[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

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

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A number of uranium(V) alkoxides were prepared by several methods, the most important of which was the exchange reaction $U(OC_2H_5)_5 + 5ROH \rightarrow U(OR)_5 + 5C_2H_5OH$.

Following the discovery of uranium(V) ethoxide,[1] which was a distillable liquid, it became of immediate importance to prepare other uranium(V) alkoxides with the hope of finding one more volatile and perhaps more stable than the ethoxide. To this end the uranium(V) alkoxides of all of the aliphatic alcohols with four or less carbon atoms and of a number of fluorinated and otherwise substituted alcohols were studied.

The same methods used for the synthesis of uranium(V) ethoxide[1] were applicable to the preparation of other alkoxides. These methods are indicated by the accompanying reactions (A) to (D).

$$UCl_4 + 4NaOR \longrightarrow U(OR)_4 \xrightarrow{(O)} U(OR)_5 \quad (A)$$

$$UCl_4 + ROH + NH_3 \longrightarrow U(OR)_4 \xrightarrow{(O)} U(OR)_5 \quad (B)$$

$$UCl_4 + 4NaOR \longrightarrow U(OR)_4 \xrightarrow{1/2Br_2} U(OR)_4Br \xrightarrow{NaOR} U(OR)_5 \quad (C)$$

$$UCl_5 + 5ROH + NH_3 \longrightarrow U(OR)_5 \quad (D)$$

A fifth and most generally satisfactory method (E) involved an exchange of alkoxide groups. The readily available uranium(V) ethoxide was mixed with another alcohol, and, after heating for a short time, the alcohols were removed by distillation. The new uranium(V) alkoxide was purified usually by distillation under high vacuum.

$$U(OC_2H_5)_5 + 5ROH \longrightarrow 5C_2H_5OH + U(OR)_5 \quad (E)$$

Those alcohols with boiling points higher than that of ethanol were used in only slightly greater than theoretical quantity, while those with boiling points near or lower than that of ethanol were used in large excess. Reaction (E) appeared to be completely reversible as demonstrated by the preparation of pure uranium(V) ethoxide by reaction of a large excess of ethanol with uranium(V) *iso*- or *t*-butoxide. Although most of the alkoxides of Table I were obtained in greater than 90% yield by reaction (E), this method did not appear to be satisfactory for the preparation of the methoxide. Even when uranium(V) ethoxide was heated with a large excess of methanol only partial replacement of the ethoxide groups took place with formation of mixed uranium(V) alkoxides containing both methyl and ethyl groups.

The *n*-alkyl uranium(V) alkoxides (Table I) with the exception of the methoxide were dark brown liquids resembling closely uranium(V) ethoxide.[1] They were generally quite stable when heated and could be distilled readily. The methoxide and the branched-chain alkoxides were crystalline solids at room temperature. Although the methoxide and isopropoxide were high-melting solids, they sublimed easily under reduced pressure, and, like the other alkoxides, they were soluble in non-polar solvents such as ether, benzene or petroleum ether. All of the alkoxides were easily hydrolyzed, and therefore it was necessary to carefully protect them from moisture.

No molecular weight determinations were made of any of the compounds of Table I. By analogy with the ethoxide,[1] however, it may be expected that the uranium(V) alkoxides are associated at ordinary temperatures and are probably best represented as $[U(OR)_5]_2$. None of the compounds of Table I was more volatile or more stable than the ethoxide. The one having the largest uranium content and therefore the most desirable in this respect for isotope separation work was the methoxide. Unfortunately the methoxide was one of the least volatile and highest melting of the group. The 2,2,2-trifluoroethoxide appeared to have approximately the same volatility as the ethoxide.

Experimental

The following experiments are illustrative of the methods used to prepare the compounds described in Table I. Only one example of each type of reaction is given.

Uranium(V) Methoxide (Method A).—Sodium metal, 18.4 g. (0.80 g. atom), was dissolved in 200 ml. of dry methanol. To the resulting solution was added in small portions and with stirring 75.1 g. (0.20 mole) of powdered, anhydrous uranium(IV) chloride. After the addition was complete the mixture was stirred and heated under reflux for several hours. The green mixture was cooled and treated with one liter of dry oxygen.[1] A red color developed. The mixture was evaporated to dryness under reduced pressure with the careful exclusion of moisture. The residue was heated under about 0.01 mm. pressure in a oil-bath, the temperature of which was gradually raised from 160 to 210° during a period of four hours. Uranium(V) methoxide was obtained as a red crystalline sublimate in a yield of 17.5 g. (23%). A sample for analysis was resublimed.

Uranium(V) *sec*-Butoxide (Method B).—Into a suspension of 15.2 g. (0.04 mole) of powdered, anhydrous uranium(IV) chloride in 75 ml. of dry *sec*-butyl alcohol was bubbled dry gaseous ammonia for four hours. Dry air was then passed through the mixture for a few minutes after which the solvent was removed by evaporation under reduced pressure. The brown residue was extracted with two 75-ml. portions of dry petroleum ether (b.p. 28–38°). The petroleum ether extract was concentrated in a distilling flask, and the residue was distilled under greatly reduced pressure.

Uranium(V) *n*-Propoxide (Method C).—A solution of sodium *n*-propoxide was prepared by dissolving 5.75 g. (0.25 g. atom) of sodium in 150 ml. of dry *n*-propanol. With stirring 23.75 g. (0.0625 mole) of powdered, anhydrous uranium(IV) chloride was added in small portions. The mixture was stirred and warmed gently for one hour, and then a solution of 1.58 ml. (0.0312 mole) of bromine in 10 ml. of benzene was added dropwise. The mixture changed color from green to dark brown. After about five minutes a solution of 0.0625 mole of sodium *n*-propoxide in

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

TABLE I

URANIUM(V) ALKOXIDES $U(OR)_5$

Empirical formula	Method of prep. (yield, %)	B.p., °C. (mm.)	Analyses, U, % Calcd.	Analyses, U, % Found
$U(OCH_3)_5$	A(23), C(60)	Sub. 190–210 (0.01)[a]	60.5	60.0
$U(OC_3H_7\text{-}n)_5$	B(33), C(73), E(97)	162–164 (0.001)[b]	44.63	44.71, 44.65
$U(OC_3H_7\text{-}iso)_5$	B(26), E(89)	Sub. 160° (0.01)[c]	44.63	44.19, 44.25
$U(OC_4H_9\text{-}n)_5$	A(41), C(38), E(95)	192–194 (0.001)[d]	39.44	39.36, 39.27
$U(OC_4H_9\text{-}iso)_5$	A(32), B(31), E(97)	192 (0.009)[e]	39.44	39.40, 39.09
$U(OC_4H_9\text{-}sec)_5$	A(33), B(21), E(91)	175–180 (0.008)[f]	39.44	39.61, 39.28
$U(OC_4H_9\text{-}t)_5$	E(95)	Solid, not sublimed[g]	39.44	40.10
$U(OCH_2CF_3)_5$	D(45)	130 (0.008)[h]	32.45	32.55, 32.33
$U(OCH_2CH{=}CH_2)_5$	B(24)	175–180 (0.015)[i]	45.5	44.6 , 44.5
$U[OCH_2CH_2N(C_2H_5)_2]_5$		Liquid, not dist.	29.1	29.3 , 28.6
$U(OCH_2CH_2SCH_2CF_3)_5$		Liquid, not dist.	23.00	22.84, 23.10

[a] Red, crystalline solid. The m.p. was above 210° but unfortunately was not carefully determined. [b] Other distillation temperatures: 151–152° (0.0003), 173–175° (0.006). [c] Brown crystalline solid; m.p. 320° dec. Soluble in petroleum ether. [d] Other distillation temperatures: 205–207° (0.008). [e] Brown crystalline solid; m.p. 100–104°. [f] Brown crystalline solid; m.p. 85°. Other distillation temperatures: 180–185° (0.009). [g] Tan crystalline solid, unfortunately no melting point was determined. [h] Brown-green crystalline solid at room temperature, no melting point was determined. [i] Some decomposition took place during distillation.

75 ml. of dry 1-propanol was added, and the mixture was stirred for one hour. Following this the mixture was concentrated in a distilling flask, and the residue was distilled under greatly reduced pressure. This procedure is described in greater detail for the preparation of uranium(V) ethoxide.

Uranium(V) 2,2,2-Trifluoroethoxide (Method D).—To a solution of 33.6 g. (0.336 mole) of dry 2,2,2-trifluoroethanol[2] in 500 ml. of anhydrous ether was added 27 g. (0.065 mole) of freshly prepared, powdered uranium(V) chloride.[3] With vigorous stirring dry ammonia gas was passed into the mixture for two hours. The mixture was filtered with careful exclusion of moisture, and the filtrate was concentrated in a distilling flask. The residue of uranium(V) 2,2,2-trifluoroethoxide was a green-brown crystalline solid. It melted when warmed and was purified by distillation under high vacuum.

Uranium(V) *n*-Butoxide (Method E).—To 74 g. (1 mole) of dry 1-butanol was added 83 g. (0.18 mole) of uranium(V) ethoxide. The solution was heated for a short time, and then the alcohols were distilled first at atmospheric pressure, finally under reduced pressure. The brown liquid residue of uranium(V) *n*-butoxide was distilled under high vacuum.

Uranium(V) Ethoxide from Uranium(V) Isobutoxide and Ethanol.—To 50 ml. of absolute ethanol was added 6.3 g. of solid uranium(V) isobutoxide. A brown solution was formed. This was heated for a short time, and then the alcohol was distilled, finally under reduced pressure. The residual brown liquid was distilled under high vacuum to give 4.4 g. (90% yield) of uranium(V) ethoxide, b.p. 127° (0.007 mm.).

Anal. Calcd. for $U(OC_2H_5)_5$: U, 51.4. Found: U, 50.1, 50.2.

Uranium(V) *t*-Butoxide.—To a solution of 3.4 g. (0.0074 mole) of uranium(V) ethoxide in 10 ml. of dry ether was added 4 ml. of dry *t*-butyl alcohol. A tan solid precipitated. The solvents were distilled, finally under reduced pressure leaving the crystalline *t*-butoxide; yield 4.2 g. (95%).

Anal. Calcd. for $U(OC_4H_9)_5$: U, 39.44. Found: U, 40.10.

The above solid was dissolved in 50 ml. of absolute ethanol and the excess solvent was distilled, finally under reduced pressure. The residual brown liquid was distilled under high vacuum; b.p. 132–135° (0.012 mm.).

Anal. Calcd. for $U(OC_2H_5)_5$: U, 51.4. Found: U, 50.6.

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(2) H. Gilman and R. G. Jones, THIS JOURNAL, **70**, 1281 (1948).

(3) O. Ruff and A. Heinzelmann, *Ber.*, **42**, 492 (1909).

[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY AND KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Anodic Reactions. II. The Mechanism of the Kolbe Electrosynthesis[1]

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Studies of the mechanism of the Kolbe electrosynthesis lead to the conclusion that only the discharged ion theory appears tenable. This is based largely on an investigation of the kinetics of the electrode processes using variable frequency square wave A-C. This technique is designed to determine the molecularity of the slow step in the sequence of reactions occurring after the initial transfer of an electron to the electrode. Results of studies using square wave A-C indicate that: (a) the order of the reaction of acetic acid at the anode to produce ethane is the same in water and in glacial acetic acid; (b) the reaction in (a) is apparently first order in acetoxy radicals; (c) the reaction of propionic acid at the anode to produce ethylene (not butane) is apparently second order in propionoxy radicals. Additional evidence is presented to support these views.

Three theories concerning the mechanism of the Kolbe electrosynthesis[3] in aqueous media have been advanced. These are the following: 1. The discharged ion theory proposed by Brown and Walker[4] in 1891. The important steps in this mechanism are the direct oxidation of the carboxylic anion and subsequent decomposition of the radicals formed. 2. The acyl peroxide theory proposed by Fichter[5] in 1925. Fichter contends that the electrode process is not direct oxidation of the

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(1) Presented before the Division of Organic Chemistry, 128th meeting of the American Chemical Society, Minneapolis, September, 1955.

(2) Hudson Foam Plastics Corpn., Yonkers, New York.

(3) H. Kolbe, *Ann.*, **69**, 279 (1849).

(4) A. Brown and J. Walker, *ibid.*, **261**, 107 (1891).

(5) F. Fichter, *Trans. Am. Electrochem. Soc.*, **45**, 131 (1924).