(Fig. 2) which will account for high melting point and brittleness, and with a resonating system of "half bonds" which should lead to high polarizability, metallic luster and high electrical conductivity, much as these properties are found in graphite. Moreover, it provides a satisfactory explanation for the uranium–uranium distances in the hydride and suggests satisfactory positions for precisely the correct number of hydrogen atoms.

The author is quite aware that it is impossible to defend the proposed structure except insofar as the proposal provides an explanation of the unusual properties, composition and metal arrangement of the hydride. This proposal is offered here because it seems unlikely that an M–H–M bridge is unique to uranium hydride. Many other metallic hydrides have rather similar properties, and though structural information is not yet complete enough to cite another good example of this type, it seems to the author that most "interstitial solution" compounds need further study. Nearly all such compounds, including hydrides, are brittle, hard and high melting, properties quite inconsistent with the weakening of metal–metal bonds unless replaced with better bonds. A number of metallic hydrides fulfill the conditions for "half bonds" as described before.[11]

Acknowledgments.—The author wishes to express his appreciation to the members of the Ames section of the Metallurgical Project for both samples and analytical data. Especial thanks are due Mr. A. S. Wilson for aid in the precise determination of hydride and deuteride spacings, to Mr. R. Nottorf, Dr. A. Newton, Messrs. W. Tucker and P. Figard for special sample preparations and to Drs. I. B. Johns and F. H. Spedding.

Summary

Uranium forms a metallic hydride, UH_3, a compound of definite composition, unique metal arrangement unrelated to that of the metal itself, and almost lacking in metal–metal bonds.

The hydride is cubic, $a = 6.631$ Å., with eight uranium atoms per unit cell at positions (a) 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and (c) $\frac{1}{4}\frac{1}{2}0$, $0\frac{1}{4}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{4}$, $\frac{3}{4}\frac{1}{2}0$, $0\frac{3}{4}\frac{1}{2}$, $\frac{1}{2}0\frac{3}{4}$ of the space group O_h^3, O^2 or T_d^4. The X-ray density is 10.92 g./cc. The deuteride spacing is 6.620 Å., definitely smaller than for the hydride.

It is proposed that the hydrogens form uranium–hydrogen–uranium bridges between metal atoms of type (a) and (c) in the structure, where the bridge contains one electron pair for the two bonds. This structure accounts for the physical properties, unique metal arrangement and formula of the hydride, and is consistent with a recently proposed theory of electron deficient structures.[10,11]

The Synthesis of Chromium Hexacarbonyl[1,2]

BY BENTON B. OWEN, JAMES ENGLISH, JR., HAROLD G. CASSIDY AND CLARISSA VANDERBILT DUNDON

Although satisfactory methods have been recorded[3] for the preparation of tungsten hexacarbonyl and molybdenum hexacarbonyl by reaction of the metals, or their salts, with carbon monoxide in the presence of reducing agents, no practical synthesis of chromium hexacarbonyl has been published. Job and Cassal[4] prepared small amounts of chromium hexacarbonyl from phenylmagnesium bromide and chromic chloride in the presence of carbon monoxide at atmospheric pressure. They obtained yields of 14% or less, and this unsatisfactory conversion was confirmed by others.[5,6] Recently, Anissimov and Nesmeya-

nov[7] carried out this same reaction at 115 atm. and reported yields as high as 22%. Our interest in this synthesis arose from an immediate need for a supply of chromium carbonyl for research purposes. Our efforts were therefore directed toward increasing the yields obtained by known methods rather than toward discovering new reactions or investigating the mechanism of old ones. In the following section we outline the procedures by which we obtained the highest yields (67% at 50 atm., and 24% at 1 atm.) by the action of carbon monoxide upon phenylmagnesium bromide and chromic chloride. In the final section we discuss results which might be of interest in a further study of the peculiar chemistry of organic chromium compounds.

Experimental

Materials.—The chromic chloride was a commercial product dried at 250° in nitrogen and screened to 40 mesh. Moisture in this material had no deleterious effect other than consumption of Grignard reagent.

All yields were calculated on the basis of per cent. of an-

(1) Published with the permission of C. L. Lee, Captain U.S.N., for the Navy Department, and R. B. Doulens, Major CAC, for the War Department.

(2) Abstracted from NDRC Report No. A-401, the first of two final reports covering the work done at Yale University under Contract OEMsr-1318 for Division One of the National Defense Research Committee, L. H. Adams, Chief.

(3) I. G. Farbenindustrie A. G., Patents; Chem. Zentr., 102, II, 2041 (1931); 103, I, 2498, 2753 (1932).

(4) A. Job and A. Cassal, Compt. rend., 183, 392 (1926).

(5) W. Hieber and E. Romberg, Z. anorg. allgem. Chem., 221, 321 (1935).

(6) M. Windsor and A. Blanchard, THIS JOURNAL, 56, 823 (1934).

(7) K. N. Anissimov and A. N. Nesmeyanov, Compt. rend. acad. sci. U. R. S. S., 26, 58 (1940).

hydrous chromic chloride converted to air-dried crude carbonyl.

Preparation of Chromium Hexacarbonyl under High Pressures of Carbon Monoxide.—Pure dry chromic chloride, 3.08 g., was suspended in 60 cc. of dry ether in a glass bomb liner[8] with stirring in a nitrogen atmosphere. The vessel was cooled to about −70° and then a solution of 27 g. of phenylmagnesium bromide in 80 cc. of dry ether was added slowly, with continued stirring, to the cold suspension. This required about thirty minutes. Much of the Grignard reagent crystallized. The liner was then removed from the cooling bath, wiped, and transferred to a bomb capable of being rocked mechanically. This was then sealed, and a pressure of carbon monoxide between 35 and 70 atm. was applied at once. The rocking was started promptly, and continued for two and three-quarter hours; about three-quarters of an hour was required for the bomb to reach room temperature, and two hours were allowed for complete reaction. Longer periods do not improve the yield of carbonyl.

At the end of this time, the carbon monoxide pressure was released, and the contents of the bomb were treated with ice water, 35 cc. of 6 N sulfuric acid was added, and then the mixture was steam distilled. Sufficient ether was added to the receiver to dissolve all of the carbonyl present, the ether layer was separated, washed with water, dried over sodium sulfate, and most of the ether evaporated through a fractionating column. Chromium carbonyl is carried over with the ether unless an efficient fractionating column is used: The residue from evaporation of most of the ether was cooled in an ice-bath, filtered, washed with cold methanol and finally washed with a little cold dry ether and dried in air.[9] The yield of crude material so obtained was from 2.3 to 2.9 g. (53 to 67% of theory). For further purification, the compound was recrystallized from dry ether, and sublimed *in vacuo*. The sublimed material forms large, highly refracting crystals.

Samples of crude and recrystallized carbonyl were analyzed[10] for chromium with the following results; crude 23.27 and 23.35%, recrystallized 23.50 and 23.46%, theoretical 23.63%.

Preparation of Chromium Hexacarbonyl at Atmospheric Pressure.—The reaction vessel was a 3-liter five-necked flask equipped with a high speed metal stirrer, a condenser cooled with Dry Ice in acetone, a gas inlet for carbon monoxide, a thermometer, and a 250-cc. buret delivering Grignard reagent. A suspension of 12 g. of dry chromic chloride in 700 cc. of dry ether was stirred at about 5000 r. p. m. and cooled to −70°. Without interrupting the stirring, 210 cc. of 2.7 N phenylmagnesium bromide in ether was added over a period of one hour. The carbon dioxide–acetone bath was then replaced by an ice-bath, and carbon monoxide was introduced through the gas inlet at a rate of 220 liters per hour. After a period of about ten minutes, the mixture warmed up to −10 or −8°, at which temperature the reaction began, as evidenced by a change in color. The reaction was allowed to proceed fifteen to thirty minutes longer. The temperature was 0° during most of this interval. To terminate the reaction, the mixture was poured over ice and treated in exactly the same manner as the high pressure runs. The yield was 21–24% of theoretical. Lower stirring speeds, lower rates of gas flow, and more concentrated solutions were found to decrease the yield.

Discussion

It appears to be essential to have the mole ratio

(8) Liners of mild steel, stainless steel, brass and copper were also used without influencing the yield.

(9) The drying in air should not be overdone as the material is volatile at room temperatures and is probably toxic. Loss of carbonyl may be incurred if the ethereal solutions are allowed to stand; a brownish fuzz precipitates on standing overnight in the dark, and decomposition in sunlight is rapid. We have been advised by English sources that an ethereal solution of molybdenum carbonyl detonated on standing.

(10) The carbonyl was analyzed by the method of A. Job and A. Cassal, *Compt. rend.*, **183**, 392 (1926).

of Grignard reagent to chromic chloride rather high.[4] We maintained this ratio at 7.5 in most of our experiments, but the yield is not sensitive to the exact value of this ratio if it is greater than 5. Various Grignard reagents were tested, but none gave a higher yield than phenylmagnesium bromide. Ethyl ether is the most suitable solvent.

As alternative sources of chromium we tried anhydrous chromic bromide and chromous chloride, and the ether-soluble liquid chromyl chloride. Chromyl chloride gave yields of only 15 and 22%, and is too dangerous to be used without elaborate precautions. Chromic bromide failed to yield any carbonyl at all under the conditions of the high pressure synthesis described above. The experiments with chromous chloride will be referred to later.

Variability in yield was reported by everyone who has synthesized chromium carbonyl. This variability is not so much a function of the conditions (temperature, pressure, time, etc.) during subjection of the reaction mixture to carbon monoxide in the bomb, as it is a function of the conditions under which the reactants are mixed prior to subjection to carbon monoxide. The extent to which phenylmagnesium bromide and chromic chloride react is apparently the crucial factor. If the two substances were allowed to react to completion before carbon monoxide was introduced, low or even zero yields were obtained. In order to get reproducible results, rigid standardization of the conditions of this initial reaction was necessary. This indicates the existence of an unstable intermediate reaction product essential to carbonyl formation. A special series of experiments designed to isolate this intermediate failed in that purpose, but it demonstrated that the intermediate was soluble in ether, and decomposed very readily in the presence of oxygen, or more slowly in the presence of an excess of Grignard reagents. A rough analytical control showed that the reaction between one mole of chromic chloride and one mole of Grignard reagent can be carried through to completion. The resulting intermediate, when treated with 6.5 moles of Grignard and quickly subjected to carbon monoxide under pressure, leads to good yields of carbonyl. Complete reaction between chromic chloride and more than one mole of Grignard reagent leads to destruction of this intermediate as evidenced by the very poor yields of carbonyl obtained from such mixtures.

It was suspected that one possible intermediate product might be chromous chloride, formed by the reducing action of the Grignard reagent. All attempts to convert chromous chloride, prepared by reduction of chromic chloride with hydrogen at 450°, to the carbonyl by the methods outlined above resulted in much lower yields than those obtained with chromic chloride under similar conditions. In those experiments in which reduction by hydrogen seemed most complete, the yield was

very low, and it is not impossible that absolutely pure chromous chloride would not react at all.

A solution of mixed phenylchromium halides, prepared according to Hein,[11] failed to yield any detectable carbonyl after treatment with carbon monoxide under pressure. On the basis of this negative result, and our experience with chromous chloride, we venture the opinion that none of the mechanisms proposed in the literature for the formation of chromium carbonyl is correct.

Acknowledgment.—The authors express their gratitude to Mr. J. F. Sweeney of the Struthers

(11) Fr. Hein. *J. prakt. Chem.*, **132**, 59 (1931).

Wells Corporation for the loan of high pressure equipment, and to Drs. P. G. Stevens and E. W. Fager for experimental assistance at the beginning of this work.

Summary

A procedure is described by which a 60% yield of chromium hexacarbonyl may be obtained by the action of carbon monoxide upon phenylmagnesium bromide and chromic chloride. The results obtained by some alternative procedures are discussed.

The Preparation of Strontium Selenide and its Properties as a Base Material for Phosphors Stimulated by Infrared[1,2]

By Arthur L. Smith,[3] R. D. Rosenstein and Roland Ward

Alkaline earth selenide phosphors have been reported by Pauli,[4] Kittleman,[5] Lenard, Tomaschek and Schmidt.[6] They prepared the selenides by heating a mixture of either the oxide or the carbonate with selenium at a high temperature in a specially constructed furnace. These workers were aware that poor yields of selenide were obtained by this procedure. Lenard[6] drew attention to the harmful effect of the presence of "inactive material" in strontium selenide activated with samarium, although Kittleman[5] stated that it did not affect the quality of the phosphors activated with other ions.

Methods for the preparation of alkaline earth selenides in reasonably pure condition have been known since the time of Berzelius. Fabre[7] and Henglein and Roth[8] obtained the selenides by reducing the corresponding selenates with hydrogen at red heat. The latter authors gave the temperatures at which reaction begins and claimed yields of 95 to 98% of theoretical. Slattery[9] prepared strontium and barium selenides for X-ray studies from the selenites by a similar process.

(1) The work reported here was carried out at the Polytechnic Institute of Brooklyn under Contract OEMsr 982 with the Office of Scientific Research and Development.

(2) Abstracted from part of theses submitted to the Graduate School of the Polytechnic Institute of Brooklyn by Arthur L. Smith in 1946 in partial fulfillment of the degree of Doctor of Philosophy and by R. D. Rosenstein in partial fulfillment of the degree of Master of Science in Chemistry.

(3) Present address: R. C. A. Victor Division, Luminescent Materials Dept., Lancaster, Pa.

(4) W. E. Pauli. *Ann. Physik.* [iv] **38**, 870 (1912).

(5) F. Kittleman. *ibid.*, [iv] **46**, 177 (1915).

(6) F. Lenard. R. Tomaschek and F. Schmidt, "Handbuch der Experimentalphysik," **1**, 23 (1928). Also R. Tomaschek. *Ann. Physik*, [iv] **75**, 109 (1924).

(7) C. Fabre. *Ann. chim. phys.*, [6] **10**, 472 (1887).

(8) F. Henglein and R. Roth. *Z. anorg. allgem. Chem.*, **126**, 227 (1923).

(9) M. K. Slattery, *Phys. Rev.* **20**, 84 (1922), **21**, 213A (1923). **25**, 333 (1925).

None of these investigators was concerned with the use of the alkaline earth selenides as phosphors.

This paper describes some further studies on the preparation of strontium selenide from strontium selenite and the preparation of infrared-stimulated phosphors from the pure selenide.

Experimental

A. Preparation of Pure Strontium Selenide.—Since the presence of metallic ions in concentrations less than 1 part per million may have profound effects upon the luminescent properties of phosphors, it is necessary to eliminate these impurities as completely as possible. The following procedure has been found to be adequate.

Reagent grade chemicals were used as source materials and all of the water was twice distilled, the second distillation being carried out in Pyrex stills.

A slurry of 2.2 kilos of strontium carbonate with one liter of distilled water is made in a 12-liter flask and 1825 to 1850 ml. of concentrated nitric acid is introduced slowly. Fifteen ml. of concentrated sulfuric acid is added to precipitate most of the barium and the mixture is boiled. The hot solution (pH about 6) is treated for thirty minutes with tank hydrogen sulfide, which is previously passed through barium hydroxide solution. The precipitate is allowed to settle and the solution is filtered. All of the filtering is accomplished, as illustrated in Fig. 1A, by drawing the solution into an evacuated flask through fritted glass filters which are protected with filter paper pulp. This technique serves to prevent contamination by dust particles.

The filtrate is treated with 100 ml. of saturated ammonium oxalate solution to remove calcium and the pH adjusted to 7 with ammonium hydroxide. The mixture is boiled and while still hot is treated with hydrogen sulfide, allowed to stand overnight, and filtered. The filtrate is acidified with nitric acid to a pH of 3. A slight excess of bromine (about 5 ml.) is added to oxidize any iron or manganese which remains at this point, and the solution is boiled till the excess bromine is removed. Ammonium hydroxide is again added until the pH is 8 when the solution is further treated with hydrogen sulfide and filtered after standing for several hours. The filtrate is again acidified to a pH of 3 with nitric acid, boiled and filtered. This solution of strontium nitrate is sufficiently free from heavy metal impurities to be used for the preparation of the phosphors.