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A Method of Preparation of Uranium(+3) Compounds from Solutions

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Introduction

Up to now, the preparation of relatively few uranium(+3) compounds have been reported. The main reasons seem to have been (a) the large sensitivity of uranium(+3) compounds to hydrolysis and oxidation and (b) the instability of its aqueous solutions.

This paper presents a method of preparation of a number of uranium(+3) compounds like $U(HCOO)_3$ [1], M_2UCl_5 (M = K, Rb and NH_4) [2, 3], $M'U_2Cl_7$ (M' = K, Rb, NH_4, $(C_6H_5)_4As$ and $(C_6H_5)_4P$) [4] and UPO_4 [4], by reduction of UCl_4 solutions in formic acid or acetonitrile.

The application of an improved apparatus for carrying out all the necessary preparative operations in an oxygen-free atmosphere is described.

Apparatus and General Method of Preparation

The apparatus which enabled reduction, precipitation and isolation in the absence of air is shown in Fig. 1. The system, the construction of which is obvious from the figure, is a modification of that presented by Herzog and Dehnert [5].

A solution of the substance to be reduced was placed in flask C to which also a 2.4% liquid zinc amalgam was added until its surface reached a distance of approximately 2 mm from the extension (p) of the reaction flask B. Next, the appropriate amount of a wash liquid was added to flask A and the system was filled with an inert gas through stopcock (2) and evacuated by means of (1) and (3). Oxygen could also be easily removed from the liquids and the apparatus by connecting stopcocks (1) and (2) to a vacuum pump and subsequently evaporating for about 20 min the solutions in flasks A and C. The apparatus with the liquid zinc amalgam was then shaken for a time span of 15 to 30 min which was necessary for a complete reduction of the solution. Precipitation may occur in either flask B or flask C. In flask C it will occur due to reduction, cooling or evaporation, whereas in flask B it will be induced by the use of appropriate precipitation agents collected in flasks A or B. The solution with the precipitate is then forced to move from flask C, through the extension (p) into flask B by gently warming flask C or by joining stopcock (2) to vacuum. Such a method of separation has been established to avoid contamination with the liquid zinc amalgam. Flasks A and B were then separated from C, put together with flasks D and E and the latter rinsed with an inert gas. Filtering, washing and vacuum drying (cold or hot) of the substance collected on the filter plate (11) could then be easily effected by connecting flask E with a vacuum system. Finally, flask D could be emptied in a stream of inert gas entering it through a stopcock (4).

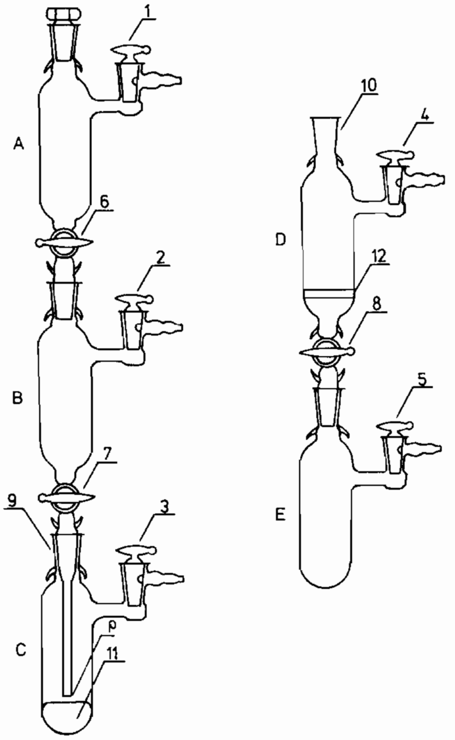

Fig. 1. System for reduction, precipitation and isolation in the absence of air. A) glass flask with a washing liquid; B, C) reaction flasks; D) filter flask with a glass frit (11); E) glass flask; 1–5 Schiff stopcocks; 6–8 stopcocks; 9, 10 some of the ground joints; 12 liquid zinc amalgam.

Reagents

Uranium tetrachloride was prepared from UO_2 according to the procedure given in ref. [1]. A 95% formic acid of analytical grade was used in the preparation of $U(HCOO)_3$. Acetonitrile was dried for several days over anhydrous Na_2SO_4 and distilled under reduced pressure. Other reagents were of analytical grade.

Preparation of Compounds

Uranium(+3) Formate

An approximately 0.25 *M* solution of UCl_4 in a 95% formic acid was reduced under an inert atmosphere in flask C, by shaking it with a 2.4% liquid zinc amalgam for 15 to 30 min. The reduction results in the change of the colour of the solution to a red-brown and in the formation, after a time, of a fine crystalline, dark olive-green precipitate. In order to obtain a better yield, the solution may be left for several days over the liquid zinc amalgam for crystallization. After separation from the zinc amalgam, the precipitate was filtered off, washed with anhydrous formic acid and dried under reduced pressure. All the operations were conducted as described in the preceding section.

Contrary to the previous report [1] it has been found that the use of a 90–95% formic acid provides a much more stable and pure product.

Attempts to prepare uranium(+3) acetate and propionate in an analogous way were unsuccessful.

Uranium(+3) complex chlorides of the M_2UCl_5 type

The synthesis of these compounds was first presented in ref. [2]. In a typical preparation, about 10 g of uranium tetrachloride was added, in small portions and under vigorous shaking, to a mixture of 5–8 g of MCl (M = K, Rb or NH_4) and 100 ml of a 50:1 solution of acetonitrile and propionic acid. The solutions were filtered from the excess of MCl, inserted into flask C and reduced for 20 to 30 min in an inert atmosphere with liquid zinc amalgam. The reduction results in the formation of fine crystalline, violet-purple precipitates. The excess of MCl is indispensable for the preparation of this type of complex. The subsequent operations have been performed as described above, using the 50:1 solution of acetonitrile and propionic acid as the wash liquid. More details about these compounds are given in ref. [1].

Uranium(+3) complex chlorides of the $M'U_2Cl_7$ type

Contrary to the previous synthesis, an excess of uranium tetrachloride is necessary for the preparation of these compounds. They were prepared by stirring about 95 ml of a 50:2 solution of acetonitrile and propionic acid with 5–8 g of M'Cl (M' = K, Rb, NH_4, $(C_6H_5)_4As$ or $(C_6H_5)_4P$) and 10 g of UCl_4. After filtering, about 5 ml of a 1 *M* solution of UCl_4 in propionic acid was added, the solution obtained transferred to the reaction flask C and reduced with zinc amalgam in an inert atmosphere. All the following operations were conducted as described above.

The reduction results in the separation of a fine crystalline, brown precipitate. Since these compounds are less stable to oxidation and more hygroscopic than those of the M_2UCl_5 type, they should be stored under an inert atmosphere in sealed tubes.

The complex chlorides dissolved easily in strong acids and numerous organic solvents such as methanol, ethanol, formic acid, acetic acid, tributylphosphate and N-methylformamide. Their electronic spectra [4] are typical for uranium(+3) but unlike the spectra of the M_2UCl_5 complexes, they do not exhibit the very broad and intense absorption bands at 17000–19000 cm^{-1}, which have been attributed to the formation of inner sphere uranium(+3) complexes [2–4, 6–8] and Laporte-allowed 5f–6d transitions [2, 3, 6–8].

Uranium(+3) phosphate

An approximately 0.1 *M* solution of uranium tetrachloride in anhydrous formic acid was reduced for about 20 min in flask C with liquid zinc amalgam and the resulting red-brown uranium(+3) solution transferred to flask B. In order to avoid a possible precipitation of the uranium(+3) formate, it is recommended to first saturate the solvent for about 5 min with gaseous hydrogen chloride. Next, the amount of Na_3PO_4 required for precipitation of UPO_4 is dissolved in about 30 ml of anhydrous formic acid, the solution inserted into flask I, and the oxygen dissolved removed by vacuum evaporation. The dropwise addition of this solution into flask B results in the separation of a voluminous, brown precipitate of UPO_4. The obtained compound was filtered off, thoroughly washed with anhydrous formic acid and vacuum dried.

The uranium(+3) phosphate is insoluble without decomposition and, when dried, is relatively stable to oxidation. The electronic spectra and magnetic susceptibility of this compound are typical for uranium(+3) [4].

Conclusions

The presented method facilitated, in a relatively simple manner, the preparation of a variety of uranium(+3) compounds. For the preparation of stable uranium(+3) solutions, by reduction of UCl_4 solutions with liquid zinc amalgam, other organic solvents besides formic acid may be used, such as methyl alcohol, ethyl alcohol and N-methylformamide. The use of a solvent is, among others, limited by its ability to dissolve zinc chloride, which is formed in the reduction process. Since it has been established that in many cases 10:2 mixtures of an organic solvent and water do not oxidize uranium both in solution and in the solid state, the number of solvents and ligands utilized may largely increase.

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References

1 B. Jeżowska-Trzebiatowska and J. Drożdżyński, *J. Inorg. Nucl. Chem., 31,* 727 (1969).

2 J. Drożdżyński, *Proc. 2nd Int. Conf. Electr. Str. Actin.,* Ed. Ossolineum (1977), Wrocław, Poland.

3 J. Drożdżyński and D. Miernik, *Inorg. Chim. Acta, 30,* 185 (1978).

4 J. Drożdżyński, to be published.

5 S. Herzog and E. Dehnert, *Z. Chem., 4,* 1 (1964).

6 M. Shiloh and V. Marcus, *Israel J. Chem., 3,* 123 (1965).

7 J. Drożdżyński and A. N. Kamenskaya, *Phys. Chem. Letters, 56,* 549 (1978).

8 J. Drożdżyński, *J. Inorg. Nucl. Chem., 40,* 319 (1978).

9 C. K. Jørgensen, *Acta Chem. Scand., 10,* 1503 (1956).

10 R. Barnard, J. I. Bullock and L. F. Larkworthy, *J. Chem. Soc. Dalton Trans., 819,* 964 (1972).