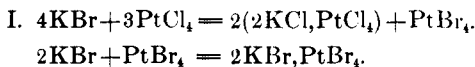


XXXVI.—ON THE FORMATION OF COMPOUND PLATINATES AND A
NEW PLATINO-POTASSIUM SALT.

BY LUCIUS PITKIN.

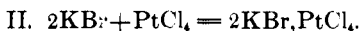
When a solution of platinum tetrachloride is mixed with a solution of potassium bromide, in some degree of concentration, a precipitate is formed, which, although resembling in many points the ordinary double chloride of platinum and potassium, is of a much darker color. The shade of color depends largely on the rapidity of the precipitation, rapid precipitation in the cold forming a dark orange powder, while a slower formation favors the production of small, reddish crystals. As will be seen further on, the amount of potassium bromide present, influences the color of the crystals, as does also the presence of hydrochloric acid in greater or less amount.

Two formulæ can be given for the reaction mentioned above. In the first we may suppose the chlorine of the platinic chloride combines directly with the potassium, forming a double chloride, while platinic bromide is left in solution; the latter then unites with a fresh portion of potassium bromide, and forms a double bromide of potassium and platinum.



In this case a mechanical mixture would be formed of two equivalents of double chloride and one of double bromide.

In the second case, however, we may suppose a direct combination of the bromide with the chloride, forming a salt with the composition $2\text{KBr}, \text{PtCl}_4$.



It is obvious that whether a mechanical mixture of double chloride and bromide takes place in the proportion of two to one, or whether a chlorobromo-platinate of potassium is formed, the percentage of each constituent remains exactly the same.

In order to determine, then, whether a new salt, of definite proportions, has been formed, or whether we are dealing with a mixture, we must resort to the use of solvents or fractional crystallization.

The percentage of platinum in both cases is 34.35, which was found to agree most closely with an analysis of the pulverulent precipitate, formed by adding platinic chloride to potassium bromide in excess.

In order to ascertain if hydrochloric acid would exercise a replacing power, and allow the formation of a double chloride, three determinations were made, of precipitates produced under varying circumstances.

In the first determination, 4 grms of potassium bromide were dissolved in a minimum amount of water, 2 c.c. of strong hydrochloric acid added, then .500 gm of PtCl_4 in solution. A pulverulent precipitate was the result—.4175 gm of which yielded .144 gm of metallic platinum, or 34.49 per cent.

The determination of platinum was made in the usual way, *i. e.*, a known amount of the thoroughly dried salt was decomposed by heat, with the aid of oxalic acid, and, after being thoroughly washed, was dried and weighed in the state of spongy metal.

The conditions of the second determination were the same, except that 1 c.c. of concentrated hydrochloric acid was used in place of the 2 c.c. of the previous experiment; .3565 gm of the precipitate gave 123 gm of metallic platinum, which is equivalent to 34.47 per cent.

In the third determination no hydrochloric acid was used, and the resulting precipitate contained 34.1 per cent. of platinum, .1444 gm being obtained from .4236 gm of the substance.

We see from this that hydrochloric acid has no effect on the chemical constitution of the precipitate, the average yield of platinum being 34.32 per cent., against a theoretical 34.35 per cent.

But the acid produced one effect which is interesting to note: without changing the constitution it produced a change in the color, which was not accidental or confined simply to these determinations, for a second trial fully confirmed the first. The change consists in the tint of the precipitate growing lighter in direct proportion to the amount of acid used.

It being thus proven that the precipitate was constant under variations in the amount of hydrochloric acid used, it remained to determine whether it were simply a mixture, or whether a new salt, not noted in any work on chemistry which I have consulted, had been formed.

The method chosen was fractional crystallization, as offering the best results for the separation, if a mixture, or for the confirmation of the definite character, if a new and constant salt.

The result has been such as to leave no doubt but that a salt of the composition $2\text{KBr}, \text{PtCl}_4$ is formed, under favorable conditions, while the investigation necessary to prove the fact has led to some interesting points in the relation of the chloro-platinates to the bromo-platinates of potassium.

In order to crystallize successive crops, a strong solution of potassium bromide was made, and platinum chloride, in solution, added, the bromide being in excess. By cautious evaporation, five crops of crystals were obtained, which it was supposed would, in the case of a mixture, yield a successive difference in the ratio of platinum, or else prove the existence of a chlorobromo-platinate, by exhibiting a constant percentage of platinum, and that percentage would be 34.35.

But neither result appeared, as the tabular view of the experiments will show. Crops 1, 3 and 5 were selected for determination :

EXPERIMENT 1.—CROP 1.

Amount ppt. used.....	.5371
Amount platinum.....	.1406
Percentage platinum.....	26.18

EXPERIMENT 2.—CROP 3.

Amount ppt. used.....	.3680
Amount platinum.....	.0960
Percentage platinum.....	26.10

EXPERIMENT 3.—CROP 5.

Amount ppt. used.....	.2688
Amount platinum.....	.0724
Percentage platinum.....	26.90

It will be seen that the crystallization has shown no change in the composition of the five specimens, but what it has shown is this, that boiling a haloid platinate of potassium with a strong solution of potassium bromide, insures the formation of a double bromide of platinum and potassium. The theoretical amount of Pt in $2\text{KBr}, \text{Pt}_4 = 26.3$ per cent., while the average of the above gives 26.39 per cent. of metallic platinum.

Here, also, a curious color change is apparent without change in chemical constitution, each successive crop becoming darker and darker.

The first crystals were bright red.

The second crystals were red.

The third crystals were brownish-red.

The fourth crystals were dark brownish-red.

The fifth crystals were blackish-red.

In order to put the question to a crucial test as to whether the boiling with potassium bromide produces double bromides, some double chloride was formed in the usual way, washed with alcohol, and then treated with boiling KBr solution. On recrystallization and

washing with alcohol, it proved to be a double bromide, yielding 26.00 platinum, while the double chloride yields 40.6 per cent.

A new set of crystals was then made by taking 2 grms of $PtCl_4$, 1404 grm of KBr , and making two solutions. Upon pouring these together a copious precipitate appeared; this was filtered, washed with alcohol and dissolved up, and from its solution successive crops of crystals formed.

It will be seen that in this case little time was given for the full action of the bromide on the chloride; and if the tendency is to form first a double chloride, which is afterwards acted on by the bromide, no chance was afforded by this process.

The resulting crystals, three crops of which were separated out, were all of the same tint—a rich, bright yellow—and gave:

First crop.....	38.3 per cent. platinum.
Second crop.....	38.0 “ “
Third crop.....	39.0 “ “

The proportions used of the bromide and chloride were capable of forming the chlorobromo-platinate, if opportunity was given for full action, and the platinic chloride were perfectly pure. It was of Merck's manufacture, and none remained to test as to purity.

For the final and decisive test, as to the existence of platinate of potassium, in which bromine and chlorine are both united, I prepared my platinic chloride from spongy platinum, and afforded full opportunity for mutual reaction, by boiling several hours. The proceeding was as follows: 2,000 grms of platinic chloride were dissolved in 20 c.c. distilled water, and added to a solution of 1,404 grms of potassium bromide, in 50 c.c. water. The solution was then boiled for four hours, and finally evaporated slowly, and three crops of crystals recovered. These crystals were all of the same tint—a rich, dark orange—and gave uniform results in the determination of the amount of platinum contained.

CROP No. 1.

Amount used.....	1.0123
Platinum found.....	.3465
Percentage platinum.....	34.22

CROP No. 2.

Amount used.....	.6311
Platinum found.....	.2205
Percentage of platinum.....	34.70

Crop No. 3.	
Amount used6479
Platinum found.....	.2228
Percentage platinum.....	34.39

These percentages strike an average of 34.43 per cent., a variation of only .08 per cent. from the theoretical composition of chlorobromoplatinate of potassium, while their absolute identity in tint supplies another strong reason for considering them as such.

To resume, then, in closing, the following facts may be taken as well established :

1st. The formation of a compound containing bromine, when potassium bromide is used with platonic chloride.

2d. The conversion of chloro-platinates into double bromides, by action of hot solution of potassium bromide.

3d. The variation in shade of color in regular gradation, of crystals separated out of boiling bromide solution, as also the color effect of hydrochloric acid.

4th. The formation of a chlorobromo-platinate, by suitable action of platonic chloride on potassium bromide, which salt is of an orange color, and crystallizes in fine octohedra.

In the commercial analysis of potassium compounds the amount is generally estimated by the weight of the dried double chloride, or by the amount of metallic platinum contained in that salt. If the latter method is pursued, no objection can be urged, as one equivalent of platinum corresponds to two of potassium, whether in the form of double chloride, bromide, iodide of chlorobromo-platinate. But it is plain that no such relation exists between the amount of potassium and the salts mentioned.

If the weight of the precipitate is also known, it becomes an easy calculation to estimate the approximate amount of chloride and bromide present together, from the ratio between the dried precipitate and the platinum obtained from it.

Fresenius, in his quantitative analysis, recommends to treat salts of potassium, other than chlorides, with hydrochloric acid, and evaporate to dryness. Rose proposes the use of chlorine water in the same way. The latter method decomposes the bromide better than the former, but is rendered unnecessary if a determination of the metallic platinum is made.

It is my intention to investigate the corresponding salts of ammonium and sodium, and make a more extended examination of the properties of potassium chlorobromo-platinate, as I may have leisure so to do.