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Reaction of Aluminum Hydride with Beryllium Chloride in Diethyl Ether

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Received July 13, 1973

The reaction of aluminum hydride with beryllium chloride in diethyl ether has been studied by infrared spectroscopy. The reaction proceeds according to the following equations: $BeCl_2 + AlH_3 \rightarrow H_2AlCl + HBeCl$; $HBeCl + AlH_3 \rightleftharpoons H_2AlCl + BeH_2$. Hydridoberyllium chloride was prepared unequivocally by the reaction of BeH_2 and $BeCl_2$ and shown to be the product of the above reaction. When AlH_3 is used in excess, BeH_2 precipitates from solution. The yield of BeH_2 depends on the amount of excess AlH_3 used. Hydridoberyllium chloride is stable to disproportionation and is dimeric in ether solvent. Difinitive beryllium-hydrogen stretching and deformation frequencies are reported.

Introduction

In a study of the reaction of lithium aluminum hydride with beryllium chloride, we[1] reported experimental results which could be explained by assuming an exchange between aluminum hydride and beryllium chloride to yield hydridoberyllium chloride and dihydridoaluminum chloride (eq 1).

$$AlH_3 + BeCl_2 \rightarrow HBeCl + H_2AlCl \tag{1}$$

The suspected HBeCl formed in this reaction was soluble in ether as was the H_2AlCl. However, Dymova[2] has reported that the reaction of lithium aluminum hydride and beryllium chloride in a 2:1 ratio yields $LiAl_2H_7$ and HBeCl which he reports to be insoluble in ether solvent

$$2LiAlH_4 + BeCl_2 \rightarrow HBeCl\downarrow + LiCl\downarrow + LiAl_2H_7 \tag{2}$$

The preparation of $HBeX \cdot NR_3$ (X = Cl, Br, I; NR_3 = *N*-methylpyrrolidine and other tertiary amines) by several different methods has been recently reported.[3]

We have undertaken to study the redistribution of AlH_3 with $BeCl_2$ in ether in order to establish (1) the true nature of the products of the reaction of $LiAlH_4$ and $BeCl_2$ in ether, (2) the physical properties of HBeCl, particularly the Be-H stretching and deformation frequencies, and (3) the value of AlH_3 as a reagent for preparing HMX compounds by redistribution of AlH_3 in ether solvent with groups II and III metal halides.

Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and water or on the bench using typical Schlenk-tube techniques.[4]

Instrumentation. Infrared spectra were obtained with a Perkin-Elmer Model 257 infrared spectrophotometer using NaCl liquid cells. Ebullioscopic molecular weight measurements were carried out as described previously.[5]

Reagents. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use. Benzene (Fisher Certified reagent) was distilled over sodium aluminum hydride immediately prior to use. Anhydrous beryllium chloride was obtained from Columbia Organic Chemical Co. To a slurry of beryllium chloride in benzene cooled to 0° was added excess diethyl ether (50% excess based on the bis(etherate) of beryllium chloride). The resulting solution was then filtered and the benzene was removed from the filtrate under vacuum. The resulting solid was dissolved in ether, and the resulting solution was then standardized by beryllium and chloride analysis. Ether solutions of anhydrous $AlCl_3$ (Fisher Certified reagent) were prepared in a manner similar to that of $BeCl_2$.

Preparation of Aluminum Hydride in Diethyl Ether. Lithium aluminum hydride was added to beryllium chloride in diethyl ether in a 2:1 ratio.[1] The resulting solution was then filtered. Analysis of the filtrate gave an Al:H:Li:Cl ratio of 1.00:3.02:0.06:0.01.

Analytical Procedures. Gas analyses were carried out by hydrolyzing samples on a standard vacuum line equipped with a Toepler pump. Aluminum analysis was carried out by titration with EDTA. Chloride was determined by potentiometric titration using Ag-glass electrodes. The sum 3 Al + 2 Be was determined by adding excess NaF to the solution at pH 7.8 and then back-titrating to pH 7.8 using standard hydrochloric acid.

Infrared Study of the Reaction of AlH_3 with $BeCl_2$ in Diethyl Ether. To 15 ml of AlH_3 in ether (0.07 *M*) in a 25-ml volumetric flask was added a volume of $BeCl_2$ in ether (0.225 *M*) calculated to give the desired AlH_3 to $BeCl_2$ ratio. The solution was then adjusted to the 25-ml mark and stirred. AlH_3:$BeCl_2$ ratios of 1:2, 1:1, and 2:1 were studied by infrared spectroscopy in this manner. The infrared spectra of these solutions are shown in Figure 1. They showed no change after 24 hr.

When the $BeCl_2$ was added to the AlH_3 solution, a white precipitate formed immediately. This precipitate redissolved when the AlH_3:$BeCl_2$ ratio was 1:2 or 1:1. In order to identify the precipitate, 30 ml of $BeCl_2$ solution (0.225 *M*) was added to 90 ml of AlH_3 in ether (0.165 *M*). The reaction mixture was then filtered. Analysis of the solid obtained from the filtration gave the following Be:H:Cl ratios: 1.00:1.87:0.25. The amount of beryllium in the solid represented 6.5% of the total beryllium added.

Infrared Study of the Reaction of AlH_3 with $AlCl_3$ in Diethyl Ether. The choloroaluminum hydrides, H_2AlCl and $HAlCl_2$, were prepared by mixing AlH_3 and $AlCl_3$ in ether in the appropriate ratios. The reaction between AlH_3 and $AlCl_3$ has been discussed by a number of authors.[6-8] The infrared spectra of AlH_3, H_2AlCl, and $HAlCl_2$ are reported in Figure 2.

Preparation of HBeCl from BeH_2 and $BeCl_2$ in Diethyl Ether. To 6.086 g of $BeBr_2 \cdot 2Et_2O$ in 100 ml of ether was added 35 ml of $LiAlH_4$ in ether (1.119 *M*). The solution was stirred overnight and then filtered. Analysis of the resulting solid gave a Be:H ratio of 1.00:1.90. To 6.80 mmol of this solid product was added 25 ml of $BeCl_2$ in ether (0.2325 *M*). The solution was stirred overnight and filtered. Analysis of the filtrate gave a H:Be:Cl ratio of 0.92:1.00:1.08. The infrared spectrum of the solution *vs.* ether showed bands at 1330, 1050, 970, 908, 840, 840 (sh), 790, and 700 cm^{-1} (see Figure 3).

The compound DBeCl was prepared from BeD_2 and $BeCl_2$ in ether. Its infrared spectrum showed that the band at 1330 cm^{-1} in HBeCl shifted in DBeCl to 985 cm^{-1}. The band at 970 cm^{-1} in HBeCl disappeared in DBeCl. All the other bands in HBeCl were the same in DBeCl. Removal of the ether from the solution of HBeCl yielded an oil which was not characterized further. Ebullioscopic molecular weight determination of HBeCl in ether indicated that this compound is a dimer in the concentration range 0.1-0.3 *m*.

Reaction of AlH_3 with $BeCl_2$ in Et_2O at 4:1 and 8:1 Ratios. To 50 ml of $BeCl_2$ in diethyl ether (0.2067 *M*) was added 17 ml of $LiAlH_4$ in ether (1.156 *M*). The solution was stirred for 1 hr and filtered. To the filtrate which was found to contain no lithium was

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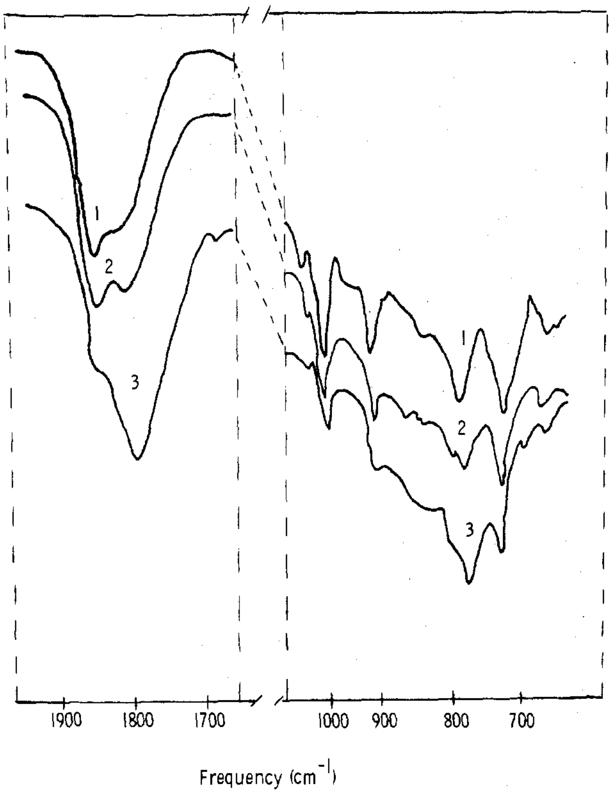


Figure 1. Infrared study of the reaction of AlH_3 with $BeCl_2$ in diethyl ether in (1) 1:2, (2) 1:1, and (3) 2:1 ratios.

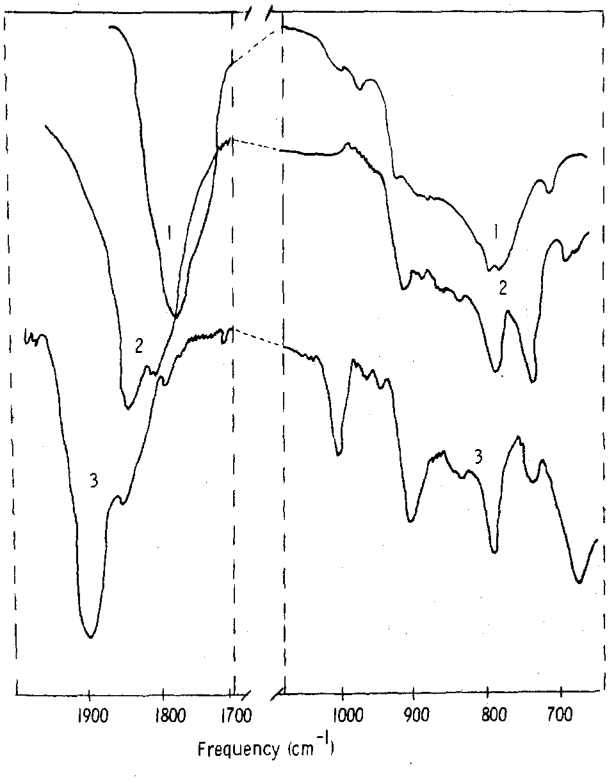


Figure 2. Infrared study of the reactions of AlH_3 with $AlCl_3$ in diethyl ether in (1) 1:0, (2) 2:1, and (3) 1:2 ratios.

added 25 ml of $BeCl_2$ in ether (0.2067 *M*) and the solution was stirred overnight. The solution was then filtered and the resulting solid gave a Be:H ratio of 1.00:1.90. This represented 34.8% of the original amount of beryllium.

In a similar experiment AlH_3 was allowed to react with $BeCl_2$ in ether in a ratio of 8:1. In this case 56% of the original beryllium was isolated in the solid.

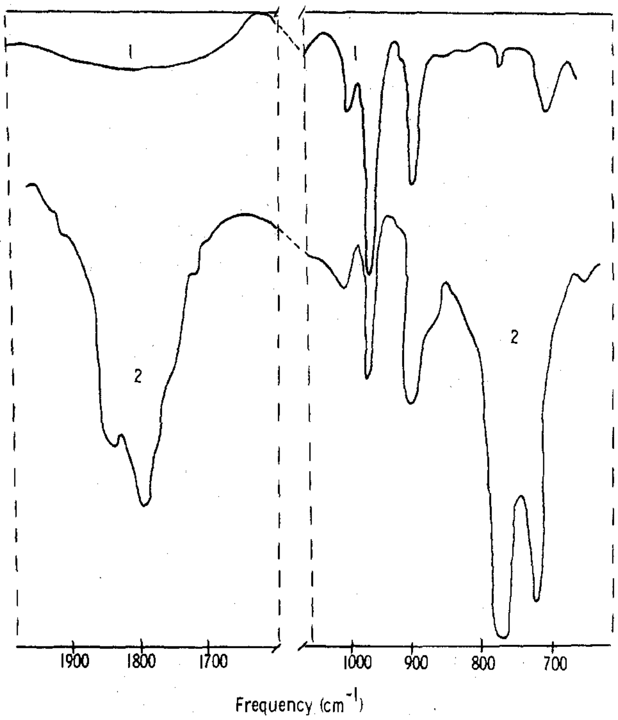


Figure 3. Infrared study of the reaction of (1) BeH_2 with $BeCl_2$ in a 1:1 ratio in diethyl ether and (2) AlH_3 with $BeCl_2$ in a 1:1 ratio in diethyl ether.

Results and Discussion

In our study of the reaction of lithium aluminum hydride with beryllium chloride in diethyl ether in 2:1 ratio, we found that the AlH_3 formed in this reaction is soluble in ether. When the above reaction was carried out in 1:1 ratio, a mixture of products was formed which was attributed to further reaction of AlH_3 with unreacted $BeCl_2$. In an effort to establish the nature of these products we decided to study the reaction of AlH_3 with $BeCl_2$ in ether in some detail.

Since hydrogen-halogen exchange in the AlH_3-$BeCl_2$ system would be expected to form hydridochloroalanes as well as HBeCl, it was decided that the hydridochloroalanes would have to be prepared first for infrared spectroscopic comparison purposes. Ether-soluble alane was found to show bands in its infrared spectrum at 1788 and 770 cm^{-1}. When AlH_3 and $AlCl_3$ were mixed in a ratio of 2:1, H_2AlCl was produced (eq 3). This compound has infrared bands at 1850, 1820 (sh), 780, and 725 cm^{-1}. The compound $HAlCl_2$ was produced when AlH_3 and $AlCl_3$ were allowed to react in 1:2 ratio (eq 4). Its infrared spectrum shows bands

$$2AlH_3 + AlCl_3 \rightarrow 3H_2AlCl \qquad (3)$$

$$AlH_3 + 2AlCl_3 \rightarrow 3HAlCl_2 \qquad (4)$$

at 1905, 1850, and 780 cm^{-1}.

When $BeCl_2$ was added to AlH_3 in ether in 2:1 ratio, a precipitate formed initially which redissolved as the $BeCl_2$ was added. When the addition was complete, the reaction solution was clear. The infrared spectrum of the solution shows bands at 1850, 970, 905, 780, and 725 cm^{-1}. It is interesting that no bands characteristic of AlH_3 or $HAlCl_2$ are present. The bands at 1850, 780, and 725 cm^{-1} can be attributed to H_2AlCl. The bands at 970 and 905 cm^{-1} were found to correspond to the compound HBeCl prepared independently from BeH_2 and $BeCl_2$. At an AlH_3 to $BeCl_2$ ratio of 1:1, the infrared spectrum of the resulting solution is unchanged. These data indicate that as $BeCl_2$ is added to AlH_3, H_2AlCl and HBeCl are formed

$$AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl \qquad (5)$$

At an AlH_3:$BeCl_2$ ratio of 2:1, the infrared spectrum showed bands at 1850 (sh), 1788, 970, 905, 772, and 725 cm^{-1}. These data correspond to a mixture of AlH_3 and H_2AlCl. The bands at 970 and 905 cm^{-1} are again attributed to HBeCl. A small amount of solid precipitated from the reaction mixture. The solid was found to be BeH_2 and represented 6% of the total beryllium added. At AlH_3:$BeCl_2$ ratios of 4:1 and 8:1 larger amounts of solid were isolated. This solid proved to be BeH_2 in yields of 34.8 and 56%, respectively. Alane was also found to reduce HBeCl in ether to BeH_2 in 63% yield (based on HBeCl) at an AlH_3:HBeCl ratio of 2:1 (eq 6).

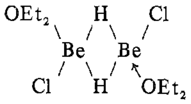
$$2AlH_3 + HBeCl \rightleftharpoons BeH_2\downarrow + H_2AlCl + AlH_3 \qquad (6)$$

The compound HBeCl was prepared independently by the redistribution of BeH_2 and $BeCl_2$ in ether (eq 7). The

$$BeH_2 + BeCl_2 \rightarrow 2HBeCl \qquad (7)$$

infrared spectrum of HBeCl in ether showed bands at 1330, 1050, 970, 908, 840 (sh), 790, and 700 cm^{-1}. The infrared spectrum of DBeCl showed that the band at 1330 cm^{-1} shifted to 985 cm^{-1} and the band at 970 cm^{-1} in HBeCl disappeared in DBeCl. This gives a ν_H:ν_D ratio of 1.35. Molecular weight determination of HBeCl in ether indicates that the compound is associated with an *i* value of 2.17 at 0.1-0.3 *m*.

Coates and Roberts[9] isolated the complex Be_2H_4·TMED which has a sharp doublet in the infrared spectrum at 1787 and 1807 cm^{-1}. They attribute these bands to terminal Be-H stretching vibrations. We find no bands in this region for HBeCl. Bell and Coates[10] have reported the compounds $[CH_3BeH·N(CH_3)_3]_2$ and $[C_2H_5BeH·N(CH_3)_3]_2$ which are dimers in benzene. These compounds exhibit strong absorption at 1333-1344 cm^{-1} (in cyclohexane) which is attributed to the Be-H-Be bridge. In the deuterated compounds, the 1344-cm^{-1} band of $[CH_3BeH·N(CH_3)_3]_2$ shifted to 1020 cm^{-1}. We therefore conclude that HBeCl is associated through Be-H-Be bridge bonds, *i.e.*



Acknowledgment. We acknowledge with gratitude support of this work by the Office of Naval Research.

Registry No. $BeCl_2$, 7787-47-5; $LiAlH_4$, 16853-85-3; AlH_3, 7784-21-6; HBeCl, 42016-55-7; $[HBeCl(OEt_2)]_2$, 42744-98-9.

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Infrared Studies of Apatites. I. Vibrational Assignments for Calcium, Strontium, and Barium Hydroxyapatites Utilizing Isotopic Substitution

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Received July 11, 1973

The infrared spectra of powdered calcium hydroxyapatite isotopically substituted with D, ^{18}O, ^{44}Ca, and ^{48}Ca and infrared spectra of powdered strontium and barium hydroxyapatites and their deuterated analogs are reported at 48 and −185° in the 4000-200-cm^{-1} region. Band assignments, based on isotopic frequency shifts, band intensity, band temperature dependency, and comparisons between corresponding bands of these structurally related apatites are presented for the above and other apatites.

Introduction

The major crystalline calcium phosphate in teeth and bones is well known to have an apatite-like structure; however, many compositional and structural details of both the *in vitro* and *in vivo* apatites have not been clearly resolved. Consequently, numerous chemical and physical studies of the biological apatites, synthetic apatites, geological apatites, and related calcium phosphates have been carried out to acquire further knowledge to define better the chemical and structural details of the apatites. One effectual physical method for studying both compositional and structural details of the apatites is infrared spectroscopy. The initial requirements to utilize effectively the infrared data for determining compositional and structural details are the complete assignment and characterization of the vibrational spectra of the pure apatite end members of controlled chemical and physical properties.

Spectral assignment and characterization should be made on oriented single crystals using polarized radiation and also on powdered samples, progressively reduced in particle size to a few unit cells. Single-crystal studies provide data necessary for more complete spectral assignments including spatial vibrational transition moments and bond directions whereas the powder data represent an average spectrum reflecting all orientations of the crystallites. The small crystal size of most apatites of controlled chemical composition generally precludes oriented single-crystal analysis, and, therefore, powder data are usually obtained. The small crystal size of many biological and other apatites render powder data appropriate along with spectral characterization of extremely small apatite crystals (a few unit cells). Extremely small pure apatite crystals may show spectral alteration due to both surface and size effects independent of vibrational perturbations expected to arise from additional sources in extremely small impure apatites. The powdered apatites examined in this study were prepared under controlled conditions in order to minimize the occurrence of absorption bands and/or perturbation in vibrational frequencies and intensities arising from, *e.g.*, nonstoichiometry, substitution of other ions, impurities, size, surface effects, and poor crystal perfection.