O_2,PtCl_2 + OH_2 = CO_2 + CO + Pt + 2HCl;$

but, as Schützenberger points out, these represent only the chief actions. Now, in neither of these reactions is platinum formed as a first result of the action. If a drop of water is added to a crystal of the substance, it immediately becomes black. But both strong hydrochloric and strong nitric acid dissolve the black substance; therefore, it cannot be either platinum or platinum dichloride, for the former is soluble in neither acid, and the latter is insoluble in nitric acid. Hence, if hydrogen chloride be formed by the action of water, it will tend to keep part of the substance in solution. Schützenberger found that a very considerable quantity of platinum remained in solution; but, in presence of a large excess of water, platinum is eventually precipitated.

The Action of Various Gases.

In order to find a suitable atmosphere into which to volatilise the substances for the vapour-density experiments, the action of various gases was tried. The results are briefly as follows:—

Action of Dry Air on $PtCl_2,2CO$.—The substance is unchanged till its melting point is reached, when carbon monoxide is evolved; the residue then solidifies, melting again at 190°. A little above this temperature, it decomposes with a slight sublimation.

Dry hydrogen has no action in the cold. At the melting point, the compound is at once reduced to metal with partial sublimation. If the hydrogen be burned, the flame becomes luminous, and deposits a film of platinum on the surface of porcelain introduced into the flame.

Dry chlorine has no action till from 80° to 90°, at which temperature the compound fuzes, losing carbon monoxide with effervescence. At 115° it solidifies. At 140° it fuzes again, and is decomposed.

Dry Carbon Dioxide.—Schützenberger says the substances can be distilled in this gas; but it is very difficult to volatilise them completely. A large residue of platinum dichloride is invariably left.

Phosgene had a peculiar action in the cold. Yellow drops of liquid were formed where the substance was in contact with the glass. This liquid could not be obtained in sufficient quantity for examination. A considerable quantity of the substance volatilised when the tube was heated, but complete vaporisation seemed impossible. It is also noteworthy that the compounds heated at 100° with liquid carbonyl chloride in a sealed tube are dissolved by it, and deposited again on cooling in large crystals. In a vacuum, the substance was also incompletely volatile. The only gas in which it seemed possible to determine the vapour density was carbon monoxide.

Vapour-Density Experiments.

These were at first conducted in a Victor Meyer's tube, in an atmosphere of carbon monoxide. The bottom of the bulb was lined with asbestos. A small block of the compact substance (experiments were made with both substances) was dropped directly from the stopper on to the asbestos.

Experiments were made at various temperatures varying between 200° and 400°. There was, however, no agreement between any of the results. In some cases decomposition was evident, in others the substance was not completely volatilised. Some experiments were made without asbestos, but in no single case, even at a very high temperature, and after the lapse of a considerable time, was volatilisation complete. A final attempt was made with a modified form of apparatus devised by Professor Lothar Meyer. The bulb of the apparatus is constricted in the middle. A small piece of platinum gauze rests on the constricted part. The substance is dropped directly on to the gauze. The vapour formed falls at once into the lower part of the tube, leaving the atmosphere surrounding the solid unsaturated. In this manner the whole of the substance was volatilised; but, on examining the tube, it was found that even at a temperature of 250° the vapour of the substance in the bottom part of the tube was decomposed in contact with the glass. The colour of the vapour is a dull red. It seemed evident that the vapour density of the compounds could not be determined when glass vessels were used.

Possibly the form of apparatus described above may be useful in determining the vapour densities of other solids with heavy vapours.

It was supposed possible that the corresponding bromine derivatives might be more volatile. An attempt was therefore made to obtain them.

Preparation of Platinum Dibromide.

Schützenberger obtained platinum dichloride by passing chlorine over heated platinum sponge. An attempt to obtain the dibromide in the same way failed. V. Meyer and Züblin obtained the tetrabromide by heating platinum sponge with bromine and hydrobromic acid in a sealed tube at 180°, evaporating to dryness, and heating to 180° (*Ber.*, 1880, **16**, 404). It is not necessary, however, to make use of sealed tubes. If platinum sponge be simply boiled for a short time with an excess of bromine and hydrobromic acid, in a flask connected with a reflux condenser, the whole is dissolved. If the solution is then evaporated to dryness and the residue heated, bromine and hydrogen bromide are evolved. According to Topsoë, this takes place slowly at 100°, but more quickly at 200°, leaving a bright brown powder which, when washed to free it from undecomposed tetrabromide, gives a brownish-green residue of the dibromide. It is, however, very doubtful whether any dibromide is formed at the lower temperature. The residue, obtained as above, was heated in an air-bath. Some dibromide was formed at 180°. This, when thoroughly washed from the tetrabromide, had not a brownish-green colour, but was coal-black. After heating another portion at 255° for five hours, some undecomposed tertrabromide still remained, but this time the colour of the dibromide was a dark, clear brown. It would seem therefore that the colour of the product is conditioned by the temperature of its formation. A third portion was heated at 310° for four hours in a current of air. Even at this temperature a residue of tetrabromide was left. The most convenient temperature for the preparation of the dibromide was found to be about 280°.

It may be here mentioned that spongy platinum is also dissolved by a hot solution of iodine in hydriodic acid, yielding a dark-red liquid. From this, the tetraiodide can be easily obtained by evaporating it to dryness, heating the residue to 180° in an air-bath, and washing away the soluble part. The iodide thus obtained is a compound of singular stability, seeing that it can be heated with sodium carbonate to the fusing point of that salt without losing all its iodine. A rough determination of the platinum in the iodide was made by reduction with magnesium and acetic acid; this gave a percentage of 28·2 of platinum, against the theoretical 27·7.

Action of Carbon Monoxide on Platinum Dibromide.

The dibromide was contained in a small boat which was placed in a combustion tube. The end of the tube was bent into a U-shape, so as to serve as a receiver for the volatile compound. The straight part of the tube was placed in a combustion furnace, which was gradually heated; in the meantime, a slow current of dry carbon monoxide was passed over the dibromide. At the cool end of the tube a sublimate was formed, consisting of yellow and white crystals, and a brick-red powder. At about 180°, the contents of the boat melted, giving a dark-red liquid which was volatilised with difficulty; so great was the difficulty of completely volatilising this liquid, that it seemed impracticable to determine its vapour density. The sublimed substance was now melted by immersing the U-tube in a heated paraffin-bath. A current of carbon monoxide was passed over the melted substance for more than an hour, in order that a maximum amount might be absorbed. From the analogy to the chlorine compounds, it was supposed that a compound $PtBr_2,2CO$ would be formed. Such, however, was not the case. On cooling, the substance solidified to a mass of bright-red needles. The platinum and bromine in this compound were estimated by heating a weighed quantity in a platinum crucible with a very large excess of carbonate of soda. That none of the substance was volatilised was evident from examination of the crucible after ignition. The resulting platinum was washed and weighed, and the bromine in the washings was estimated in the usual way. In this and in many other analyses, the carbonate of soda was tinged a darkish-blue. This may have been due to the formation of a subbromide of sodium, corresponding to the subchloride of potassium described by Bunsen (*Ann. Phys. Chem.*, 1861, **113**, 445).

The following results were obtained .—

	I.	II.	
Percentage of platinum,	50·44	50·33;	mean, 50·38
,, bromine,	41·504	1·03;	,, 41·26
,, CO,	8·06	8·67;	,, 8·36

This approximates closely enough to the constitution of a compound having the formula $PtBr_2,CO$, which has the following percentage composition:—Platinum, 50·90; bromine, 41·79; CO, 7·31. It would appear, therefore, that this compound, which may be called "carbonylbromoplatinite," does not absorb carbon monoxide at its melting point.

Properties of Carbonylbromoplatinite.

The melting points of two different specimens were taken with a delicate thermometer with the following results: (1) 177·5°, (2) 177·5°, (3) 178°, (4) 178°. Mean result 177·7°. It is bright-red and crystallises in well-defined needles. It is much less sensitive to the action of moisture than the corresponding chlorine compound. Indeed, it may be exposed to the air for a considerable time without darkening in colour. When treated with water, it first dissolves, giving a red solution, which, however, almost instantly blackens. The black product is soluble in hydrobromic acid. Absolute alcohol dissolves the substance without blackening, giving a dark-brown solution. When melted in a stream of carbon dioxide, it loses carbon monoxide, and appears to be converted into the dibromide of platinum.

In conclusion, I must express my very sincere thanks to Professor Lothar Meyer for the great assistance which he has given me. It was he who suggested the work, and he who, during its progress, aided me with very many suggestions and much personal help.

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