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PREPARATION OF METAL FLUOBORATES

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This invention relates to an electrochemical method of preparing metal fluoborates.

Metal fluoborates were first prepared by the reaction of a metal carbonate with fluoboric acid. Lithium and aluminum fluoborates are formed as by-products in the reaction of lithium aluminum hydride with boron trifluoride ethyl etherate but the main product is diborane. Similarly, sodium and potassium fluoborates are produced as by-products in the preparation of diborane from sodium and potassium borohydrides and boron trifluoride. In the production of diborane it is necessary to recover BF_3 from the fluoborates which are produced as by-products of reaction. Sodium and potassium fluoborates decompose to produce BF_3 when heated to a very high temperature. Other fluoborates, such as alkaline earth fluoborates decompose to produce BF_3 at a much lower temperature. It has therefore become important to provide a method for readily converting sodium and potassium fluoborates to less stable fluoborates.

It is one of the objects of this invention to provide a new and improved method for the preparation of metal fluoborates in substantial yields from readily available fluoborates such as sodium or potassium fluoborate.

Another object of this invention is to provide a new and improved method for preparing metal fluoborates from sodium fluoborate by electrolysis.

A further object is to provide a new and improved method for preparing metal fluoborates in which sodium fluoborate is dissolved in a non-aqueous solvent and electrolyzed using a mercury or platinum cathode and a sacrificial metal anode.

Other objects of this invention will become apparent throughout the specification and claims as hereinafter related. This process will be described more fully in the specification and the novelty thereof will be particularly pointed out and distinctly claimed.

In this invention, a solution of an ionic fluoborate MBF_4 in an ionizing non-aqueous solvent is electrolyzed using either a mercury cathode or an inert cathode and a sacrificial metal anode comprised of the metal (M^1) of the fluoborate desired. The metal M of the dissolved fluoborate is deposited at the cathode as an amalgam if a mercury cathode is used. The metal M^1 must form an amalgam less readily than does metal M. At the same time the metal M^1 ions will go into solution from the anode. If the resultant fluoborate M^1BF_4 is soluble in the solvent, the reaction will go to completion only if the amalgam of the metal M^1 is higher in the electromotive series for the solvent used than the M amalgam. If the desired fluoborate M^1BF_4 is substantially insoluble in the solvent the M^1 and BF_4 ions will immediately react to precipitate M^1BF_4 at the anode.

In a particular experiment, 300 ml. of a saturated solution of sodium fluoborate in tetraethyleneglycol dimethyl ether [$CH_3(C_2H_4O)_4OCH_3$] was electrolyzed between a magnesium anode and a platinum cathode. A total of 0.5 amp. current with 30 applied volts was passed at an anode current density of 20 ma. per cm^2. The temperature of the cell during the electrolysis was approximately 30° C. A deposit of metallic sodium was observed at the cathode and a gelatinous precipitate, magnesium fluoborate, deposited in the cell during the electrolysis. In other experiments it has been found that this reaction proceeds more satisfactorily with a mercury cathode which forms an amalgam with the discharged sodium. By the use of a mercury cathode it has been found possible to prepare fluoborates of metals which are normally lower in the electromotive series than sodium.

Other experiments indicate that substantial yields of fluoborates may be obtained by using various polyethylene glycol ethers [$RO(C_2H_4O)_nR$, where R is an alkyl group and n is an integer] or lower organic amines such as ammonia, methylamine, ethylamine and dimethylamine as solvents. By judicious selection of the electrolytic solvent the resulting fluoborate may be obtained either as the anhydrous salt or as a solvate. Selection of the solvent to be employed in a particular instance will be governed by the extent and nature of solvation which can be tolerated in the product.

Metals which may be used as anodes include any desired metal the amalgam of which is more electropositive than sodium amalgam or whose fluoborate is insoluble in the solvent used for the electrolysis. It is also possible to use fluoborates of metals other than sodium as the solute in this process. The necessary requisites are that the dissolved fluoborate must dissociate ionically in the solvent and the resultant fluoborate must be insoluble in the solvent or the amalgam of the metal anode must be more electropositive than the amalgam of the metal deposited by electrolysis of the dissolved fluoborate. The term more electropositive as used herein is used in the sense that one metal is more electropositive than another metal when the one metal is less noble than the other metal and stands higher than the other metal in the electromotive series for the particular solvent in which the determination of electrochemical activity was made. It is to be understood that because of the different solvation energies of metal ions in different solvents the relative order of metals in the electromotive series varies slightly from one solvent to another. It is apparent therefore that, subject to the aforementioned requisites, this process may be employed as a method of preparation of any desired metal fluoborate from another metal fluoborate.

While we have described a few embodiments of our invention it is to be understood that within the scope of the claims appended hereto this invention may be practiced otherwise than as specifically described.

Having thus described our invention what we desire to claim and secure by Letters Patent of the United States is:

1. A method of preparing metal fluoborates comprising electrolyzing a non-aqueous solution of an ionic metal fluoborate with an anode of the desired metal in a solvent in which the desired metal fluoborate is substantially insoluble and recovering the fluoborate precipitated at the anode.

2. A method according to claim 1 in which the non-aqueous solvent is of the group consisting of polyethyleneglycoldialkylethers, liquid ammonia, and lower organic amines.

3. A method according to claim 1 in which the non-aqueous solvent is a polyethyleneglycol dialkyl ether.

4. A method according to claim 1 in which the non-aqueous solvent is liquid ammonia.

5. A method according to claim 4 in which non-aqueous solvent is a lower organic amine.

6. A method according to claim 1 in which the ionic metal fluoborate is of the group consisting of sodium fluoborate and potassium fluoborate.

7. A method according to claim 1 in which the anode

is comprised of a metal which is less noble than the metal of the dissolved fluoborate.

8. A method according to claim 7 in which the cathode is mercury.

9. A method of preparing metal fluoborates comprising electrolyzing a non-aqueous solution of an ionic fluoborate having the general formula MBF_4, where M is a metal whose fluoborate is soluble in the solvent, using a mercury cathode and a sacrificial metal anode of a metal M^1, where M^1 is the desired metal ion and forms an amalgam less readily than M, to produce the desired metal fluoborate M^1BF_0 and (M) amalgam, and recovering the fluoborate thus formed.

10. A method according to claim 9 in which the desired fluoborate M^1BF_4 is insoluble in the solvent.

11. A method of preparing magnesium fluoborate comprising electrolyzing a solution of sodium fluoborate in a polyethyleneglycol dimethyl ether using a cathode of a metal of the group consisting of mercury and platinum and a magnesium anode and recovering the fluoborate precipitated at the anode.

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