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Abstract

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NEW ROUTES TO THE PREPARATION OF HEXAFLUOROPLATINATES

FLUORINATION WITH CHLORINE TRIFLUORIDE

In a previous communication ([1]), a survey was given of methods for the synthesis of complex fluorides of tetravalent platinum, and the authors' work on the synthesis of potassium hexafluoroplatinate starting from bromine pentafluoride and metallic platinum was described. A fluorination mechanism was established, based on the formation of bromine monofluoride and difluorobromonium hexafluoroplatinate. The present work was undertaken with the aim of developing more convenient methods for preparing potassium hexafluoroplatinate.

As is known, of all fluorine compounds the most active fluorinating agent is chlorine trifluoride. In addition, it has the further advantage that, as a result of fluorination, no by-products are formed together with potassium hexafluoroplatinate, which eliminates the need for a prolonged heating operation under vacuum to remove the halogen fluoride.

Taking these circumstances into account, we studied the action of chlorine trifluoride on a mixture of platinum with potassium bifluoride, and also on potassium hexachloroplatinate. It was found that, when a nickel boat containing a mixture of 5 g of platinum black with 3 g of potassium bifluoride was heated to 200° in a stream of chlorine trifluoride, the platinum was completely converted into potassium hexafluoroplatinate, which was then separated from the excess potassium bifluoride by recrystallization from hot water.

Even better results were obtained in the conversion of potassium hexachloroplatinate into potassium hexafluoroplatinate by means of chlorine trifluoride. Although, as experiments showed, liquid ClF_3 has almost no effect on K_2PtCl_6, and after this salt had stood for 24 hours with liquid chlorine trifluoride in a Teflon beaker at 0° only an extremely small amount of a more lightly colored phase had formed, the reaction at 500° with gaseous ClF_3 rapidly leads to complete replacement of chlorine by fluorine. The experiments were carried out in a quartz tube into which a nickel boat with potassium hexachloroplatinate (15 g) was placed. The transformation could be followed by the lightening of the product and the evolution of chlorine. At the end of the reaction the color of the salt became pale yellow, and the loss in weight corresponded exactly to that calculated from the equation

$$K_2PtCl_6 + 2ClF_3 = K_2PtF_6 + 4Cl_2. \quad (1)$$

After this it is necessary to make sure that chlorine is absent from the sample of the substance obtained.

Under the conditions described, the process was completed in approximately 1½ hours. It should be borne in mind that at high temperature K_2PtF_6 reacts with atmospheric moisture; therefore the boat should not be removed from the quartz tube until it has cooled. The purity of the potassium hexafluoroplatinate obtained in this way is determined only by the purity of the starting K_2PtCl_6. If necessary, the preparation can be purified by recrystallization from water. The crystals separated in this process are completely identical with those obtained previously. The composition of the salt is confirmed both by the loss in weight

in agreement both with equation (1) and with the analytical data. For the analysis of potassium hexafluoroplatinate, a method had been developed involving pyrohydrolysis of the weighed sample with superheated steam, as reported earlier ([1]). However, this method required a considerable expenditure of time; therefore we developed another analytical method, distinguished by sufficient accuracy and rapid execution.

A weighed portion of the salt, 0.2–0.4 g, was mixed with calcined soda (1 g) in a platinum boat. The mixture was covered from above with a layer of soda. The boat was placed in a quartz tube and heated in a stream of hydrogen for 15–20 min at 400°.

After cooling and weighing the boat, a loss in weight was observed, corresponding to the loss in weight calculated from the equation

$$K_2PtF_6 + H_2 + 2Na_2CO_3 = 2KF + 4NaF + Pt + 2H_2O + 2CO_2.$$

The sample was then leached on a filter with hot water; the platinum remaining on the filter was ignited and weighed. In the filtrate, fluorine was determined in the form of PbClF and potassium as K_2PtCl_6. The entire analysis can be carried out in one day.

Results of the analysis of potassium hexafluoroplatinate:

Found, %:	Pt 50.7 ± 0.2;	F 29.5 ± 0.3;	K 20.0
K_2PtF_6. Calculated, %:	Pt 50.37;	F 29.43;	K 20.13

The density of the synthesized preparation, determined pycnometrically, proved to be 4.79 g/cm^3. The literature value is 4.83 g/cm^3.

The results of experiments carried out under the same conditions with replacement by gaseous fluorine showed that in this case K_2PtCl_6 is also converted

into potassium hexafluoroplatinate; however, the yield of product is significantly lower, and as a result the preparation requires purification by recrystallization.

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Note: Figure translations are in progress. See original paper for figures.