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PREPARATION OF URANIUM TRICHLORIDE BY THERMAL VACUUM DECOMPOSITION OF AMMONIUM TETRACHLOROURANATE(III) TETRAHYDRATE

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Abstract—Ammonium tetrachlorouranate(III) tetrahydrate may easily be converted into uranium trichloride at a non-static high-vacuum of 10^{-5}–10^{-6} Pa and temperatures ranging from 20–400°C.

The chemical literature reports several methods of preparation of uranium trichloride,[1] however this compound has been found to be difficult to obtain in a state of high purity. The most successful large scale synthesis involves the reaction of finely divided uranium metal or uranium hydride with gaseous hydrogen chloride at 250–300°C,[2,3] as well as the reduction of UCl_4 with hydrogen[3,4] or metallic zinc[5] at 450–650°C. The product obtained by any of these methods usually needs purification by chemical transport with iodine vapour.[3] Since uranium trichloride at higher temperatures is very sensitive to oxidation and hydrolysis, the preparative procedures need to be carried out under strict moisture- and oxygen-free conditions. Hence, the synthesis of UCl_3 requires a more or less complex apparatus as well as some experience and pure starting materials.

This paper presents a relatively simple method for the preparation of uranium trichloride by thermal decomposition of tetrachlorouranate(III) tetrahydrate. The method seems to be the most convenient in cases where only gram amounts of the compound are needed.

For the preparation of ammonium tetrachlorouranate(III) tetrahydrate, 1–5 g of uranium tetrachloride with a large excess of ammonium chloride was added to a solution consisting of 80 cm^3 methyl cyanide, 2.5 cm^3 water and 3.5 cm^3 propionic acid.[6] The mixture was shaken until all the tetrachloride dissolved, and was left standing for a couple of hours. Next, the solution was filtered off from the undissolved ammonium chloride and reduced in an inert atmosphere by gentle shaking with a 2.4% liquid zinc amalgam. The reduction resulted in the immediate formation of a well defined crystalline, violet–red precipitate of $NH_4UCl_4 \cdot 4H_2O$. An excess of water may result in the formation of a separate, oily phase consisting probably of a different, hydrated uranium(III) complex chloride. The precipitate was filtered off and washed under an inert atmosphere with degassed methylcyanide and freshly distilled ether, dried under reduced pressure at 25–35°C for about 20 min, and stored in sealed tubes at temperatures below 15°C. The yield of the reaction is *ca.* 80%.

The synthesis was carried out in a relatively simple all-glass apparatus as previously described.[7] The inert atmosphere glove box as well as by using a set necting the apparatus with a vacuum pump and evacuating the solutions and wash liquids for *ca.* 3 min. The synthesis may also be performed in an inert atmosphere glove box as well as by using a set of Schlenk tubes.

The compound crystallizes much easier and seems also to be much more resistant to oxidation by air, compared with the earlier obtained hydrated and anhydrous complex chlorides.[8–10] The physical and chemical properties of $NH_4UCl_4 \cdot 4H_2O$ along with its potassium and rubidium analogues will be given elsewhere.[11]

The ammonium tetrachlorouranate(III) tetrahydrate obtained in the above manner was converted into UCl_3 by a thermal high vacuum decomposition. For this purpose 1–3 g of $NH_4UCl_4 \cdot 4H_2O$ together with an excess (*ca.* 1.5 times) of NH_4Cl were placed in the bottom of the sealed off end of a quartz tube, 40 cm long and 2 cm in diameter. About 10 cm from the bottom, the tube narrowed and therefore the section of the tube with the product could be easily sealed off. The other end of the tube was fitted with a joint and vacuum stopcock. A furnace was slipped over the tube and the system was pumped off to *ca.* 10^{-6} Pa. Decomposition proceeds first between 25–80°C for at least 7 h. The temperature was never raised at a pressure higher than 10^{-4} Pa. At the end of the process the temperature was slowly rasied to 400°C. Samples of UCl_3 prepared in this manner are olive green in colour. The pyknometrically determined density of the compound is 5.46 g cm^{-3}. From X-ray data[11] a value of 5.51 g cm^{-3} was obtained. Found: U, 69.6; Cl, 31.1. Calc. for UCl_3: U, 69.1; Cl, 30.9%.

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