NEW METHODS OF PREPARING TRIPOTASSIUM LEAD HYDROGEN OCTAFLUORIDE.

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Introduction.

These experiments were made in connection with the problem of preparing free fluorine. Tripotassium lead hydrogen octafluoride evolves fluorine when heated above 300°, but the preparation of the octafluoride by the known methods was found to be slow and the yields were low. Therefore, new methods of preparing the salt were sought.

The excellent paper by Clark[1] gives complete working details of perhaps the best of the known methods. Potassium plumbate is first formed by heating a mixture of lead peroxide, potassium hydroxide and water. The residue is added to strong hydrofluoric acid and the pure salt, tripotassium lead hydrogen octafluoride, is obtained by crystallization of the filtrate. The review omitted the method[2] of treating lead tetraacetate with hydrofluoric acid and potassium hydrogen fluoride. This, however, is a slow and expensive method. Ruff[3] states that both the ammonium and the potassium double salts can be easily made but no details of the method are given.

Experimental.

Action of Anhydrous Hydrofluoric Acid upon Peroxides of Lead.—Lead peroxide and red lead (Pb_3O_4) are apparently unacted upon by the ordinary conc. hydrofluoric acid (50%). However, the nearly anhydrous acid (96%) acts readily upon the red lead or freshly prepared lead peroxide with formation of good yields of lead tetrafluoride in each case. The reaction with the red lead is very vigorous. The lead peroxide which is split off from the red lead dissolves very quickly in the anhydrous hydrofluoric acid but the waste of the anhydrous acid in the formation of the lead difluoride is objectionable. No black color is noticed except for short intervals in places where the red lead happens to be in excess. Lead peroxide (c. p.) from Eimer and Amend is insoluble in the anhydrous hydrofluoric acid even on standing for several hours. Freshly prepared lead peroxide dissolved in the anhydrous acid but not in the 50% acid. This lead peroxide was prepared by treating red lead with an excess of nitric acid, washing and drying at a low temperature. The undried paste was not soluble. This was probably due to the dilution of the acid. It seemed to make no difference if the dried lead peroxide was used at once or after several days. The tetrafluoride solutions thus obtained were

[1] This Journal, 41, 1477 (1919).

[2] Brauner, *Z. anorg. Chem.*, 7, 1 (1894); *J. Chem. Soc.*, 65, 393 (1894); Winterfeld, Doktor Dissertation zu Berlin, 1894.

[3] *Z. angew. Chem.*, [2] 20, 1218 (1907).

quickly hydrolyzed by dilution with water—a black precipitate of plumbic hydroxide being formed. The addition of potassium or ammonium fluoride, before dilution, lessens the tendency to hydrolysis. A yield of 62% of the tetrafluoride, based on lead peroxide, was obtained. The only serious objection to this method is the use of anhydrous hydrofluoric acid, which is so very difficult to make and to keep and is disagreeable to use.

By Fusion of Lead Peroxide with Potassium Hydrogen Fluoride.—Any sample of lead peroxide reacts with fused potassium hydrogen fluoride with formation of a double fluoride of lead. Equal weights of potassium hydrogen fluoride (dried by fusion) and lead peroxide in platinum or copper vessels, were used. This gives approximately 3 molecules of potassium hydrogen fluoride to one of lead peroxide, which is the quantity of potassium for the desired salt, but there is insufficient available hydrofluoric acid for complete reaction upon the lead peroxide. It is better to supply the required hydrofluoric acid by the scheme described below than to start with larger quantities of the potassium hydrogen fluoride. The latter substance was fused over a free flame at a temperature of about 200° and the lead peroxide added slowly with stirring. A gas, probably water, was evolved during the reaction. The heating, which need last only for a few minutes, should be discontinued as soon as the mass becomes very pasty. Increase in temperature decomposes the octafluoride. The mass remains black in color. About 30 to 40% of the lead peroxide was changed to a double fluoride at this point. After cooling, the mass was moistened with conc. hydrofluoric acid, the lumps were crushed and the mass thoroughly stirred with a carbon rod. This treatment regenerates potassium hydrogen fluoride. The vessel was then heated in an oven for several hours at about 225°. The residue became much whiter during the heating, thus showing that the lead peroxide was being acted upon. By repeating once or twice the treatment with the hydrofluoric acid followed by the heating, the residue became practically white. Analyses showed that 80% to 86% of the lead peroxide was changed to octafluoride. Analysis was made by extracting the residue with conc. hydrofluoric acid, filtering and washing the residue with 1 : 1 hydrofluoric acid. The filtrate was treated with 5 cc. of conc. nitric acid, and titrated with excess hydrogen peroxide followed with potassium permanganate. Direct fusion with larger amount of potassium hydrogen fluoride (4 : 1) without any further treatment with hydrofluoric acid or heating gave yields of 65% to 70%.

Pure crystals of the double salt, tripotassium lead hydrogen octafluoride, were prepared by digesting the crude residue with conc. hydrofluoric acid, filtering and crystallizing. Analysis, by electrodeposition of lead peroxide from nitric acid solution, gave 50.3% of lead peroxide while that calculated was 50.09%.

A stronger acid was required to avoid hydrolysis of the octafluoride when no excess of potassium was present. One part of hydrofluoric acid (50%) to 0.05 part of water gave no hydrolysis of the pure salt when heated upon a water bath, but one of acid to one of water gave hydrolysis. However, one part of acid, 2 of water and 0.2 part of potassium hydrogen fluoride gave no hydrolysis. Cold solutions hydrolyzed less easily than hot ones. In extracting the crude residue, conc. hydrofluoric acid should be used as otherwise some hydrolysis is likely to occur. Pure crystals of the double salt in glass containers blackened upon the surface. Crystals could be kept without discoloration when sealed in paraffin containers.

Preparation of Fluorine Gas by Heating Tripotassium Lead Hydrogen Octafluoride.—The heating of pure crystals of the double fluoride, $3KF.HF.PbF_4$, as a method of making free fluorine is practically a failure. Heating in an open dish (a platinum retort was not available) has never given enough free fluorine for the writer to detect its odor—a really sensitive test. However, sufficient fluorine is produced to etch the platinum dish. Ruff,[1] who has done more with fluorine and fluorides than anyone except Moissan, says that this method is not successful, although he obtained a sufficient quantity from a platinum retort to detect its odor.

These experiments with the complex octafluoride were discontinued as soon as the really satisfactory method of easily making free fluorine by the electrolysis of melted potassium hydrogen fluoride was discovered.[2]

Summary.

Tripotassium lead hydrogen octafluoride, $3KF.HF.PbF_4$, can easily be prepared by fusing potassium hydrogen fluoride with lead peroxide, followed by treatment with conc. hydrofluoric acid and drying at 225°. The treatment with hydrofluoric acid and drying should be repeated until the residue is almost white. Yields of 86% of the octafluoride can be obtained.

Yields of 62% of the tetrafluoride were obtained by direct solution of freshly prepared lead peroxide in almost anhydrous hydrofluoric acid.

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[1] *Loc. cit.*

[2] *Trans. Am. Electrochem. Soc.*, 35, 335 (1919); *J. Phys. Chem.*, 23, 348 (1919); *Chem. Eng.*, 27, 107 (1919).