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An Investigation of the Direct Synthesis of Group Ia Hexahydridoaluminates

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An evaluation of the direct synthesis of the hexahydridoaluminates (M_3AlH_6) of lithium, sodium, and potassium from the alkali metals, aluminum, and hydrogen is presented in this report. Although Na_3AlH_6 and K_3AlH_6 can be readily prepared from the elements, no satisfactory conditions for the direct synthesis of Li_3AlH_6 were found. Evidence is presented which indicates that the direct synthesis of K_3AlH_6 is an equilibrium process and that a similar equilibrium may acount for some reactions of Na_3AlH_6 in THF. K_3AlH_6, although insoluble in the common organic solvents, was shown to reduce benzophenone to benzhydrol and tri-*n*-butyltin chloride to the corresponding hydride. Attempts to prepare $Mg_3(AlH_6)_2$ by the reaction of Na_3AlH_6 and magnesium chloride were not successful.

Introduction

The preparation of the first hexahydridoaluminate, trisodium hexahydridoaluminate (Na_3AlH_6), was reported by Zakharkin and Gavrilenko[2] in 1962. These workers prepared the new hydride by the reaction of sodium hydride and sodium tetrahydridoaluminate ($NaAlH_4$) in heptane at elevated temperature

$$2NaH + NaAlH_4 \longrightarrow Na_3AlH_6 \qquad (1)$$

Since this time we have reported the direct synthesis of Na_3AlH_6 from the elements.[3] The procedure used to make this compound was similar to the one used earlier to prepare sodium tetrahydridoaluminate from the elements[4]

$$Na + Al + 2H_2 \longrightarrow NaAlH_4 \qquad (2)$$

$$3Na + Al + 3H_2 \longrightarrow Na_3AlH_6 \qquad (3)$$

More recently, the physical and chemical properties of Na_3AlH_6 have been studied,[5-7] and the reducing properties of the compound were uncovered. The only report of K_3AlH_6 is that presented by Chini and coworkers,[7] who prepared the compound from KH and $KAlH_4$ in toluene at 180°.

A number of procedures providing varying yields of the analogous Li_3AlH_6 were reported by Ehrlich and coworkers[8]—the preferred reaction being the reduction of *n*-butyllithium with excess $LiAlH_4$. It has also been reported that Li_3AlH_6 and Na_3AlH_6 are produced by thermal decomposition of the respective tetrahydridoaluminates[3,9]

$$3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2 \qquad (4)$$

The direct synthesis of hexahydridoaluminates from the elements represents a more convenient and potentially more economic route to this interesting class of compounds than reactions employing the tetrahydridoaluminates. For this reason, we have attempted to extend our earlier studies concerning the direct synthesis of Na_3AlH_6 also to include other group Ia metals.

Experimental Section

Materials.—Sodium, lithium, and potassium metals (reagent grade) were obtained from Fisher Scientific Co., Inc. These were cut under dry toluene in a nitrogen-filled drybox and stored under the appropriate dry diluent in a stoppered flask. Lithium hydride was obtained from Alfa Inorganics, Inc., as a 50% mixture in mineral oil and used as received. Aluminum powder was obtained from Metals Disintegrating, Inc. (Grade MD-201), and activated prior to use by either of the methods outlined below. Triethylaluminum was obtained from Air Products, Inc. All solvents and diluents were distilled from $NaAlH_4$ prior to use and stored over sodium wire.

Equipment.—A 300-ml Magne-Drive autoclave (Autoclave Engineers) was used in a high-pressure laboratory. The reactor was loaded and unloaded in a nitrogen-filled drybox. The drybox was provided with a recirculating system in which the atmosphere was continuously passed through Dry Ice–acetone traps in order to remove solvent vapors and manganese oxide columns in order to remove oxygen.[10]

Infrared spectra were obtained using a Perkin-Elmer 621 high-resolution grating spectrophotometer.

X-Ray powder pattern data were recorded from samples loaded in the drybox and sealed in 0.5-mm glass capillaries. The data were obtained using a Norelco 114.6-mm diameter camera employing Cu Kα radiation.

Activation of Aluminum Powder.—The hydriding reaction does not occur with metallic aluminum unless the powder is initially activated. An excellent method (the "Ziegler procedure") involves heating aluminum powder with triethylaluminum under hydrogen.[4,11] The activated powder was stored under dry hexane.

Another effective procedure, employed when toluene was used as the diluent in the syntheses, simply involves vigorous stirring (~2000 rpm) of the aluminum powder with a 1.5% solution of triethylaluminum in toluene under hydrogen pressure (about 1000 psi) for 16 hr at room temperature.[5]

Trisodium Hexahydridoaluminate, Na_3AlH_6.—Aluminum powder (4.784 g, 0.166 g-atom) in 90 ml of dry toluene was activated as described above using 1.5 ml of triethylaluminum. The autoclave was then depressurized, sodium metal (12.226 g, 0.532 g-atom; Na:Al = 3:1) was added, and the mixture was heated to 165° with rapid stirring, under 4000 psi of dry hydrogen. The reaction was exothermic, but power to the heating jacket was

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(1) To whom all inquiries should be sent.

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(9) V. I. Mikheeva and S. M. Arkhipov, *Russ. J. Inorg. Chem.*, **12**, 1066 (1967).

(10) T. L. Brown, D. W. Dickerhoff, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

(11) H. E. Redman, U. S. Patent 2,885,314 (1959).

controlled so that the temperature did not rise above 195°. Hydrogen uptake appeared complete after about 4 hr, but heating was continued for 16 hr to ensure maximum conversion. The reaction vessel was allowed to cool and was depressurized; the mixture was then filtered through a medium-porosity glass frit. The resultant solid was washed with three 50-ml portions of dry THF and dried *in vacuo*. The X-ray powder pattern of the compound, together with its pyrophoric nature in air and its extreme insolubility in common organic solvents, was in complete agreement with the properties previously reported.[3,6] The THF washings contained a small amount of hydrolyzable hydrogen and an infrared spectrum indicated a weak band at 1680 cm^{-1}, presumably due to $NaAlH_4$.

Attempted Purification of Na_3AlH_6 by Soxhlet Extraction.—A portion (~10 g) of the Na_3AlH_6 formed above was extracted with dry THF in a Soxhlet apparatus for 7 days. No obvious reduction in solid volume was noted and no solid appeared in the receiver flask. However, evaporation of the THF under vacuum left a small amount (~1 g) of a white solid residue, identified as $NaAlH_4$ from its X-ray powder pattern. No lines of NaH or Na_3AlH_6 were observed.

Tripotassium Hexahydridoaluminate, K_3AlH_6.—In all cases, the attempted syntheses were carried out in a manner similar to that employed for Na_3AlH_6 except for the temperature and metal ratio variations indicated in Table I.

TABLE I

EXPERIMENTAL CONDITIONS INVESTIGATED IN THE PREPARATION OF K_3AlH_6

Expt no.	Amt, g		K:Al g-atom ratio	Amt of toluene, ml	Reaction temp, °C	Reaction time, hr	Product K:Al
	K	Al					
1	22.38	5.147	3:1	95	160	16	3.20:1
2	21.56	4.961	3:1	90	160	24	3.45:1
3	21.23	4.882	3:1	90	180	24	3.13:1
4	23.16	5.811	2.75:1	110	200	24	2.94:1

Preparations involving KH in toluene appear prone to produce a green color, possibly due to the formation of a potassium alkyl or aryl. In each case, a green pyrophoric solid was isolated. Washing with diglyme or THF followed by diethyl ether removed the green color. Drying of the solid *in vacuo* gave a gray material containing excess potassium hydride as evidenced by the X-ray powder pattern and chemical analyses. The diglyme washings contained a large amount of hydrolyzable hydrogen and infrared spectra of these solutions always showed a strong band near 1660 cm^{-1}, suggesting $KAlH_4$. Addition of a large excess of dry ether to the diglyme washings from preparation 2 precipitated approximately 1.7 g of a white solid, shown to be $KAlH_4$ from its X-ray powder pattern.

A preparation similar to no. 4 but with K:Al = 2.5:1 (amounts used: K metal, 25.68 g, 0.658 g-atom; Al metal, 7.06 g, 0.262 g-atom; toluene, 136 ml) gave a product which appeared to be the purest K_3AlH_6 sample, with K:Al:H = 3.05:1.00:5.88. The strongest lines of KH in the X-ray powder pattern appeared only very weakly, the remainder being identical with the pattern published[7] for K_3AlH_6. Preparations at temperatures above 180° gave purer final products but the associated green color of the solid was deeper and required prolonged diglyme washing for its removal. The final product obtained was a pyrophoric, gray solid, insoluble in THF, diglyme, ether, benzene, and toluene.

Lithium Hexahydridoaluminate, Li_3AlH_6.—Since the melting point of metallic lithium is considerably higher than that of sodium or of potassium, in attempting two syntheses directly from the metal the Li–Al mixture in toluene was heated above 185° and stirred vigorously for 1 hr to form a good lithium dispersion before the system was pressurized; otherwise the same procedure was adopted as for Na_3AlH_6. (See Table II.) In both instances the products were shown by their X-ray powder patterns to be mixtures of LiH and Al powder.

TABLE II

EXPERIMENTAL CONDITIONS INVESTIGATED IN THE PREPARATION OF Li_3AlH_6 FROM LITHIUM DISPERSION

Expt no.	Amt, g		Li:Al g-atom ratio	Amt of toluene, ml	Reaction conditions
	Li	Al			
1	4.445	5.760	3:1	105	195° for 24 hr at 4000 psi
2	5.634	7.301	3:1	135	225° for 24 hr at 4000 psi, reduced to 160° for 24 hr, finally to 90° for 24 hr

The synthesis of Li_3AlH_6 was then attempted from lithium hydride. (See Table III.) In all of these experiments the aluminum powder was activated beforehand using the Ziegler procedure and the amount estimated so as to provide an excess for soluble $LiAlH_4$ to be obtained as the by-product. In all reactions 2 ml of triethylaluminum/100 ml of diluent was added as catalyst.

TABLE III

EXPERIMENTAL CONDITIONS INVESTIGATED IN THE PREPARATION OF Li_3AlH_6 FROM LITHIUM HYDRIDE

Expt no.	Amt of 50% LiH, g	Approx wt of Al, g	Li:Al	Vol of diluent	Reaction conditions
3	10.075	6.1	2.79:1	200 ml of THF	80 hr at 95°
4	6.698	3.9	2.89:1	110 ml of THF	18 hr at 95°, then 150° for 24 hr
5	9.746	5.7	2.88:1	135 ml of $(C_2H_5)_2O$	16 hr at 95°, then 7 hr at 135°, finally 17 hr at 150°
6	13.24	7.7	2.89:1	165 ml of $N(C_2H_5)_3$	18 hr at 95°, then 50 hr at 140°

The results of the examination of the products of these reactions are shown in Table IV.

Reduction Reactions Using K_3AlH_6. A. Benzophenone.—A 25-ml aliquot of a benzophenone solution (2.417 g in 100 ml of dry ether) was stirred for 1.5 hr in the drybox with excess (0.646 g) finely powdered K_3AlH_6. The mixture was then carefully hydrolyzed and the residue was dissolved in sulfuric acid. The ether layer was separated and dried over anhydrous magnesium sulfate. A portion of this solution was shown by gas chromatography at 200° on 4-ft Carbowax columns to contain mainly unchanged benzophenone with approximately 10% benzhydrol.

B. Tri-*n*-butyltin Chloride.—Tri-*n*-butyltin chloride (10.627 g) was dissolved in ~50 ml of dry ether, the solution added slowly to a suspension of 7.1 g of K_3AlH_6 in dry ether, and the mixture stirred under nitrogen for 25 hr. At the end of this time, the mixture was filtered. The filtrate showed an intense absorption near 1805 cm^{-1}, characteristic of the Sn–H stretching frequency. Gas chromatography at 190° with an SE 30 column gave no evidence for the presence of more than one component.

Reaction of Na_3AlH_6 with Magnesium Chloride in Tetrahydrofuran.—A. A 100-ml aliquot of 0.406 *M* magnesium chloride in THF[12] was added to a 2.782-g (27.2-mmol) portion of finely ground Na_3AlH_6 and the mixture was refluxed under nitrogen for 7 days protected from light. The flask and contents were cooled to room temperature and the mixture was filtered. The gray residue was washed with 20 ml of dry THF and the washings were added to the filtrate. The residue was dried *in vacuo*. The solvent was evaporated from the filtrate *in vacuo* giving 5.2 g of a

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

TABLE IV

SUMMARY OF RESULTS OF ATTEMPTS TO PREPARE Li_3AlH_6 FROM LiH, Al, AND H_2

Residue			Filtrate			
Expt no.	Active hydrogen content	X-Ray	Active hydrogen content	Analysis	Infrared Al–H absorption	Yield of $LiAlH_4$,[a] %
3	High	LiH	High	Al:Li = 0.99:100	1690	~92
4	High	LiH	High	Al:Li = 0.98:100	1690	~95
5	High	LiH + Al	Moderate	35 mequiv of Li^+ total in filtrate	1740	~17
6	High	LiH + Al	None	No Li^+	None	0

[a] Based on Al metal converted.

colorless, crystalline solid. Found: Cl:Mg:Al:Na = 1.50:1.32:1.00:0.0. An X-ray powder pattern indicated that the product was best described as mainly $ClMgAlH_4 \cdot 4THF$ with the presence of a small amount of unreacted $MgCl_2$. Analysis of the gray residue revealed that, although containing active hydrogen, it was largely sodium chloride. Found: Na:Cl:Mg:Al = 6.82:4.50:1.58:1.00. The X-ray powder pattern confirmed the presence of a considerable quantity of sodium chloride and the presence of at least one other compound (unidentified) but no evidence for the presence of sodium hydride.

B. A 50-ml aliquot of 0.444 *M* magnesium chloride in THF was added to 6.217 g (61.0 mmol) of finely ground Na_3AlH_6; the mixture was refluxed 8 days and treated as before. The evaporated filtrate yielded 0.82 g of white crystals, shown by their X-ray powder pattern to be $NaAlH_4$ with negligible contamination. The powder pattern of the residue showed intense bands due to NaCl and Na_3AlH_6 and very weak bands of another component, having *d* values of 2.50, 2.34, 2.15, and 1.23 Å. The same *d* values were observed in the insoluble residue described in the previous experiment.

Results and Discussion

The synthesis of metal hexahydridoaluminates directly from the elements promises to be the most convenient and economic route to this important class of compounds. In addition to economics and convenience, the considerably higher thermal stabilities of the hexahydridoaluminates makes them more attractive than their tetrahydridoaluminate counterparts for many applications.

Details for the synthesis of Na_3AlH_6 from sodium, aluminum, and hydrogen have already been reported by us[3] and others.[4] Activation of aluminum powder is essential in direct synthetic procedures for the hydriding reaction to occur. Aluminum containing a small amount of titanium is known to operate effectively without other activation in the synthesis of triethylaluminum from aluminum, hydrogen, and ethylene, and it was hoped that this type of aluminum might function conveniently in reaction 3. Unfortunately, this source of aluminum yielded no Na_3AlH_6 in several attempted syntheses. Aluminum activated by the "Ziegler procedure" can be stored and protected under dry hexane for an indefinite period of time. Activation by this procedure, however, is time consuming and the resulting aluminum wet with $(C_2H_5)_2AlH$–hexane solution is consequently difficult to weigh accurately. It was found that aluminum powder was simply and effectively activated by rapid stirring with a 1.5% solution of triethylaluminum in toluene,[5] thus avoiding an inconvenient ball-milling procedure reported earlier by Russian workers.[13,14]

The reaction of sodium with aluminum in 3:1 ratio in the presence of excess H_2 proceeds rapidly and completely at about 160°, but the exact purity of the Na_3AlH_6 product is not known. Recently, Zakharkin and coworkers reported[13] that Na_3AlH_6, obtained by the direct synthesis, is less thermally stable than the product obtained from reaction of sodium hydride and sodium tetrahydridoaluminate. They suggested that heavy-metal impurities and/or unreacted aluminum may be present in the former product which can catalyze the decomposition of the compound. In addition, a small quantity of a soluble aluminate species was always observed when the reaction product was washed with THF, following the synthesis. It is possible that this could arise in two ways. (1) The equilibrium in the system

$$2NaH + NaAlH_4 \rightleftharpoons Na_3AlH_6 \qquad (5)$$

does not lie completely to the right. (2) The triethylaluminum catalyst reacts with the product Na_3AlH_6 or the reactant NaH or Na under the conditions of the synthesis

$$Na_3AlH_6 + 2Al(C_6H_5)_3 \longrightarrow 3NaAlH_2(C_2H_5)_2{}^{14} \qquad (6)$$

$$4Al(C_2H_5)_3 + 3Na \longrightarrow 3NaAl(C_2H_5)_4 + Al^{9} \qquad (7)$$

$$NaAl(C_2H_5)_4 + NaAlH_4 \longrightarrow 2NaAlH_2(C_2H_5)_2{}^{9} \qquad (8)$$

$$Al(C_2H_5)_3 + NaH \longrightarrow NaAl(C_2H_5)_3H^{9} \qquad (9)$$

In considering equilibrium 5, it is interesting that Zakharkin and coworkers reported that, in the direct synthesis of $NaAlH_4$, the hexahydridoaluminate Na_3AlH_6 is formed initially and that this reacts further with aluminum and hydrogen to give the product.[14] On the other hand, the same group reported that preparation of the hexahydridoaluminate from the tetrahydridoaluminate and sodium hydride requires an excess of $NaAlH_4$ to obtain a product of the highest purity.[14] In this respect, then, it is advantageous to employ a slightly greater than stoichiometric quantity of aluminum in the direct synthesis reaction effectively to increase the quantity of $NaAlH_4$ formed in the reaction mixture. The excess is easily removed later by THF washing of the product. In any event, the im-

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(13) V. V. Gavrilenko, G. A. Egorenko, L. M. Antipin, and L. I. Zakharkin, *Russ. J. Inorg. Chem.*, **12**, 317 (1967).

(14) L. I. Zakharkin, V. V. Gavrilenko, L. M. Antipin, and Y. J. Struchkov, *ibid.*, **12**, 607 (1967).

purity level was such that $NaAlH_4$ was not noted in the X-ray powder pattern.

It is noteworthy that the equilibrium (eq 10) apparently lies further to the left than in the corresponding sodium case.

$$2KH + KAlH_4 \rightleftharpoons K_3AlH_6 \qquad (10)$$

With the starting K:Al ratio at 3:1, the product always contained appreciable amounts of potassium hydride. The soluble by-product in this case was shown to be $KAlH_4$ on isolation. Increasing the reaction temperature apparently helped to displace the equilibrium further to the right. Only when the proportion of aluminum in the mixture was significantly increased (giving effectively excess $KAlH_4$) was K_3AlH_6 obtained without residual KH. The only previous report of K_3AlH_6 was that given by Chini.[6] From the quantities quoted in the experimental section of that paper, the compound he isolated necessarily contained excess potassium hydride. Also the compound was reported to be a green solid. K_3AlH_6 prepared by the direct synthesis was initially green in color; however, the color was removed by washing with diglyme or THF. When dried, K_3AlH_6 was a light gray powder.

The direct synthesis of Li_3AlH_6 presented a greater problem. Lithium metal or lithium hydride does not react with activated aluminum powder in toluene between 90 and 225° at hydrogen pressures up to 4000 psi. On the other hand, lithium hydride is known to react with hydrogen and activated aluminum powder in THF[9] to form $LiAlH_4$. In THF, either at 95 or 150°, $LiAlH_4$ was formed, but did not react with more LiH to form Li_3AlH_6. Neither did thermal decomposition of the $LiAlH_4$ occur at the higher temperature to form Li_3AlH_6. Zakharkin and coworkers reported that sodium hydride and sodium aluminum hydride react only very slowly forming Na_3AlH_6 when THF and diglyme are used as solvents.[14] These workers ascribed this phenomenon to Na_3AlH_6 coating the surface of the NaH, preventing further reaction. If this were the case, it is hardly likely that NaH and $NaAlH_4$ would react together in hydrocarbons[2] to form Na_3AlH_6 since all three compounds are totally insoluble. In tetrahydrofuran, the reaction of LiH with Al powder and H_2 proceeds only as far as the $LiAlH_4$ stage (in excellent yield). The lack of reaction between $LiAlH_4$ and LiH in tetrahydrofuran may be caused by the fact that the free energy for the reaction (eq 11) is insufficient to overcome the solvation of the $LiAlH_4$ by THF.

$$2LiH + LiAlH_4 \longrightarrow Li_3AlH_6 \qquad (11)$$

On the other hand, it is reasonable that this reaction proceeds to completion in the sodium and potassium cases due to the greater ionic character of these compounds and hence greater thermal stability of the products and ease of formation. The greater solvation by THF of $LiAlH_4$ as compared to that of $NaAlH_4$ and $KAlH_4$ is probably also an important consideration concerning the question as to why the reaction of LiH, Al, and H_2 in THF stops at the $LiAlH_4$ stage rather than proceeding further with additional LiH to form $LiAlH_6$. Alternatively, the lack of further reaction could be a property of the lithium hydride since Ehrlich reported that $LiAlH_4$ did not react with commerical LiH.[8] However, the LiH did readily react to form $LiAlH_4$; therefore it should not be resistant to further reaction. At present, the optimum synthesis for Li_3AlH_6 involves first the preparation of $LiAlH_4$ followed by reaction of unsolvated $LiAlH_4$ with LiH in toluene as described by Chini.[6]

The infrared spectra of both sodium and potassium hexahydridoaluminate display two moderately strong bands expected for an AlH_6^{3-} ion of O_h symmetry, centered around 1300 and 800 cm^{-1}. The higher energy band, which may be assigned to an asymmetric Al–H stretching mode, is of considerably lower frequency than the corresponding mode associated with the AlH_4^- ion—although the forms of these vibrations appear markedly different.[15] The frequency is also significantly different from that reported[8] for Li_3AlH_6 (1720 cm^{-1}). The 800-cm^{-1} band may be assigned to an Al–H deformation mode. These results are in agreement with an apparent generalization that the Al–H stretching frequency decreases with increasing coordination number about the aluminum atom.[16] The higher energy 3d orbitals on aluminum are necessarily utilized as the coordination number is increased, and the Al–H bond may be expected to be correspondingly weakened. This is perhaps somewhat surprising in view of the fact that the hexahydridoaluminates are more thermally stable than the tetrahydridoaluminates. The thermal stability of the hexahydridoaluminates may be a consequence of a more stable crystal lattice structure. If so, it is necessarily a substantial effect, since the heat of formation of Li_3AlH_6 from $LiAlH_4$ has been estimated[9] as exothermic by 159 kcal/mol.

Preliminary investigations were carried out using K_3AlH_6 as a reductant with benzophenone and tributyltin chloride. Although effective, its utility is obviously hindered by its extreme insolubility. The possibility of metathesis of Na_3AlH_6 with magnesium chloride in THF to form $Mg_3(AlH_6)_2$ was also examined, but the results proved rather inconclusive. Sodium chloride was positively identified as a product of the reaction, but the fate of the magnesium species was less clear. In one instance $ClMgAlH_4 \cdot 4THF$[17] was isolated from the filtrate and, on another occasion, $NaAlH_4$ was the soluble product. These results suggest that, in THF, Na_3AlH_6 exists in an equilibrium situation, as in eq 5, with the equilibrium lying slightly to the left and possibly being kinetically slow. This is also in agreement with the result from the attempted Soxhlet extraction of Na_3AlH_6. No sodium hydride was noted, however, suggesting that further reaction to

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[15] See, for example, K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

[16] H. Roszinsky, R. Dautel, and W. Zeil, *Z. Physik. Chem.* (Frankfurt), **36**, 26 (1963).

[17] E. C. Ashby, R. D. Schwartz, and B. D. James, unpublished work.

some species such as Na_2MgH_4 might be produced in such reactions. In fact, a few weak lines in the powder patterns of the insoluble residue were observed which could not be attributed to NaCl, Na_3AlH_6, or NaH.

$$3MgCl_2 + 2Na_3AlH_6 \longrightarrow 2ClMgAlH_4 + Na_2MgH_4 + 4NaCl \quad (12)$$

While further work is required to clarify these reactions, it appears that $Mg(AlH_6)_2$ is not formed exclusively, if at all.

The major problem with K_3AlH_6 is avoidance of contamination in the dry powder. One 20-g sample, which had been stored in a screw-top sample jar for several months, exploded violently as a surface layer of oxidized material was being removed with a metal spatula in a drybox. The compound should be stored under dry, inert diluent in a firmly stoppered flask, preferably in a drybox with a good atmosphere. Residual K_3AlH_6 should be destroyed if there is any doubt as to its purity. It is not clear how this danger arises. The synthetic procedure might leave a small percentage of unhydrided, dispersed metallic potassium which can then react with oxygen on long standing to form potassium superoxide. It is possible that the hydride then reacts with the superoxide under the influence of shock or local heating caused by the spatula.

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Some Properties of Potassium Hexafluoronickelates(III) and -(IV). Absorption Spectra of Nickel(III) and -(IV) in Hydrogen Fluoride Solutions[1a]

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Visible and near-ultraviolet absorption spectra have been obtained for K_3NiF_6, K_2NiF_6, and solutions of K_2NiF_6 in hydrogen fluoride. Spectra of the solutions are shown at several stages during the reduction of nickel(IV) to nickel(III) and -(II). Nickel(III) and -(IV) species have also been produced by anodic oxidation of nickel metal in hydrogen fluoride solutions. The highly reactive species may be intermediates in the fluorination of organic compounds by the Simons process, since nickel anodes are used in Simons electrolysis cells. Infrared spectra of K_3NiF_6, K_2NiF_6, and solid phases from the nickel solutions are reported. Oxygen is shown to be the chief gaseous product in hydrolysis reactions of the complex salts.

Introduction

It has been shown recently that the reaction of Na_2PrF_6 with hydrogen fluoride yields praseodymium tetrafluoride,[2,3] although the tetrafluoride cannot be obtained by direct fluorination of praseodymium trifluoride. We have studied the effect of hydrogen fluoride on the complex salts K_2NiF_6 and K_3NiF_6 and found that the first salt dissolves in this solvent, forming red solutions of nickel(IV), whereas the second partially disproportionates to nickel(II) and -(IV). A very reactive brown solid is formed in the reaction of K_3NiF_6 with liquid hydrogen fluoride, and a similar product is formed in the reduction of nickel(IV) solutions. Some spectral and chemical properties of the brown phase, the potassium hexafluoronickelate salts, and nickel(III) and -(IV) solutions are reported in the present article. It is shown that nickel(III) and -(IV) species can be formed by anodic oxidation of nickel metal in hydrogen fluoride solutions.

Experimental Section

Preparation of Complex Salts.—K_2NiF_6 and K_3NiF_6 were prepared by a modification of the method of Klemm and Huss[4] from 2:1 and 3:1 molar mixtures of potassium chloride and nickel dichloride. Potassium chloride (Baker and Adamson, reagent grade) was dried at 120° in air and nickel dichloride (Alfa Inorganics, reagent grade) was dried at 275° in an atmosphere of nitrogen and carbon tetrachloride vapor. The mixtures were intimately ground in a drybox, heated in nickel boats for 3 hr at 300° with fluorine at 300 mm pressure, and then were reground and refluorinated for 6–8 hr at 1000 mm pressure. Red, crystalline K_2NiF_6 was obtained from the 2:1 mixtures. However, the products from the 3:1 mixtures were shown by infrared analyses to contain both nickel(III) and -(IV). The latter were heated to 450° under vacuum to decompose nickel(IV) and then were reground and refluorinated until violet, crystalline K_3NiF_6 was obtained.

Anal. Calcd for K_2NiF_6: K, 31.17; Ni, 23.40; F, 45.43. Found: K, 31.09, 31.78; Ni, 23.04, 23.61; F, 45.6, 46.1. Calcd for K_3NiF_6: K, 40.45; Ni, 20.24; F, 39.31. Found: K, 41.28, 40.96; Ni, 19.65, 19.82; F, 39.0, 39.3.

X-Ray powder patterns of both salts were obtained with a 114.59-mm diameter Phillips camera and copper $K\alpha$ radiation. These were indexed for face-centered cubic cells with lattice constants of 8.11 Å (K_2NiF_6) and 8.49 Å (K_3NiF_6). Similar constants have been reported previously by Klemm and coworkers

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(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) Honors Program Participant, Alfred University. (c) Honors Program Participant, Monmouth College.

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