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Organic Compounds of Uranium. II. Uranium(IV) Amides, Alkoxides and Mercaptides

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Uranium(IV) diethylamide, a green, low melting, distillable compound, was prepared from uranium(IV) chloride and lithium diethylamide. Uranium(IV) ethyl and *n*-butylmercaptides were prepared from uranium(IV) diethylamide and the corresponding mercaptans. These light green solids were pyrophoric. Uranium(IV) methoxide and ethoxide were obtained from reactions of the alcohols with uranium(IV) diethylamide. They were light green solids, readily decomposed by air or moisture.

Early in the studies on volatile uranium compounds[1] a number of organic derivatives of uranium(IV) were prepared. Among the most interesting of these was uranium(IV) diethylamide which could be distilled and from which pure samples of uranium(IV) alkoxides and mercaptides were synthesized.

Uranium(IV) diethylamide was prepared by the reaction of lithium diethylamide with uranium(IV) chloride using ether as solvent. The product was isolated by distillation under greatly reduced pressure. It was obtained as an emerald-green liquid that crystallized when cooled and melted at 35.5–36.5°. The best yields were 25–30%, and these low yields were probably a result of decomposition during distillation. The reaction of lithium diethylamide with uranium(V) chloride gave also uranium(IV) diethylamide as the only product isolated.

Attempts to prepare other uranium(IV) dialkylamides were unsuccessful. The lithium derivatives of dimethylamine, diallylamine, diisopropylamine, di-*n*-butylamine and piperidine were allowed to react with uranium(IV) chloride, and in all cases exothermic reactions took place with probable formation of the desired uranium amides. From none of these reactions, however, could any products be isolated by distillation; complete decomposition took place. Possibly the products could have been isolated from the reaction mixtures by extraction with appropriate solvents.

$$4LiN(C_2H_5)_2 + UCl_4 \longrightarrow U[N(C_2H_5)_2]_4 + 4LiCl$$

Uranium(IV) diethylamide was readily soluble in non-polar solvents such as ether, benzene or petroleum ether. It was very readily hydrolyzed and also was extremely sensitive to oxygen. The slightest contact with air caused it to turn brown; thus, the preparation, isolation and all subsequent operations were carried out in an atmosphere of dry nitrogen.

The reaction of uranium(IV) diethylamide with ethyl mercaptan in ether solution gave uranium (IV) ethyl mercaptide as a light green solid. It was purified by washing with ether. In the same way uranium(IV) *n*-butyl mercaptide was prepared from *n*-butyl mercaptan. These compounds did not melt but decomposed when heated to high temperatures. They were very sensitive to water or oxygen. When samples were exposed to the open air they spontaneously burst into flames and burned vigorously.

$$U[N(C_2H_5)_2]_4 + 4RSH \longrightarrow U(SR)_4 + 4(C_2H_5)_2NH$$

The uranium(IV) alkoxides like the mercaptides were readily prepared by reactions of alcohols with uranium(IV) diethylamide in ether solution. The tetramethoxide and the tetraethoxide were obtained analytically pure by this method. These compounds were light green solids, insoluble in ether, sparingly soluble in alcohol, and they decomposed without melting when heated. They were readily hydrolyzed and were highly sensitive to oxygen. The slightest exposure to air caused them to turn brown. Unlike the mercaptides, the alkoxides were not pyrophoric, but when exposed to the air the brown colored and stable penta-alkoxides appeared to be formed. These will be discussed in subsequent papers.

$$U[N(C_2H_5)_2]_4 + 4ROH \longrightarrow U(OR)_4 + 4(C_2H_5)_2NH$$
$$UCl_4 + 4LiOR \longrightarrow U(OR)_4 + 4LiCl$$

Although small pure samples of the uranium(IV) alkoxides were prepared from the diethylamide, the method was impractical for larger quantities. Uranium(IV) methoxide was obtained in quantity and in a reasonably pure state from uranium(IV) chloride and lithium methoxide in methanol. Since lithium chloride is quite readily soluble in methanol whereas uranium(IV) methoxide is insoluble, isolation of the product was accomplished by centrifugation of the reaction mixture followed by washing the solid in the centrifuge bottle with methanol and ether. In the same way uranium(IV) ethoxide was prepared but the yield in this case was only about 50% because of the appreciable solubility of the compound in ethanol. Preliminary experiments indicated that the solubilities of the uranium(IV) alkoxides increased with increasing size of the alcohol groups. The tertiary butoxide appeared to be soluble even in petroleum ether.

Reactions of uranium(IV) chloride with sodium alkoxides gave the uranium(IV) alkoxides admixed with sodium chloride. This reaction was generally used as an intermediate step in preparation of the uranium(V) alkoxides to be described in subsequent papers. Ammonia and/or potassium amide reacted with uranium(IV) chloride and various

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[1] H. Gilman, R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. F. Nobis, J. R. Thirtle, H. L. Yale and F. A. Yoeman, THIS JOURNAL, **78**, 2790 (1956).

alcohols to form uranium(IV) alkoxides. In this way pure uranium(IV) *t*-butoxide was prepared. This compound was unusual in two respects. It was readily soluble in low-boiling petroleum ether, and when this solution was evaporated large green crystals were obtained. It was much less sensitive to air oxidation than other uranium(IV) alkoxides, and apparently was not readily converted to $U(t\text{-}OC_4H_9)_5$.

$$UCl_4 + 4KNH_2 \longrightarrow [U(NH_2)_4] \xrightarrow{t\text{-}C_4H_9OH} U(t\text{-}OC_4H_9)_4 + 4NH_3$$

Experimental

Uranium(IV) Diethylamide.—Methyllithium, about 1.5 to 2.0 molar, was prepared in the usual way from methyl chloride. The solution was standardized by titration of an aliquot with acid, and then a quantity of the solution containing 0.4 mole of CH_3Li was transferred by means of a pipet to a dry 500-cc. three-necked flask. The flask was provided with a rubber sealed stirrer, dropping funnel and reflux condenser and was previously swept out with nitrogen. To the methyllithium solution was added dropwise and with stirring, 29.2 g. (0.40 mole) of pure diethylamine which had been dried over metallic sodium. Methane was evolved rapidly, and a clear ether solution of lithium diethylamide was formed.

A 250-ml. Claisen flask with ground glass joints was provided with a dropping funnel, nitrogen inlet, and condenser and receiver. In the flask were placed 38 g. (0.10 mole) of powdered, anhydrous uranium(IV) chloride and 20 ml. of dry ether. From the dropping funnel was added slowly the ether solution containing 0.4 mole of lithium diethylamide. Reaction took place immediately but soon became slow because the uranium(IV) chloride in the presence of ether coalesced into a compact mass. The flask was placed in a warm water-bath, and ether was distilled from the mixture as the lithium diethylamide solution was added so that the volume was kept at about 200 ml. After all of the diethylamide solution had been added, the dropping funnel was replaced with a rubber sealed stirrer, care being taken that no air entered the flask, and the mass of UCl_4 was cautiously broken up to allow the reaction to proceed. The reaction appeared to be complete in about one to two hours. The ether was then removed by distillation, and the dark brown residue was heated on a water-bath at 60–80° under about 20 mm. pressure for 1.5 hours. The flask was refilled with dry nitrogen, then connected to the high vacuum system and heated gradually up to 120° in an oil-bath. At 60° the pressure in the system was 0.059 mm. of mercury. At a bath temperature of 80° the first distillate began to collect. After 2.5 hours at 115 to 125° the distillation was complete, and the apparatus was refilled with dry nitrogen. The yield of pure uranium(IV) diethylamide was usually 10.5 to 14 g. (20–27%). The best yields were obtained when the distillation was carried out at the lowest possible pressure. At 115–125° appreciable decomposition took place, and above 130° decomposition became very rapid.

For analysis, samples were collected in small tared bulbs with capillary stems.[2] The bulbs were broken under dilute sulfuric acid with which the contents reacted violently. The mixture was made basic with sodium hydroxide and distilled. Diethylamine was determined in the distillate by titration with standard acid. Uranium was determined, as usual, with 8-hydroxyquinoline.

Anal. Calcd. for $U[N(C_2H_5)_2]_4$: U, 45.25; $(C_2H_5)_2N$-, 54.75. Found: U, 44.89, 44.84; $(C_2H_5)_2N$-, 54.94, 54.61.

The molecular weight of uranium(IV) diethylamide was determined by the freezing point lowering of benzene. The experiment was carried out in an atmosphere of nitrogen.[3] The values observed were 471 and 525 while the simplest formula weight for $U[N(C_2H_5)_2]_4$ is 526.

Uranium(IV) Ethoxide.—An ether solution of uranium (IV) diethylamide was prepared by dissolving 6 g. of the pure compound in 10 ml. of anhydrous ether. The solution was carefully protected by a nitrogen atmosphere. A 2-ml. portion of this dark green solution was added, with a pipet, to a solution of 1 ml. of absolute ethanol in 2 ml. of dry ether. This was contained, under a nitrogen atmosphere, in a small filtering beaker with a sintered glass disc. A vigorous reaction took place immediately with evolution of heat and the formation of a voluminous light green precipitate. The ether was removed through the filter disc, and the precipitate was washed with three 5-ml. portions of dry ether. The product was dried in a slow current of nitrogen.

Anal. Calcd. for $U(OC_2H_5)_4$: U, 56.94. Found: U, 56.86.

Uranium(IV) Methoxide.—This was prepared in the same way as the ethoxide.

Anal. Calcd. for $U(OCH_3)_4$: U, 65.75. Found: U, 65.00.

When exposed to the air this product quickly turned brown, and with water it turned black.

Uranium(IV) Ethylmercaptide.—In a small filtering beaker was placed a solution of 1 ml. of dry ethyl mercaptan in 3 ml. of ether. To this was added by pipet 2 ml. of ether solution containing about 1 g. of uranium(IV) diethylamide. A black gelatinous precipitate instantly formed, and this immediately began to change to a flocculent green precipitate with the evolution of heat. The ether solution was filtered under nitrogen from the green precipitate and the latter was washed by suspension in four 5-ml. portions of dry ether. The mercaptide was dried by gently warming in a current of nitrogen.

Anal. Calcd. for $U(SC_2H_5)_4$: U, 49.38. Found: U, 49.55.

Uranium(IV) *n*-Butylmercaptide.—This was prepared in the same way as the ethylmercaptide.

Anal. Calcd. for $U(SC_4H_9)_4$: U, 40.07. Found: U, 40.66 and 40.64.

Uranium(IV) *t*-Butoxide.—Potassium amide was prepared by adding a total of 6.25 g. (0.16 g. atom) of potassium metal in small portions to one liter of dry liquid ammonia containing a little ferric oxide as catalyst. When the addition was complete the mixture was stirred for 45 minutes during which time the blue color disappeared and the mixture became orange-red. To this potassium amide in liquid ammonia was added 15.2 g. (0.04 mole) of powdered, anhydrous uranium(IV) chloride in small portions with stirring. After 1.5 hours, 14.8 g. (0.20 mole) of dry *t*-butyl alcohol was added and stirring was continued for two hours. The ammonia was allowed to evaporate, and the residue was extracted with 500 ml. of dry petroleum ether (b.p. 28–38°). The petroleum ether extract was colored bright green. It was allowed to evaporate and large green crystals of uranium(IV) *t*-butoxide were obtained. The yield was not determined.

Anal. Calcd. for $U(OC_4H_9)_4$: U, 44.9. Found: U, 45.1.

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[2] E. Krause and P. Dittmar, *Ber.*, **63**, 2401 (1930).

[3] E. Krause and P. Dittmar, *ibid.*, **63**, 2347 (1930).