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

Concerning the Preparation of Magnesium Aluminum Hydride. A Study of the Reactions of Lithium and Sodium Aluminum Hydrides with Magnesium Halides in Ether Solvents

BY E. C. ASHBY,[1] R. D. SCHWARTZ, AND B. D. JAMES

Received September 4, 1969

The reactions of alkali metal aluminum hydrides with magnesium halides in ether solvents were investigated as possible routes to magnesium aluminum hydride [$Mg(AlH_4)_2$]. The ability of these reactions to produce $Mg(AlH_4)_2$ depended on the nature of the alkali metal, the halide, the solvent, and the solubility of the alkali metal halide by-product. Contrary to previous reports $Mg(AlH_4)_2$ could not be prepared by the reaction of $LiAlH_4$ and magnesium bromide in diethyl ether. This reaction regardless of the nature of the halogen or solvent was found to produce an equilibrium mixture ($LiAlH_4 + MgBr_2 \rightleftarrows LiBr + BrMgAlH_4$) which varied in its composition depending on the amount of $LiAlH_4$ used but which did not contain any detectable amount of $Mg(AlH_4)_2$. Magnesium aluminum hydride was prepared in a pure form as the ether solvate by the reactions of $NaAlH_4$ and $MgCl_2$ in tetrahydrofuran and $NaAlH_4$ and $MgBr_2$ in diethyl ether. Magnesium aluminum hydride is insoluble in both diethyl ether and tetrahydrofuran; thus it was separated from the NaCl and NaBr by-products by Soxhlet extraction. Because of the solubility of NaI in tetrahydrofuran, $Mg(AlH_4)_2$ as the tetrakis(tetrahydrofuran) solvate was prepared halogen free by the reaction of sodium aluminum hydride and magnesium iodide. Halogenomagnesium aluminum hydrides ($XMgAlH_4$, where X = Cl and Br) were prepared in tetrahydrofuran by the reaction of sodium aluminum hydride and the magnesium halide in 1:1 stoichiometry. Infrared spectra and powder diffraction data are presented for all of the compounds prepared.

Introduction

The preparation of magnesium aluminum hydride ($Mg(AlH_4)_2$) was first reported in 1950 by Wiberg and Bauer.[2-4] The preparation of this new hydride was reported by three different synthetic routes represented by eq 1–3. Magnesium hydride (MgH_2) was reported

$$4MgH_2 + 2AlCl_3 \longrightarrow Mg(AlH_4)_2 + 3MgCl_2 \quad (1)$$

$$MgH_2 + 2AlH_3 \longrightarrow Mg(AlH_4)_2 \quad (2)$$

$$2LiAlH_4 + MgBr_2 \longrightarrow Mg(AlH_4)_2 + 2LiBr \quad (3)$$

to react with both aluminum hydride (AlH_3) and aluminum chloride ($AlCl_3$)[2-4] in diethyl ether to produce $Mg(AlH_4)_2$ whereas the third method involved the reaction of $LiAlH_4$ with $MgBr_2$ in diethyl ether.[2,3] The $Mg(AlH_4)_2$ produced was reported to be soluble in diethyl ether and to decompose at 140°; however few experimental details concerning the preparations were given.

Hertwig[5] reported the preparation of $Mg(AlH_4)_2$ by hydrogenolysis of a Grignard reagent in diethyl ether followed by the addition of aluminum chloride to the reaction product. Reactions 4–6 were suggested to describe the course of the reaction. However again few

$$4RMgX + AlX_3 + 4H_2 \longrightarrow XMgAlH_4 + 3MgX_2 + 4RH \quad (4)$$

$$3RMgX + AlX_3 + 3H_2 \longrightarrow AlH_3 + 3MgX_2 + 3RH \quad (5)$$

$$2XMgAlH_4 \longrightarrow Mg(AlH_4)_2 + MgX_2 \quad (6)$$

experimental details were given. Hertwig's[5] report seemed reasonable since earlier we had shown[6] that hydrogenolysis of Grignard reagents produces a mixture of MgH_2 and magnesium halide. Therefore, the MgH_2 produced by hydrogenolysis of the Grignard compound in the reaction reported by Hertwig could have reacted with $AlCl_3$ to form $Mg(AlH_4)_2$ in a similar way to that previously reported by Wiberg. The suggested $XMgAlH_4$ could then have arisen from the redistribution of $Mg(AlH_4)_2$ and $MgCl_2$.

Some time ago we had the occasion to prepare $Mg(AlH_4)_2$ by the reaction of $NaAlH_4$ and $MgCl_2$ in dimethyl ether[7] and noticed that the physical properties of this compound were different from the properties reported by Wiberg for $Mg(AlH_4)_2$. The $Mg(AlH_4)_2$ prepared by us was insoluble in diethyl ether and decomposed at 180°.

In 1966 Czech workers[8] verified the preparation of $Mg(AlH_4)_2$ by the reaction of $NaAlH_4$ and $MgCl_2$. Although elemental analysis data were presented, no infrared or X-ray powder diffraction data were given.

It would appear that there is some confusion in the literature concerning the preparation and properties of $Mg(AlH_4)_2$. Since the reaction of a complex metal hydride with MgX_2 in ether solvent to produce $Mg(AlH_4)_2$ is such a fundamental reaction, we decided to study this reaction in detail.

Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and water[9] 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 spectrophotom-

(1) To whom all inquiries should be sent at the Department of Chemistry, Georgia Institute of Technology, Atlanta, Ga. 30332.
(2) E. Wiberg and R. Bauer, *Z. Naturforsch.*, **5b**, 397 (1950).
(3) E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).
(4) E. Wiberg and R. Bauer, *Z. Naturforsch.*, **7b**, 131 (1952).
(5) A. Hertwig, German Patent 921,986 (1955).
(6) W. E. Becker and E. C. Ashby, *J. Org. Chem.*, **29**, 954 (1964).
(7) Ethyl Corp., British Patent 905,985 (1962).
(8) J. Plesek and S. Hermanek, *Collection Czech. Chem. Commun.*, **31**, 3060 (1966).
(9) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

Table I

X-Ray Powder Patterns (Main Lines)

Compd	d, Å	I/I_0	Compd	d, Å	I/I_0
$Mg(AlH_4)_2 \cdot 4THF$	8.76	ms	$IMgAlH_4 \cdot (C_2H_5)_2O$	11.6	s
	7.22	vs		4.58	s
	5.84	m		3.24	ms
	5.50	m		2.83	ms
	4.13	vs			
	3.82	m	$BrMgAlH_4 \cdot (C_2H_5)_2O$	11.6	s
	3.22	m		10.4	m
				8.9	m
$BrMgAlH_4 \cdot 4THF$	11.7	s		4.6	m
	9.71	m			
	8.04	s	$Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$	10.5	s
	7.11	s		7.9	m
	6.19	m		5.9	s
	4.385	vs		5.6	w
	3.86	m		5.1	w
				4.03	w
$ClMgAlH_4 \cdot 4THF$	11.5	m		3.85	w
	9.4	m		3.65	w, b
	8.0	m		3.50	m
	7.0	m		3.25	w
	6.15	m		2.96	w
	5.69	m		2.90	vw
	5.24	m		2.80	vw
	4.75	m		2.75	w
	4.1	s		2.40	w
				2.18	w

eter. Sodium chloride cells were used. Spectra of solids were obtained in Nujol which had been dried over sodium wire and stored in a drybox. No change was observed in the spectra of either solutions or mulls after standing in the cell for some time. It is therefore concluded that no interaction of the products studied with the cell windows takes place.

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 benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately before use. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use.

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

Lithium and sodium aluminum hydrides were obtained from Ventron Metal Hydrides Division. Diethyl ether and tetrahydrofuran solutions of these complex metal hydrides were prepared by adding dry, freshly distilled solvent to an appropriate amount of the solid complex metal hydride. The resulting solution was then filtered through a coarse glass fritted filter funnel to which had been added dried Celite filter aid. The resulting clear solutions were standardized by EDTA titration of aluminum.

Preparation of Magnesium Halides in Diethyl Ether and Tetrahydrofuran.[10,11]—In a typical preparation of magnesium halides in ether solvents, 2 g of magnesium was added to 20 g of the appropriate mercuric halide in a 500-ml round-bottom flask with a magnetic stirring bar. Two hundred and fifty milliliters of diethyl ether was then distilled into the flask containing the mixture. The solution was stirred overnight and filtered. The solutions were then standardized by magnesium analysis (EDTA) and halogen analysis (Volhard method). The magnesium to halogen ratio was 1.0:2.00 $\pm$ 0.05 in all cases. A qualitative test for residual mercury in the solutions was negative using ferrocyanide and 2,2′-dipyridyl. The solutions were also tested for solvent impurities by hydrolyzing a sample of the solution with distilled water in benzene. The organic matter was then salted out of the water layer into the benzene. The benzene layer was then subjected to analysis by glpc. Only diethyl ether was found to be present in the original solution of MgX_2.

A different method for the preparation of magnesium chloride in diethyl ether had to be used. This was necessary since $MgCl_2$ is insoluble in diethyl ether and it would have been difficult to separate the $MgCl_2$ from the Hg by-product in the previous method. Anhydrous hydrogen chloride in diethyl ether was added to a diethyl ether solution of ethylmagnesium chloride at room temperature in 1:1 molar ratio. The precipitate which was formed was washed with diethyl ether and dried under vacuum. *Anal.* Calcd for $MgCl_2 \cdot (C_2H_5)_2O$: Mg, 14.36; Cl, 41.89. Found: Mg, 14.30; Cl, 41.29.

Analytical Procedures.—Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis was carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanolamine. Lithium analysis was carried out by flame photometry. Hydridic hydrogen analysis was carried out by hydrolyzing a weighed sample of the compound and measuring the volume of gas evolved after passing it through a Dry Ice–acetone trap to remove ether. The amount of ether solvated to a compound was assumed by difference.

General Procedures for Infrared Studies.—A measured amount of magnesium halide in solution was added to a three-neck, 500-ml, round-bottom flask equipped with a three-way stopcock, an addition funnel, and a Dry Ice condenser. The solution of alkali metal aluminum hydride was added in a stepwise fashion in order to establish $MAlH_4$:MgX_2 mole ratios of 0.5:1.0, 1.0:1.0, 1.5:1.0, 2.0:1.0, and 3.0:1.0. After each addition the solution was stirred for 15 min and any precipitate formed was allowed to settle. A sample of the supernatant liquid was taken with a syringe through the three-way stopcock (under strong nitrogen flush) and the infrared cell filled in the drybox. All

(10) B. K. Lewis, *Dissertation Abstr.*, **20**, 2544 (1960).

(11) E. C. Ashby and R. C. Arnott, *J. Organometal. Chem.* (Amsterdam), **14**, 1 (1968).

TABLE II

INFRARED DATA (SOLUTION SPECTRA, cm^{-1})

$Mg(AlH_4)_2 \cdot 4THF$	$BrMgAlH_4 \cdot 4THF$	$LiAlH_4 \cdot (C_2H_5)_2O$
1730 m	1725 s	1740 s
800 w	795 m	755 m
750 m	760 m	
$ClMgAlH_4 \cdot 4THF$	$BrMgAlH_4 \cdot (C_2H_5)_2O$	$LiAlH_4 \cdot THF$
1715 s	1780 s	1691 s
795 m	760 m	760 m
760 m		
		$NaAlH_4 \cdot THF$
		1680 s
		772 m

reactions were carried out such that the resulting concentration of the reaction mixture was between 0.1 and 0.2 *M*.

General Procedure for the Isolation of Intermediates.—The alkali metal aluminum hydride was added to the magnesium halide in a ratio of 1.0:1.0. Any solid formed at this ratio was filtered and analyzed, and its infrared spectrum and X-ray powder pattern were obtained. The resulting solutions were then fractionally crystallized, the separate fractions were analyzed, and their infrared spectra and X-ray powder patterns were obtained.

A. Reactions of $NaAlH_4$ and MgX_2 in Tetrahydrofuran. (1) **Reaction of Sodium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran.**—When $NaAlH_4$ was added to $MgCl_2$ in THF in a mole ratio of 0.5:1.0, a precipitate was formed. The infrared spectrum of the solution at this point showed bands at 1715, 795, and 760 cm^{-1}. At a $NaAlH_4$:$MgCl_2$ ratio of 1.0:1.0 the bands at 1715 and 795 cm^{-1} increased in intensity and more precipitate was formed. Elemental analysis and an X-ray powder pattern of this solid showed it to be NaCl. At a $NaAlH_4$:$MgCl_2$ ratio of 1.5:1.0 the intensity of the infrared bands noted above decreased and more precipitate was formed. At a 2.0:1.0 ratio, no infrared bands appeared in the Al–H stretching and deformation regions and more precipitate was formed. At a 3.0:1.0 ratio bands appeared at 1680 and 772 cm^{-1} characteristic of $NaAlH_4$ in tetrahydrofuran. No more precipitate was formed. The solid was filtered and gave an X-ray powder pattern consisting of lines for NaCl and some other substance. This solid was then subjected to Soxhlet extraction with tetrahydrofuran. A white solid was obtained from this extraction which gave lines in the powder pattern which were the same as the lines in the previous pattern with the NaCl lines subtracted (see Table I). The infrared spectrum of this solid showed absorption bands at 1725, 1025, 920, 875, 785, and 740 cm^{-1}. A 77% yield of $Mg(AlH_4)_2 \cdot 4THF$ was obtained. *Anal.* Calcd for $Mg(AlH_4)_2 \cdot 4THF$: Mg, 6.49; Al, 14.41; H, 2.13. Found: Mg, 7.06; Al, 14.90; H, 2.24.

In a separate experiment, $NaAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in a mole ratio of 1.0:1.0. A precipitate formed which was filtered. The resulting filtrate was then subjected to crystallization by solvent removal. The infrared spectrum of this solid in Nujol gave bands at 1730, 1070, 1030, 920, 880, and 745 cm^{-1}. For the major lines in the X-ray powder pattern see Table I. *Anal.* Calcd for $ClMgAlH_4 \cdot 4THF$: Cl, 9.36; Mg, 6.41; Al, 7.12; H, 1.05. Found: Cl, 9.58; Mg, 6.77; Al, 7.22; H, 1.13.

(2) **Sodium Aluminum Hydride and Magnesium Bromide in Tetrahydrofuran.**—The course of the reaction of $NaAlH_4$ and $MgBr_2$ in tetrahydrofuran was followed by infrared analysis. The results were similar to those reported for the previous system.

In a separate experiment, the solution containing the reaction product of $NaAlH_4$ and $MgBr_2$ in a mole ratio of 1.0:1.0 was treated in the same way as the $ClMgAlH_4$ solution. The infrared spectrum of the solid in Nujol gave absorption bands at 1715, 1070, 1030, 915, 875, 795, and 745 cm^{-1}. The X-ray powder pattern is shown in Table I. *Anal.* Calcd for $BrMgAlH_4 \cdot 4THF$: Br, 18.88; Mg, 5.74; Al, 6.37; H, 0.94. Found: Br, 19.49; Mg, 6.40; Al, 6.91; H, 0.96.

TABLE III

INFRARED DATA (MULL SPECTRA, cm^{-1})

$Mg(AlH_4)_2 \cdot 4THF$	$Mg(AlH_4)_2 \cdot 2THF$	$Mg(AlH_4)_2$
1725 s	1785 s	1855 s
1025 s	1730 s	1830 s
920 w		
875 m		
785 s		
740 s		
$Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$	$ClMgAlH_4 \cdot 4THF$	$ClMgAlH_4 \cdot 2THF$
1800 s	1730 s	1775 s
1285 w	1070 w	1030 m
1190 w	1030 m	880 m
1150 m	920 w	810 m
1090 m	880 m	745 m
1045 s	745 s	$ClMgAlH_4$
995 w		1850 s
895 w		1830 s
740 s		
$BrMgAlH_4 \cdot 4THF$	$BrMgAlH_4 \cdot (C_2H_5)_2O$	$IMgAlH_4 \cdot (C_2H_5)_2O$
1715 s	1830 s	1800 s
1070 w	1290 w	1285 w
1030 m	1260 w	1190 w
915 w	1190 w	1150 w
875 m	1150 w	1090 m
795 s	1090 m	1050 m
745 s	1040 m	900 m
	1000 w	890 w
	900 w	810 s
	750 s	
	720 s	

(3) **Sodium Aluminum Hydride and Magnesium Iodide in Tetrahydrofuran.**—At 0.5:1.0 addition of a solution of $NaAlH_4$ in tetrahydrofuran to solid MgI_2 in tetrahydrofuran, the infrared analysis of the filtrate showed an absorption band at 1730 cm^{-1}. At a 1.0:1.0 ratio, a shoulder appeared on the low-frequency side of the absorption band noted above. The intensity of the band at 1730 cm^{-1} was not increased. The X-ray powder pattern of the solid after the 1:1 addition showed it to be a mixture of $MgI_2 \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$. Further addition of $NaAlH_4$ increased the intensity of the shoulder until at a ratio of 10:1.0 the entire band centered at 1680 cm^{-1}. A yield of 58% for $Mg(AlH_4)_2 \cdot 4THF$ was obtained. The solid at 10:1.0 addition was analyzed. *Anal.* Calcd for $Mg(AlH_4)_2 \cdot 4THF$: Mg, 6.49; Al, 14.41; H, 2.13; I, 0.0. Found: Mg, 7.06; Al, 14.93; H, 2.24; I, 0.0. Infrared and X-ray powder pattern data are given in Tables I–III.

B. Reactions of $LiAlH_4$ and MgX_2 in Tetrahydrofuran. (1) **Lithium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran.**—At a 0.5:1.0 ratio of $LiAlH_4$ in tetrahydrofuran to $MgCl_2$ in tetrahydrofuran, infrared analysis of the clear filtrate showed absorption bands at 1715, 795, and 760 cm^{-1}. At a 1.0:1.0 ratio these bands increased in intensity and broadened somewhat. At 1.5:1.0 ratio the bands increased in intensity, and a shoulder appeared at the low-frequency side of the 1715-cm^{-1} band. At a 2.0:1.0 ratio these bands increased in intensity, and at a 3.0:1.0 ratio, what was the shoulder in the previous addition became the main band and was centered around 1691 cm^{-1}. The band at 760 cm^{-1} broadened and its intensity increased to a greater extent than the 795-cm^{-1} band. ($LiAlH_4$ in tetrahydrofuran has infrared absorption bands at 1691 and 763 cm^{-1}.) No precipitate was observed even at 3.0:1.0 addition.

In a separate experiment, $LiAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in 1:1 ratio. The solvent was then removed under vacuum and the infrared spectrum and X-ray powder pattern of the resulting solid were obtained. The solid was shown to be a mixture of LiCl and $ClMgAlH_4 \cdot 4THF$.

(2) **Lithium Aluminum Hydride and Magnesium Bromide in Tetrahydrofuran.**—Similar results were obtained as in the

previous system. No precipitate was observed even at $LiAlH_4$ to $MgBr_2$ ratios as high as 5.0:1.0.

(3) **Lithium Aluminum Hydride and Magnesium Iodide in Tetrahydrofuran.**—When $LiAlH_4$ in tetrahydrofuran was added to MgI_2 in tetrahydrofuran, no absorption bands appeared in the infrared spectrum of the solution which were different from those of pure solvent until a $LiAlH_4$:MgI_2 ratio of greater than 2.0:1.0 was attained. At this point absorption bands at 1691 and 760 cm^{-1} appeared indicative of $LiAlH_4$ in solution. The precipitation of solid material in this reaction was obscured by the fact that the MgI_2 reactant is insoluble in THF. The X-ray powder diffraction pattern of the solid product showed the compound to be $Mg(AlH_4)_2 \cdot 4THF$. A yield of 85% for $Mg(AlH_4)\cdot$ 4THF was obtained.

C. Reactions of $NaAlH_4$ and MgX_2 in Diethyl Ether. Sodium Aluminum Hydride and Magnesium Bromide in Diethyl Ether.—Magnesium bromide in diethyl ether was added to $NaAlH_4$ in diethyl ether in a ratio of 1.0:2.0. The solution was stirred for 4 days. At the end of this time no bands in the Al–H stretching and deformation regions were found in the infrared spectrum of the solution. An X-ray powder pattern of the solid showed lines due to NaBr and some other compound which was not $MgBr_2$ or $NaAlH_4$. The infrared spectrum of the solid had bands at 1800, 1285, 1190, 1150, 1090, 1045, 995, 895, and 740 cm^{-1}. The white solid was subjected to Soxhlet extraction. The infrared spectrum of the resulting solid in Nujol exhibited absorption bands at 1800, 1285, 1190, 1150, 1090, 1045, 995, 895, and 740 cm^{-1}. The X-ray powder diffraction pattern is given in Table I. The total yield of $Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$ was 80%. *Anal.* Calcd for $Mg(AlH_4)_2 \cdot 2C_2H_5O$: Mg, 10.37; Al, 23.03; H, 3.41. Found: Mg, 9.43; Al, 23.96; H, 3.50.

D. Reactions of $LiAlH_4$ and MgX_2 in Diethyl Ether. (1) **Lithium Aluminum Hydride and Magnesium Chloride in Diethyl Ether.**—Lithium aluminum hydride in diethyl ether was added to $MgCl_2$ in diethyl ether in a mole ratio of 2.0:1.0. The solution was stirred for 2 days. The solid obtained was analyzed. *Anal.* Found: Cl, 50.43; Mg, 2.96; Al, 7.27. The X-ray powder pattern showed only LiCl. The infrared spectrum of the solid gave no definite bands in the Al–H stretching region. After removing some of the solvent from the filtrate a solid was obtained and analyzed. *Anal.* Found: Cl, 16.17; Mg, 12.53; Al, 24.02; Li, 3.15. The X-ray powder pattern gave lines for LiCl and some other compounds. The infrared spectrum of the solid gave bands at 1845, 1780, 1190, 1150, 1090, 1040, 995, and 900 cm^{-1}.

When $LiAlH_4$ was added to $MgCl_2$ in diethyl ether in a mole ratio of 1.0:1.0, the precipitate obtained was analyzed. *Anal.* Found: Cl, 43.91; Mg, 7.25; Al, 11.66; Li, 6.17. The X-ray powder pattern showed lines for LiCl and another compound which did not correspond to the compound in the 2:1 case. The solid obtained by removing the solvent from the filtrate was analyzed. *Anal.* Found: Cl, 22.42; Mg, 12.99; Al, 10.84; Li, 1.27. The X-ray powder pattern gave lines for LiCl. In addition to the lines for LiCl, other lines were observed which corresponded to the second solid in the 2:1 case. The infrared spectrum of this solid gave bands at 1800, 1260, 1195, 1150, 1095, 1045, 1000, and 900 cm^{-1}. The solution spectra of the 2:1 and 1:1 case both gave absorption bands at 1780 cm^{-1} and shoulders on the low-frequency side.

(2) **Lithium Aluminum Hydride and Magnesium Bromide in Diethyl Ether.**—At a 0.5:1.0 ratio of $LiAlH_4$ to $MgBr_2$ in diethyl ether, absorption bands at 1780 and 760 cm^{-1} appeared in the infrared spectrum of the solution. At a 1.0:1.0 ratio a shoulder on the low-frequency side of the 1780-cm^{-1} band appeared. At a 1.5:1.0 ratio, the bands increased in intensity and the band at 760 cm^{-1} broadened. At a 2.0:1.0 ratio, the bands at 1780 and 1740 cm^{-1} were of equal intensity. At a 3.0:1.0 ratio the bands at 1740 cm^{-1} increased in intensity.

A precipitate was initially formed which gave an indefinite analysis. However, it contained only 2% of the total magnesium.

In a separate experiment, lithium aluminum hydride in diethyl ether was added to $MgBr_2$ in diethyl ether in a mole ratio of 1.0:1.0. The solvent was then removed and a solid was obtained. The X-ray powder pattern showed LiBr but not $LiAlH_4$ or $MgBr_2 \cdot (C_2H_5)_2O$. For the infrared spectrum of the solid in Nujol see Table III. *Anal.* Calcd for LiBr + $BrMgAlH_4 \cdot 2(C_2H_5)_2O$: Li, 1.89; Br, 43.65; Mg, 6.64; Al, 7.37. Found: Li, 1.87; Br, 40.74; Mg, 6.45; Al, 6.45.

(3) **Lithium Aluminum Hydride and Magnesium Iodide in Diethyl Ether.**—No infrared absorption bands other than diethyl ether appeared up to a $LiAlH_4$:MgI_2 ratio of 1.0:1.0. A white solid was obtained up to this ratio and analyzed. *Anal.* Calcd for $IMgAlH_4 \cdot (C_2H_5)_2O$: I, 49.53; Mg, 9.49; Al, 10.53. Found: I, 49.23; Mg, 9.52; Al, 10.67. Addition of more $LiAlH_4$ gave infrared bands corresponding to $LiAlH_4$. A yield of product was 72%. For the X-ray powder diffraction pattern and infrared spectrum of the solid see Tables I and III.

Reaction of Magnesium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran.—When equimolar amounts of $Mg(AlH_4)_2$ and $MgCl_2$ in THF were mixed, the resulting solution gave an infrared spectrum corresponding to that of $ClMgAlH_4$. The removal of the solvent gave a solid whose infrared spectrum and X-ray powder pattern were identical with those of $ClMgAlH_4 \cdot 4THF$.

Reaction of Lithium Bromide and Magnesium Aluminum Hydride in Diethyl Ether.—When equimolar amounts of LiBr and $Mg(AlH_4)_2$ were mixed in diethyl ether, the resulting solution exhibited infrared absorption bands at 1780, 1740 (both of equal intensity), 793, and 762 cm^{-1}. See Figure 2.

Results and Discussion

In the present study $LiAlH_4$ and $NaAlH_4$ were allowed to react with $MgCl_2$, $MgBr_2$, and MgI_2 in diethyl ether and tetrahydrofuran. It is important that this reaction was studied in such detail since the course of the reaction is dependent on the nature of the alkali metal, the halide, the solvent, and the solubility of the alkaki metal halide by-product. The discussion will be divided roughly into two parts (eq 7), namely, those combinations of reactants that produce $Mg(AlH_4)_2$ as the reaction product and those combinations of reactants that either stop at the $XMgAlH_4$ stage or produce an equilibrium mixture of products.

$$MAlH_4 + MgX_2 \longrightarrow MX + XMgAlH_4 \xrightarrow{MAlH_4} MX + Mg(AlH_4)_2 \quad (7)$$

When $NaAlH_4$ was allowed to react with $MgCl_2$ in tetrahydrofuran in a mole ratio of 1.0:1.0, a white precipitate appeared which was shown by elemental and X-ray powder pattern analyses to be NaCl. The infrared spectrum of the reaction solution showed bands at 1715, 795, and 760 cm^{-1}. None of these bands corresponds to $NaAlH_4$ but they are characteristic of the Al–H stretching and deformation regions. When this solution was subjected to fractional crystallization, successive fractions gave elemental analyses corresponding to the empirical formula $ClMgAlH_4 \cdot 4THF$. The X-ray powder pattern of this solid shows no lines due to $MgCl_2 \cdot 2THF$, $Mg(AlH_4)_2 \cdot 4THF$, $NaAlH_4$, or NaCl. Furthermore, the infrared spectrum of this solid shows bands at 1730, 1070, 1030, 920, 880, and 745 cm^{-1} which are not characteristic of either $MgCl_2$ or $Mg(AlH_4)_2 \cdot 4THF$. Also no bands characteristic of Mg–H were observed. It would appear then that the product produced in this reaction is $ClMgAlH_4 \cdot 4THF$ and not a physical mixture of $MgCl_2$ and $Mg(AlH_4)_2$ or $MgCl_2$, MgH_2, and AlH_3.

As one adds more $NaAlH_4$ to the $MgCl_2$ in tetrahydrofuran until the mole ratio is 2.0:1.0, more precipitate is formed and the infrared spectrum of the solution shows no bands in the Al–H or Mg–H stretching and deformation regions. The infrared spectrum of this solid in Nujol shows bands at 1725, 1025, 920, 875, 785, and 740 cm^{-1}. The X-ray powder pattern of the solid showed NaCl in admixture with some other compound. The elemental analysis of the solid was consistent with a mixture of NaCl and $Mg(AlH_4)_2 \cdot 4THF$. Soxhlet extraction of this solid with tetrahydrofuran yielded crystals which produced an analysis consistent with $Mg(AlH_4)_2 \cdot 4THF$. The infrared spectrum of the solid-extracted product was the same as the original product mixture and the X-ray powder pattern showed all the lines of the mixture after subtracting out the lines due to NaCl. The infrared and powder pattern data of the extracted solid were not consistent with the description of the product as a physical mixture of MgH_2 and AlH_3. Thus it appears clear that the reaction of $NaAlH_4$ and $MgCl_2$ in tetrahydrofuran proceeds stepwise to produce first the soluble $ClMgAlH_4$ and then the insoluble $Mg(AlH_4)_2$

$$NaAlH_4 + MgCl_2 \xrightarrow{THF} ClMgAlH_4 + NaCl \qquad (8)$$

$$ClMgAlH_4 + NaAlH_4 \xrightarrow{THF} Mg(AlH_4)_2 + NaCl \qquad (9)$$

When $MgCl_2$ in tetrahydrofuran was added to $Mg(AlH_4)_2 \cdot 4THF$, the insoluble $Mg(AlH_4)_2$ dissolved. The resultant solution produced an infrared spectrum identical with that exhibited by $ClMgAlH_4$. Fractional crystallization of the solution yielded solid fractions whose X-ray powder patterns and infrared analyses were consistent with those of $ClMgAlH_4 \cdot 4THF$ prepared from $NaAlH_4$ and $MgCl_2$ in 1:1 stoichiometry

$$MgCl_2 + Mg(AlH_4)_2 \xrightarrow{THF} 2ClMgAlH_4 \qquad (10)$$

Since the reaction of $NaAlH_4$ with $MgCl_2$ in tetrahydrofuran is a stepwise reaction to produce $ClMgAlH_4$ and then $Mg(AlH_4)_2$, any $Mg(AlH_4)_2$ formed in the initial stages of the reaction would rapidly redistribute with $MgCl_2$ to form $ClMgAlH_4$. The $Mg(AlH_4)_2$ formed in these reactions was insoluble in tetrahydrofuran, diethyl ether, and the common nonprotic organic solvents contrary to the earlier reports by Wiberg.[2-4]

When $NaAlH_4$ was allowed to react with $MgBr_2$ in THF, results similar to the reactions with $MgCl_2$ were observed; *i.e.*, at a 1:1 ratio $BrMgAlH_4$ was formed and at a 2:1 ratio $Mg(AlH_4)_2$ was formed. Since sodium bromide is also insoluble in tetrahydrofuran, $Mg(AlH_4)_2$ produced in this reaction contains 2 molar equiv of NaBr.

Magnesium aluminum hydride could be prepared essentially halogen free by allowing $NaAlH_4$ and MgI_2 to react in tetrahydrofuran at a mole ratio of 10:1.0. Since the NaI by-product is soluble in THF, $Mg(AlH_4)_2$ precipitates from solution halogen free. Attempts to prepare $IMgAlH_4$ in THF were unsuccessful owing to the disproportionation of this compound to MgI_2 and $Mg(AlH_4)_2$ in tetrahydrofuran. Since both MgI_2 and $Mg(AlH_4)_2$ are insoluble in THF, elemental analysis indicates an empirical formula $IMgAlH_4$. However infrared and powder diffraction analyses show that this solid is a physical mixture of MgI_2 and $Mg(AlH_4)_2$ (eq 11). This disproportionation was demonstrated

$$NaAlH_4 + MgI_2 \xrightarrow{THF} NaI + [IMgAlH_4] \longrightarrow 0.5MgI_2\downarrow + 0.5Mg(AlH_4)_2\downarrow \qquad (11)$$

further by adding $IMgAlH_4 \cdot (C_2H_5)_2O$ to tetrahydrofuran (eq 12). The reaction was very exothermic and

$$2IMgAlH_4 + (C_2H_5)_2O \xrightarrow{THF} MgI_2 \cdot 6THF\downarrow + Mg(AlH_4)_2 \cdot 4THF\downarrow + (C_2H_5)_2O \qquad (12)$$

the resultant solid produced an infrared spectrum and X-ray powder pattern consistent with those of a mixture of $MgI \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$.

A second reaction which produces $Mg(AlH_4)_2$ essentially halogen free is that between $LiAlH_4$ and MgI_2 in tetrahydrofuran at a mole ratio of 3:1 or 4:1. Here again the disproportionation of $IMgAlH_4$ to MgI_2 and $Mg(AlH_4)_2$ prevents the isolation of $IMgAlH_4$ in THF. The solubility of the LiI by-product enables the $Mg(AlH_4)_2$ to be obtained halogen free

$$2LiAlH_4 + MgI_2 \xrightarrow{THF} Mg(AlH_4)_2 + 2LiI \qquad (13)$$

When $NaAlH_4$ was allowed to react with $MgBr_2$ in diethyl ether at a mole ratio of 2.0:1.0, a white precipitate formed. This solid was shown by X-ray powder diffraction and infrared data to be a mixture of NaBr and $Mg(AlH_4)_2$ (eq 14). Thus it is possible to prepare

$$2NaAlH_4 + MgBr_2 \xrightarrow{(C_2H_5)_2O} Mg(AlH_4)_2 + 2NaBr \qquad (14)$$

$Mg(AlH_4)_2$ in both tetrahydrofuran and diethyl ether using the specific combination of reagents described.

The reactions described until now have been reasonably straightforward. When the alkali metal aluminum hydrides were added to the MgX_2 in 1:1 stoichiometry, $XMgAlH_4$ was formed. Upon addition of more $MAlH_4$, the $XMgAlH_4$ reacted further to form $Mg(AlH_4)_2$. In most of these cases the insolubility of the alkali metal halide by-product or of the MgI_2 seems to play an important role. If now we concentrate on the reactions where the alkali metal halide by-product is soluble, we see that the reaction proceeds in a somewhat different fashion.

When $LiAlH_4$ was allowed to react with $MgCl_2$ in tetrahydrofuran in a 1.0:1.0 ratio, the reaction filtrate exhibited infrared absorption bands corresponding to $ClMgAlH_4$ as was observed in the reaction of $MgCl_2$ with $NaAlH_4$ in tetrahydrofuran. No precipitate formed in the reaction since LiCl is soluble in tetrahydrofuran. When the 1.0:1.0 ratio of reactants was exceeded, the bands due to $ClMgAlH_4$ did not decrease in intensity as in the previous cases. Instead as more $LiAlH_4$ was added, bands due to the $LiAlH_4$ increased in intensity. Thus, instead of $Mg(AlH_4)_2$ being produced, an equilibrium resulted as shown in eq 15.

$$LiAlH_4 + MgCl_2 \overset{THF}{\rightleftharpoons} ClMgAlH_4 + LiCl \qquad (15)$$

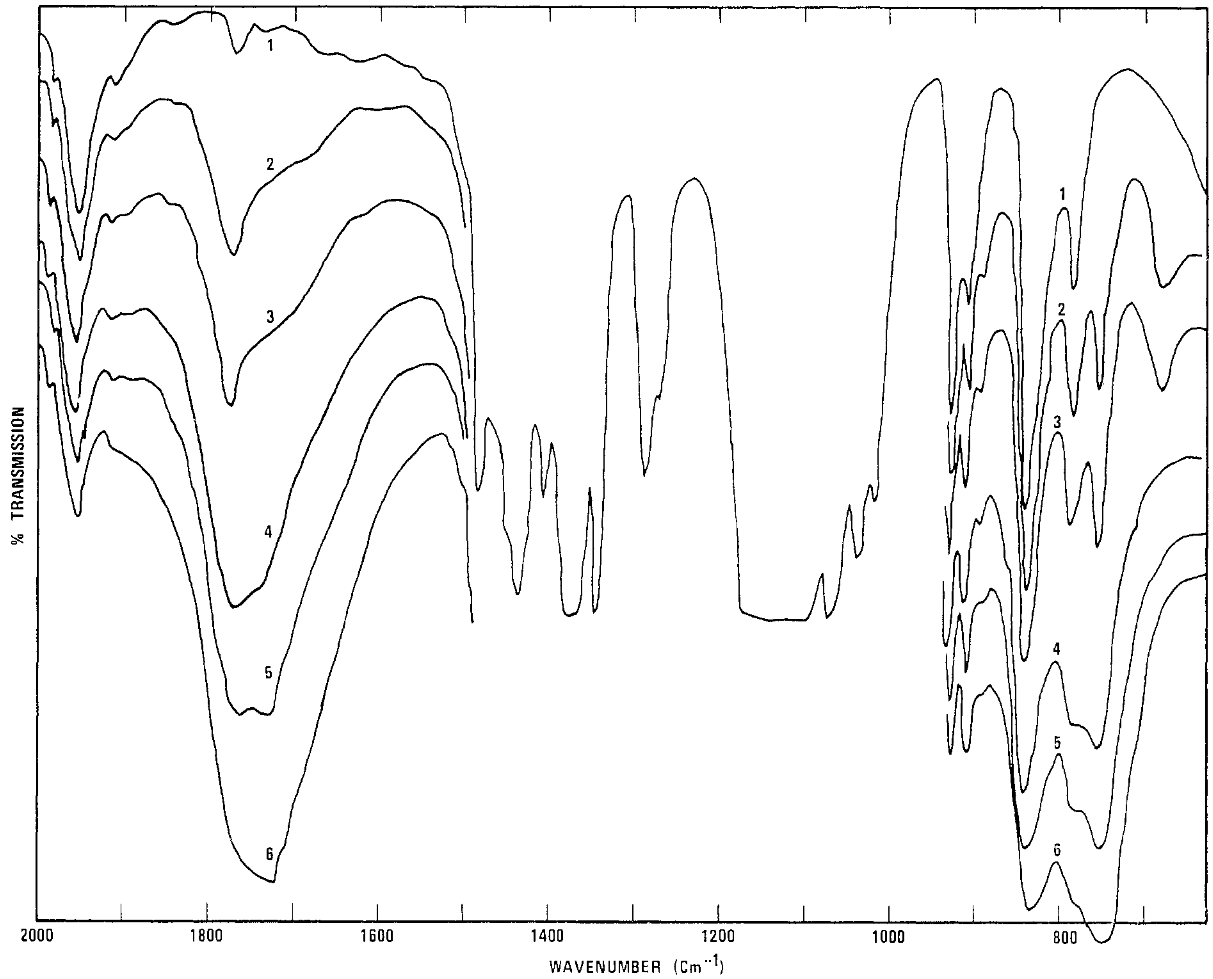

Figure 1.—Reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether. Ratio of $LiAlH_4$:$MgBr_2$: (1) $(C_2H_5)_2O$, (2) 0.5:1.0, (3) 1.0:1.0, (4) 1.5:1.0, (5) 2.0:1.0, (6) 3.0:1.0.

In order to determine if $ClMgAlH_4$ was the actual intermediate being formed, $LiAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in a 1:1 ratio. The solution was then fractionally crystallized and the resulting solids were subjected to X-ray, infrared, and elemental analyses. All of the analyses showed that $ClMgAlH_4 \cdot 4THF$ and LiCl were the major products present.

Similar results were obtained when $LiAlH_4$ and $MgBr_2$ were allowed to react in tetrahydrofuran (eq 16). The products of this reaction are $BrMgAlH_4 \cdot 4THF$ and LiBr. Here no solid was formed in the reaction even when the $LiAlH_4$:$MgBr_2$ ratio was 5.0:1.0, once again indicating the lack of formation of $Mg(AlH_4)_2$ (insoluble in tetrahydrofuran). Lithium bromide is soluble in tetrahydrofuran.

$$LiAlH_4 + MgBr_2 \underset{}{\overset{THF}{\rightleftharpoons}} BrMgAlH_4 + LiBr \quad (16)$$

The reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether, previously reported by Wiberg to form $Mg(AlH_4)_2$, also showed this equilibrium behavior. The equilibrium in diethyl ether may not lie as far to the right as in tetrahydrofuran (eq 16) since the $LiAlH_4$ appears in the solution spectrum sooner than in tetrahydrofuran. A small amount of initial precipitate was formed; however it was found to contain less than 2% of the total magnesium in the reaction. No additional precipitate was formed even at an $LiAlH_4$:$MgBr_2$ ratio of 3:1. The equilibrium nature of the reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether was verified by the infrared examination of the reaction solution as the $LiAlH_4$ was added to the $MgBr_2$. Figure 1 shows that even at an $LiAlH_4$:$MgBr_2$ ratio of 0.5:1.0, unreacted $LiAlH_4$ is present in the reaction mixture. The Al–H stretching band (1740 cm^{-1}) and the Al–H deformation band (755 cm^{-1}) characteristic of $LiAlH_4$ in diethyl ether increases as the $LiAlH_4$:$MgBr_2$ ratio increases. At the $LiAlH_4$:$MgBr_2$ ratio of 2:1 it is clear that the spectrum represents a mixture of $BrMgAlH_4$ and $LiAlH_4$ in approximately equimolar quantities rather than $Mg(AlH_4)_2$ reported by Wiberg (compare the spectrum for $Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$ in Figure 2).

In order to test the equilibrium hypothesis an ether solution of LiBr was added to $Mg(AlH_4)_2$ obtained by the reaction of $NaAlH_4$ and $MgBr_2$ in diethyl ether. The resulting solution (eq 17) produced absorption

$$LiBr + Mg(AlH_4)_2 \xrightarrow{(C_2H_5)_2O} BrMgAlH_4 + LiAlH_4 \quad (17)$$

bands of equal intensity at 1780 and 1740 cm^{-1}. ($LiAlH_4$ in diethyl ether has an absorption band at 1740 cm^{-1} and $BrMgAlH_4$ has an absorption band at 1780

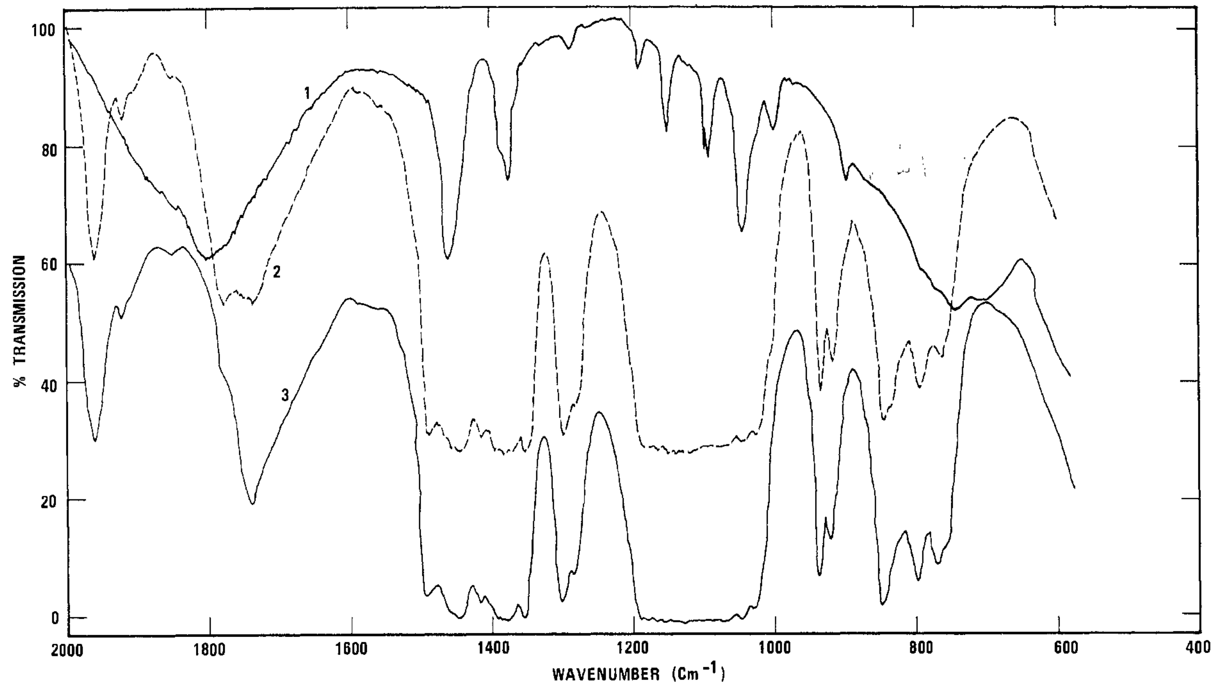

Figure 2.— $Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$ in Nujol; (2) $Mg(AlH_4)_2 + LiBr \xrightarrow{(C_2H_5)_2O} LiAlH_4 + BrMgAlH_4$; (3) $LiAlH_4$ in $(C_2H_5)_2O$.

cm^{-1} in diethyl ether.) The infrared spectrum (Figure 2) was consistent with that expected for a mixture of $LiAlH_4$ and $BrMgAlH_4$. The spectrum was also identical with the solution spectrum of the 2.0:1.0 addition product of $LiAlH_4$ to $MgBr_2$ (eq 18).

$$2LiAlH_4 + MgBr_2 \xrightleftharpoons{(C_2H_5)_2O} BrMgAlH_4 + LiBr + LiAlH_4 \quad (18)$$

In diethyl ether the reaction of $LiAlH_4$ with MgI_2 (eq 19) was found to proceed in a similar fashion to the reaction of $LiAlH_4$ and $MgBr_2$. At a stoichiometry of 1:1, a white solid was obtained which was shown by infrared, X-ray powder diffraction, and elemental analyses to be $IMgAlH_4 \cdot (C_2H_5)_2O$. Further addition of $LiAlH_4$ did not produce $Mg(AlH_4)_2$.

$$LiAlH_4 + MgI_2 \xrightarrow{(C_2H_5)_2O} IMgAlH_4 + LiI \quad (19)$$

The results of the reaction of $LiAlH_4$ and $MgCl_2$ in diethyl ether are somewhat confusing. There is evidence that both $ClMgAlH_4$ and $Mg(AlH_4)_2$ are formed. Both the 1:1 and 2:1 reaction mixtures appear to contain $ClMgAlH_4$. In the 2:1 case there is evidence also that some $Mg(AlH_4)_2$ is formed.

Infrared studies in the solid state of the compounds prepared indicate that the degree of covalent bonding between the magnesium and the tetrahydridoaluminate group is dependent upon the degree of solvation. This is especially true in the case of the tetrahydrofuran solvates. Both $Mg(AlH_4)_2$ and $ClMgAlH_4$ are obtained from tetrahydrofuran solution as the tetrakis(tetrahydrofuranates). The four tetrahydrofuran solvate molecules probably exist in a tetrahedral arrangement about the magnesium atom. This would increase the size of the cation thereby stabilizing the molecule. The solid-state infrared spectra of $Mg(AlH_4)_2 \cdot THF$ and $ClMgAlH_4 \cdot THF$ both exhibit single sharp bands (25–50 cm^{-1} half-width) at 1725 and 1730 cm^{-1}, respectively. Since the bands are not split, the four hydrogens on the AlH_4 group must be equivalent with no bridging. This would be consistent with an ionic model.

On the other hand, when two of the tetrahydrofuran solvate molecules are removed from the tetrakis solvate, the infrared spectrum of the resulting solid shows that the Al–H stretching band has moved to a higher frequency and split into two bands at 1785 and 1730 cm^{-1}. This indicates that the compound has become more covalent and that there are probably bridging hydrogens as indicated by the two bands. If $Mg(AlH_4)_2$ is completely desolvated, the Al–H stretching frequency shifts to an even higher frequency and remains split with bands at 1855 and 1830 cm^{-1}.

When $ClMgAl_4 \cdot 4THF$ is dissolved in benzene and recrystallized, the solid obtained contains only two THF solvate molecules. The infrared spectrum of this solid shows that the Al–H stretching band has shifted to a higher frequency. However, the band is not split, although it is somewhat broad and is centered at 1775 cm^{-1}. Upon complete desolvation the Al–H stretching band again shifts to a higher frequency and this time splits into two bands: 1850 and 1830 cm^{-1}.

These data indicate that upon desolvation $Mg(AlH_4)_2$ and $ClMgAlH_4$ exhibited more covalent character through bridging hydrogens. Lithium aluminum hydride in the solid state, which is considered to be covalent, has two bands in the solid-state infrared spectrum at 1770 and 1625 cm^{-1}.

Summary

In summary, the reactions of complex metal hydrides with magnesium halides in ether solvents can be divided into two classes. The first class includes those reactions which produce an insoluble alkali metal halide by-product. These reactions produce at a 1:1 $MAlH_4 + MgX_2$ stoichiometry an isolatable $XMgAlH_4$ compound and upon addition of more $MAlH_4$ produce $Mg(AlH_4)_2$ in good yield. An exception to this is the MgI_2 case in THF. Here the "$IMgAlH_4$" disproportionates to MgI_2 and $Mg(AlH_4)_2$ immediately so that "$IMgAlH_4$" cannot be isolated from tetrahydrofuran solution. The second class includes those reactions where the alkali metal by-product is soluble. Here an equilibrium is produced according to

$$MAlH_4 + MgX_2 \rightleftharpoons XMgAlH_4 + MX \qquad (20)$$

Magnesium aluminum hydride is not formed even when $MAlH_4$ is added in excess.

Acknowledgments.—We are indebted to the National Aeronautics and Space Administration (Grant NAG-657) and the Office of Naval Research (Contract N0014-67-A-0159-0005) for their support of this work. We also wish to thank Dr. J. A. Bertrand for the use of his X-ray powder diffraction instrumentation.

CONTRIBUTION FROM THE CHEMICAL ENGINEERING AND CHEMISTRY DIVISIONS, ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS 60439

The Thermochemistry of Aqueous Xenon Trioxide[1]

BY P. A. G. O'HARE, GERALD K. JOHNSON, AND EVAN H. APPELMAN

Received September 4, 1969

Solution calorimetric measurements of the enthalpies of the reactions of $XeO_3(aq)$ with HI(aq) and of $I_2(c)$ with HI(aq) have been used to determine a value of 99.94 ± 0.24 kcal mol^{-1} for $\Delta H_f°(XeO_3 \cdot 96.15H_2O)$ at 298.15°K. The electrode potentials of the Xe–XeO_3 couple in acidic solution and of the Xe–$HXeO_4^-$ couple in basic solution were deduced to be 2.10 ± 0.01 and 1.24 ± 0.01 V, respectively.

Introduction

Xenon trioxide, XeO_3, and its derivatives are perhaps the most unexpected of the noble gas compounds. Solid xenon trioxide is explosively unstable and has an enthalpy of formation of 96 ± 2 kcal mol^{-1}.[2] Solutions of XeO_3 in dilute aqueous acid, although they are potent oxidizers,[3] show no evidence of spontaneous decomposition, and because of this, they have received more experimental attention than has the dangerous solid. A reliable quantitative determination of the thermodynamic oxidizing power of these solutions is therefore of considerable practical value. Inasmuch as reactions of aqueous XeO_3 are irreversible, this oxidizing power can only be measured thermodynamically.

The present investigation was undertaken to obtain a precise value for the enthalpy of formation at 298.15°K of aqueous XeO_3, $\Delta H_f°_{298.15}[XeO_3(aq)]$, from calorimetric measurements of the enthalpies of the reactions between $XeO_3(aq)$ and HI(aq) and between $I_2(c)$ and HI(aq) according to the processes

$$XeO_3(aq) + 9I^-(aq) + 6H^+(aq) \longrightarrow Xe(g) + 3I_3^-(aq) + 3H_2O(l) \qquad (1)$$

$$I_2(c) + I^-(aq) \longrightarrow I_3^-(aq) \qquad (2)$$

These results, when combined with auxiliary thermochemical data from the literature, yielded a precise value for $\Delta H_f°(XeO_3 \cdot 96.15H_2O)$.

Experimental Section

Materials. XeO_3(aq).—Xenon trioxide was prepared by hydrolysis of XeF_6, which was synthesized by the reaction of xenon with a large excess of fluorine at 300° and about 100 atm pressure.[4] Hydrolysis was effected by passing a stream of argon over the XeF_6 and then through water.[5] The product was purified by treatment with magnesium oxide, hydrous zirconium phosphate, and hydrous zirconium oxide.[3] A rotary evaporator was used to concentrate the resulting solution at room temperature. The XeO_3 assay, 3.1394 ± 0.0006 (standard deviation) equiv kg^{-1} (*in vacuo*), was determined by iodometric titration,[3] using a thiosulfate solution that had been standardized against Mallinckrodt Primary Standard grade KIO_3 (manufacturer's assay, 99.95–100.05%).

Potentiometric titration of the XeO_3 solution indicated the presence of 0.010 equiv kg^{-1} of strong acid, presumably perchloric acid introduced during the purification operations.[3] Measurements with a fluoride electrode (Orion Research, Inc.) revealed the presence of 6×10^{-5} mol kg^{-1} of fluoride. No metallic impurities were detected by emission spectrography.

HI(aq).—Constant-boiling hydriodic acid was prepared by fractionation of reagent grade 48% HI, followed by dilution to the required concentration with argon-saturated, twice-distilled water. The distillation and dilution operations were carried out in an inert atmosphere and in subdued light to prevent premature oxidation of the HI. Two HI solutions were made, the concentrations of which were determined to be 0.197 and 0.177 *M* by titration with standardized NaOH. The H_2O:HI molar ratios for these solutions were calculated to be 279.18 and 310.90, respectively, based on the published densities.[6] The solutions were stored in dark bottles in an inert atmosphere.

I_2(c).—Iodine crystals (Electronic Space Products, Inc., Los

(1) This work was performed under the auspices of the United States Atomic Energy Commission.

(2) S. R. Gunn in "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 149.

(3) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(4) C. L. Chernick and J. G. Malm, *Inorg. Syn.*, **8**, 258 (1966).

(5) B. Jaselskis, T. M. Spittler, and J. L. Huston, *J. Am. Chem. Soc.*, **88**, 2149 (1966).

(6) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 55.