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Abstract

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NEW ROUTES FOR OBTAINING HEXAFLUOROPLATINATES

Hexafluoroplatinates have so far not been obtained by the usual methods in aqueous solution, owing to irreversible hydrolysis. It is known that even hot 40% hydrofluoric acid does not react with $Pt(OH)_4$ (^{1}). It is also impossible to obtain hexafluoroplatinates by the action of anhydrous hydrogen fluoride on hexachloroplatinates (^{2}).

Potassium hexafluoroplatinate was first obtained by Schlesinger and Tapley by fusing the complex salt $3KF \cdot PbF_4 \cdot HF$ with finely divided platinum (^{3}). Water-soluble hexafluoroplatinates of some rare-earth metals were successfully prepared by the action of fluorine at 525° on platinum foil coated with a rare-earth fluoride ($^{4-6}$). By the action of bromine trifluoride on platinum tetrabromide and evaporation of the resulting solution in vacuum, Sharp (^{7}) obtained a product of composition $PtBr_2F_{10}$, to which the formula of difluorobromonium hexafluoroplatinate, $(BrF_2)_2PtF_6$, was assigned. Upon addition of potassium fluoride to a solution of this compound in BrF_3, potassium hexafluoroplatinate is formed according to the equation

$$(BrF_2)_2PtF_6 + 2KBrF_4 \rightleftharpoons K_2PtF_6 + 4BrF_3.$$

Since this reaction is reversible, the product is obtained in a mixture with the starting substances. Its yield does not exceed 40%. We found that a mixture of bromine with bromine pentafluoride rather rapidly dissolves metallic platinum. Meanwhile, pure BrF_5 has no action at all on metallic platinum. By simple evaporation of the solution, a dark-yellow crystalline compound of composition $PtBr_2F_{10}$ was isolated.

The salt obtained is instantly hydrolyzed by water with evolution of bromine vapors; it fumes in air, does not dissolve in hydrogen fluoride, ignites on contact with alcohol, and does not react with CCl_4. When heated in vacuum to 200°, the compound loses BrF_3 and PtF_4 remains in the residue; in bromine pentafluoride about 10 g of the salt dissolves per 100 ml of BrF_5 with formation of a red solution. In bromine trifluoride the product is very readily soluble, forming a clear red solution, to which, upon addition of potassium fluoride and subsequent removal of the solvent under vacuum at room temperature, there remains a light-yellow residue of composition $K_2PtF_6 \cdot 1.1\,BrF_3$. The latter, when heated in vacuum at 250°, decomposes with liberation of bromine trifluoride. After leaching the residue with hot water and filtering the solution, lemon-yellow crystals of potassium hexafluoroplatinate separated from it.

When potassium fluoride is added to a solution of platinum in the indicated mixture, the reaction proceeds according to the scheme:

$$(BrF_2)_2PtF_6 + 4KF = K_2PtF_6 + 2KBrF_4.$$

The reaction can be used to obtain potassium hexafluoroplatinate in high yield.

2.5 g of platinum in the form of wire or foil was placed in a Teflon test tube (capacity 12 cm^3) with a stopper. The test tube was then filled to 3/4 with a reaction mixture of Br_2 and BrF_5 in a ratio of 1:2 by volume, closed

was closed with a stopper and placed in a container hermetically sealed with flanges. The container was placed in an air thermostat having a temperature of 40°. The platinum dissolved completely within a week. At room temperature this requires 3 weeks. After the time required for dissolution had elapsed, the container was cooled to 0°, opened, the contents of the test tube were poured into a Teflon cup, and evaporated to dryness under a hood with heating. Care must be taken that the heating is stopped immediately as soon as the liquid phase has been removed. As long as even traces of liquid remain, the product does not react with atmospheric moisture. The resulting difluorobromonium hexafluoroplatinate was washed from the cup with bromine pentafluoride, in 50 cm^3 portions, into a Teflon beaker of 100 cm^3 capacity. To this solution, well-ground potassium fluoride (3 g) was added in small portions with stirring. The contents of the beaker should be cooled with dry ice in order to prevent vigorous boiling. After all the potassium fluoride had been added, the beaker was placed in a hermetically sealed container and left overnight. Then the solvent was evaporated under a hood at room temperature to a pasty mass, and the beaker together with its contents was placed in a quartz box, the ground joint of which was lubricated with a perfluoride grease. In the lid of the box there was an outlet connected to a quartz trap immersed in a Dewar vessel with liquid nitrogen. The trap was connected to an oil pump. First, at room temperature, the remaining bromine pentafluoride was distilled off in vacuo; then the residue was heated to 280° to decompose $KBrF_4$. There must be no leak in the vacuum system, in order to avoid decomposition of the product by atmospheric moisture.

After complete removal of bromine, the light-yellow residue, consisting of a mixture of KF with K_2PtF_6, was leached with boiling water (about 200 cm^3) in 20 cm^3 portions until the characteristic crystals of potassium hexafluoroplatinate were no longer detected in the filtrate. The hot solution was filtered, and the filtrate was cooled to 0°. The precipitated crystals were suction-filtered on a platinum funnel and recrystallized from hot water. By evaporating the mother liquor under vacuum, an additional portion of the substance is isolated. The yield is about 80%. Analysis for fluorine and potassium was carried out after removal of platinum from the solution of the weighed sample with hydrazine hydrochloride. Fluorine was determined in an aliquot portion of the solution as lead fluorochloride (9), and potassium—as sulfate. Platinum was determined in a separate sample by precipitation with thioacetamide according to the method of V. A. Golovnya and S. K. Sokol (10). In addition, an analytical method was used based on pyrohydrolysis of a weighed sample of the salt in a stream of water vapor at 400°.

The results of the analyses are presented in Table 1. Below are the results obtained by other methods.

Table 1

Results of analysis by the pyrohydrolytic method and calculated according to the formula K_2PtF_6 (in percent)

Nos. of analyses	Pt found	Pt calculated	Distilled-off fluorine found	Distilled-off fluorine calculated	Residue found	Residue calculated	KF found	KF calculated
1	50.3	50.4	20.2	19.6	80.2	80.2	29.9	30.0
2	50.2		20.2		80.2		30.0	

By the method of V. A. Golovnya and S. K. Sokol, Pt 50.1 ± 0.1%; K 20.1 ± 0.1% was found. Determination of K and F after removal of platinum with hydrazine hydrochloride:

$$\text{Found \%: } K\ 20.4 \pm 0.1;\ F\ 30.0 \pm 0.3;$$
$$K_2PtF_6.\ \text{Calculated \%: } K\ 20.2 \quad F\ 29.4 \quad Pt\ 50.4$$

As can be seen from the analytical results, during pyrohydrolysis 4 atoms of fluorine out of six are split off, which is additional evidence for the absence-

substitution of fluorine by OH or H_2O groups. The appearance and properties of the potassium hexafluoroplatinate obtained coincided exactly with the descriptions available in the literature. The appearance of the crystals differs sharply from that of analogous salts with other halides, which is in complete agreement with the literature data (11, 12). The density of the salt obtained, measured pycnometrically, was equal to 4.81 ± 0.01 g/cm^3. According to the measurements of Wiler and co-workers it is equal to 4.83 g/cm^3.

The dissolution of platinum in a mixture of bromine with bromine pentafluoride described in the present work is explained by the formation in this mixture of bromine monofluoride, which rather rapidly attacks platinum (13); moreover, we found and confirmed by analysis of the final products that, along with bromonium hexafluoroplatinate, bromine trifluoride is also formed.

The process of dissolution of platinum may be represented by the equations

$$Br_2 + BrF_5 \rightleftharpoons Br_2F_2 + BrF_3, \qquad (1)$$

$$5Br_2F_2 + Pt = (BrF_2)_2PtF_6 + 4Br_2. \qquad (2)$$

Equation (1) was given by Ruff and Braida in explaining the mechanism of preparation of bromine monofluoride by fluorinating bromine with fluorine ([14]). The overall equation $Br_2 + 5BrF_5 + Pt = (BrF_2)_2PtF_6 + 5BrF_3$ agrees with the data obtained by us from analysis of the final reaction products.

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