

Studies of Lithium Hydride²

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Introduction

The negative character of the hydrogen in lithium hydride was first postulated by Lewis (1) and later by Nernst (2). Their predictions were substantiated by Moers (3) and Peter (4) who were able to show that, in the electrolysis of lithium hydride, hydrogen is liberated at the anode. The fact that the negative hydrogen present in lithium hydride and other salt-like hydrides is a powerful reducing agent is well known (5). However, very little specific information relative to the reducing properties of lithium hydride is available in the literature. These investigations were undertaken in the hope that additional information concerning the behavior of lithium hydride toward inorganic compounds, particularly those of elements of the transition groups might be gained. It was also desired to find a reaction medium in which lithium hydride is soluble and stable and to develop the necessary techniques for studying reactions with lithium hydride in such a medium.

Two different types of reactions were studied. In the first case, solid-solid reactions involving mixtures of lithium hydride with various chlorides and oxides were investigated. It was found that lithium hydride is soluble without decomposition in the fused lithium chloride-potassium chloride eutectic (40 mole per cent potassium chloride) which melts at 350°C. The second series of reactions studied was between suspensions of certain oxides in this melt and lithium hydride dissolved in the melt.

Experimental

The lithium hydride used in these investigations was obtained from the Fairmount Chemical Company of Newark, New Jersey. For use in these studies it was necessary to grind the hydride to a fineness of about 100 mesh. A solenoid-operated vacuum grinder was used for this purpose to prevent the reaction of the hydride with moisture in the air during the grinding process.

All of the reactions studied were performed in an apparatus similar to that shown in Figure 1. The reaction vessel consisted of a stainless steel crucible. A large thick-walled test tube heated by an electric muffle formed the reaction vessel. The type of manometer used depended

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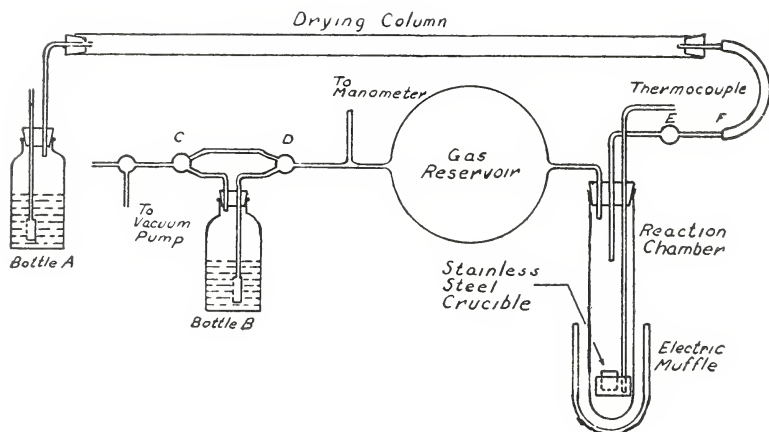


Figure 2 Apparatus for Studying Reactions

upon the reaction being studied. A Wegner distillation pump capable of reducing the pressure to 0.01 mm. Hg. was used to evacuate the apparatus. Gases admitted to the apparatus passed through Bottle (A), containing a strong potassium hydroxide solution, and the drying column which was packed with Drierite. Carbon dioxide and water were thus removed from the admitted gases. Bottle (B) contained a standardized sodium hydroxide solution and the two three-way stopcocks (C) and (D) provided a means whereby the gaseous products generated during a reaction could be pumped through the standard base solution.

(I) *Solid-Solid Reactions of Lithium Hydride with Alkali Chlorides.*—A series of four reactions was studied in which mixtures of solid lithium hydride with, successively, the solid chlorides of sodium, potassium, rubidium, and cesium were heated under reduced pressure. For these reactions a Zimmerli manometer was attached to the apparatus to permit the determination of small departures from zero pressure. The reactions were all performed in essentially the same manner. A small, known quantity of ground lithium hydride was placed in the stainless steel crucible and heated, under vacuum, to a temperature of about 550°C. for one-half hour to remove any traces of moisture. When cooled, a weighed quantity of the alkali chloride was added and mixed intimately with the lithium hydride. The alkali chlorides had been previously ground and then dried at temperatures slightly below their melting points. The mixture was then heated to 300°C. under vacuum (continuous pumping). At that temperature the system was closed to permit any gas generated by the reaction to be retained in the apparatus.

In each case, at temperatures around 500°C. there occurred a sudden increase in pressure and a mirror-like deposit formed on the walls of the reaction chamber above the heated zone. The reaction usually continued for about thirty minutes. When the apparatus had

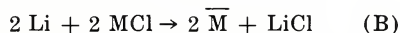
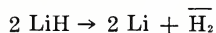
cooled to room temperature, the pressure was noted and the amount of gas produced was calculated by use of the gas law.

Air was then admitted to the apparatus through Bottle (A). Bottle (B) contained a standard sodium hydroxide solution. The gases in the apparatus were then pumped through Bottle (B) and the resulting solution was titrated with standard hydrochloric acid solution.

The distilled material in the mirror-like deposit and the residue remaining in the crucible were examined separately for lithium and the other alkali metal concerned by standard analytical procedures. The data obtained in these experiments are shown in Table 1. It is to be noted that in no case was any hydrogen chloride produced. Also it is of interest that reduction of the alkali metal chloride to the metal is nearly complete in each case and the quantity of gas produced corresponds roughly to one-half mole of hydrogen per mole of alkali chloride reduced. In view of these observations it was concluded that the reactions were probably of the type



These reactions were repeated using metallic lithium in place of the lithium hydride. The alkali metal chlorides were reduced to the metals in these reactions in the same manner and at about the same temperature as when lithium hydride was used. Consequently, one cannot be certain whether a reaction mechanism as illustrated by the following equations is responsible for the reductions observed when lithium hydride is used rather than that represented by Equation (A).



The same relative quantity of gas would be produced in either case. However, the pressures attained in the reactions involving lithium hydride ranged from 16 to 26 mm. Hg. while the decomposition pressure of lithium hydride is given as 0.07 mm. Hg. at 500°C. Hence, for the reaction as represented by (B) to continue, the lithium hydride would have to decompose against a pressure of hydrogen much in excess of its decomposition pressure at the reaction temperature.

(II) *Solid-Solid Reactions of Lithium Hydride With Oxides of Groups IV and V.*—These reactions were performed in essentially the same manner as those involving the alkali halides except that the preheating of the lithium hydride to remove moisture was not done and the gases evolved were not checked for the presence of acidic constituents. No products distilled out of the reaction vessel in these reactions. Pressures and temperatures were noted and the quantity of gas evolved was calculated, although no coordination between the quantity of gas evolved and the degree of reduction attained was found. Since the decomposition pressure of lithium hydride is about 15 mm. Hg. at the temperatures reached in these experiments (ca. 600°C.) it is

TABLE 1. Reaction of Lithium Hydride with Alkali Chlorides.

Alkali Chloride	m. Moles LiH	m. Moles Alkali Chloride	Mole Ratio LiH/MCl	m. Moles Gas Per m. Mole MCl	m. eq. HCl formed	MCl Left in Residue	Temp. of Initial React.	Max. Temp
NaCl	9.72	1.22	7.96	0.50	0	absent	500	520
KCl	9.08	1.13	8.01	0.51	0	absent	490	517
RbCl	13.0	1.58	8.22	0.53	0	ca. 5 mg. present	472	530
CsCl	6.95	0.881	7.88	0.58	0	trace	480	530

TABLE 2. Reactions of Lithium Hydride with Group IV and Group V Oxides.

Oxide	m. Moles Oxide	LiH m. Moles	Mole Ratio LiH Oxide	Max. Temp. °C.	m. Moles Gas Per m. Mole Oxide	Color of Product	Possible Formula Product
ThO ₂	1.825	7.86	4.31	600	0.53	White	ThO ₂
ZrO ₂	1.62	6.71	4.13	610	0.70	Black	Zr, (ZrO, Zr ₂ O ₃)
TiO ₂	1.99	12.32	6.2	600	0.715	Black	Ti ₂ O ₃
SiO ₂	2.675	10.56	3.95	600	1.33	Black	Si
GeO ₂	1.19	5.97	5.02	610	1.79	Black	GeO
Cb ₂ O ₅	0.469	3.95	8.43	605	3.33	Black	Cb ₂ O ₃ , CbO ₂

entirely possible that the decomposition of the hydride produced the major portion of the gas evolved. The data obtained for the solid-solid reactions between lithium hydride and thorium dioxide, zirconium dioxide, titanium dioxide, silicon dioxide, germanium dioxide and columbium pentoxide are given in Table 2.

The determination of the composition of the products of these reactions was difficult because of the instability of these elements in their lower oxidation states. The reaction product was, in each case, treated with water to remove the excess lithium hydride and any lithium oxide or metallic lithium formed in the reaction. The solutions were filtered and an attempt was made in each case to identify the residue by solubility tests. The probable formulas of the reduction products are given in Table 2.

(III) *Reactions of Lithium Hydride in a Lithium Chloride—Potassium Chloride Melt.*—In performing these reactions the apparatus shown in Figure 1 was used. An open J-tube manometer was used for pressure measurement since these reactions were studied under an atmosphere of helium at near atmospheric pressure. The following procedure was followed for all of the reactions studied. About one gram of lithium chloride was placed in a weighed stainless steel crucible and heated for one hour under vacuum (continuous pumping) and at a temperature of about 550°C. When cool, the crucible was weighed and the proper amount of potassium chloride previously dried by heating, was added to produce the eutectic. This mixture was heated under vacuum to a temperature of 300°C. Helium was then admitted through Bottle (B) to bring the apparatus to atmospheric pressure. Heating was continued until the mixture had fused completely. When again cool, a weighed amount of ground lithium hydride was added and the mixture was heated until fusion occurred and the lithium hydride dissolved in the melt following the same procedure as when the potassium chloride was added.

When the apparatus was again cool, a weighed amount of the compound to be reacted with the lithium hydride was added. The mixture was then heated under vacuum to a temperature of 300°C. Helium was then admitted through Bottle (B) and the heating was continued. At some definite temperature, usually 345°C., the apparatus was allowed to come to atmospheric pressure. The system was then closed off and heating was continued until fusion occurred. In each case studied, a rapid reaction occurred immediately after fusion of the mixture. Heating was continued until the reaction was complete as indicated by a constant pressure. As the apparatus cooled, the pressure in the apparatus was noted when the temperature reached that at which the system was closed during heating. The pressure was again noted when the apparatus had cooled to room temperature. The atmospheric pressure was also noted. From the pressure and temperature data taken, the quantity of gas generated in the reaction could be calculated roughly. The gases in the apparatus were pumped through a standard sodium hydroxide solution in Bottle (B) and the resulting solution was titrated with standard hydrochloric acid solution.

TABLE 3. Reactions of Ta₂O₅, Cb₂O₅, V₂O₅, and Eu₂O₃ in a KCl-LiCl Melt.

Oxide	Run	m. Moles Oxide	m. Moles LiH	Mole Ratio $\frac{\text{LiH Oxide}}{\text{m. Moles Compound}}$	m. Moles Gas Formed	m. Moles Acidic Gas Formed	mg. Product	mg. Starting Material	Possible Formula Product
Ta ₂ O ₅	A	0.786	12.64	16.1	1.86	0	345.0	348.2	TaO ₂
Ta ₂ O ₅	B	0.5797	9.13	15.5	1.97	0	264.6	256.8	TaO ₂ •H ₂ O
Cb ₂ O ₅	A	1.364	21.8	16.0	2.52	0	334.0	363	Cb ₂ O ₃
Cb ₂ O ₅	B	.7304	11.41	15.6	...	0	147.7	194.4	Cb ₂ O ₃
Cb ₂ O ₅	C	.4419	6.98	15.8	2.50	0	106.0	117.6	Cb ₂ O ₃
V ₂ O ₅	A	1.902	24.7	13.0	3.86	0	215.2	346	VO
Eu ₂ O ₃	B	0.435	6.4	14.9	1.5	0	133.3	152.9	Eu ₂ SO ₄
Eu ₂ O ₃	A	0.430	6.8	15.7	1.5	0	53.5	151.7	Eu ₂ SO ₄

Treatment of the residues differed according to the reaction being studied. Table 3 presents the data obtained in the study of the reaction of lithium hydride with tantalum pentoxide, columbium pentoxide, vanadium pentoxide, and europium trioxide.

Summary

Lithium hydride reacts with sodium chloride, potassium chloride, rubidium chloride, and cesium chloride under reduced pressure and at temperatures around 500°C. In each case a gas (probably hydrogen) is evolved and the alkali metal other than lithium is distilled from the hot zone to the cooler parts of the reaction chamber. The results obtained indicate that the reaction is probably of the type



Many oxides of Group IV and Group V elements react with lithium hydride under reduced pressure and at temperatures around 500°C. The product of the reduction may be the element or oxides of the element in lower oxidation states. The experiments performed indicate that the following reductions occur under these conditions.

Thorium dioxide is not reduced.

Zirconium dioxide is reduced to the metallic state.

Titanium dioxide is reduced to the trivalent state.

Silicon dioxide is reduced to amorphous silicon.

Germanium dioxide is reduced at least to the bivalent state and perhaps to the metal.

Columbium pentoxide is reduced, possibly to the trivalent state.

The lithium chloride-potassium chloride eutectic, at its melting point, will dissolve lithium hydride. The resulting solution may be used as a reaction medium for the study of reactions of lithium hydride with solids not soluble in the eutectic. The reactions of the pentoxides of tantalum, columbium, and vanadium with lithium hydride in the eutectic were studied.

The identification of the products obtained in these reactions was difficult due to the instability of these elements in their lower oxidation states. The evidence obtained indicates that tantalum is reduced at least to the trivalent state and that vanadium is reduced to the bivalent state. The identification of these oxidation states was not rigorous and the results obtained are indicative only.

Europic oxide reacts with lithium hydride in a potassium chloride-lithium chloride melt. The europium may be recovered as europous sulfate by disintegrating the product obtained with dilute sulfuric acid. Quantitative recovery was not achieved.

This study is being continued in this laboratory.

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