[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Methyl Derivatives of Uranium(IV) Borohydride[1]

BY H. I. SCHLESINGER, HERBERT C. BROWN, L. HORVITZ, A. C. BOND, L. D. TUCK AND A. O. WALKER

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Treatment of uranium(IV) borohydride with trimethylboron at 50 to 70° results in the formation of methylated derivatives. Two products, a monomethyl and a tetramethyl derivative of uranium(IV) borohydride, have been isolated. On the basis of their reactions with water and hydrogen chloride, the structures $U(BH_4)_3(BH_3CH_3)$ and $U(BH_3CH_3)_4$ have been assigned. The monomethyl derivative is more volatile than the parent compound and is the most volatile known derivative of tetravalent uranium. Uranium borohydride is alkylated also by triethylboron and higher alkyl borons. However, pure compounds were not isolated from the reaction products.

Treatment of uranium borohydride[2] with trimethylboron at 50 to 70° results in the formation of methyl diboranes and of a green, moderately viscous liquid. From this liquid it is possible to isolate two products by fractional distillation and sublimation. The less volatile of these was a crystalline solid, almost colorless in thin layers, lavender to almost black in thicker crystals. The more volatile product was obtained as deep green crystals.

The composition and structures of the compounds were established by their analyses, and by their behavior toward water and toward hydrogen chloride. The volatile products, obtained when the green compound is treated with water, contain hydrogen and methyl boric acid. Of the former approximately 15 moles are liberated; oxidation of the remaining volatile material produces carbon dioxide in an amount corresponding to the presence of one methyl group per gram atomic weight of uranium in the original compound. These results indicate that the green compound is B-methyluranium(IV) borohydride, $U(BH_4)_3BH_3CH_3$, and are in agreement with the equation

$$U(BH_4)_3(BH_3CH_3) + 12H_2O \longrightarrow U(OH)_4 + 15H_2 + CH_3B(OH)_2 + 3HBO_2$$

Further evidence for the proposed structure is derived from the treatment of the compound with hydrogen chloride. The reaction yields hydrogen, diborane and methylboron chlorides, as would be expected according to the equation

$$U(BH_4)_3BH_3CH_3 + 6HCl \longrightarrow UCl_4 + 6H_2 + 3/2B_2H_6 + CH_3BCl_2$$

Because of the readiness with which methylboron chlorides disproportionate, as well as of the difficulty in separation of the products, no attempt was made to obtain quantitative data for the reaction.

The lavender compound, on the other hand, when treated with hydrogen chloride produces no diborane or diborane derivatives; instead there is obtained all of the hydrogen to be expected from the equation

$$U(BH_3CH_3)_4 + 12HCl \longrightarrow UCl_4 + 12H_2 + 4CH_3BCl_2$$

The presence of methylboron chloride was demonstrated by its conversion to methylboric acid. Combustion of the latter with nitric acid showed the presence of 4 methyl groups per gram atomic weight of uranium in the original sample. These facts, together with the analyses later reported, indicate that the lavender compound is B,B′,B″,B‴-tetramethyluranium borohydride, $U(BH_3CH_3)_4$.

It is interesting to compare the behavior of uranium borohydride toward hydrogen chloride with that of its tetramethyl derivative. The former yields hydrogen and diborane almost quantitatively, according to the equation

$$U(BH_4)_4 + 4HCl \longrightarrow UCl_4 + 4H_2 + 2B_2H_6$$

Practically no chlorodiborane is formed since the reaction of hydrogen chloride on diborane is slow. The tetramethyl derivative might, therefore, be expected to produce dimethyldiborane on treatment with hydrogen chloride.

$$U(BH_3CH_3)_4 + 4HCl \longrightarrow UCl_4 + 2B_2H_4(CH_3)_2 + 4H_2$$

As already mentioned, no diborane derivatives were obtained in the reaction, and all of the methyl groups appear as methylboron chlorides. The difference is explicable on the assumption that methyl groups attached to boron increase the reactivity of boron–hydrogen bonds toward hydrogen chloride. Unfortunately the investigation

$$B_2H_6 + HCl \xrightarrow[\text{slow}]{UCl_4} B_2H_5Cl + H_2$$

$$(CH_3)_2B_2H_4 + 4HCl \xrightarrow[\text{fast}]{UCl_4} 2CH_3BCl_2 + 4H_2$$

had to be terminated before the explanation just given could be verified experimentally.

B,B′,B″,B‴-Tetramethyluranium(IV) borohydride melts at 72–74°. The melting point of the B-methyluranium(IV) borohydride is in doubt. A purified sample melted at 85°. However, slow sublimation of this material yielded fractions of gradually increasing melting points up to 95°. It is not certain whether this increase in melting point was due to increasing purity of the sample, or was caused by slow disproportionation of the monomethyl derivative into the simple borohydride and more highly methylated products.

Both compounds are quite volatile. The monomethyl derivative exhibits a vapor pressure of 8.5 mm. at 50° as contrasted with the value of 1.4 mm. for the unsubstituted compound. The tetramethyl compound is somewhat less volatile, with a vapor pressure of 0.4 mm. at the same temperature. The increase in volatility of the monomethyl over the parent compound, in spite of the increased molecular weight, is presumably due to a lower crystal lattice energy. (Uranium(IV) borohydride shows no signs of melting below 100°.[2])

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[1] New Developments in the Chemistry of Diborane and the Borohydrides. XI. The nomenclature employed is explained in paper I of this series. THIS JOURNAL, **75**, 186 (1953).

[2] H. I. Schlesinger and H. C. Brown, *ibid.*, **75**, 219 (1953).

There was considerable evidence that compounds intermediate between the monomethyl and tetramethyl derivatives exist. When the former was treated with a mixture of diborane and trimethylboron, the color darkened and the crystalline form seemed to change. The resulting material had a carbon content intermediate between that of the mono- and the tetramethyl derivatives. These products of intermediate composition seemed to be mixtures, probably containing both di- and trimethyl derivatives. Since they did not offer any points of interest beyond those of the mono- and tetramethyl compounds, they were not investigated in detail.

Uranium borohydride was treated with triethylboron and several higher trialkylborons. In each case reaction occurred and green liquids were obtained which were apparently mixtures of the mono- and higher alkylated derivatives. Fractionation by our usual methods failed to effect separation into pure compounds.

Experimental Part

Preparation[3] **of B-Methyluranium(IV) Borohydride,** $U(BH_4)_3BH_3CH_3$.—Uranium(IV) borohydride, 1.8 g. (6.1 mmoles) and 58.7 ml. (2.62 mmoles) of trimethylboron were introduced into a reaction vessel under high vacuum conditions. The vessel had dimensions such that the maximum calculated pressure would not exceed 3 atm. The sealed vessel was heated to 60° for 4 hours. The tube was opened to a vacuum line free of mercury vapor and the volatile contents were passed through a series of U-tubes at −10, −80 and −196°, respectively. (A non-volatile brown decomposition product remained in the reaction vessel. Although its bulk was moderately large, it was very finely divided and its total weight was relatively small. Like the residues obtained from the decomposition of uranium borohydride, this residue reacted vigorously with air.) After two hours, a green liquid had condensed in the −80° tube and a small amount of lavender crystals in the −10° tube. The contents of the −80° tube were again passed through a U-tube at −10° and condensed at −80° in a weighed U-tube, which was then sealed off. About 0.6 g. (1.93 mmoles) of the green compound was obtained.

The product obtained in this way was slightly richer in carbon than the calculated value for a monomethyl derivative. For purification of the crude product, a 1.00-g. sample was treated with 100 ml. of gaseous diborane at room temperature for 48 hours. During this time the sample was occasionally sublimed from one U-tube to another to expose fresh surfaces to the diborane. In a few hours the appearance of the sample had completely changed. Instead of an amorphous, or at best microcrystalline mass of green solid, obviously contaminated with materials of lighter color, the purified sample consisted of clusters of moderately dark green, well-defined crystals. Sublimation from the reaction vessel left behind some of the brown non-volatile decomposition product already described. But the product, once removed from this non-volatile residue, could be sublimed from a 0° bath, leaving no tetramethyl derivative behind. It is to be noted that if the mixture of the monomethyl derivative and diborane is warmed, partial transformation to the simple uranium(IV) borohydride occurs.

Preparation of B′,B,B″,B‴-Tetramethyluranium(IV) Borohydride, $U(BH_3CH_3)_4$.—Uranium(IV) borohydride, 7.2 g. (24 mmoles), and 1606 ml. (72 mmoles) of trimethylboron were heated at 75° for 12 hours in a vessel of such dimensions that the maximum calculated pressure would be about 2 atm. The contents of the vessel were then fractionated as described for the monomethyl derivative. The bulk of the volatile product was the tetramethyl derivative, which was retained in the −10° bath. This material was resublimed several times from a container at room temperature in a train consisting of a −10 and a −80° bath. The material collected in the −10° bath was then treated with trimethylboron at room temperature for several hours to ensure complete transformation of any of the monomethyl derivative into the desired product. The total amount of tetramethyl derivative obtained was 1.8 g. or 5.4 mmoles.

Analysis and Molecular Weight.—The analyses of the mono- and tetramethyl derivatives were carried out by hydrolysis and by reaction with hydrogen chloride. The hydrolytic procedure will be described for the monomethyl compound; the hydrogen chloride procedure for the tetramethyl.

A weighed sample of the monomethyl compound, 0.127 g., was distilled into a small "bomb" tube attached to the vacuum system and a small quantity of water was introduced to hydrolyze the compound. (As little water as possible was used to avoid dilution of the nitric acid later added.) All volatile products, except hydrogen, were trapped at liquid nitrogen temperature; the hydrogen was removed by a Toepler pump and measured. The remaining volatile material (water and methylboric acid) was recondensed in the bomb tube to which an appropriate amount of fuming nitric acid was added. The tube was sealed and heated for 3–4 hours at 350 to 400°. The gaseous product resulting from this treatment was passed repeatedly over copper, heated to redness in a quartz tube, to reduce oxides of nitrogen. The carbon dioxide was separated from nitrogen by condensing the former and was measured. The contents of the bomb tube were washed out with nitric acid and evaporated to dryness. The residue was treated with sulfuric acid and methanol to determine boron in the usual manner. The uranium was determined with 8-hydroxyquinoline.

Anal. U, 95.2 mg.; CO_2, 8.7 ml.; H_3BO_3, 0.1 *N* base, 16.0 ml.; H_2, 130.0 ml.

The hydrogen refers to hydrolyzable hydrogen; the hydrogen in the methyl group was not determined. The ratios correspond to the formula: $U_{1.00}B_{4.00}(CH_3)_{0.98}H_{14.5}$.

The molecular weight, determined by the method described for uranium(IV) borohydride,[2] was 339, somewhat higher than the 311 value calculated for the monomer. The sample used was one that had been prepared before development of the diborane procedure for removing the last traces of more highly alkylated derivatives. The presence of these impurities, and the fact that the measurements were necessarily made at pressures near saturation, probably account for the high value. However, the result definitely supports the monomeric formula for the vapor.

For analysis of the tetramethyl derivative, 0.1382 g. was placed in a small tube, and an excess of hydrogen chloride was introduced. After several hours the tube was opened and the hydrogen was removed by a Toepler pump, while other volatile material was trapped with liquid nitrogen. A total of 105.2 ml. of hydrogen was found. The contents of the trap were re-evaporated and the excess of hydrogen chloride was removed from them by fractional condensation. The remaining material consisted mainly of methylboron chlorides. These were only slightly contaminated with compounds containing active hydrogen, as shown by the fact that hydrolysis of the material produced only 1.3 ml. of hydrogen gas. The methylboric acids, obtained by the hydrolysis, were analyzed for carbon and boron as previously described. Uranium was determined as the 8-hydroxyquinolate.

Anal. U, 96.3 mg.; CO_2, 33.6 ml.; H_3BO_3, 0.1 *N* base, 15.8 cc.; H_2, 106.5 ml.

These data correspond to the ratio $U_{1.00}B_{3.91}(CH_3)_{3.71}H_{11.8}$.

Attention is again called to the fact that treatment of unmethylated uranium borohydride with hydrogen chloride liberates only 25% of the available hydrogen in elementary form; the remaining 75% appears as diborane. In the corresponding reaction of the tetramethyl derivative, 99% of the active hydrogen is generated in elementary form and no appreciable diborane formation occurs. These facts, together with the identification of methylboron chloride in the reaction product, indicate that each methyl group is attached to a different boron atom.

Because of the relatively low vapor pressures of the compound, its molecular weight was not determined. In view of the fact, however, that the compound is at all volatile and that both the parent compound and the monomethyl derivative are monomeric in the vapor state, there is little reason to doubt that the same thing is true of the tetramethyl derivative.

Vapor Pressures.—The measurements were made in an apparatus with an all-glass Bourdon gage as previously

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[3] Volumes of gases and vapors are reduced to N. T. P.

described for uranium(IV) borohydride.[2] The data for the monomethyl compound are recorded in Table I.

TABLE I

VAPOR PRESSURES OF THE MONOMETHYL DERIVATIVE OF URANIUM(IV) BOROHYDRIDE

The calculated pressures were obtained from the equation:

$$\log P = -3{,}160/T + 10{,}690$$

Temp., °C.	25.1	31.4	38.1	45.4	50.7	58.0	65.6
P, mm., obsd.	1.06	2.13	3.37	5.56	8.52	14.6	25.8
P, mm., calcd.	1.24	2.05	3.44	5.87	8.53	14.0	23.4

In Table II the data for the tetramethyl derivative are recorded.

TABLE II

VAPOR PRESSURES OF THE TETRAMETHYL DERIVATIVE OF URANIUM(IV) BOROHYDRIDE

The calculated pressures were obtained from the equation:

$$\log P = -2{,}960/T + 8.815$$

Temp., °C.	40.1	45.6	53.2	60.3	65.3	70.6	73.7
P, mm., obsd.	0.24	0.34	0.51	0.84	1.03	1.66	1.93
P, mm., calcd.	0.23	0.34	0.55	0.86	1.17	1.60	1.91

Triethylboron and Uranium Borohydride.—Uranium borohydride, 9.6 mmoles, and 5.0 mmoles of triethylboron were heated in an evacuated reaction tube at 60° for two hours. The contents of the tube were then distilled through a series of U-tubes at −20, −80 and −196°. The −20° tube showed a tinge of green within a few minutes and within 20 min. there was green color in the −80° tube. Since very little material distilled from the reaction vessel at room temperature, the latter was heated to 70°. A ring of colorless, oily liquid was noted in the reaction vessel, just above the heating bath. The liquid might have been a compound analogous to the tetramethyl derivative but insufficient material was obtained to attempt its purification and identification.

The material collected at −20° was distilled through a second series of U-tubes at 0, −20 and −80° for 18 hours. About 100 mg. passed through the −20° trap into the −80° tube. The condensate in the latter was, however, obviously still a mixture of green and of lighter colored material. Neither the bulk of the material, trapped at 0°, nor that collected at −20° was very volatile and could not be handled effectively in the vacuum equipment. The difficulty of purification was enhanced by the fact that the volatility of the ethyldiboranes, formed in the reaction, does not differ greatly from that of the uranium compounds.

Analyses (which need not be reported in detail) of the various fractions obtained, showed that the uranium-to-boron ratio in all fractions was approximately 1:4, but the carbon content did not correspond to any of the possible ethyluranium borohydrides.

Uranium borohydride was also treated with triisopropylboron and tri-*t*-butylboron. However, the results were similar—no pure compound could be isolated from the complex reaction mixtures.

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CHICAGO, ILL.

NOTES

A Suggested Reaction Mechanism for the Copolymerization of Ethylene and Carbon Monoxide

BY W. G. BARB

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Brubaker, Coffmann and Hoehn[1] have recently discovered that polyketones can be prepared by copolymerizing carbon monoxide and ethylene in cyclohexane solution, using di-(*t*-butyl) peroxide as catalyst. Their paper gives, amongst other data, information about the effect of the monomer ratio and of the total pressure on the composition of the resulting copolymer and the yield obtained in a given time.

There is an obvious formal similarity between this reaction and the formation of polysulfones from olefins and sulfur dioxide. The kinetics of the latter have recently been investigated[2,3] and it has been shown that sulfur dioxide units are incorporatedin to the polymer chain by reaction of a 1:1 complex of sulfur dioxide and the olefin; this contrasts with copolymerizations of two vinyl compounds, where it is generally accepted that the original monomeric units react (see, *e.g.*, review by Mayo and Walling[4]). It is therefore of interest to examine whether the similarity between polysulfone and polyketone formation extends to the reaction mechanisms. One feature of the data of Brubaker, *et al.*,[1] immediately suggests that the usual copolymer composition equation[4] which holds for vinyl copolymerizations, and which only involves the *ratio* of the monomer concentrations, is not directly applicable in this system; namely, the composition of the copolymer obtained at a given monomer ratio varies greatly with the total pressure, *i.e.*, with the absolute monomer concentration.

It is therefore suggested that the reaction occurs by the usual type of free-radical polymerization processes but that, by analogy with polysulfone formation,[2] the reactants are the olefin M and a 1:1 complex C of the olefin and carbon monoxide; and that the concentration [C] of the complex is given by

$$[\mathrm{C}] = K[\mathrm{M}][\mathrm{CO}]$$

where [M] and [CO] are the total concentrations of olefin and carbon monoxide (*i.e.*, the equilibrium constant *K* is assumed to be small).

From the four possible propagation reactions (R = remainder of polymer radical), *viz.*

$$\begin{array}{llll}
\mathrm{R{-}C\cdot} + \mathrm{C} & \longrightarrow & \mathrm{R{-}C\cdot} & k_{\mathrm{CC}} \\
\mathrm{R{-}C\cdot} + \mathrm{M} & \longrightarrow & \mathrm{R{-}M\cdot} & k_{\mathrm{CM}} \\
\mathrm{R{-}M\cdot} + \mathrm{C} & \longrightarrow & \mathrm{R{-}C\cdot} & k_{\mathrm{MC}} \\
\mathrm{R{-}M\cdot} + \mathrm{M} & \longrightarrow & \mathrm{R{-}M\cdot} & k_{\mathrm{MM}}
\end{array}$$

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[1] M. M. Brubaker, D. D. Coffmann and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952).

[2] W. G. Barb, *Proc. Roy. Soc.* (*London*), **A212**, 66, 177 (1952).

[3] F. S. Dainton and K. J. Ivin, *ibid.*, **A212**, 96, 207 (1952).

[4] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).