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Organic Compounds of Uranium. III. Uranium(V) Ethoxide

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Uranium(V) ethoxide, a dark-brown, thermally stable, distillable liquid, was prepared by several methods. Its physical properties and some of its reactions are described.

The reaction of powdered anhydrous uranium(IV) chloride with sodium ethoxide in ethanol gave a light green precipitate that apparently consisted of a mixture of uranium(IV) ethoxide[1] and sodium chloride. When the mixture was exposed to air it assumed a dark brown color, and its appearance offered little hope that any pure compound could be separated from the mixture. The green uranium(IV) ethoxide, when heated in a nitrogen atmosphere, charred and decomposed without melting. Uranium(IV) ethoxide, therefore, seemed quite unpromising as a route to volatile uranium compounds. Nevertheless, a preparation was carried out using sodium ethoxide and uranium(IV) chloride in a molar ratio of four to one; the solvent was removed by evaporation, and the residue was heated under greatly reduced pressure. Surprisingly, a small quantity of brown liquid distilled at about 110° under a pressure of 10^{-4} mm. of mercury. The astonishing fact was that this liquid contained a high percentage of uranium. The experiment was repeated a number of times varying the ratio of reactants, but the best yields were obtained when the original four-to-one ratio was used and when no great care was taken to exclude air from the reaction. Indeed, when air was deliberately passed through the mixture prior to distillation, still higher yields of the brown liquid were obtained. The product from a number of preparations consistently had the same boiling point and the same uranium content indicating a pure compound. Analyses for carbon, hydrogen, uranium and ethoxyl content established the empirical formula as $U(OC_2H_5)_5$. Evidently oxygen of the air or heat, or perhaps both had, in some way, converted $U(OC_2H_5)_4$ to $U(OC_2H_5)_5$.

Once the existence of uranium(V) ethoxide and its empirical formula had been established, a number of methods of preparation were suggested. Under carefully controlled conditions the reaction of uranium(IV) ethoxide in alcohol suspension with one-half mole of dry oxygen gave as high as 65% conversion to uranium(V) ethoxide. The mechanism of this reaction is not clear; however, one possibility is that part of the uranium is converted to oxide as indicated by the accompanying equation.

$$5U(OC_2H_5)_4 + O_2 \longrightarrow 4U(OC_2H_5)_5 + UO_2$$

On this basis the yields of $U(OC_2H_5)_5$ were about 80%.

Oxidizing agents other than oxygen itself successfully converted $U(OC_2H_5)_4$ to $U(OC_2H_5)_5$. The best of these was bromine. When one mole of uranium(IV) ethoxide was treated with one-half mole of bromine followed by one mole of sodium ethoxide, yields of uranium(V) ethoxide in the range of 90 to 95% were obtained.

$$U(OC_2H_5)_4 + {}^1/_2Br_2 \longrightarrow U(OC_2H_5)_4Br \xrightarrow{NaOC_2H_5} U(OC_2H_5)_5 + NaBr$$

This was the method of choice for the preparation of uranium(V) ethoxide and other related alkoxides to be described in following papers.

The reaction of uranium(V) chloride with five moles of sodium ethoxide in ethanol gave uranium(V) ethoxide in 64% yield. This method, although direct, was inconvenient because it involved the tedious preparation of uranium(V) chloride.[2]

$$UCl_5 + 5NaOC_2H_5 \longrightarrow U(OC_2H_5)_5 + 5NaCl$$

Uranium(V) ethoxide was a dark brown, mobile liquid having a density at 25° of 1.711. It distilled readily under reduced pressure boiling at about 123° (0.001 mm.); 134° (0.005 mm.); 145° (0.01 mm.) and 160° (0.05 mm.). Decomposition began at temperatures between 180 and 200°, but below 170° the compound was remarkably stable. A sample sealed in a glass tube was heated at 125° for four weeks and no decomposition took place. Ninety-nine per cent. of the material was recovered unchanged by distillation. A sample heated at 170° for four weeks underwent some decomposition, but even after this treatment, 78% was recovered by distillation. The compound was stable and miscible in all proportions with the following solvents: ethanol, ether, benzene, petroleum ether, ethyl acetate, carbon tetrachloride, chloroform, carbon disulfide, pyridine, 1,4-dioxane, mineral oil, tetraethyllead, epichlorohydrin and nitrobenzene. It dissolved but underwent change as evidenced by formation of precipitates with the following: acetone, methanol, *t*-butyl alcohol, glycerol, liquid ammonia, diethylamine, ethylenediamine and acetic anhydride. It was not miscible with acetonitrile.

The values for the molecular weight of uranium(V) ethoxide determined by the freezing point depression of benzene were 864 and 840 and by the freezing point depression of naphthalene 926 and 951. These figures correspond most closely with 926 which is double the formula weight of $U(OC_2H_5)_5$. The compound, therefore, may be expressed as $U_2(OC_2H_5)_{10}$, $[U(OC_2H_5)_5]_2$ or $U(OC_2H_5)_4{\cdot}U(OC_2H_5)_6$. The latter implies an association of one molecule each of uranium(IV) and uranium(VI) ethoxide. Indeed, when the compound was hydrolyzed with dilute acid exactly equal quantities of the U^{+4} and UO_2^{+2} were obtained. These ions, however, could have been formed by disproportionation of a uranium(V) compound at the time of hydrolysis. Uranium(V) ethoxide itself showed no tendency to disproportionate into

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[1] R. G. Jones, G. Karmas, G. A. Martin, Jr., and H. Gilman, THIS JOURNAL, **78**, 4285 (1956).

[2] O. Ruff and A. Heinzelmann, *Ber.*, **42**, 492 (1909).

uranium(IV) ethoxide and uranium(VI) ethoxide (a well-characterized compound to be described in a subsequent paper). It could be distilled repeatedly without change, and the relatively low boiling point indicated that the compound may exist as unassociated $U(OC_2H_5)_5$ in the vapor state although no molecular weight determinations were carried out with the vapor. From all appearances, uranium(V) ethoxide is a true compound of five-valent uranium, but it is very much more stable than uranium(V) chloride[3] which spontaneously decomposes even at room temperature to form UCl_4 and Cl_2.

Uranium(V) ethoxide reacted instantly with water to form uranium oxides and ethanol. For this reason it was necessary to carefully protect it from moisture during preparation and handling. Its reaction with alcohols, hydrogen halides, other metal alkoxides and oxidizing agents will be discussed in following papers.

Experimental

Uranium(V) Ethoxide. Oxygen Method.—In a 1-liter three-necked flask provided with a reflux condenser and rubber-sealed stirrer was placed 800 ml. of absolute ethanol to which was added as rapidly as practicable 46 g. (2 g. atom) of sodium cut into small pieces. Toward the end of the addition the mixture was heated under reflux and stirred to bring about complete reaction of the sodium. The solution was cooled to room temperature and protected from moisture with a calcium chloride tube. With rapid stirring, 190 g. of finely powdered uranium(IV) chloride[4] was added in approximately 20-g. portions at intervals of about five minutes. Heat was evolved, and to keep the ethanol from boiling too vigorously the flask was surrounded with a bath of cold water. When the exothermic reaction had subsided the flask was placed in a steam-bath and the mixture heated under reflux with vigorous stirring for two hours. During this time the mixture became a thick light green colored paste.

After the mixture had cooled to room temperature, one neck of the flask was fitted with a rubber stopper carrying a T-tube. One branch of the T-tube was connected to an aspirator, the other was connected through a calcium chloride drying tube to a suitable gas holder containing 2.5 l. (0.1 mole) of oxygen. The tube leading to the oxygen was closed as was the remaining opening of the flask and the flask was partially evacuated (to about 50 mm.) by means of the aspirator. The tube to the aspirator was then closed, and that leading to the oxygen holder was carefully opened allowing the oxygen to be drawn into the reaction mixture. The mixture was rapidly stirred and as the oxygen was absorbed the color changed from light green to dark brown. Some heat was evolved. Stirring was continued for about one-half hour.

About one-third of the mixture was transferred with minimum exposure to the air to a dry 500-ml. Claisen flask provided with a condenser for distillation. In the straight neck of the Claisen flask was placed a rubber-sealed stirrer. The flask was immersed in an oil-bath, the temperature of which was gradually raised to 150°, and, with stirring to prevent bumping, the alcohol was distilled. Another portion of the reaction mixture was then transferred to the Claisen flask, and the process was repeated until almost all the alcohol had been removed and the mixture was concentrated in the Claisen flask. To remove the last of the alcohol, the stirrer was replaced with a stopper and the flask was heated in the bath at 150° under 2-3 mm. pressure. During all the manipulations the contents of the flask were carefully protected from moisture.

The flask containing the almost solid residue of sodium chloride and the desired uranium(V) ethoxide was attached through a short condenser to a vacuum system consisting of a mercury vapor pump backed by a large capacity mechanical vacuum pump. A deep oil-bath was placed around the flask and heated gradually. The product began to distil under 0.001-0.004 mm. pressure at a bath temperature of 180°, and the collection of distillate was continued up to a bath temperature of 240°. When the distillation was complete the pump was stopped, and the apparatus was allowed to cool before dry air was readmitted.

The yield was 150 g. (65% based on uranium(IV) chloride used). It was pure uranium(V) ethoxide, and upon redistillation it all came over at 129-131° (0.002 mm.). The compound was a brown, mobile, heavy liquid.

Bromine Method.—Uranium (IV) chloride, 0.5 mole, was allowed to react with 2 moles of sodium ethoxide in absolute ethanol as described above. The mixture was cooled to room temperature and with rapid stirring a solution of 40 g. (0.5 g. atom) of bromine in 20 ml. of dry benzene was added dropwise during 15 minutes. The color of the mixture changed from light green to brown to gray and was finally dark green at the end of the addition. Some heat was evolved.

The mixture was well stirred and to it was added rapidly a solution of sodium ethoxide made by dissolving 11.5 g. (0.5 g. atom) of sodium in 200 ml. of absolute ethanol. The color immediately changed from dark green to brown. The mixture was concentrated and the product distilled as described above. Yields of uranium(V) ethoxide ranged from 184 to 217 g. (80-94%).

Preparations as large as 1.25 moles were carried out and distilled to yield up to 500 g. of product in a single batch. Experiments in which attempts were made to remove the sodium chloride and bromide by filtration before distillation were not satisfactory because of the finely divided character of the salt. Filtration was slow and tedious. The presence of the salt in the distilling flask offered no particular difficulties.

Uranium(V) Ethoxide from Uranium(V) Chloride.—Freshly prepared uranium(V) chloride,[2] 9.2 g. (0.023 mole), was added in portions to a solution of sodium ethoxide made by dissolving 2.3 g. (0.1 g. atom) of sodium in 50 ml. of absolute ethanol. The reaction was vigorous. After the addition, the mixture was heated under reflux for four hours, and then the solvent was removed by distillation under reduced pressure. The residue was subjected to distillation under high vacuum and 4.7 g. (64% yield) of pure uranium(V) ethoxide was obtained.

Another variation of this method was to use dry ammonia as the base in place of sodium ethoxide. To a solution of 7 ml. of dry ethanol in 7 ml. of dry ether was added 1.4 g. of freshly prepared, powdered uranium(V) chloride. The mixture was stirred and dry ammonia was passed in until saturated. The mixture turned dark brown and became thick with precipitated ammonium chloride. An additional 30 ml. of dry ether was added, and the mixture was centrifuged. The ether solution was concentrated in a small flask and the residue distilled under high vacuum yielding 1.1 g. (72%) of uranium(V) ethoxide.

Analysis.—Samples of uranium(V) ethoxide were redistilled for analysis. Boiling points varied somewhat depending on the rate of distillation. Some typical temperatures and pressures were: 119-122° (0.0018 mm.), 128-130° (0.0048 mm.). Samples were burned with potassium chlorate for carbon and hydrogen determinations. Uranium was determined in the usual way with 8-hydroxyquinoline.

Anal. Calcd. for $U(OC_2H_5)_5$: C, 25.90; H, 5.43; U, 51.39. Found: C, 25.84, 25.90; H, 5.69, 5.59; U, 50.68, 50.60.

Many analyses were made for uranium on numerous samples of $U(OC_2H_5)_5$ and the values were always consistently low. No explanation for this was found.

A weighed sample of uranium(V) ethoxide was decomposed under nitrogen with 5% sulfuric acid solution. The U^{+4} ion was separated from the UO_2^{+2} ion by addition of potassium iodate according to the method of Kaufman.[5] The only modification was that sodium bisulfite was used in place of oxalic acid to destroy excess iodate. The uranium contents of the precipitate and the filtrate were determined separately by the 8-hydroxyquinoline method.

Anal. Calcd. for $U(OC_2H_5)_5$: U, 51.39. Found: U^{+4}, 25.86; UO_2^{+2}, 25.94; total 51.80.

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[3] H. Martin and K. H. Eldau, *Z. anorg. allgem. Chem.*, **251**, 295 (1943) [*C. A.*, **37**, 5328 (1943)].

[4] Obtained from Harshaw Chemical Company.

[5] L. Kaufman, *Compt. rend. acad. Sci.* (*U.S.S.R.*), **27**, 807 (1940) [*C. A.*, **35**, 1724 (1941)].