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The Direct Fluorination of Borohydrides and Lithium Aluminium Hydride. A New Route to Fluoroborates and Fluoroaluminates

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The controlled reactions of the extremely reactive species sodium borohydride, potassium borohydride, lithium borohydride and lithium aluminium hydride with elemental fluorine have been investigated. The products obtained are sodium tetrafluoroborate, $NaBF_4$; potassium tetrafluoroborate, KBF_4; lithium tetrafluoroaluminate, $LiAlF_4$. This direct fluorination process establishes a new preparation for the fluoroborates and has produced the new compound lithium tetrafluoroaluminate. Yields near 100% have been obtained.

Introduction

Fluoroborates have been prepared by many different synthetic routes. Some can be formed by bubbling boron trifluoride metal fluoride melts. The most common approach is the fluorination of some inorganic boron compound with a fluorinating agent such as hydrogen fluoride, Na_2SiF_6, or boron trifluoride. Fluoroaluminates such as Li_3AlF_6, Na_3AlF_6, $NaAlF_4$, and $KAlF_4$ are well-known compounds which are formed by fusing the alkali metal fluorides with aluminium trifluoride. Lithium tetrafluoroaluminate has not been prepared in the solid phase at room temperature.

The most common laboratory preparation of sodium fluoroborate utilizes the reaction of orthoboric acid and sodium carbonate with hydrogen fluoride.[1]

Similarly KBF_4 may be formed using potassium hydroxide for the potassium source in a 90% yield.[1]

$$H_3BO_3 + 4HF + KOH \xrightarrow{20^\circ C} KBF_4 + 4H_2O$$

Also sodium, potassium and lithium fluoroborate may be obtained as byproducts during the formation of lower boranes in the reaction of boron trifluoride with $NaBH_4BH_3$.[2]

The fluorination in diglyme solution of lithium hydride and lithium borohydride has been reported.[3]

$$6LiH + 8BF_3 \xrightarrow{\text{diglyme}} 6LiBF_4 + B_2H_6$$

$$3LiBH_4 + 4BF_3 \xrightarrow{\text{diglyme}} 3LiBF_4 + 2B_2H_6$$

It was also reported that no reaction occurred between lithium borohydride and gaseous boron trifluoride.

Lithium tetrafluoroaluminate, $LiAlF_4$, has been reported as a gaseous species in a mass spectroscopic study. Porter and Zeller[4] observed the $(LiF \cdot AlF_3)$ species in the mass spectra of a mixture of AlF_3 and LiF. They also reported the species $(LiF)_2AlF_3$ and $(LiFAlF_3)_2$. The direct fluorination of potassium, sodium, and lithium borohydrides and of lithium aluminum hydride has not been previously reported.

The fluorination process used to prepare the compounds in this paper (the LaMar process) has been previously discussed.[5] Essentially, this process employs initial fluorine concentrations diluted with helium at room temperature over a 24-hour period of time to allow for dissipation of the energy released in the highly exothermic reaction.

Experimental Section

Materials and Apparatus

The hydrides were reagent grade and obtained from Alfa Inorganics. The $LiAlH_4$ starting material was purified by extracting with ether until a pure white compound was obtained. The fluorine was supplied by Allied Chemical Corp. (98% purity typical). The apparatus used in this work has been described.

Analytical and Analytical Apparatus

The elemental analyses were done by Schwartzkopf Analytical Laboratories, Woodside, New York. The infrared spectra were recorded on a Beckman IR8 using KBr disc samples. The X-ray powder patterns were taken on a Phillips Electronics Model 12045 B/3 X-ray spectrometer with a Type 5205610 powder pattern camera. Copper (1.5405 Å) radiation was used in all X-ray spectra reported.

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General Procedure

The general procedure is as follows. A fluorine flow of about 2 cm^3/min with a helium flow of 6 cc/min was introduced into a 1″ nickel tube reactor containing the finely powdered hydride in a nickel boat. The chamber was flushed with helium before starting the fluorine flow. The reaction proceeds at room temperature and this flow was continued for 16 hours. Then the flow was changed to 3 cc/min fluorine and the helium flow was terminated. This flow was continued for 48 hours. The reactor was then purged with helium and the product was removed. Shorter reaction times are possible but this procedure has been designed for nearly complete fluorinations. The reactions were essentially complete with 6 hours of diluted flow and 18 hours of pure fluorine flow.

The Reaction of Sodium Borohydride with Fluorine

About 1/2 gram of finely powdered sodium borohydride was placed in a nickel boat in the 11′ nickel reaction chamber. The chamber was flushed with a 4 cc/min helium flow for 30 minutes. Care must be taken that the chamber is dry to avoid decomposition of the hydride. Flow rate procedures were identical with those of the general procedure. The product was a white powder. The X-ray powder patterns were taken and prominent *d* spacings were found at 3.8, W; 3.4, VS; 3.12, W; 2.84, M; 2.73, W; 2.55, W; 2.30, S; 2.14, M; 2.03, M; 1.91, W; and 1.84, W.

All of these lines plus several more very weak lines agree exactly in position and intensity with those reported by Norment, Henderson and South for sodium tetrafluoroborate, ($NaBF_4$).[6]

The Reaction of Potassium Borohydride with Fluorine

The fluorination procedure, flow rates and times were identical with those for sodium borohydride. A white powdered compound was obtained. The X-ray powder pattern was taken and *d* spacings were found at 3.41, VS; 3.24, S; 3.06, S; 2.07, 3.51, 2.80, 2.09, and 2.23. These lines are identical to those reported for potassium tetrafluoroborate (KBF_4) in the ASTM powder pattern diffraction file.[7]

In addition, lines at 3.87, 2.45, 2.31, 2.02 and 1.9 (very weak) were seen. All 31 lines matched exactly with the powder pattern X-ray of a sample of KBF_4 obtained from Alfa Inorganics.

The Reaction of Lithium Borohydride with Fluorine

The fluorination procedure, flow rates and fluorination time were identical with those for potassium and sodium borohydride. A white finely powdered compound was obtained.

The X-ray powder pattern has *d* spacings of 4.8, M; 3.2, VS; 3.35, S; 2.57, M; 2.41, M–S; 2.365, M; 2.27, W; 2.045, VS; 1.685, M; 1.608, W; 4.23, 3.8, 2.845, 2.75, 1.87, 1.82, 1.785, 1.75, 1.425 and 1.23. These lines were identical to the lines obtained from the X-ray powder pattern of a commercial sample of lithium tetrafluoroborate ($LiBF_4$).

The Reaction of Lithium Aluminium Hydride with Fluorine

The procedure, flow rates, and exposure times were identical to those reported for the borohydrides. A light grey powdered sample was obtained.

The infrared spectra showed only a very strong broad stretch from 850 cm^{-1} to somewhere beyond 600 cm^{-1}, centered at 617 cm^{-1}. A small node occurred at 730 cm^{-1}. The bands are due to the aluminium fluoride stretch in the tetrahedral AlF_4 group. Stretches at 645 cm^{-1} and 746.5 cm^{-1} have been previously reported by Lecomte, Duval and Wadier[11] for the aluminum fluoride stretch in potassium fluoroaluminate ($KAlF_4$). The compound was very hygroscopic and features due to water appeared in the spectra when the compound was allowed to remain in air for a short period of time. The mass spectra of this compound at 650° C and 50 ev. contained the following species: $Li_2AlF_4^+$, 117; $LiAlF_3^+$, 91, AlF_2^+, 64; AlF^+, and $LiAl^+$, 34. These spectra were identical with those which were obtained in the Porter and Zeller study of the gaseous $LiAlF_4$ species which was previously mentioned. This previous study of appearance potentials indicated that the $LiAlF_3^+$ species is formed from the $LiAlF_4$ gaseous species and that no parent ion exists in the system. Absent from our spectra were the LiF^+ and Li_2F species that were characteristic of the LiF vapor species in the Porter and Zeller study. The $LiAlF_4$ *d* spacings index well into a tetragonal unit cell which would be the most probable structure for such a compound. It is also noteworthy that none of the lines observed are due to the LiF or AlF_3 powder diffraction lines.

The X-ray powder pattern had *d* spacings of 4.105, S; 3.900, W; 3.517, W; 2.970, W; 2.852, W; 2.711, W; 2.339, M; 2.272, W; 2.196, M; 2.133, M; 2.092, W; 2.026, M; 1.882, W; 1820, W; 1.771, W; 1.591, W; 1.428, W; 1.227, W; and 1.174, W. It is interesting to observe that seven lines were observed in close proximity of the prominent lines in the mineral cryolithionite $Na_3Li_3Al_2F_{12}$,[12] occurring at 3.03, 2.71, 2.37, 2.21, 1.75, 1.43 and 1.22.

Anal.: Calcd. for $LiAlF_4$; Li, 6.33%; Al, 24.54%; F, 68.139%; Found: Li, 6.56%; Al, 24.17%; F, 65.79%

Results and Discussion

The compounds $NaBF_4$, sodium tetrafluoroborate, KBF_4, potassium tetrafluoroborate, $LiBF_4$, lithium tetrafluoroborate, and $LiAlF_4$, lithium tetrafluoroaluminate have been prepared in near 100% yield by direct fluorination (Table I).

TABLE I. Fluorination of Borohydrides and Lithium Aluminum Hydride.

Reaction	Temp.	Approx. Yield
$NaBH_4 + 4F_2 \rightarrow NaBF_4 + 4HF$	20° C	~100%
$KBH_4 + 4F_2 \rightarrow KBF_4 + 4HF$	20° C	~100%
$LiBH_4 + 4F_2 \rightarrow LiBF_4 + 4HF$	20° C	~100%
$LiAlH_4 + 4F_2 \rightarrow LiAlF_4 + 4HF$	20° C	~100%

The preparation of the fluoroborates seems to be very good high yield preparation. The fact that no *d* spacings are observed for alkali halides etc. and the analytical purity obtained indicate that this reaction provides material of high purity not always characteristic of the usual molten reactor syntheses. The preparation of the lithium tetrafluoroaluminate shows that new compounds may be prepared by this process when there is a known hydride precursor. The formation of $LiAlF_4$ has a precedent since it is very similar to a preparation of Wilburg and Lacal[13] where an ethereal solution of $LiAlH_4$ was titrated in vacuo with an ethereal solution of I_2 at −100° C. A white compound was formed with the empirical formula $LiAlI_4$. If $LiAlF_4$ is exhaustively fluorinated, one obtains a white substance of unknown structure but presumable a higher fluoride of this system. It is therefore likely that still other compounds exist in the Li–Al–F system.

Possibly the most striking result of this investigation is the fact that the normally explosive reaction of elemental fluorine with metal hydrides can be smothly and successfully controlled.

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