the usual explanations for displaced C–H deformation vibrations. It is not present in diethyl acetoxyethylphosphonate.

Experimental

2-Bromoethyl Esters.—These were prepared by the reaction of the highly purified fatty acid with 2-bromoethanol (Eastman Organic Chemical), followed by vacuum distillation as described in the previous publication,[4] with the exception of 2-bromoethyl palmitate and stearate. These esters were purified by recrystallization from acetone at 0 to 5°. The boiling point (or melting point), $n^{30}\text{D}$ and yield of the 2-bromoethyl esters are: caproate, 116–118° (20 mm.), 1.4505, 74%; laurate, 114–119° (0.5 mm.), 1.4564, 84%; myristate, 157–160° (0.9 mm.), 1.4539, 59%; palmitate, 43.0–43.5°, 1.4507 (55°), 81%; stearate, 49–50°, 1.4500 (55°), 84%; oleate, 185–186° (0.6 mm.) 1.4669, 74%. 2-Bromoethyl acetate, b.p. 160–161°, was an Eastman Organic Chemical.

Dialkyl Acyloxyethylphosphonates.—The preparation of diethyl lauroxyethylphosphonate has been described in a previous publication.[4] The preparation of the other diethyl acyloxyethylphosphonates followed this procedure with only minor variations. Dry nitrogen was passed through the reaction mixture which was refluxed from 4 to 5 hours at 155–165°. Diethyl acetoxyethylphosphonate was distilled through a short packed column to achieve good separation from the unused triethyl phosphite. Di-*n*-butyl- and di-*n*-hexyl lauroxyethylphosphonate were prepared by heating 2-bromoethyl laurate with the appropriate trialkyl phosphite in 33% excess for 5 to 6 hours at 180 to 200°. Properties of these compounds are shown in Table I.

Hydrolysis Experiments.—The medium for hydrolysis was freshly prepared for each run by adding 1 volume of 0.5 *N* HCl solution to 4 volumes of acetone. The resulting solution was thus 0.1 *N* with respect to the HCl and contained 20% water by volume.

Two to three grams of the sample was weighed accurately into a 100-ml. volumetric flask. The hot hydrolysis solution was added to the mark and the contents of the flask thoroughly mixed. The solution was transferred to a reaction flask where it was maintained at reflux temperature (61°). Ten-ml. aliquots were removed periodically, added to 60–70 ml. of 95% ethanol and the solution was titrated with 0.1 *N* NaOH. A blank consisting of the hydrolysis solution containing no sample was treated in exactly the same way. The sample titration minus the blank titration indicated the degree of hydrolysis of the sample.

Infrared Absorption Spectra.—The procedure and instrument used to obtain the infrared spectra were the same as previously reported.[4]

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organic Compounds of Uranium. V. Derivatives of Uranium(V) Alkoxides

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Uranium(V) ethoxide reacts with sodium ethoxide, calcium ethoxide and aluminum ethoxide to give the salt-like compounds $NaU(OC_2H_5)_6$, $Ca[U(OC_2H_5)_5]_2$ and $Al[U(OC_2H_5)_6]_3$, respectively. Uranium(V), 2,2,2-trifluoroethoxide, forms a series of addition complexes with aliphatic amines. Compounds of the type $U(OR)_4Cl$, $U(OR)_3Cl_2$ and $U(OR)_2Cl_3$ are obtained by reactions of $U(OR)_5$ with hydrogen chloride.

Uranium(V) ethoxide behaves as an acid and forms complexes or salts with other more basic metal alkoxides. The purpose of this paper is to describe these salts and some related compounds derived from $U(OR)_5$ types.

When a solution of uranium(V) ethoxide in absolute ethanol was treated with one mole of sodium ethoxide, the characteristic dark brown color was discharged and a clear green solution was formed. Uranium(V) ethoxide can be titrated with sodium ethoxide solution in ethanol using phenolphthalein as an outside indicator. The red color with phenolphthalein appeared when the theoretical one mole of sodium ethoxide had been added. Evaporation of the green alcohol solution left a green crystalline solid that was recrystallized from absolute ethanol. Analysis showed it to be $NaU(OC_2H_5)_6$. The compound was not volatile but decomposed when heated under reduced pressure. The reaction of the sodium compound with dry hydrogen chloride in ether gave uranium(V) ethoxide of the highest purity.

$$NaU(OC_2H_5)_6 + HCl \longrightarrow NaCl + C_2H_5OH + U(OC_2H_5)_5$$

Calcium ethoxide formed a complex with uranium(V) ethoxide and this product was somewhat volatile. By heating under greatly reduced pressure the compound was obtained as a light green sublimate, and analyses were consistent with the formula $Ca[U(OC_2H_5)_6]_2$. An aluminum complex with the formula $Al[U(OC_2H_5)_6]_3$ was prepared from aluminum ethoxide and three moles of uranium(V) ethoxide. This compound was quite volatile and was obtained as a green liquid in 97% yield after distillation. Triethyl borate, ethyl orthosilicate or tin(IV) ethoxide failed to form complexes with uranium(V) ethoxide.

The formation of $NaU(OC_2H_5)_6$ in quantitative yield lends support to the idea that the uranium(V) alkoxides are actually compounds of five-valent uranium and are best represented by the formula $[U(OR)_5]_2$ or perhaps $(RO)_5U–U(OR)_5$.

$$2NaOR + [U(OR)_5]_2 \longrightarrow 2NaU(OR)_6$$

Another suggested structure,[1] $[U(OR)_4]^+[U(OR)_6]^-$ appears to be less plausible. Reaction of the latter with a sodium alkoxide would be expected to give a mixture of $NaU(OR)_5$ and $NaU(OR)_7$, but these compounds apparently do not exist. When pure uranium(IV) ethoxide was treated with sodium ethoxide there was no evidence that any reaction took place to form $NaU(OC_2H_5)_5$. Likewise, uranium(VI) ethoxide (to be described in a later

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

paper) did not appear to form a definite complex with sodium ethoxide.

Meerwein and Bersin[2] have studied a large number of metal alkoxide complexes or salts similar to these of uranium. The compounds such as $NaU(OC_2H_5)_6$ and $Al[U(OC_2H_5)_6]_3$ described here appear to fit into the general class of complex metal alkoxides described by the German authors.

Another demonstration of the acidic character of the $U(OR)_5$ compounds was the ability of some of them to form addition complexes with amines. Uranium(V) 2,2,2-trifluoroethoxide was studied in this connection. On a number of occasions, during the distillation of $U(OCH_2CF_3)_5$ prepared from UCl_5 and trifluoroethanol with excess ammonia,[3] a light green liquid with a lower boiling point than $U(OCH_2CF_3)_5$ was obtained. It proved to be a complex of the latter with ammonia, but the ammonia was lost easily when the complex was heated. The quantity of ammonia contained in the complex was variable. Analyses of a number of different samples indicated values for x of 6 to 12 in the formula $U(OCH_2CF_3) \cdot xNH_3$.

More stable complexes were formed between uranium(V) 2,2,2-trifluoroethoxide and various low-molecular weight mono-, di- and trialkyl amines. The quantity of amine in the complex varied between two and three moles depending on the amine. For the formula $U(OCH_2CF_3)_5 \cdot xNRR'R''$, x was 2 when $NRR'R''$ was trimethylamine, *n*-propylamine, di-*n*-propylamine or isopropylamine, but x was 3 when $NRR'R''$ was dimethylamine or ethylenimine. These complexes are tabulated in the Experimental part. They were green liquids and were more volatile than the parent $U(OCH_2CF_3)_5$ which was a brown solid. The complexes were relatively unstable, however, losing the amine when heated and reverting to the parent $U(OCH_2CF_3)_5$.

Reactions of uranium(V) alkoxides with acidic rather than basic reagents brought about cleavage of one or more of the OR groups. With one, two and three moles of hydrogen chloride, uranium(V) ethoxide gave $U(OC_2H_5)_4Cl$, $U(OC_2H_5)_3Cl_2$ and $U(OC_2H_5)_2Cl_3$; the first two were isolated and purified by distillation. These compounds containing both alkoxy and chlorine groups were green liquids, soluble in non-polar solvents including low-boiling petroleum ether. They readily reacted with sodium alkoxides or alcohols and ammonia to form uranium(V) alkoxides.

$$U(OR)_4Cl + ROH + NH_3 \longrightarrow NH_4Cl + U(OR)_5$$

Cleavage of uranium(V) ethoxide with two moles of ethyl 2,2,2-trifluoroacetoacetate gave a uranium(V) compound containing both ethoxide and β-ketoester groups.

$$U(OC_2H_5)_5 + 2CF_3COCH_2CO_2C_2H_5 \longrightarrow \\ 2C_2H_2OH + U(OC_2H_5)_3(CF_3COCHCO_2C_2H_5)_2$$

The same uranium compound was obtained when only one mole or when four moles of ethyl trifluoroacetoacetate were used. In the latter case, however, a second product, the known and highly stable uranium(IV) chelate, $U(CF_3COCHCO_2C_2H_5)_4$,[4] was obtained in high yield. Thus part of the uranium(V) had been reduced to uranium(IV).

Reaction of uranium(V) ethoxide with two moles of ethyl acetoacetate did not give the expected $U(OC_2H_5)_3(CH_3COCHCO_2C_2H_5)_2$. Aside from unchanged $U(OC_2H_5)_5$, the only product isolated was a green uranium(IV) compound that on the basis of analysis appeared to be the hitherto unknown $U(CH_3COCHCO_2C_2H_5)_4$.

Experimental

Uranium(V) Ethoxide and Sodium Ethoxide.—A solution of 0.3696 g. (0.000798 mole) of pure uranium(V) ethoxide in 25 ml. of anhydrous ethanol in a dry nitrogen atmosphere was titrated with a 0.0788 *N* solution of sodium ethoxide in absolute ethanol. The end-point was determined with phenolphthalein as an outside indicator. Equilibrium was reached rather slowly, but a definite end-point occurred after the addition of 10.02 ml. of the sodium ethoxide solution. Based upon the anticipated reaction, $U(OC_2H_5)_5 + NaOC_2H_5 \rightarrow NaU(OC_2H_5)_6$, 10.12 ml. should have been required.

To 10 ml. of absolute ethanol solution containing 0.0037 mole of sodium ethoxide was added 1.00 ml. (1.713 g., 0.0067 mole) of uranium(V) ethoxide. The resulting green solution was evaporated under reduced pressure to about 3 ml., whereupon a crystalline solid separated. The solvent was removed with a pipet, 2 ml. of absolute ethanol was added and the mixture warmed. The solid dissolved and separated again when the solution was cooled. After two such recrystallizations the green solid was dried under reduced pressure and analyzed.

Anal. Calcd. for $NaU(OC_2H_5)_5$: Na, 4.3; U, 44.8. Found: Na, 4.7; U, 44.6.

This compound resembled ferrous sulfate in appearance, it was soluble in alcohol or ether, sparingly soluble in benzene or petroleum ether, and instantly hydrolyzed with water. When heated under reduced pressure it charred and decomposed without melting or subliming.

Calcium Ethoxide Complex with Uranium(V) Ethoxide.—Calcium ethoxide was prepared by heating 0.37 g. (0.0092 g. atom) of calcium metal and a trace of mercuric chloride in 75 ml. of absolute ethanol. To the resulting solution was added 5.0 ml. (8.55 g., 0.0184 mole) of uranium(V) ethoxide. The solvent was removed by distillation and the residue was heated slowly up to 200° under 0.001 mm. pressure. A light green sublimate was obtained. This was washed with a little petroleum ether, dried in a current of dry nitrogen and analyzed. The yield was not measured.

Anal. Calcd. for $Ca[U(OC_2H_5)_6]_2$: Ca, 3.79; U, 45.06. Found: Ca, 3.66, 3.45; U, 44.36, 44.11.

Aluminum Ethoxide Complex with Uranium(V) Ethoxide.—Aluminum ethoxide was prepared by heating under reflux for three hours, 0.167 g. (0.0062 g. atom) of aluminum foil, a trace of iodine and a trace of mercuric chloride in 40 ml. of absolute ethanol. To the resulting solution was added 5.0 ml. (8.55 g., 0.0184 mole) of uranium(V) ethoxide, and the mixture was heated under reflux for seven hours. After removal of the alcohol by distillation the residual liquid was distilled under reduced pressure, b.p. 111–115° (0.0012 mm.). The yield of green product was 9.4 g. (97%).

Anal. Calcd. for $Al[U(OC_2H_5)_6]_3$: Al, 1.74; U, 46.02. Found: Al, 1.56, 1.50; U, 46.03, 45.85.

Hydrogen Chloride on the Sodium Ethoxide Complex with Uranium(V) Ethoxide.—Sodium ethoxide was prepared from 0.84 g. (0.037 g. atom) of sodium sand and 2.15 g. (0.037 mole) of absolute ethanol in 100 ml. of dry ether. To this was added 17.0 g. (0.037 mole) of uranium(V) ethoxide. After stirring for several hours the sodium ethoxide had dissolved, the brown color of the $U(OC_2H_5)_5$ had disappeared and a light green solution had formed.

To this solution was added a dry ether solution containing 0.037 mole of hydrogen chloride. The mixture immediately

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(2) H. Meerwin and T. Bersin, *Ann.*, **476**, 113 (1929).

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

(4) 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. Yeoman, *ibid.*, **78**, 2790 (1956).

TABLE I

Formula	B.p. °C.	B.p. Mm.	Yield, %	Uranium, % Calcd.	Uranium, % Found
$U(OCH_2CF_3)_5\cdot 2(CH_3)_3N$	95–100	0.02	24	27.97	27.50, 27.60
$U(OCH_2CF_3)_5\cdot 2C_3H_7NH_2$	105–107	.009	34	28.00	28.25
$U(OCH_2CF_3)_5\cdot 2(CH_3)_2CHNH_2$	100–103	.01	30	28.00	28.45, 28.50
$U(OCH_2CF_3)_5\cdot 2(C_3H_7)_2NH$	97–100	.006	4.5	25.45	25.45
$U(OCH_2CF_3)_5\cdot 3(CH_3)_2NH$	95–100	.01	10	27.4	27.0, 27.5
$U(OCH_2CF_3)_5\cdot 3\underbrace{CH_2{-}CH_2}_{NH}$	125–128	.002	40	27.60	27.85

turned brown. The solution was filtered from the precipitated sodium chloride, the ether was removed by distillation and the residue distilled to yield 14.5 g. (85%) of uranium(V) ethoxide, b.p. 118–119° (0.0015 mm.).

Anal. Calcd. for $U(OC_2H_5)_5$: U, 51.4. Found: U, 51.30, 51.35.

Amine Complexes with Uranium(V) 2,2,2-Trifluoroethoxide.—A solution of 5.0 g. (0.0068 mole) of uranium(V) 2,2,2-trifluoroethoxide in 10 ml. of ether was treated with five equivalents (0.034 mole) of the carefully dried amine. The initially brown solution turned green. After removal of the ether and excess amine by evaporation under reduced pressure at temperatures below 40°, the residue was distilled under high vacuum. The amine complex distilled first as a green liquid followed by unchanged uranium(V) 2,2,2-trifluoroethoxide as a green-brown liquid that crystallized when cooled, b.p. 125–130° (0.002), 135–140° (0.01). In this way the compounds listed in Table I were prepared.

$U(OC_2H_5)_4Cl$.—To a solution of 8.5 g. (0.0184 mole) of uranium(V) ethoxide in 15 ml. of dry ether cooled in an ice-bath was added dropwise with stirring under a nitrogen atmosphere, 28.4 ml. of 0.652 *N* hydrogen chloride in dry ether (0.0185 mole of HCl). The color changed from brown to green. After standing for several hours, the solution was evaporated under reduced pressure, and the residual green liquid was distilled under high vacuum. The fraction distilling at 145–155° (0.005 mm.) was redistilled and that distilling at 145–150° (0.005 mm.) was taken for analysis. The yield of brown liquid was 6.9 g. (83%).

Anal. Calcd. for $U(OC_2H_5)_4Cl$: Cl, 7.82; U, 52.49. Found: Cl, 7.72; U, 52.50; mol. wt. by freezing point depression of benzene 890, 807 (calcd. for $[U(OC_2H_5)_4Cl]_2$, 907).

Another preparation of $U(OC_2H_5)_4Cl$ was made by adding 3.4 g. (0.0074 mole) of uranium(V) ethoxide to a solution of 0.7 g. (0.0018 mole) of uranium(IV) chloride in 10 ml. of absolute ethanol. The solvent was removed by evaporation under reduced pressure and the residue was distilled to yield 3.0 g. (88%) of brown liquid, b.p. 140–147° (0.003 mm.).

Anal. Calcd. for $U(OC_2H_5)_4Cl$: Cl, 7.82; U, 52.49. Found: Cl, 7.81; U, 52.26.

The compound was soluble in ethanol, ether, benzene or petroleum ether.

$U(OC_3H_7\text{-}n)_4Cl$.—This was prepared from uranium(V) *n*-propoxide and dry hydrogen chloride in ether solution in the same way as described above for the preparation of $U(OC_2H_5)_4Cl$. The product was distilled and obtained in a yield of 81%, b.p. 186–192° (0.095 mm.).

Anal. Calcd. for $U(OC_3H_7\text{-}n)_4Cl$: Cl, 6.96. Found: Cl, 6.35, 6.33.

$U(OC_2H_5)_3Cl_2$.—A solution of 8.5 g. (0.0184 mole) of uranium(V) ethoxide in 15 ml. of dry ether was treated with 0.037 mole of dry hydrogen chloride in 56 ml. of dry ether. The dark green solution was evaporated under reduced pressure at about 80° leaving a green sirup.

Anal. Calcd. for $U(OC_2H_5)_3Cl_2$: Cl, 15.97. Found: Cl, 14.98.

Decomposition occurred during attempted distillation of the product under high vacuum. The compound was soluble in petroleum ether.

$U(OC_2H_5)_2Cl_3$.—This was prepared in dry ether solution from uranium(V) ethoxide and three equivalents of hydrogen chloride. The brilliant green liquid obtained after evaporation of the solvents under reduced pressure turned brown when heated. It completely decomposed when distillation under high vacuum was attempted.

$U(OC_2H_5)_3(CF_3COCHCO_2C_2H_5)_2$.—To a solution of 8.5 g. (0.0184 mole) of uranium(V) ethoxide in 35 ml. of dry ether was added with stirring under a nitrogen atmosphere 6.77 g. (0.0368 mole) of ethyl trifluoroacetoacetate. An immediate reaction took place and the solution turned dark green. The ether was removed by evaporation under reduced pressure and the residue was distilled to yield 12.5 g. (92%) of green liquid, b.p. 95–98° (0.001 mm.).

Anal. Calcd. for $U(OC_2H_5)_3(CF_3COCHCO_2C_2H_5)_2$: U, 32.2. Found: U, 32.6.

$U(OC_2H_5)_3(CF_3COCHCO_2CH_3)_2$.—This was prepared in the same way as the above ethyl ester compound, b.p. 93–95° (0.001 mm.).

Anal. Calcd. for $U(OC_2H_5)_3(CF_3COCHCO_2CH_3)$: U, 33.4. Found: U, 33.0.

$U(OC_2H_5)_3(CF_3COCHCO_2C_4H_9\text{-}n)_2$.—This was prepared in the same manner as the above ethyl ester compound, b.p. 110° (0.005 mm.).

Anal. Calcd. for $U(OC_2H_5)_3(CF_3COCHCO_2C_4H_9)_2$: U, 30.0. Found: U, 30.6.

$U(OCH_3)_3(CF_3COCHCO_2C_2H_5)_2$.—In 25 ml. of anhydrous methanol was dissolved 4 g. of $U(OC_2H_5)_3(CF_3COCHCO_2C_2H_5)_2$, and the solution was allowed to stand under nitrogen for 24 hours. The solvent was removed by evaporation under reduced pressure and the residue was distilled, b.p. 95–97° (0.002 mm.). The yield of green liquid was quantitative.

Anal. Calcd. for $U(OCH_3)_3(CF_3COCHCO_2C_2H_5)_2$: U, 34.2. Found: U, 34.3.

Reaction of Uranium(V) Ethoxide with One and with Four Equivalents of Ethyl Trifluoroacetoacetate.—A reaction between 8.5 g. (0.0184 mole) of uranium(V) ethoxide and 3.39 g. (0.0184 mole) of ethyl trifluoroacetoacetate in 35 ml. of dry ether yielded, after distillation, a forerun of $U(OC_2H_5)_3(CF_3COCHCO_2C_2H_5)_2$ followed by a larger quantity of unchanged $U(OC_2H_5)_5$; b.p. 130° (0.007 mm.).

A reaction between 8.5 g. (0.0184 mole) of uranium(V) ethoxide and 13.54 g. (0.0737 mole) of ethyl trifluoroacetoacetate in 25 ml. of dry ether gave, after distillation, 2.0 g. (15% yield) of $U(OC_2H_5)_3(CF_3COCHCO_2C_2H_5)_2$, a light green liquid, b.p. 100–105° (0.004 mm.), and 10 g. of a dark green compound that crystallized in the receiver, b.p. 120–125° (0.005 mm.). The latter compound was identified as $U(CF_3COCHCO_2C_2H_5)_4$, m.p. 65°, mixed melting point with an authentic sample 65°.

Anal. Calcd. for $U(CF_3COCHCO_2C_2H_5)_4$: U, 24.65. Found: U, 24.60.

Reaction of Uranium(V) Ethoxide with Ethyl Acetoacetate. $U(CH_3COCHCO_2C_2H_5)_4$.—A solution of 8.5 g. (0.0184 mole) of uranium(V) ethoxide and 4.78 g. (0.0368 mole) of ethyl acetoacetate in 25 ml. of dry petroleum ether (b.p. 90–100°) was heated under reflux for two hours. The mixture was distilled to give 6.8 g. (80%) of unchanged $U(OC_2H_5)_5$; b.p. 130° (0.007 mm.) followed by 1.5 g. of dark green oil; b.p. about 160° (0.007 mm.). This crystallized on cooling, but unfortunately, the melting point was not determined. It was redistilled, and a middle cut was taken for analysis.

Anal. Calcd. for $U(CH_3COCHCO_2C_2H_5)_4$: U, 31.65. Found: U, 31.60.

When $U(OC_2H_5)_5$ was allowed to react with a large excess of ethyl acetoacetate no recognizable products could be isolated.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

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

BY R. G. JONES, E. BINDSCHADLER, D. BLUME, G. KARMAS, G. A. MARTIN, JR., J. R. THIRTLE, F. A. YEOMAN AND H. GILMAN

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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).

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