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CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA 30332

Concerning the Reactions of Lithium, Sodium, and Potassium Hydrides with Magnesium Halides in Ether Solvents. A Convenient and Economic Route to Reactive Magnesium Hydride

BY E. C. ASHBY* AND R. D. SCHWARTZ

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The reactions of lithium, sodium, and potassium hydrides with magnesium chloride, bromide, and iodide in diethyl ether and tetrahydrofuran, as a route to reactive magnesium hydride, have been studied. Magnesium hydride was formed in quantitative yield by the reaction of sodium hydride with magnesium bromide in tetrahydrofuran and by the reaction of sodium hydride or potassium hydride with magnesium iodide in diethyl ether. In the latter reactions the sodium iodide by-product was separated from magnesium hydride by extraction with tetrahydrofuran, and potassium iodide was separated by extraction with diglyme. Commercially available lithium hydride was found not to react with magnesium halides in tetrahydrofuran at room temperature although some reaction was detected at reflux temperatures. Lithium hydride prepared by hydrogenolysis of *tert*-butyllithium was found to react slowly with magnesium bromide in tetrahydrofuran and not at all with magnesium chloride in the same solvent. No complexes of the type M_nMgH_{2+n} were detected when excess alkali metal hydrides were used in these experiments.

Introduction

There are three general methods for preparing magnesium hydride.[1] The equations used to represent these methods are

$$(C_2H_5)_2Mg \xrightarrow{175^\circ} MgH_2 + 2C_2H_4 \tag{1}$$

$$LiAlH_4 + 2Mg(C_2H_5)_2 \longrightarrow 2MgH_2 + LiAl(C_2H_5)_4 \tag{2}$$

$$Mg + H_2 \xrightarrow[200\ \text{atm}]{570^\circ} MgH_2 \tag{3}$$

The pyrolysis of diethylmagnesium[2] (eq 1) produces an active form of magnesium hydride which is pyrophoric in air and reacts violently with water and other protic compounds. The reaction of lithium aluminum hydride with diethylmagnesium[3] (eq 2) also produces active magnesium hydride. The formation of magnesium hydride from the elements (eq 3) occurs at 570° and 200 atm using magnesium iodide as a catalyst.[4] This method is obviously an economic one and the magnesium hydride prepared by this method is commercially available. Unfortunately MgH_2 prepared by this method is quite unreactive even to air and water.

In 1951 Wiberg,[5] in a short note concerning the preparation of BeH_2, made a one-sentence statement that excess lithium hydride and magnesium chloride in diethyl ether react to form either magnesium hydride or Li_nMgH_{2+n}. Since a mixture of excess LiH and MgH_2 could not be distinguished from Li_nMgH_{2+n} except by powder diffraction analysis, one cannot be sure what was formed in this reaction and to what extent. No subsequent report has appeared.

The reaction of alkali metal hydrides with magnesium halides in ether solvents represents a substantially more convenient and economic route to reactive magnesium hydride than the methods now available. Ideally it was hoped that in a particular solvent an insoluble metal hydride would react with a soluble magnesium halide to form insoluble MgH_2 and soluble magnesium halide. Thus active MgH_2 could be easily isolated in a pure form by filtration. We therefore decided to explore the general scope and utility of the reaction MH + MgX_2 (where M = Li, Na, K and X = Cl, Br, I) in an attempt to produce active magnesium hydride free from the alkali metal halide by-product. We also wished to determine whether Li_nMgH_{2+n} is formed in the reaction of LiH and $MgCl_2$ and, if so, isolate the compound.

Experimental Section

All operations were carried out either in a nitrogen-filled glove

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* To whom correspondence should be addressed.

(1) K. M. Mackay, "Hydrogen Compounds of the Metallic Elements," Wilmer Brothers Ltd., Birkenhead, Cheshire, England, 1966, p 39.

(2) E. Wiberg and R. Bauer, *Z. Naturforsch. B*, **5**, 396 (1950).

(3) G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **73**, 4585 (1951).

(4) E. Wiberg, H. Goeltzer, and R. Bauer, *Z. Naturforsch. B*, **6**, 394 (1951).

(5) E. Wiberg and R. Bauer, *ibid.*, *B*, **6**, 171 (1951).

box equipped with a recirculating system to remove oxygen and water[6] or on the bench using typical Schlenk-tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation.—Infrared spectra were obtained using a Perkin-Elmer Model 621 high-resolution infrared spectrophotometer. Cesium iodide cells were used. Spectra of solids were obtained in Nujol which had been dried over sodium wire and stored in a drybox.

X-Ray powder diffraction patterns were run using a Debye–Scherrer camera of 114.6-mm diameter using Cu Kα (1.540 Å) radiation with a nickel filter. Single-walled capillaries of 0.5-mm diameter were used. These were filled in the drybox and sealed with a microburner.

Reagents.—Tetrahydrofuran and diethyl ether (Fisher Certified reagent) were distilled over sodium aluminum hydride and lithium aluminum hydride, respectively, immediately before use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium, obtained from Dow Chemical Co., was washed with diethyl ether and dried under vacuum prior to use.

Sodium hydride was obtained from Alfa Inorganics as a 57% suspension in mineral oil. Potassium hydride was obtained from Alfa Inorganics as a 50% suspension in mineral oil. Lithium hydride was obtained from Alfa Inorganics as a dry powder. *tert*-Butyllithium in pentane solution was obtained from Foote Mineral Co.

Analytical Procedures.—Halogen analysis was carried out by the Volhard method. Magnesium analysis was carried out by titration with EDTA. Hydridic hydrogen analysis was carried out by hydrolyzing a weighed sample of the compound on a high-vacuum line and transferring the gas to a calibrated measuring bulb with a Toepler pump after passing the gas through a liquid nitrogen trap. Lithium analysis was carried out by flame photometry.

Preparation of Magnesium Halides in Diethyl Ether and Tetrahydrofuran.—Magnesium halides in ether solvents were prepared as described previously.[7]

Preparation of Lithium Hydride.—To an autoclave (300-ml chamber) was added 150 ml of *tert*-butyllithium in pentane. The autoclave was then pressurized to 3000 psi with hydrogen and the contents were allowed to stir overnight at room temperature. The resulting solution was not filtered and the white solid product was never allowed to become dry. The supernatant liquid showed no activity and analysis of the solid as a slurry in pentane gave a lithium to hydrogen ratio of 1.0:1.0.

Reactions of Alkali Metal Hydrides with Magnesium Halides in Ether Solvents at Room Temperature.—Alkali metal hydrides were allowed to react with magnesium halides in diethyl ether and THF at room temperature in order to determine the general extent of the reaction. The results are summarized in Table I. An example of the general reaction is given below.

To 83.4 ml of magnesium bromide in THF (0.1436 mol) was added 1.15 g of sodium hydride (57% in mineral oil) and the solution was stirred for 2 days. The solution was then filtered and the analysis of the filtrate showed no magnesium or bromide in solution. The infrared spectrum and X-ray powder pattern of the solid indicate a mixture of sodium bromide and magnesium hydride.

Reactions of Alkali Metal Hydrides with Magnesium Halides in Ether Solvents at Reflux Temperatures.—In order to obtain some idea of the order of reactivity based on solvent, halide, or alkali metal, the alkali metal hydrides were allowed to react with the magnesium halides under a set of standard conditions. These conditions involved a 2:1 ratio of alkali metal hydride to magnesium halide and refluxing the solvent for 5 hr. The solutions were then cooled and filtered and the amount of magnesium hydride in the solid was determined by elemental analysis. The results are summarized in Table II.

TABLE I

SUMMARY OF RESULTS OF REACTIONS OF METAL HYDRIDES WITH MAGNESIUM HALIDES IN ETHER SOLVENTS

Reactants	Solvent	Reaction conditions	Yield of MgH_2, %
$NaH + MgI_2$	$(C_2H_5)_2O$	Room temp; 2 days	100[a]
$NaH + MgI_2$	$(C_2H_5)_2O$	Reflux; 36 hr	100
$NaH + MgI_2$	THF	Room temp; 3 days	No reaction
$NaH + MgBr_2$	THF	Room temp; 2 days	100
$NaH + MgCl_2$	THF	Room temp; 4 days	20
$NaH + MgCl_2$	THF	Reflux; 4 days	11
$LiH + MgCl_2$	THF	Room temp; 2 days	No reaction
$LiH + MgBr_2$	THF	Reflux; 2 days	50
$LiH + MgCl_2$[b]	THF	Room temp; 2 days	No reaction
$LiH + MgBr_2$[b]	THF	Room temp; 1 day	33
$KH + MgI_2$	$(C_2H_5)_2O$	Reflux; 1 day	100
$LiH + MgBr_2$[b]	THF	Reflux; 12 hr	86

[a] NaI can be removed by extraction with THF. [b] LiH was prepared by hydrogenation of *tert*-butyllithium.

TABLE II

RELATIVE REACTIVITY OF ALKALI METAL HYDRIDES TOWARD MAGNESIUM HALIDES[a]

$2MH + MgX_2$	Solvent	Yield of MgH_2, %	$2MH + MgX_2$	Solvent	Yield of MgH_2, %
$LiH + MgCl_2$	THF	0[b]	$NaH + MgBr_2$	THF	15
$LiH + MgBr_2$	THF	0[b]	$KH + MgBr_2$	THF	4.4
$LiH + MgCl_2$	THF	64[c]	$NaH + MgBr_2$	Ether	10
$LiH + MgBr_2$	THF	74[c]	$KH + MgBr_2$	Ether	19
$LiH + MgI_2$	THF	15.9[c]	$NaH + MgI_2$	Ether	2.5

[a] All reactions run in refluxing solvent for 5 hr. [b] Commercial grade LiH. [c] LiH was prepared by hydrogenolysis of *tert*-butyllithium.

Results and Discussion

In the present study alkali metal hydrides were allowed to react with magnesium halides (eq 4) in THF and diethyl ether. The purpose of this investigation

$$2MH + MgX_2 \longrightarrow 2MX + MgH_2 \qquad (4)$$

was to study the possibility of reaction of alkali metal hydrides with magnesium halides as a convenient and economic route to active magnesium hydride.

Commercial grade lithium hydride obtained as a dry powder did not react with magnesium bromide in THF at room temperature. Even after stirring at room temperature for several days only the unreacted starting materials were recovered. Under conditions of reflux for 2 days, some reaction did take place as the Mg:Br ratio in solution rose to 1.0:4.16. Since LiBr is soluble in THF, this ratio indicates the removal of magnesium from solution, presumably as insoluble MgH_2 (eq 5).

$$\underset{\text{(insoluble)}}{2LiH} + \underset{\text{(soluble)}}{MgBr_2} \xrightarrow{\text{THF}} \underset{\text{(insoluble)}}{MgH_2} + \underset{\text{(soluble)}}{2LiBr} \qquad (5)$$

In order to obtain a more reactive form of lithium hydride, *tert*-butyllithium in pentane was hydrogenated at 3000 psi and 25°. Lithium hydride was obtained as a pentane slurry and remained active as long as it was not allowed to become dry. However, reaction of this LiH with $MgCl_2$ in THF at room temperature afforded only unreacted starting material after 2 days. The reaction

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[6] T. L. Brown, D. W. Dickerhoff, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, **33**, 491 (1962).

[7] E. C. Ashby, R. D. Schwartz, and B. D. James, *Inorg. Chem.*, **9**, 325 (1970).

of this active form of LiH with $MgBr_2$ in THF gave MgH_2 in 33% yield after stirring overnight. Since the reaction was not complete, some weak lines corresponding to LiH were found along with lines for MgH_2 in the X-ray powder pattern of the solid product.

The main advantage of using LiH is that the lithium halide by-products are soluble in either diethyl ether or THF thus making separation from insoluble MgH_2 simple. However if one must obtain the LiH from *tert*-butyllithium, then the convenience and economics of the reaction would no longer be an advantage. With this in mind attention was focused on the use of sodium hydride which is inexpensive and is readily available as a 50% dispersion in mineral oil. Since it is sold as a dispersion, the sodium hydride is able to retain its reactivity. Sodium hydride readily reacts with $MgBr_2$ in THF to yield MgH_2 (eq 6). If excess $MgBr_2$ is used, no sodium hydride is found in the solid product; however the MgH_2 product is mixed with 2 mol of the insoluble NaBr by-product. Nevertheless, for many purposes this will cause no difficulty.

$$2NaH + MgBr_2 \longrightarrow MgH_2 + 2NaBr \qquad (6)$$

Sodium hydride was found not to react with MgI_2 in THF. This is unfortunate since NaI is soluble in THF and thus pure MgH_2 could be easily isolated. The lack of reactivity is attributed to the insolubility of MgI_2 in THF (MgI_2 forms an insoluble hexatetrahydrofuran etherate). However, sodium hydride was found to react with MgI_2 in diethyl ether (eq 7). Ninety per

$$2NaH + MgI_2 \longrightarrow MgH_2 + 2NaI \qquad (7)$$

cent of the diethyl ether insoluble NaI was removed simply by stirring the physical mixture of MgH_2 and NaI in THF. One can effect complete removal of the NaI by high-speed stirring at room temperature. Potassium hydride was found to react with magnesium iodide in diethyl ether to yield magnesium hydride quantitatively (eq 8). The KI by-product was removed by extraction with diglyme.

$$2KH + MgI_2 \longrightarrow MgH_2 + 2KI \qquad (8)$$

In order to obtain some idea of the relative rates of the reactions between alkali metal hydrides and magnesium halides, a series of reactions was run for 5 hr in refluxing solvent. The yield of magnesium hydride was then determined. The results are summarized in Table II. As can be seen from the table, sodium hydride is more reactive than potassium hydride in THF. The position of lithium hydride in the reactivity scale is not clear since there are two sources of LiH. The relative rates of the halides are Br > Cl > I. The slower rate of the iodide can be understood as due to the insolubility of the $MgI_2 \cdot 6THF$.

In diethyl ether solvent, reaction between alkali metal hydrides and magnesium halides is slower than in THF. The reactivity of halogen is Br > I; however, the reactivity of the alkali metal hydride is reversed to K > Na. The reactivity of magnesium chloride with NaH and KH in diethyl ether was not determined since both magnesium chloride and the alkali metal chloride by-product are insoluble in diethyl ether, thus making the yield of MgH_2 difficult to determine. In addition, reaction of magnesium chloride with NaH in THF produced MgH_2 in only 11% yield after 4 days of reflux in THF, a solvent in which one of the reactants ($MgCl_2$) is soluble.

There are a number of factors affecting the relative reactivities of the alkali metal hydrides and the magnesium halides. One might expect a simple increase or decrease in reactivity as the alkali metal increases or decreases in electropositivity. However the solubilities and the degree of solvation of the magnesium halides and the alkali metal halides which fluctuate for various temperatures and from solvent to solvent will affect the order observed by changing the free energy of the reaction as well as affecting the kinetic path of the reaction. The source of the alkali metal hydride can also affect the relative reactivity as can be seen by the dramatic change between commercial LiH and that prepared from the high-pressure hydrogenation of *tert*-butyllithium.

In summary then, the reaction of alkali metal hydrides with magnesium halides in ether solvents provides an excellent method for the preparation of pure, active magnesium hydride in high yield. The reaction of commercial grade lithium hydride with magnesium halides to produce MgH_2 is very slow; however, the reaction using active lithium hydride prepared by hydrogenolysis of *tert*-butyllithium proceeds at a reasonable rate. Unfortunately generating active lithium hydride by this method is not very convenient. On the other hand, reaction of commercial grade sodium hydride with magnesium bromide in THF provides a rapid and economic method for preparing active magnesium hydride although by-product NaBr is present as well. If pure magnesium hydride is desired, this preparation can be accomplished by reaction of sodium hydride with magnesium iodide in diethyl ether followed by extraction of the by-product NaI with THF. Evidence for compounds of the type Li_nMgH_{2+n} suggested earlier by Wiberg to be formed in the reaction of lithium hydride with magnesium chloride was not found.

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