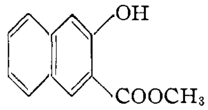
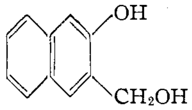
small measure of success was achieved in the preparation of this desired material by the formation of the cobaltinitrite complex of the diazotized amine[8a] and the decomposition of this complex using Starkey's[8d] procedure to give a 10–15% yield of 2-methyl-3-nitronaphthalene.

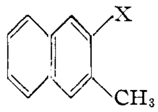
Many efforts were made to condense 2-methyl-3-nitronaphthalene with ethyl oxalate under various conditions.[9,10] When ether was used as the solvent no reaction occurred. When benzene was employed it appeared that traces of the condensation product had formed, but it could not be obtained in sufficient quantity to permit isolation in pure form and characterization. This result is in contrast to that obtained with 1-nitro-2-methylnaphthalene which did condense with ethyl oxalate in diethyl ether to give ethyl 1-nitro-2-naphthylpyruvate in 86.5% yield.



I



II



III

a, X = OH
b, X = NH_2
c, X = NO_2

Experimental[11]

3-Hydroxymethyl-2-naphthol (II).—A solution of 375 g. (1.99 moles) of 3-hydroxy-2-naphthoic acid in 1500 ml. of methanol and 75 ml. of concd. sulfuric acid was heated under reflux for 18 hours. Upon cooling, the ester, which separated as needles, was collected on a filter. The filtrate was concentrated to obtain a second crop of crystals. The two crops were combined, dissolved in ether, washed with 5% aq. sodium bicarbonate and finally water. The ether solution was evaporated to dryness and the residual methyl 3-hydroxy-2-naphthoate(I)[3] was recrystallized from methanol; m.p. 73–74°. The yield was 357 g. or 88.6% of the theoretical amount.

A 3-l. three-necked flask was fitted with an efficient reflux condenser protected with a calcium chloride drying tube, a dropping funnel similarly protected and a Hershberg stirrer fitted with a ground glass sleeve. This apparatus had been dried overnight in an oven at 110°; the ester prepared above was dried in an oven at 60°. A solution of 37 g. (0.98 mole) of lithium aluminum hydride in 1-l. of dry diethyl ether was prepared in the flask. To this solution was added dropwise 121 g. (0.60 mole) of the above ester dissolved in 600 ml. of dry diethyl ether. When this addition was completed, the reaction mixture was stirred for two additional hours. About 200 ml. of water was added slowly followed by approximately 1600 ml. of 10% aq. sulfuric acid to make the mixture acid to congo red paper. The solid product was extracted with 10 l. of diethyl ether. This solution was washed with 5% aq. sodium bicarbonate, then water and was finally evaporated to dryness. The resulting residue was recrystallized three times from methanol to give colorless flakes, m.p. 189.5–190.5° (reported[5] 190–191°). The yield was 91.6 g. or 87.9% of the theoretical amount.

3-Methyl-2-naphthol (IIIa).—A solution of 53.9 g. (0.31 mole) of 3-hydroxymethyl-2-naphthol (II) in 150 ml. of absolute ethanol was treated with hydrogen at 204 atmospheres and 142° in the presence of 6 g. of copper–chromium oxide catalyst.[12] The hydrogen uptake was completed after 45 minutes at which time the autoclave was cooled and the catalyst was separated on a filter. The ethanol solution was boiled with charcoal, filtered and evaporated to dryness. The residue was sublimed at 150° (0.01 mm.) and recrystallized from cyclohexane, from which it gave colorless plates; m.p. 156–157° (reported 155–156°[2]). The yield was 42.5 g. or 87% of the theoretical amount.

3-Methyl-2-naphthylamine (IIIb).—Anhydrous, powdered calcium chloride was placed in a 2-l., three-necked flask, fitted with a mechanical Hershberg stirrer and gas inlet and outlet tubes, and stirred vigorously while a constant stream of anhydrous ammonia gas was introduced until heat was no longer evolved. Since this complex is unstable in air it was used immediately.

A pulverized mixture of 15 g. of 3-methyl-2-naphthol (IIIa) and 75 g. of calcium chloride–ammonia complex was placed in a stationary autoclave and heated at 270° for eight hours. After removal from the cooled autoclave, the product was extracted with diethyl ether and the residual calcium chloride was dissolved in water. The water solution was extracted with diethyl ether and the combined ether extracts were washed with 2% aq. sodium hydroxide. Acidification of the alkaline solution afforded the recovery of unchanged starting material. After evaporation of the ether solution to dryness, the residue was sublimed at 110° (0.05 mm.) and recrystallized from cyclohexane. The yield, based upon starting material initially used, was 16.4 g. (82.5%) of pale yellow plates; m.p. 135–136° (reported[2] 135–135.5°).

2-Methyl-3-nitronaphthalene (IIIc).—A mixture of 13 ml. of hydrochloric acid (sp. gr. 1.18), 46 ml. of water and 5 g. (0.032 mole) of 3-methyl-2-naphthylamine (IIIb) was heated to give a clear solution. The solution was then cooled rapidly to obtain a finely divided precipitate of the amine hydrochloride. When the temperature of the mixture was below 0°, a solution of 2.6 g. of sodium nitrite in 13 ml. of water was added rapidly with vigorous stirring. The resulting diazonium salt solution was filtered and poured into a mixture of powdered calcium carbonate, ice and diethyl ether (to abate frothing). This mixture was filtered into a solution of 5.28 g. of sodium cobaltinitrite in 26 ml. of water contained in the filter flask. The diazonium–cobaltinitrite complex separated as a bright orange precipitate which was collected on a filter, washed with water and then with diethyl ether. This moist complex was stirred into a slurry with 20 ml. of water and was added to a solution of 80 g. of sodium nitrite in 160 ml. of water in which 10 g. of powdered copper was suspended by means of a mechanical stirrer. After stirring for three hours at room temperature, the solid material was collected on a filter and was extracted with diethyl ether. The residue, which remained after the evaporation of the ether, was sublimed at 120° (0.6 mm.) and recrystallized from cyclohexane to give 0.9 g. (15%) of pale yellow prisms; m.p. 120–120.5° (reported[2] 117–118.1°).

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[9] K. G. Blaikie and W. H. Perkin, Jr., *J. Chem. Soc.*, **125**, 296 (1924).

[10] W. Wislicenus and E. Mundiger, *Ann.*, **436**, 62 (1924).

[11] All melting points are uncorrected.

[12] T. W. Riener, THIS JOURNAL, **71**, 1130 (1949).

A New Form of Uranium Hydride[1]

BY R. N. R. MULFORD, F. H. ELLINGER AND W. H. ZACHARIASEN

RECEIVED AUGUST 6, 1953

We have discovered the presence of a new crystal form of uranium hydride which appears under certain conditions of preparation. For reasons given below, we believe this new form to be an alternate structure of the compound UH_3, and thus we propose to name this new crystal form α-UH_3, and to call the common form of uranium hydride β-UH_3. This nomenclature will be followed in the subsequent report.

During the course of some work involving uranium hydride, extra lines were noticed in X-ray diffraction patterns of uranium hydride preparations. These lines could not be satisfactorily explained on the basis of extraneous compounds pres-

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[1] Work done under the auspices of the A.E.C.

ent as impurities, and the presence of the extra lines could be roughly correlated with experimental conditions. Further investigation led to the discovery that the extra lines could be attributed to a diffraction pattern from a cubic cell with $a_0 = 4.160 \pm 0.005$ Å.

The common form of UH_3, the structure of which has been determined by Rundle,[2] has 8 U atoms per cubic unit cell with $a_0 = 6.63$ Å.

It was found that mixtures of this new crystal form with ordinary UH_3 could be produced by allowing hydrogen to react with powdered uranium at low temperatures, say 25 or $-80°$, and that, roughly, the percentage of the new crystal form was higher the lower the temperature of reaction. Thus, for example, at $-80°$ a mixture of normal UH_3 (β-UH_3) and the new form (α-UH_3) containing approximately 50% of α-UH_3 was obtained in one experiment. Since the reaction between uranium and hydrogen is quite exothermic, and since the powdered metal and hydride are both poor thermal conductors, some caution was necessary to keep the temperature of the reaction mixture low. Best results were obtained by adding the hydrogen in small doses and allowing time for the heat generated by the reaction to dissipate between doses.

Heat treatment of mixtures of the α- and β-hydrides produced information as to the temperature stability of the new form. The heat treatment experiments were done on specimens contained in silica capillary tubes for the Debye powder camera. Holding a mixture of approximate composition 33% α-UH_3 and 67% β-UH_3 at 250° for 100 hours converted the mixture to 100% β-UH_3. Further treatment of the same specimen at 100° for 100 hours produced no change in the diffraction pattern. Another specimen, however, consisting of a 50–50 mixture of the two forms was unchanged after 675 hours at 100°. Thus, α-UH_3 appears to be quite stable with respect to β-UH_3 at 100°, but will transform to β-UH_3 at 250°. The reverse transformation, however, from β-UH_3 to α-UH_3, can apparently not be effected in a reasonable time. This leads us to believe that α-UH_3 represents a transition, or metastable form which appears only by virtue of being formed more rapidly than it decomposes at low reaction temperatures. This explanation was suggested by J. E. Ricci.

Determination of the composition of the new form was done by more or less indirect chemical means. The compositions of mixtures produced by reaction of purified hydrogen with powdered uranium at low temperatures were measured by measuring the quantity of gas that a weighed sample of uranium would take up. When reaction was complete, Debye powder samples of the product were made, and the proportion of α-UH_3 to β-UH_3 was determined from photometric measurements of the relative intensities of the diffraction patterns. Since, as yet, we have only been able to produce the new hydride mixed with β-UH_3, no standard is available to help in estimating relative amount from pattern intensity, so that the percentages given for the various mixtures are only approximate.

The over-all compositions of 6 different preparations, together with the conditions of preparation and the relative amounts of α- and β-UH_3 as estimated from the powder patterns are shown in Table I. The last preparation listed is uranium deuteride. This sample contained as much of the α-phase as any hydride we have yet prepared, and it is believed that this may be a consequence of the fact that deuterium reacts with powdered uranium at a much slower rate than hydrogen.

TABLE I

Final comp. H:U ratio	Ratio $\alpha:\beta$	Preparation temp., °C.	Final hydrogen pressure, mm.
2.94	30:70	25	10
3.00	15:85	125	61
2.93	35:65	25	36
2.95	25:75	25	44
2.96	40:60	25	50
3.00	50:50	25	28

It will be seen that, regardless of the proportion of α to β, the composition is always very close to $UH_{3.00}$, thus providing chemical evidence that the α-form has the composition UH_3, since the composition of the β-form has been well established to be UH_3 by other investigators.

The powder diffraction pattern of α-UH_3 corresponds to a cubic unit cell with $a_0 = 4.160 \pm 0.005$ Å. Only the body-centered reflections occur. The observed intensities require two uranium atoms per unit cell in the positions (0, 0, 0) ($^1/_2$, $^1/_2$, $^1/_2$), and it is natural to suppose that the two uranium atoms are structurally equivalent. Thus, there are two possible structures for placing the hydrogen atoms

Structure I, space group Im3m, 6H in 6b.
Structure II, space group Pm3n, 6H in 6c (or 6d)

In structure I each uranium atom is bonded to six hydrogen atoms with U–6H = 2.08 Å., a hydrogen atom forming a bridge between two uranium atoms. Two objections that can be raised against this structure are: (1) the distance U–H = 2.08 Å. is small when compared with the value U–H = 2.32 Å. observed in the usual form of UH_3 and with the value Th–H = 2.3 to 2.5 Å. observed in thorium hydrides, and (2) this type of hydrogen bridge structure has not been encountered in other hydrides. Structure II gives U–12H = 2.32 Å. and each hydrogen atom is bonded to four uranium atoms which form a tetrahedron, four edges of which are 3.60 Å. long, and two edges, 4.16 Å.

Both the interatomic distances and the atomic configuration of structure II are reasonable when compared with the results for other hydrides of the heavy elements.

It has been concluded that the crystal structure of α-UH_3 is simple cubic, with $a_0 = 4.160 \pm 0.005$ Å., and with two molecules per unit cell. The space group is Pm3n and the atomic positions are

$$2\text{U in } (0,0,0)(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})$$
$$6\text{H in } \pm(\tfrac{1}{4},0,\tfrac{1}{2})(\tfrac{1}{2},\tfrac{1}{4},0)(0,\tfrac{1}{2},\tfrac{1}{4})$$

The interatomic distances, U–12H = 2.32 Å., are exactly the same as in the known form of UH_3.

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[2] R. E. Rundle, THIS JOURNAL, 73, 4172 (1951).