[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organic Compounds of Uranium. VI. Uranium(VI) Alkoxides

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Uranium(VI) ethoxide, a dark-red, distillable liquid, was prepared by oxidation of the sodium ethoxide complex of uranium(V) ethoxide with benzoyl peroxide. Other less efficient oxidizing agents were oxygen, bromine and lead tetraacetate. Other related uranium(VI) alkoxides were synthesized by the benzoyl peroxide method, but more conveniently they were obtained by exchange reactions between uranium(VI) ethoxide and various alcohols. The uranium(VI) alkoxides, although relatively volatile, were unstable toward heat.

During the early work on the preparation of uranium(V) ethoxide[1] a very small quantity of by-product in the form of a bright red liquid was often encountered. This red compound was usually obtained when oxygen was employed in the preparation of $U(OC_2H_5)_5$ or when the latter was exposed to dry air for extended periods of time. The red liquid was more volatile than $U(OC_2H_5)_5$ and was collected as a forerun during the distillation. Eventually enough was obtained for characterization, and the analyses for uranium, carbon and hydrogen were consistent with the formula $U(OC_2H_5)_6$. This new compound was of great interest because of its relatively high volatility, and therefore its preparation and reactions were studied. Several related uranium(VI) alkoxides were prepared. Although in this group were found the most highly volatile of the organic compounds of uranium, in general the $U(OR)_6$ derivatives were of limited stability. Even moderate heating caused decomposition, and for this reason they showed little promise as useful substances for isotope separation.

Initially, attempts were made to convert uranium(V) ethoxide to the uranium(VI) compound by reaction with oxygen under various conditions. Although small quantities of the desired compound were obtained, this method proved to be impractical. Other oxidizing agents such as magnesium peroxide, hydrogen peroxide–urea complex, chlorine, iodine and nitrosyl chloride gave negative results. Reactions of uranium(V) ethoxide with bromine and sodium ethoxide gave low yields (5–10%) of uranium(VI) ethoxide. Better yields (about 20%) were obtained by treating the sodium ethoxide salt of uranium(V) ethoxide[2] with lead tetraacetate. These reactions were carried out in ether or petroleum ether; in alcohol none of the uranium(VI) compound was formed.

$$NaU(OC_2H_5)_6 + {}^1/_2Br_2 \longrightarrow U(OC_2H_5)_6 + NaBr$$

$$NaU(OC_2H_5)_6 + {}^1/_2Pb(OAc)_4 \longrightarrow U(OC_2H_5)_6 + NaOAc + {}^1/_2Pb(OAc)_2$$

The best method for the preparation of uranium(VI) ethoxide involved the use of benzoyl peroxide as oxidizing agent and ethanol as the solvent. The product was isolated by distillation from the reaction mixture and purified by fractionation under high vacuum. Yields were 40 to 60% based on uranium(V) ethoxide.

$$U(OC_2H_5)_5 + NaOC_2H_5 \longrightarrow NaU(OC_2H_5)_6$$

$$2NaU(OC_2H_5)_6 + (C_6H_5CO)_2O_2 \longrightarrow 2U(OC_2H_5)_6 + 2NaO_2CC_6H_5$$

Uranium(VI) ethoxide was a red, mobile liquid having a density of 1.563. It distilled at 74–76° (0.003 mm.); 93° (0.18 mm.). Values for the molecular weight, as determined by the freezing point depression of benzene were 613 and 630. These correspond most closely with the simplest formula weight, 508, for $U(OC_2H_5)_6$. Thus the compound appeared not to be appreciably associated in benzene solution.

A sample of uranium(VI) ethoxide in a sealed glass tube was heated at 86° for 66 hours. During this time it had largely decomposed. Less than 20% of the $U(OC_2H_5)_6$ was recovered, and the main product, obtained in about 50% yield, was $U(OC_2H_5)_5$. Uranium(VI) ethoxide was readily soluble in such liquids as benzene, ether, petroleum ether, etc. It was extremely reactive toward moisture, and was hydrolyzed to form uranyl hydroxide. For analysis samples were allowed to react with cold, dilute sulfuric acid to yield solutions of uranyl sulfate. The uranium was then determined by the usual 8-hydroxyquinoline method.

As expected, uranium(VI) ethoxide was a rather powerful oxidizing agent. It was easily reduced to the stable uranium(V) ethoxide by heating with ethyl mercaptan, diethylamine or ethyl cyanoacetate. A reaction between uranium(VI) ethoxide and uranium(IV) ethoxide[3] gave uranium(V) ethoxide.

$$U(OC_2H_5)_6 + U(OC_2H_5)_4 \longrightarrow 2U(OC_2H_5)_5$$

One mole of dry hydrogen chloride reacted with uranium(VI) ethoxide to give a liquid compound that appeared to have the formula $U(OC_2H_5)_5Cl$. When uranium(VI) ethoxide was treated with sodium ethoxide there was no evidence that reaction took place or that a salt was formed. Alcohols readily entered into exchange reactions with uranium(VI) ethoxide just as with uranium(V) ethoxide.[4]

$$U(OC_2H_5)_6 + 6ROH \longrightarrow U(OR)_6 + 6C_2H_5OH$$

Presumably, a series of mixed uranium(VI) alkoxides like $U(OR)_5(OR')$, $U(OR)_3(OR')_3$, etc., also were formed in reactions of this type. With a large excess of methanol, uranium(VI) ethoxide reacted to form uranium(VI) methoxide. The

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(1) R. G. Jones, E. Bindschadler, G. Karmas, F. A. Yeoman and H. Gilman, THIS JOURNAL, **78**, 4287 (1956).

(2) R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. R. Thirtle and H. Gilman, *ibid.*, **78**, 6027 (1956).

(3) R. G. Jones, G. Karmas, G. A. Martin, Jr., and H. Gilman, *ibid.*, **78**, 4285 (1956).

(4) R. G. Jones, E. Bindschadler, G. Karmas, G. A. Martin, Jr., J. R. Thirtle, F. A. Yeoman and H. Gilman, *ibid.*, **78**, 4289 (1956).

latter also was prepared from $NaU(OCH_3)_6$ and benzoyl peroxide. The methoxide was a deep red crystalline solid that melted at 62–64° and distilled at 87° (0.01 mm.). Uranium(VI) isopropoxide, prepared from the ethoxide and isopropyl alcohol, was also a dark red solid melting at 167–168°. It sublimed when heated under vacuum. The *n*-propoxide was prepared from *n*-propyl alcohol and uranium(VI) ethoxide, and, like the latter, it was a red liquid. It was relatively unstable, however, and underwent some decomposition during distillation. Uranium(VI) *n*-butoxide appeared to be formed from uranium(VI) ethoxide and *n*-butyl alcohol. The compound, a red liquid, decomposed completely when it was heated under 0.007 mm. pressure and the only product, obtained as a distillate, was the stable, brown uranium(V) *n*-butoxide.[4]

Experimental

Uranium(VI) Ethoxide.—In a dry, 500-ml. three-necked flask fitted with a gas-tight stirrer and a gas inlet tube connected to a source of dry nitrogen was placed 300 ml. of absolute ethanol. In this was dissolved 1.69 g. (0.074 g. atom) of sodium. After the sodium had all dissolved the solution was allowed to cool in an atmosphere of nitrogen, and then 20 ml. (34 g., 0.074 mole) of uranium(V) ethoxide[1] was added from a pipet. The brown color of the uranium (V) ethoxide was discharged and a clear, light green solution of $NaU(OC_2H_5)_6$ was formed. This solution was rapidly stirred, and 8.90 g. (0.037 mole) of dry, powdered benzoyl peroxide was added through the side neck of the flask in three equal portions at 10-minute intervals. The mixture quickly turned dark red, and a gelatinous precipitate of sodium benzoate separated. A little heat was evolved. Stirring was continued at room temperature under a nitrogen atmosphere for one hour.

About one-half of the above reaction mixture was transferred under a nitrogen atmosphere to a 250-ml. claisen flask attached to a condenser and receiver for vacuum distillation. The alcohol was distilled at atmospheric pressure by heating on a steam-bath. When the contents of the flask had been reduced in volume, more of the reaction mixture was added and distillation of the alcohol was continued until the reaction mixture had been concentrated in the claisen flask. The flask was now heated in an oil-bath gradually up to 140° under 5 to 10 mm. pressure to remove the remaining alcohol. Distillation was continued under high vacuum (about 0.003 mm. pressure) and a bath temperature of 100–140°. The crude uranium(VI) ethoxide came over as a dark red liquid; the yield was about 20 g. Small quantities of impurities such as uranium(V) ethoxide and ethyl benzoate were removed by redistillation under high vacuum. The yield of pure product was 16 g. (43%), b.p. 72–74° (0.001 mm.).

Anal. Calcd. for $U(OC_2H_5)_6$: C, 28.34; H, 5.95; U, 46.84. Found: C, 28.58, 28.46; H, 6.16, 6.00; U, 45.90, 46.23.

The carbon and hydrogen analyses were carried out in the same manner as described for uranium(V) ethoxide.[1] For uranium analysis a thin-walled glass bulb containing a weighed sample of the compound was broken under ice-water. The solution was acidified with sulfuric acid, and uranyl-8-hydroxyquinoline compound was precipitated, dried and weighed.

The preparation was carried out many times and yields ranged from 30 to 70%. Best yields appeared to be obtained when a 10 to 20% excess of benzoyl peroxide was used. One preparation using 0.02 mole of $NaU(OC_2H_5)_6$ in 25 ml. of ether solution and 0.01 mole of lead tetraacetate as oxidizing agent, carried out and worked up essentially as described above, gave 2.1 g. (20% yield) of uranium(VI) ethoxide.

Uranium(VI) Methoxide.—This was prepared from uranium(V) methoxide,[4] sodium methoxide and benzoyl peroxide in methanol solution in the same way as described for the preparation of uranium(VI) ethoxide. The compound distilled as a red liquid at 87° (0.01 mm.), 96–98° (0.5 mm.). After cooling it crystallized to a deep red solid, m.p. 62–64°. The yield was 20%.

Anal. Calcd. for $U(OCH_3)_6$: U, 56.13. Found: U, 55.42, 55.49.

Uranium(VI) methoxide also was prepared by dissolving 7.82 g. (0.015 mole) of uranium(VI) ethoxide in 25 ml. of carefully dried methanol and allowing the solution to stand for several hours. The mixture was distilled, and after removal of the alcohol the uranium(VI) alkoxide was distilled under high vacuum. The red distillate was again treated with methanol, and the process was repeated four times. Eventually 4.4 g. (67% yield) of uranium(VI) methoxide was obtained; b.p. 92° (0.3 mm.), m.p. 62–64°.

Uranium(VI) Isopropoxide.—To 25 ml. of dry isopropyl alcohol in a small distilling flask was added 6.0 g. (0.012 mole) of uranium(VI) ethoxide. The solution, under nitrogen, was allowed to stand for 24 hours after which it was heated on the steam-bath under about 10 mm. pressure to remove the alcohols. The solid residue was heated in an oil-bath at 135° under 0.004 mm. pressure. The uranium (VI) isopropoxide sublimed rapidly and collected as a dark red crystalline solid, m.p. 167–168°, yield 3.0 g. (42%).

Anal. Calcd. for $U(OC_3H_7)_6$: U, 40.20. Found: U, 40.46, 40.30.

Uranium(VI) *n*-Propoxide.—This was prepared from uranium(VI) ethoxide and dry *n*-propyl alcohol in the same way as uranium(VI) isopropoxide. It was obtained in about 40% yield as a deep red liquid, b.p. 115° (0.004 mm.), 105–107° (0.001 mm.).

Anal. Calcd. for $U(OC_3H_7)_6$: U, 40.2. Found: U, 40.6, 40.5.

The chief by-product from this preparation appeared to be uranium(V) *n*-propoxide,[4] brown liquid, b.p. 165° (0.004 mm.). When the uranium(VI) *n*-propoxide was redistilled, more uranium(V) *n*-propoxide was formed.

When uranium(VI) ethoxide was allowed to react with dry *n*-butyl alcohol followed by distillation of the excess alcohols a red liquid, presumably uranium(VI) *n*-butoxide, was obtained. This was distilled under 0.007 mm. pressure, but the only product isolated was the brown uranium(V) *n*-butoxide, b.p. 205° (0.007 mm.). The latter apparently was formed by thermal decomposition of the uranium(VI) *n*-butoxide.

Preparation of $U(OC_2H_5)_5Cl$.—To a solution of 5.7 g. (0.012 mole) of uranium(VI) ethoxide in 25 ml. of dry ether was added 52.5 ml. (0.012 mole) of 0.221*M* hydrogen chloride in dry ether solution. The resulting solution which had turned from red to dark red-brown in color, was stirred for one hour and, after evaporation of the solvent, the residue was fractionally distilled. The main fraction came over at 90–110° (0.003 mm.). This was redistilled to give a liquid, b.p. 104–107° (0.007 mm.).

Anal. Calcd. for $U(OC_2H_5)_5Cl$: Cl, 7.12. Found: Cl, 6.99, 6.96.

Reduction of Uranium(VI) Ethoxide.—To a solution of 7.8 g. (0.015 mole) of uranium(VI) ethoxide in 25 ml. of dry ether was added 5.7 g. (0.092 mole) of ethyl mercaptan. The color of the solution changed from red to dark brown. After heating under reflux for two hours the solvent was evaporated, and the residue was distilled under high vacuum to yield 6.5 g. (96%) of uranium(V) ethoxide, b.p. 128–130° (0.001 mm.).

Anal. Calcd. for $U(OC_2H_5)_5$: U, 51.39. Found: U, 50.75.

A reaction carried out as above except that 6.75 g. (0.092 mole) of dry diethylamine was used in place of ethyl mercaptan gave 6.0 g. (87% yield) of uranium(V) ethoxide identified by distillation point and analysis.

To 7.82 g. (0.015 mole) of uranium(VI) ethoxide was added 5.65 g. (0.05 mole) of freshly distilled ethyl cyanoacetate. After 24 hours the mixture was distilled and the only uranium compound isolated was 3.1 g. (45% yield) of brown uranium(V) ethoxide, b.p. 125–127° (0.001 mm.).

Anal. Calcd. for $U(OC_2H_5)_5$: U, 51.39. Found: U, 50.68.

Reaction of Uranium(VI) Ethoxide with Uranium(IV) Ethoxide.—Uranium(IV) ethoxide was prepared by adding, under nitrogen, a dry ether solution containing 1.6 g. (0.003 mole) of uranium(IV) diethylamide[3] to 5 ml. of absolute ethanol. The solvents were removed by evaporation under reduced pressure, and the green powder was suspended in 10 ml. of dry petroleum ether (b.p. 60–68°). To this was added 1.0 ml. (0.003 mole) of uranium(VI) ethoxide. The green solid slowly disappeared and a brown solution was formed. After removal of the petroleum ether by evaporation, the residual brown liquid was distilled giving 2.5 g. (78% yield) of uranium(V) ethoxide identified by boiling point and analysis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Reactions of Perfluoronitriles. I. Synthesis of Derivatives of Perfluoroamidines, N-Substituted Perfluoroamidines and Perfluorothioamides[1,2]

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Trifluoroacetonitrile, pentafluoropropionitrile and heptafluorobutyronitrile react with alkyl amines to produce N-alkyl perfluoroamidines and with hydrogen sulfide to give perfluorothioamides. Perfluoroamidines, which result from the reaction of perfluoronitriles with ammonia, react with silver oxide or mercuric oxide to form salts and also with hydrogen sulfide to give perfluorothioamides.

The strong electronegative effect of the fluorocarbon group in the perfluoronitriles has been found to increase considerably the reactivity at the carbon to nitrogen unsaturated linkage in these compounds, presumably by increasing the positive character of the carbon site. This condition has produced a reactivity different from that of organic nitriles that do not contain a fluorocarbon group and the products of several types of reactions have properties that are not found in the organic analog.

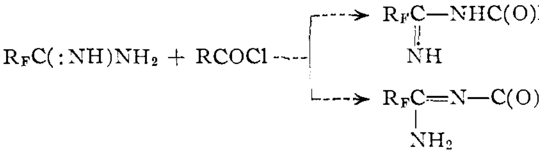
This paper describes the reactions of three perfluoronitriles with primary and secondary amines to produce N-alkyl perfluoroamidines and with hydrogen sulfide to produce perfluorothioamides. Modification of the procedure reported by Husted[3] for the preparation of the free perfluoroamidines is presented with some derivatives formed by these unusual compounds.

N-Alkyl substituted perfluoroamidines were prepared from the perfluoronitriles with primary and secondary alkyl amines. The properties of these compounds are shown in Table I. Although the primary and secondary alkyl amines reacted rapidly with the perfluoronitriles at the reflux temperature of the mixture, aromatic amines, for example, aniline, did not react even at a higher temperature. This indicates that the basicity of the amine is an important consideration in this reaction. Aniline, being a weaker base than either ammonia or alkyl amines, would furnish a relatively poor anionoid nitrogen to take part in the formation of the substituted amidine.

The perfluoroamidines are sufficiently acidic to form certain metallic salts. The silver and mercury salts shown in Table I are white crystalline solids that decompose on heating. The perfluoroamidines appear to function as monoprotic acids since in no case did the analyses indicate that more than one hydrogen was replaced by silver or mercury.

Basic properties are shown by the perfluoroamidines in their ability to form salts with inorganic, organic and perfluoroacids in anhydrous organic solvents. Salts prepared by reaction of perfluoroamidines with acetic and heptafluorobutyric acids are shown in Table I.

Acylation of the perfluoroamidines proceeds readily to form the N-acyl derivatives. Two tautomeric products are possible from this reaction



$$R_FC(:NH)NH_2 + RCOCl \dashrightarrow \begin{cases} R_FC(=NH)\text{—}NHC(O)R & \text{I} \\ R_FC(NH_2)\text{=}N\text{—}C(O)R & \text{II} \end{cases}$$

The complete structure of the acylated product has not been defined. Structure I might be expected to be acidic and to hydrolyze to the secondary amide III while Structure II would probably be a very weak acid or neutral molecule and

$R_FC(:O)NHC(:O)R$ III $\quad$ $R_FC(:O)NH_2 + RC(:O)NH^2$ IV

hydrolyze to a mixture of amides IV. Actually, the N-benzoyl derivative of perfluorobutyramidine is a neutral compound insoluble in aqueous alkali. The acetyl derivative of $C_3F_7C(NH)NH_2$ was easily hydrolyzed by aqueous base to form perfluorobutyramide and acetamide. These properties suggest that even if a tautomeric equilibrium is operative, structure II is the reactive form in basic hydrolysis.

Perfluorothioamides were prepared by the reaction of hydrogen sulfide with either the perfluoronitrile or the perfluoroamidine and are shown in Table I. The reaction of the perfluoronitriles with hydrogen sulfide at room temperature was vigorous; in the synthesis of perfluorothioacetamide from perfluoroacetonitrile and hydrogen sulfide, the reactants were maintained at 0° to prevent charring. Preparation of the perfluorothioamides from the respective amidines was carried out in ethyl ether with good yields. These com-

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[1] This paper represents a part of the dissertation presented by William L. Reilly to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] D. Husted, U. S. Patent 2,676,985 (April, 1954).