[CONTRIBUTION FROM THE CHEMICAL DIVISION, AEROJET-GENERAL CORPORATION]

The Reaction between Aluminum and Atomic Hydrogen

BY BERNARD SIEGEL

RECEIVED SEPTEMBER 4, 1959

The purpose of the present investigation was to ascertain whether direct hydrogenation of aluminum could be achieved with atomic hydrogen. It was found that whereas a preformed aluminum film will undergo only a surface reaction with atomic hydrogen, a hydride is formed if aluminum is evaporated in an atmosphere of atomic hydrogen provided a sufficiently cold surface is available and the rate of aluminum evaporation is very slow. The products collected had H/Al ratios of 0.1 to 1.02 depending on the experimental conditions, but it is believed that these products included aluminum atoms and that the hydride, AlH_x, had an x value greater than unity. The hydride is stable at −78° but decomposes at higher temperatures at rates corresponding to an energy of activation of 14.4 kcal./mole.

Introduction

The objective of this investigation was to explore the possibility of forming a hydride of aluminum directly from the elements. Although at very high temperatures AlH has been observed spectroscopically from the interaction of aluminum and hydrogen,[1] there has been no reported isolation of a group III hydride (boron, aluminum or gallium) by the reaction of a group III metal with molecular hydrogen.[2] The only hydride of aluminum that has thus far been isolated is AlH_3, which is believed to be polymeric and is usually denoted as $(AlH_3)_x$. The latter has been prepared in a Lewis base medium by the reaction between $LiAlH_4$ and $AlCl_3$ and the resulting aluminum hydride is always isolated as a complex with the base. This aluminum hydride is too unstable to permit complete dissociation of the base by a heating process without decomposing to aluminum and hydrogen.[3]

A low temperature reaction between aluminum and atomic hydrogen seemed an interesting possibility for the successful synthesis of an aluminum hydride, keeping in mind the thermal instability of $(AlH_3)_x$. The literature contains several examples of hydride synthesis with atomic hydrogen; phosphine, for example, can be synthesized in this manner.[4]

Experimental

The reactor shown in cross section in Fig. 1 was connected to a high vacuum line. The two parts of the reactor were connected by a 2″ pipe joint seal, using a butyl rubber O-ring. All filament and electrical lead material was of tungsten. The heating elements consisted of two separate filaments (0.024″ diameter, while the electrical leads were 0.080″ diameter), one to vaporize aluminum and the other to dissociate H_2 into atomic hydrogen. Each filament was heated to the desired temperature by a variable transformer, operating at currents between 0–20 amp. At gas pressures of up to 1.5 mm., with the reactor submerged in a bath at −195°, the maximum filament temperature attainable was 1500°, as measured with an optical pyrometer.

Prior to each run the glass parts of the reactor were baked out and the latter was evacuated overnight; this resulted in pressures of 10^{-6} mm. with a degassing rate of 5×10^{-5} mm./hr. Extra-dry grade hydrogen was purified further by several hours of recycling past a 400° copper furnace and a liquid nitrogen bath. The filament used to evaporate aluminum was weighed and a weighed sample of aluminum wire (8–20 mg.) was wrapped around its trough. After introducing a known amount of hydrogen gas and placing a liquid nitrogen bath around the reactor, both filaments were heated to the appropriate temperatures. Periodic pressure readings were then taken on a McLeod gauge. Hydrogen was dissociated at filament temperatures of 1100° and 1500°. When hydrogen was dissociated at the higher temperature, it was difficult to maintain a slow rate of evaporation of aluminum at the second filament and consequently most of the runs were performed with hydrogen dissociation at 1100°.

The amount of aluminum which had been evaporated was determined by weighing the appropriate filament at the end of the experiment. Thermal stability of hydrides prepared by this method was studied by replacing the liquid nitrogen bath in which the reactor had been submerged with baths from −78° to 43° and by following the subsequent evolution of hydrogen.

Results

I. Reaction between Atomic Hydrogen and an Aluminum Film.—Aluminum has been reported to be impermeable to the diffusion of hydrogen atoms.[5] Nevertheless experiments were performed to investigate the effect of hydrogen atoms on a preformed film of aluminum. These experiments confirmed that only a surface reaction could be obtained under these conditions. A typical run is shown in Fig. 2. In the latter an aluminum film of approximately 570 atomic layers was vacuum deposited on the wall of the reactor which was at room temperature during the film deposition. This film then was attacked by atomic hydrogen generated by dissociation of molecular hydrogen at a filament at 1500° with the reactor in a bath at −195°. After an initial uptake of hydrogen, which corresponded to the small value of 0.094 for the composite hydrogen to aluminum ratio of the final product, no further reaction was observed.

TABLE I

Rate of Al evap. (mg./min.)	Composite H/Al ratio of product	Temp. filament at which H_2 dissoc. (°C.)	Temp. react. bath (°C.)
19[a]	0.19	1100	−195
4.9[a]	.45	1100	−195
0.3[a]	.71	1100	−195
.1[a]	1.02	1100	−195
.4[a]	0.077	1100	− 78
2.4[a]	.87	1500	−195
0.1[b]	.35	1100	−195
0.1[c]	.50	1500	−195

[a] Using reactor described in Experimental section. [b] Using reactor of 96 mm. i.d. [c] Using reactor of 96 mm. i.d., with H· generating filament 4 inches below filament charged with aluminum.

---

[1] AlH was observed spectroscopically when H_2 was slowly admitted to aluminum vapor heated to 1700°, E. Hulthen and R. V. Zumstein, *Phys. Rev.*, **28**, 13 (1926); Hulthen concluded that the formation of AlH was due to the reaction of aluminum atoms and atomic hydrogen. AlH also was observed spectroscopically in the high temperature reaction between an aluminum cathode and hydrogen in a discharge tube, H. Haber, *Physik Z.*, **40**, 541 (1939).

[2] D. Hurd, "Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 73.

[3] A. E. Finholt, *et al.*, THIS JOURNAL, **69**, 1199 (1947).

[4] I. Langmuir, *ibid.*, **34**, 1310 (1912).

[5] W. Baukloh and W. Wenzel, *Chem. Abst.*, **32**, 2066 (1938).

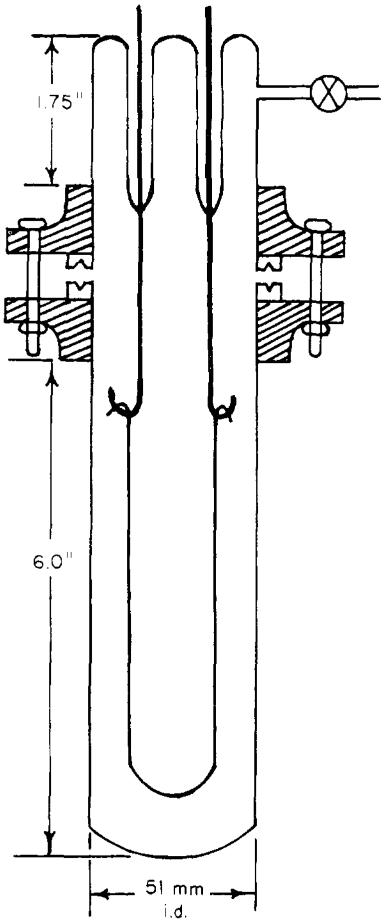

Fig. 1.—Reactor cross-section.

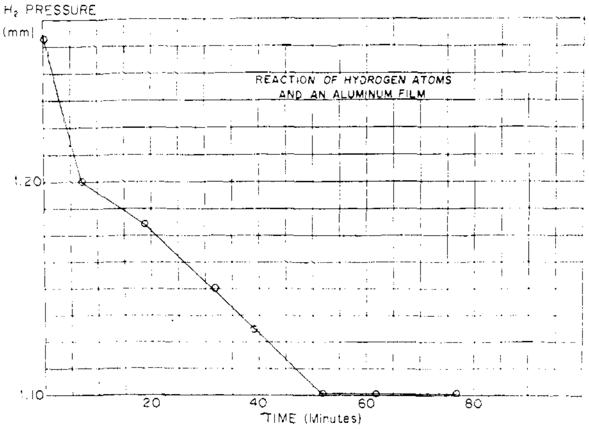

Fig. 2.

II. Reaction between Atomic Hydrogen and Evaporating Aluminum.—However, a significant reaction was observed between atomic hydrogen and evaporating aluminum and large conversions to an aluminum hydride could be obtained. The results of a study of various reaction parameters are summarized in Table I.

The rate of disappearance of hydrogen gas for a constant rate of aluminum evaporation is shown in Fig. 3. The data fit a straight line plot for $p^{1/2}$, indicating a one-half order rate law.

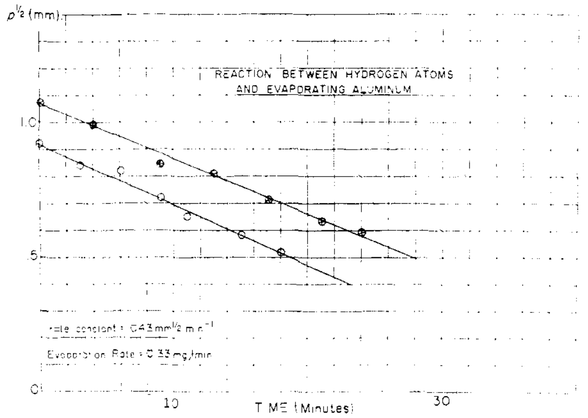

Fig. 3.

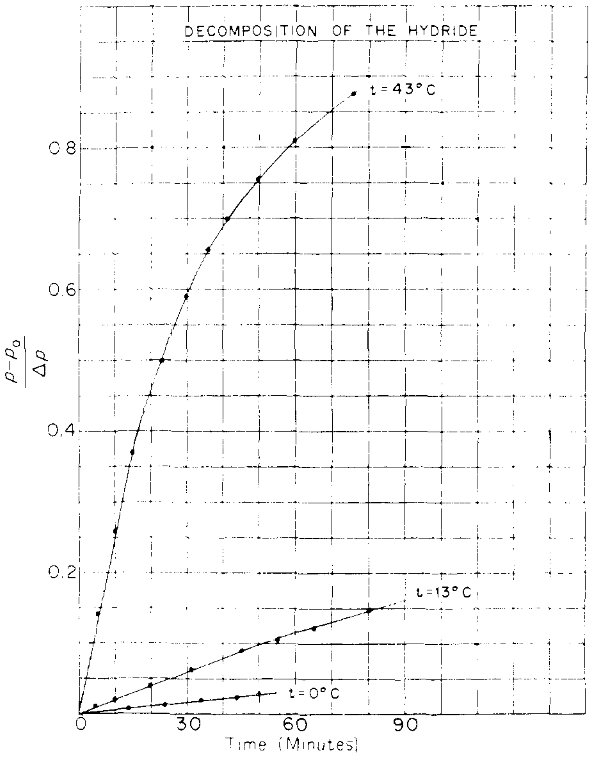

Fig. 4.

III. Decomposition of the Hydride.—The rates of thermal decomposition of samples with composite hydrogen to aluminum ratios of 0.9 to 1.0 are shown in Fig. 4. The ordinates are $p-p_0/\Delta p$ where $(p-p_0)$ is the increase in hydrogen pressure and Δp was the total hydrogen pressure decrease in the formation reaction. There was no observable decomposition at −78°, after 1 hr. The activation energy was calculated from the initial linear portions of the curves and gave a value of 14.4 kcal./mole.

Discussion

The marked increase in reaction which accompanies a slower rate of aluminum evaporation is probably attributable to the fact that aluminum atoms, which are covered by successive layers on the wall before they can react, are lost to the reaction. Also, significantly smaller conversions were obtained when the hydrogen atom concentration near the wall was lowered by increasing the path between filament and wall. The necessity for providing a very cold surface and the stability problem were shown by the drastic reduction in reaction product when a bath of −78° was substituted for the −195° bath. These observations lead to the hypothesis that at least the last, if not all, of the reaction steps leading to the formation of the hydride occur at the wall and that the continuous evaporation of aluminum serves the purpose of providing a constantly renewed film surface. However, the data do not eliminate the possibility that this is essentially a gas phase rather than a heterogeneous reaction.

The experimental determination of half-order kinetics for this reaction is in line with similar kinetics that previously were found when hydrogen was dissociated into atoms at a glowing tungsten filament.[6,7] Roberts and Bryce have explained their kinetics in terms of the mechanism of dissociation of hydrogen at the tungsten surface over a temperature range that coincides with the present study. It may thus be reasonably assumed that the rate determining step in the present process is the production of hydrogen atoms at the filament. The geometry of the apparatus supports this conclusion since the probability of hydrogen collisions with the filament is considerably lower than gas phase or wall collisions.

That the hydride formed was a chemical compound rather than physical adsorption of hydrogen was demonstrated by the decomposition kinetics. The activation energy of 14.4 kcal./mole establishes that the bonding is in the class of chemical compounds.[8] A physical desorption process would have an activation energy of approximately 1–2 kcal./mole.[8,9]

It should be emphasized that the composite H/Al ratios in Table I do not necessarily represent the compositions of the hydride molecules because these ratios also include unreacted aluminum atoms and aluminum atoms which resulted from the decomposition of initially formed hydrides. Since aluminum distilled to the wall of the reactor where the surface was constantly covered by successive layers, it is extremely unlikely that all aluminum atoms could react, keeping in mind that covered atoms were lost to the reaction. The drastic reduction in product when the wall bath was at −78°, a temperature at which the hydride is normally quite stable, proves that the hydride molecules at the constantly changing surface were exposed to a disruptive environment. This consisted of constant attack by hydrogen atoms with H recombination reactions liberating 103 kcal./mole while hydride molecules with an activation energy for decomposition of 14.4 kcal./mole served as third bodies; in addition radiation and conduction energy was transferred from the glowing filaments. Since a composite value of H/Al = 1.02 was achieved under these conditions, it is reasonable to postulate that for the actual hydride, AlH_x, x was greater than unity.[10]

Acknowledgments.—The author gratefully acknowledges the interest and advice of Dr. A. Wheeler, Dr. E. Mishuck and D. Seedman and is indebted to Dr. Seymour Siegel for critically reading the manuscript. The Bureau of Ordnance of the U. S. Dept. of the Navy sponsored this investigation under Contract NOrd-18386.

(6) J. K. Roberts and G. Bryce, *Proc. Cambridge Phil. Soc.*, **32**, 653 (1936).

(7) I. Mochan, *Chem. Abst.*, **36**, 3091 (1942).

(8) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," chapter on Heterogeneous Processes, McGraw-Hill Book Co., New York, N. Y., 1941, and R. Gomer and C. S. Smith, "Structure and Properties of Solid Surfaces," chapter on Chemisorption, Univ. Chicago Press, Chicago, Illinois, 1952.

(9) A. Eucken and W. Hunsmann, *Chem. Abst.*, **34**, 666 (1940).

(10) The instability of AlH_x at ambient temperatures and the fact that the hydride was isolated admixed with surface-active aluminum have made its chemical characterization difficult; for example, both AlH_x and aluminum deposited in the present apparatus react completely with water to liberate H_2.

AZUSA, CALIFORNIA

[CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY, LAMP DEVELOPMENT DEPARTMENT]

On the Preparation of the Phosphides of Aluminum, Gallium and Indium

BY ARRIGO ADDAMIANO

RECEIVED AUGUST 26, 1959

The phosphides of aluminum, gallium and indium can be prepared by reaction between those metals and zinc phosphide, Zn_3P_2, in a neutral atmosphere (argon, hydrogen) at about 800–900°. The reactions proceed according to the scheme

$$2Me + Zn_3P_2 \rightarrow 2MeP + 3Zn\uparrow \qquad (Me = Al, Ga, Zn)$$

with formation of the phosphides of the third group elements and evolution of zinc vapors. X-Ray and analytical data are given. The yield of reaction is a maximum for AlP, while some metal is left unreacted in the preparation of GaP and InP.

Introduction

The phosphides of aluminum, gallium and indium all have been prepared by direct synthesis from the elements.[1–7] Of them the least known is perhaps the phosphide of aluminum, while gallium and indium phosphide have been prepared in the form of single crystals[4,5,7] and considered for applications such as electroluminescence and high-temperature rectification. It seemed interesting

(1) W. E. White and A. H. Bushey, THIS JOURNAL, **66**, 1666 (1944).

(2) E. Montignie, *Bull. soc. chim. France*, 276 (1946).

(3) J. W. Mellor, "Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., London, second impression, 1947, p. 845.

(4) G. Wolff, P. H. Keck and J. D. Broder, *Phys. Rev.*, (2) **94**, 753 (1954).

(5) G. A. Wolff, R. A. Hebert and J. D. Broder, "Semiconductors and Phosphors," M. Schön and H. Welker, Editors, Interscience Publishers, Inc., New York, N. Y., 1958, p. 547.

(6) G. A. Wolff, L. Toman, Jr., N. J. Field and J. C. Clark, *ibid.*, p. 463.

(7) R. J. Guire and K. Weiser, U. S. P. 2,871,100 (1959).