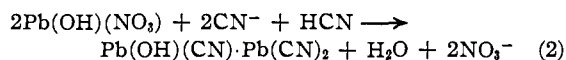


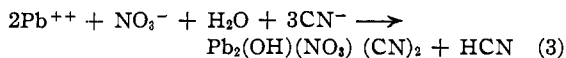
and



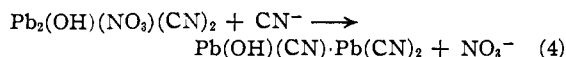
The sudden decrease in  $p\text{H}$  between the two endpoints is accounted for by the assumption that the concentration of cyanide ion must reach a certain value before reaction (2) is initiated, but that, once started, it progresses to a point at which most of the free cyanide ion has been removed.

The products formed during the titration in aqueous medium were prepared by adding known volumes of standard potassium cyanide to known volumes of standard lead nitrate solution, filtering, and air-drying. They were analyzed as described above. Addition of 1.50 mole of cyanide per mole of lead gave another new compound. Found:  $\text{PbO}$ , 81.8, 81.8; calculated for  $\text{Pb}_2(\text{OH})(\text{NO}_3)(\text{CN})_2$ , 81.85%. This compound evolved nitrogen dioxide during its decomposition. The substance formed at a mole ratio of 2.00 (*i.e.*, after the downward break) was again the hydroxytricyanide described above.

Consequently, the stoichiometry of the reactions in aqueous medium is described by the equations



and



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## The Structure of Uranium Hydride

BY LINUS PAULING AND FRED J. EWING

R. E. Rundle<sup>1</sup> has recently reported the results of an X-ray investigation of uranium hydride,  $\text{UH}_3$ . He found that there are eight molecules of this substance in the unit cube, with  $a_0 = 6.631 \text{ \AA}$ ., and that the uranium atoms have the  $\beta$ -tungsten arrangement, with two UI at 000 and  $1/2 \ 1/2 \ 1/2$  and six UII at  $1/2 \ 1/4 \ 0$ , etc. He suggested that each uranium I atom is surrounded by twelve hydrogen atoms, on the lines connecting the UI atom with the twelve surrounding UII atoms, and that there are half-bonds between hydrogen and each of the two uranium atoms ligated to it.

In this note we point out that consideration of the interatomic distances supports this proposal, and, moreover, leads to the conclusion that uranium hydride contains a new form of uranium, with small valence, similar to the low-valent forms of chromium and manganese previously reported.<sup>2</sup>

A hydrogen atom in a metallic hydride may be at the center of a tetrahedron of metal atoms, or

of an octahedron of metal atoms.<sup>3</sup> In zirconium hydride,  $\text{ZrH}$ , for example, the zirconium atoms are in a cubic closest packed arrangement, and it seems likely from consideration of the interatomic distances that the hydrogen atoms occupy tetrahedral positions, corresponding to the sphalerite structure. The single-bond radius of hydrogen is then calculated from the zirconium-hydrogen distance  $2.06 \text{ \AA}$ ., with use of the zirconium single-bond radius  $1.454 \text{ \AA}$ . and the correction  $0.36 \text{ \AA}$ . for bond-number  $1/4$ , to be  $0.25 \text{ \AA}$ . In palladium hydride,  $\text{PdH}_x$ , the tetrahedral positions are too small for hydrogen atoms, which instead occupy octahedral positions; the palladium-hydrogen distance  $2.03 \text{ \AA}$ ., with palladium single-bond radius  $1.28 \text{ \AA}$ . and correction  $0.47 \text{ \AA}$ . for bond-number  $1/6$ , then leads to  $0.28 \text{ \AA}$ . for the hydrogen radius. This radius lies between  $0.25$  and  $0.32 \text{ \AA}$  in most metallic hydrides, in good agreement with the range of values for non-metallic hydrides,  $0.28$  to  $0.32 \text{ \AA}$ .<sup>4</sup>

In uranium hydride the U-H distance of  $1.85 \text{ \AA}$ . (assuming the hydrogen to be midway between UI and UII) is approximately equal to that predicted, namely, the single-bond radius of uranium,  $1.42$ , plus the radius of hydrogen,  $0.27$ , plus the correction for bond number  $1/2$ ,  $0.18$ , a total of  $1.87 \text{ \AA}$ . There is no satisfactory position in the uranium hydride structure for hydrogen with coordination number larger than two. In  $\text{UH}_3$  each UI atom forms twelve bonds with bond number  $1/2$  with the surrounding hydrogen atoms, corresponding to a valence of six for uranium I. Each UII forms four such bonds with four surrounding hydrogen atoms, and also forms two bonds with adjacent UII atoms, at  $3.316 \text{ \AA}$ ., the calculated bond-number for these bonds being  $0.16$ . This leads for uranium II to the value  $2.3$  for the valence. No form of uranium metal or intermetallic compound of uranium has been reported so far in which uranium has this low valence, but a low-valent form of chromium and one of manganese have already been reported, so that a similar form for uranium is not entirely unexpected.

It is interesting to point out that the Brillouin-zone treatment of the  $\beta$ -tungsten structure provides some basis of understanding of the stability of this structure for both  $\beta$ -tungsten and uranium hydride. The first expected Brillouin zones correspond to the strong reflections  $\{210\}$  and  $\{211\}$ , which lead to about 16 electrons per unit cube. There then occurs another Brillouin polyhedron, bounded by the strong reflections  $\{222\}$ ,  $\{320\}$ , and  $\{400\}$ . (A fourth strongly reflecting form,  $\{321\}$ , does not further truncate this polyhedron.) The content of this polyhedron is  $53.5$  electrons

(3) G. Hägg, *Z. physik. Chem.*, **B11**, 433 (1930); **B12**, 33 (1931). Hägg's assignment of the hydrogen atoms to these positions was based on the assumption that the effective radius of hydrogen in metallic hydrides is about the same as in non-metallic hydride molecules.

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940, p. 168.

(1) R. E. Rundle, *THIS JOURNAL*, **69**, 1719 (1947).

(2) L. Pauling, *ibid.*, **69**, 542 (1947).

per unit cube. The brittleness of uranium hydride suggests that it has a filled-Brillouin-polyhedron structure. The number of electrons per unit calculated from the formula and the assumed valences 6 for UI, 2.3 for UII, and 1 for H is 49.8, which is slightly less than the theoretical value. It is possible that UII actually has valence 3 (like the low-valent form of its congener chromium), each atom forming four half-bonds with hydrogen and two (somewhat strained) half-bonds with its two UII neighbors; this valence would then lead to 54 valence electrons in the unit cube, in excellent agreement with the theoretical value.

The possibility that somewhat different effective radii, corresponding to difference in hybridization of the orbitals, should be used for metals in forming bonds with hydrogen than with other metal atoms may be mentioned. It has been pointed out before<sup>5</sup> that the very strong metal-metal bonds in gallium,  $\beta$ -tungsten, and  $\alpha$ -uranium, for which bond numbers of about 1.3 are calculated from the metallic radii, may really be single bonds, the effective radii being a few hundredths of an ångström less than usual for these bonds and greater for the other bonds. Thus in ZrH each of the twelve bonds formed by a zirconium atom with its zirconium ligands is calculated with the usual radius 1.454 Å. to have bond number 0.17, which leads to the low valence 3.04 for zirconium. In order for the valence 4 of zirconium to be effective, the single-bond radius of the metal in its Zr-Zr bonds would have to be taken as 1.50 Å. Similarly the single-bond radius of palladium effective in the Pd-Pd bonds in PdH is required to be 1.33 Å. instead of 1.278 Å. to conform with the valence 5.78. An increase in effective single-bond radius of UII for the U-U bonds in UH<sub>3</sub> and a decrease for the H-UII bonds would permit UII to be exercising the valence 3, found for its congener chromium in the A3 modification of this element.

The electron number per unit cube in  $\beta$ -tungsten itself is 48 (for valence 6) or 46.24 (for valence 5.78, as assumed in Ref. 2), corresponding to a metallic structure with partial filling of a Brillouin zone.

(5) L. Pauling, "The Nature of the Bonds in Metals and Inter-metallic Compounds," paper presented before Section 1, 11th International Congress of Pure and Applied Chemistry, London, July 1947.

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### Nitrogen-substituted Chloroalkylamines<sup>1</sup>

BY RICHARD F. PHILLIPS, CLIFFORD H. SHUNK AND KARL FOLKERS

Two nitrogen-substituted  $\beta, \beta'$ -dichlorodiethyl-

(1) This paper is based in part on work done for the Office of Scientific Research and Development under Contract OEMsr-1124 with Merck & Co., Inc.

amines were prepared by a procedure in which the Mannich reaction<sup>2</sup> is an essential step.

**4-( $\beta, \beta'$ -Dichlorodiethylamino)-2-butanone Perchlorate.**—To 10 g. of  $\beta, \beta'$ -dichlorodiethylamine hydrochloride<sup>3</sup> dissolved in 40 ml. of absolute ethanol, 15 ml. of acetone and 3 g. of paraformaldehyde were added. After heating at reflux for ten minutes, an additional gram of paraformaldehyde was added; heating was continued for fifteen minutes. Evaporation at 40° under reduced pressure left an oil, which did not crystallize. The oil was dissolved in 75 ml. of water. After filtering, 10 g. of 70% perchloric acid was added to the filtrate. On cooling, 12.0 g. of crystalline material was deposited, m. p. 112–115°. On recrystallization from water, the melting point reached a constant value of 115–116°. A sample was dried at room temperature in a vacuum desiccator.

*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>O<sub>3</sub>NCl<sub>3</sub>: C, 30.74; H, 5.16; N, 4.48; Cl, 34.03. Found: C, 31.19; H, 5.65; N, 5.00; Cl, 32.89 (Parr bomb).

Apparently some perchloric acid was lost by dissociation on crystallization from water.

**4-( $\beta, \beta'$ -Dichlorodiethylamino)-2-butanone Hydrobromide.**—To a suspension of 10 g. of the perchlorate in 50 ml. of water, a solution of 5 g. of sodium hydroxide in 10 ml. of water was added while cooling in ice. The colorless oil which separated was extracted with ether. The ether extract was dried over potassium carbonate, filtered, cooled in ice-salt mixture and saturated with dry hydrogen bromide. An oil was precipitated which crystallized on treatment with a small amount of acetone; wt. 9.2 g., m. p. 90–100°. Recrystallization of the salt from acetone raised the melting point to 108–111°; further recrystallization from absolute ethanol gave a constant melting point of 112–113°. The analytical sample was dried at room temperature in a vacuum desiccator.

*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>ONCl<sub>2</sub>·HBr·0.5H<sub>2</sub>O: C, 31.80; H, 5.67; N, 4.64; Br<sup>-</sup>, 26.45. Found: C, 31.65; H, 5.38; N, 4.75; Br<sup>-</sup>, 26.52 (Volhard titration).

**4-( $\beta, \beta'$ -Dihydroxydiethylamino)-2-butanone Hydrochloride.**—Ten grams of diethanolamine was converted to the hydrochloride by treatment with 9 ml. of concentrated hydrochloric acid. Water was removed by evaporation under reduced pressure. The residue was treated with absolute ethanol and evaporated again. After this treatment had been repeated once more, the residual viscous oil was dissolved in a mixture of 40 ml. of absolute ethanol and 16 ml. of acetone. Five grams of paraformaldehyde was added. After heating at reflux for twelve hours, evaporation of the clear solution at 60° under reduced pressure gave a viscous oil which crystallized from ethanol-acetone. The crystalline product was deliquescent. After storage in a vacuum desiccator it weighed 15 g. and melted at 75–80° in a sealed capillary tube. Two further recrystallizations of this product raised the melting point to a constant value of 83–85°. The substance appears to be unstable on heating. At 57° *in vacuo*, a sample lost 15% of its original weight in three hours.

*Anal.* Calcd. for C<sub>8</sub>H<sub>17</sub>O<sub>2</sub>N·HCl: Cl<sup>-</sup>, 16.75. Found: Cl<sup>-</sup>, 16.42 (Volhard titration, sample dried at room temperature in a vacuum desiccator).

**4-( $\beta, \beta'$ -Dihydroxydiethylamino)-2-butanol.**—A solution of 10 g. of 4-( $\beta, \beta'$ -dihydroxydiethylamino)-2-butanone hydrochloride in 125 ml. of methanol was shaken with 0.4 g. of platinum oxide catalyst and hydrogen at a pressure of 30–45 lb. per sq. in. The theoretical amount of hydrogen was absorbed within six hours. The catalyst was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was dissolved in 30 ml. of water. An excess of concentrated potassium hydroxide solution was added while cooling the flask in

(2) "Organic Reactions," Vol. I, John Wiley and Sons, New York, N. Y., 1942, Chapter 10, p. 303.

(3) Mann, *J. Chem. Soc.*, 464 (1934); Ward, *This Journal*, **57**, 915 (1935).