partitioning of the products results, at least in part, from the observed phase separation as well as from the large difference in the condensation rates. On the other hand, it appears that when CH_3PCl_2 undergoes condensation with $CH_3P(O)(OCH_3)_2$, mixed products are formed. However, these molecular structures do not seem to correspond to regular alternation,[11] since more of the $CH_3P(O)<$ than the $CH_3P<$ moiety is consistently incorporated into the products formed during condensation.

Acknowledgment. We wish to thank the National Science Foundation (Grant GP-28698X) for partial financial support of this work.

Registry No. CH_3PCl_2, 676-83-5; $CH_3P(OCH_3)_2$, 20278-51-7; $CH_3P(OCH_3)Cl$, 51934-48-6; $CH_3OP(CH_3)P(O)(CH_3)P(O)(CH_3)OCH_3$, 51934-49-7; $(CH_3PO)_8$, 51934-50-0; CH_3Cl, 74-87-3; $CH_3P(O)Cl_2$, 676-97-1; $CH_3P(O)(OCH_3)_2$, 756-79-6.

[11] J. R. Van Wazer and S. H. Cook, *Inorg. Chem.*, 12, 909 (1973).

Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

Reaction of Alkali Metal Hydrides with Zinc Halides in Tetrahydrofuran. A Convenient and Economical Preparation of Zinc Hydride

JOHN J. WATKINS and E. C. ASHBY*

Received March 14, 1974

AIC40176O

A convenient and economical preparation of ZnH_2 is reported. The reaction of KH with $ZnCl_2$ in 1:2, 1:1, 2:1, and 3:1 molar ratios has been investigated. In these reactions zinc hydride and KCl are initially formed; however, the KCl reacts further with $ZnCl_2$ to form KZn_2Cl_5 and K_2ZnCl_4. The reaction of NaH with $ZnCl_2$ in 1:1 molar ratio forms only ZnH_2 and NaCl. Likewise, the reaction of LiH with $ZnBr_2$ and NaH with ZnI_2 in 2:1 molar ratio produced only ZnH_2 and the corresponding alkali metal halide. A more thermally stable form of ZnH_2, which is also more reactive than that prepared by any of the known methods, is produced in these reactions.

Introduction

We have been interested for some time in the preparation of complex metal hydrides where the central metal atom is other than boron or aluminum. Since $NaBH_4$ and $LiAlH_4$ have become such important reagents in synthetic organic chemistry, it would seem important to evaluate complex metal hydrides of other main-group elements for their possible stereoselective properties as reducing agents. In this connection we have reported the preparation of $KMgH_3$,[1] Li_2ZnH_4,[2] $LiCuH_2$,[3] and other complex metal hydrides by the reaction of the corresponding "ate" complex with $LiAlH_4$ (*e.g.*, eq 1 and 2).[2] This synthetic scheme has turned out to be quite good since the complex metal hydride is insoluble in ether and the lithium dimethyldihydridoaluminate is soluble. Thus, the separation of product from byproduct is easy and the reaction proceeds in quantitative yield.

$$2CH_3Li + (CH_3)_2Zn \rightarrow Li_2Zn(CH_3)_4 \quad (1)$$

$$Li_2Zn(CH_3)_4 + 2LiAlH_4 \xrightarrow{Et_2O} Li_2ZnH_4\downarrow + 2LiAl(CH_3)_2H_2 \quad (2)$$

It is clear that a more convenient and economical method for the preparation of these compounds would involve the reaction of an alkali metal hydride with the group II metal hydride (*e.g.*, eq 3). This scheme is reasonable since both $NaBH_4$ and $LiAlH_4$ can be prepared in this manner,[4,5] *i.e*

$$3NaH + ZnCl_2 \rightarrow NaZnH_3 + 2NaCl \quad (3)$$

$$4NaH + (CH_3O)_3B \rightarrow NaBH_4 + 3NaOCH_3 \quad (4)$$

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl \quad (5)$$

The purpose of this study, therefore, was to prepare complex metal hydrides of zinc (*e.g.*, $KZnH_3$, K_2ZnH_4, K_3ZnH_5, etc.) by the reaction of an alkali metal hydride with zinc chloride, bromide, or iodide. The hope was that even if such complex metal hydrides could not be prepared by this method, it may be possible to prepare ZnH_2 and/or HZnX compounds and, in addition, elucidate the chemistry of reactions of alkali metal hydrides with zinc halides.

Experimental Section

Apparatus. Reactions were performed under nitrogen using Schlenk tube techniques.[6] Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system.[7]

X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually.

Analytical Work. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[6] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration. Zinc in the presence of aluminum was determined by masking the aluminum with triethanolamine and titrating the zinc with EDTA. Zinc alone was determined by EDTA titration. Halide was determined by the Volhard procedure.

Materials. Potassium and sodium hydride were obtained from Alfa Inorganics as a slurry in mineral oil. Lithium hydride was prepared by hydrogenolysis of *tert*-butyllithium at 4000 psig for 24 hr. A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared in tetrahydrofuran in the usual manner. Anhydrous zinc chloride, bromide, and iodide were obtained from Fisher Scientific. Tetrahydrofuran (Fisher Certified reagent grade)

---

[1] E. C. Ashby, R. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, 92, 2182 (1970).

[2] E. C. Ashby and J. J. Watkins, *Inorg. Chem.*, 12, 2493 (1973).

[3] E. C. Ashby, T. Korenowski, and R. Schwartz, *J. Chem. Soc., Chem. Commun.*, in press.

[4] A. E. Finholt, A. C. Bond, and H. F. Schlesinger, *J. Amer. Chem. Soc.*, 69, 1199 (1947).

[5] H. F. Schlesinger, H. C. Brown, H. R. Hoekstra, and L. R. Rapp, *J. Amer. Chem. Soc.*, 75, 199 (1953).

[6] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[7] E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, 51, 65 (1974).

Table I. X-Ray Powder Patterns of Solids from the Reaction of Alkali Metal Hydrides with $ZnCl_2$

Solid from 1:1 reacn of KH with $ZnCl_2$		Solid from 1:2 reacn of KH with $ZnCl_2$		Solid from 2:1 reacn of KH with $ZnCl_2$		Solid from 3:1 reacn of KH with $ZnCl_2$		Solid from 1:1 reacn of KCl with $ZnCl_2$		Solid from reacn of KCl + $ZnCl_2$ filtrate with AlH_3		Solid from 1:1 reacn of NaH with $ZnCl_2$		$ZnCl_2$[a]		KCl[b]		KH[b]		Zn[b]		NaCl[b]	
d, Å	I/I_0[c]	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
5.06	m	6.10	w	3.12	vs	3.28	m	6.10	m	3.12	s	3.22	w	7.6	vs	3.146	s	3.30	vs	2.473	m	3.22	w
3.59	m	5.08	m	2.82	m	3.12	s	5.08	s	2.20	s	2.80	s	6.85	vs	2.224	ms	2.86	s	2.308	m	2.80	s
3.45	vw	4.44	w	2.60	m	2.84	m	4.44	m	1.80	m	2.45	ms	6.31	mw	1.816	m	2.02	s	2.091	s	1.98	s
3.28	vw	3.58	m	2.46	m	2.80	m	3.93	w	1.56	mw	2.31	ms	5.61	w	1.573	w	1.72	s	1.687	m	1.72	w
3.12	s	3.10	vw	2.20	s	2.60	m	3.57	s	1.395	mw	2.08	vs	5.10	vs	1.407	m	1.65	m	1.342	m	1.62	m
2.80	ms	2.89	w	2.08	m	2.46	m	3.40	w	1.273	w	1.98	ms	4.75	vw	1.284	m	1.43	m	1.332	m	1.401	w
2.65	w	2.82	ms	1.90	w	2.20	s	3.10	mw	1.101	vw	1.72	w	4.20	m	1.1126	w	1.31	m	1.237	w	1.256	mw
2.59	ms	2.67	w	1.80	m	2.09	m	2.98	w	1.041	w	1.68	m	4.04	s	1.049	w	1.28	m	1.173	m		
2.44	ms	2.60	ms	1.68	w	2.00	m	2.87	m	0.987	w	1.62	m	3.77	mw	0.9951	w	1.17	m	1.154	w		
2.21	s	2.53	w	1.62	vw	1.90	w	2.67	ms	0.942	w	1.401	w	3.61	s	0.9486	w	1.10	m	1.124	w		
2.01	w	2.46	ms	1.56	mw	1.80	m	2.53	m	0.866	vw	1.333	m	3.31	m	0.9083	vw	1.01	w	1.091	w		
1.90	mw	2.33	w	1.46	m	1.71	m	2.40	w	0.837	vw	1.321	m	3.22	mw	0.8727	w			1.046	w		
1.80	m	2.29	w	1.395	m	1.68	w	2.33	mw			1.256	mw	3.12	s	0.8410	w						
1.71	w	2.25	w	1.360	w	1.64	w	2.25	mw			1.230	w	2.99	w								
1.62	mw	2.08	ms	1.33	w	1.56	mw	2.14	mw			1.169	m	2.95	m								
1.56	mw	1.90	m	1.329	w	1.48	m	2.07	mw			1.148	mw	2.84	w								
1.47	m	1.86	w	1.169	w	1.40	m	1.94	w			1.119	m	2.76	mw								
1.40	m	1.81	vw	1.119	w	1.30	w	1.87	m			1.086	w	2.58	w								
1.378	vw	1.68	w	1.09	w	1.276	m	1.83	mw			1.040	w	2.52	w								
1.280	m	1.62	mw			1.170	w	1.78	w			0.941	w	2.49	w								
1.109	w	1.475	ms			1.109	w	1.70	w					2.45	mw								
1.091	vw	1.370	m			1.043	mw	1.65	w					2.36	s								
1.045	w	1.335	w			0.991	mw	1.57	w					2.25	vw								
1.011	vw	1.329	w					1.54	w					2.18	vw								
0.946	w	1.169	w					1.50	w					2.03	s								
0.939	vw	1.119	w					1.47	w					1.96	w								
0.905	w	1.09	w					1.44	vw					1.88	mw								
0.871	w													1.82	ms								
0.840	w													1.77	ms								
														1.73	ms								

[a] Sample obtained by stripping a THF solution of $ZnCl_2$ to dryness. [b] ASTM file. [c] Key: w, weak; m, medium; s, strong; v, very; d, diffused.

was distilled under nitrogen over $NaAlH_4$. Alane was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF. Li_2SO_4 was removed by filtration and a lithium-free solution of AlH_3 in THF was obtained.[8]

Potassium, sodium, and lithium hydride were used as a slurry in THF. Each slurry was prepared by washing the respective hydride several times with generous portions of benzene and then several times with THF to remove soluble impurities. The resulting solid, while still under THF, was transferred to a round-bottom flask and more THF was added.

Zinc chloride was fused under vacuum in order to make it anhydrous prior to dissolving in THF. Zinc bromide and iodide were sublimed under vacuum prior to dissolving in THF. The final zinc halide solutions were prepared by stirring the dried zinc halide with THF overnight and filtering the next morning. The zinc iodide solution was stored in the dark.

Reaction of KH with $ZnCl_2$ in THF. (a) **Reaction of KH with $ZnCl_2$ in 1:1 Molar Ratio.** Potassium hydride slurry (5 mmol) in THF was added to 5 mmol of $ZnCl_2$ in THF. A solid remained during the entire reaction period. After 2 days of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. An analysis of the filtrate revealed that it contained K, Zn, Cl, and H in molar ratios of 1.01:2.00:4.91:0.00. The filtrate contained 1.71 mmol of the starting zinc. An analysis of the solid revealed that it contained K, Zn, Cl, and H in molar ratios of 1.28:1.00:1.71:1.51. The solid contained 3.33 mmol of the starting zinc. The X-ray powder diffraction pattern of the solid is given in Table I.

(b) **Reaction of KH with $ZnCl_2$ in 1:2 Molar Ratio.** Potassium hydride slurry (5 mmol) in THF was added to 10 mmol of $ZnCl_2$ in THF. A solid remained during the entire reaction period. After 24 hr of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. Analysis of the filtrate revealed that it contained K, Zn, Cl, and H in molar ratios of 0.29:1.00:2.27:0.00. The filtrate contained 5.86 mmol of the starting zinc. Analysis of the solid revealed that it contained K, Zn, Cl, and H in molar ratios of 0.82:1.00:1.62:1.19. The solid contained 4.20 mmol of the starting zinc. The X-ray powder diffraction pattern of the solid is given in Table I.

(c) **Reaction of KH with $ZnCl_2$ in 2:1 Molar Ratio.** Potassium hydride slurry (10 mmol) in THF was added to 5 mmol of $ZnCl_2$ in THF. A solid remained during the entire reaction period. After 2 days of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. Analysis of the filtrate showed that it contained none of the starting zinc. Analysis of the solid showed that it contained K, Zn, Cl, and H in molar ratios of 3.08:1.00:1.94:2.97. The solid contained all the starting zinc. Its X-ray powder diffraction pattern is shown in Table I.

Reaction of KCl with $ZnCl_2$ in 1:1 Molar Ratio in THF. A 1.1250-g (15.09-mmol) amount of dry KCl was placed in a 250-ml round-bottom flask and 80 ml of THF was added. $ZnCl_2$ (15.09 mmol) in THF was then added. The mixture was stirred for 4 days, during which time a white solid was always present. The mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. An analysis of the filtrate showed that it contained K, Zn, and Cl in molar ratios of 1.06:2.00:4.94. The filtrate contained 10.06 mmol of the starting zinc. Analysis of the solid showed that it contained K, Zn, and Cl in molar ratios of 1.96:1.00:3.94. The solid contained 5.05 mmol of the starting zinc. The X-ray powder pattern of the solid is shown in Table I.

Reaction of AlH_3 with the Filtrate from the Reaction of KCl with $ZnCl_2$ in THF. Alane in THF (20 mmol) was added to the filtrate from the reaction of KCl with $ZnCl_2$ (analysis indicated KZn_2Cl_5). A white precipitate appeared immediately. This slurry was stirred for 1 hr, and then the solid was separated by filtration. The solid was dried under vacuum at room temperature. Analysis of the filtrate showed it to contain K, Zn, Al, Cl, and H in molar ratios of 0.00:0.00:1.00:1.08:2.07. The filtrate contained all of the aluminum. An analysis of the solid showed that it contained K, Zn, Cl, H, and Al in molar ratios of 0.46:1.00:0.52:2.00:0.00. The solid contained all the potassium and zinc. The X-ray powder pattern of the solid is shown in Table I.

Reaction of NaH with $ZnCl_2$ in 1:1 Molar Ratio in THF. Sodium hydride slurry (10 mmol) in THF was added to 10 mmol of $ZnCl_2$ in THF. A solid remained during the entire reaction period. After 1 day of stirring the mixture was separated by filtration. The solid had turned black while being stirred overnight. The solid was dried under vacuum at room temperature. Analysis of the filtrate showed that it contained Na, Zn, Cl, and H in molar ratios of 0.00:1.00:1.96:0.00. The filtrate contained 5.12 mmol of the starting zinc. Analysis of the solid showed that it contained Na, Zn, Cl, and H in molar ratios of 1.94:1.00:1.97:1.27. The solid contained 4.98 mmol of the starting zinc. The X-ray powder pattern of the solid is shown in Table I.

Table II. X-Ray Powder Patterns of Solids from the Reaction of Alkali Metal Hydrides with $ZnBr_2$ and ZnI_2

ZnH_2 from 2:1 reacn of LiH with $ZnBr_2$		ZnH_2 from 2:1 reacn of NaH with ZnI_2		ZnH_2[a] from reacn of $LiAlH_4$ with $(C_2H_5)_2Zn$ in diethyl ether		ZnH_2[b] from reacn of $LiAlH_4$ with $(CH_3)_2Zn$ in diethyl ether	
d, Å	I/I_0[c]	*d*, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
4.90	w	4.90	w	4.51	vw	6.27	w
3.79	w	3.79	w	4.23	s	4.50	m
2.82	s	2.82	s	3.80	vw	4.16	m
2.60	s	2.60	s	3.40	m	3.79	m
2.46	s	2.46	s	2.97	vw	3.27	w
2.29	m	2.29	m	2.828	vw	3.12	m
2.08	s	2.08	s	2.608	w	2.94	w
1.90	ms	1.90	ms	2.468	vw	2.83	w
1.68	m	1.68	m	2.387	m	2.61	vw
1.62	ms	1.62	ms	2.290	m	2.50	w
1.475	s	1.475	s	2.225	m	2.40	w
1.370	ms	1.370	ms	2.135	w	2.29	w
1.335	m	1.335	m	2.085	w	2.23	m
1.329	m	1.329	m	2.107	vw	2.18	m
1.300	w	1.300	w	1.905	w	2.14	vvw
1.234	w	1.234	w	1.764	w	2.08	m
1.169	m	1.169	m	1.688	vw	2.02	vw
1.150	w	1.150	w	1.630	vw	1.98	vw
1.119	m	1.119	m	1.562	vw	1.90	vw
1.09	m	1.09	m	1.486	vw	1.77	w
1.04	mw	1.04	mw	1.464	vw	1.63	vvw
1.013	mw	1.013	mw	1.416	vw	1.61	vvw
0.974	mw	0.974	mw	1.336	vw	1.57	vvw
				1.305	vw	1.51	w
				1.295	vw	1.42	vw
				1.259	vw	1.35	w
				1.219	vw		
				1.172	vw		
				1.157	vw		
				1.123	vw		

[a] See ref 5. [b] See ref 8. [c] Key: w, weak; m, medium; s, strong; v, very; d, diffused.

Reaction of LiH with $ZnBr_2$ in 2:1 Molar Ratio in THF. Lithium hydride slurry (5 mmol) in THF was added to 2.5 mmol of $ZnBr_2$ in THF. A solid remained during the entire reaction period. After 2 days of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. Analysis of the filtrate showed it to contain Li, Zn, Br, and H in molar ratios of 1.00:0.02:0.98:0.00. The filtrate contained 0.20 mmol of the starting zinc. Analysis of the solid showed it to contain Li, Zn, Br, and H in molar ratios of 0.03:1.00:0.04:1.89. The solid contained 2.41 mmol of the starting zinc. An X-ray powder diffraction pattern of the solid is shown in Table II.

Reaction of NaH with ZnI_2 in 2:1 Molar Ratio in THF. Sodium hydride slurry (20 mmol) in THF was added to 10 mmol of ZnI_2 in THF. A solid remained during the entire reaction period. After 2 days of stirring the mixture was separated by filtration. The resulting white solid was dried under vacuum at room temperature. An analysis of the filtrate showed it to contain Na, Zn, I, and H in molar ratios of 1.06:0.01:1.00:0.00. The filtrate contained 0.21 mmol of the starting zinc. Analysis of the solid showed it to contain Na, Zn, I, and H in molar ratios of 0.06:1.00:0.05:1.97. The solid contained 9.89 mmol of the starting zinc. The X-ray powder diffraction pattern of the solid is shown in Table II.

Reaction of NaH with ZnI_2 in 2:1 Molar Ratio in THF in the Presence of $(C_2H_5)_3Al$. A slurry of sodium hydride (15.192 mmol, 30.5 ml) in THF was added to 7.596 mmol (40 ml) of ZnI_2 in THF containing a few drops of $(C_2H_5)_3Al$. The mixture was stirred for a minute and then allowed to settle at room temperature. Analysis of a small portion (1.0 ml) of the clear liquid showed 1.932 mmol of the original zinc in solution. The mixture was stirred further and the

---

(8) H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, **88**, 1464 (1966).

clear supernatent liquid was analyzed for zinc at 30 min, 1 hr, 2 hr, and 5 hr intervals. After 5 hr the analysis of clear liquid showed only 0.94 mmol of the original zinc and it was noticed that the color of the reaction mixture gradually turned black. The reaction mixture was stirred for 20 hr and then filtered. Analysis of the filtrate showed it to contain Na, Zn, I, and H in molar ratios of 1.02:0.02:1.00:0.00 and the filtrate contained 0.30 mmol of the original zinc. Analysis of the black residue showed it to contain only zinc.

Results and Discussion

The reaction of LiH with $ZnBr_2$ and NaH with ZnI_2 in 2:1 molar ratio in THF proceeds according to eq 6 and 7. In

$$2LiH + ZnBr_2 \rightarrow 2LiBr + ZnH_2 \qquad (6)$$

$$2NaH + ZnI_2 \rightarrow 2NaI + ZnH_2 \qquad (7)$$

both cases the alkali metal halide remains in solution while the ZnH_2 precipitates. In both cases all of the alkali metal and halide are found in solution, while all of the zinc and active hydride precipitate from solution. The X-ray powder patterns of the ZnH_2 obtained from these two reactions are shown in Table II. Also given in Table II are the X-ray powder patterns of ZnH_2 prepared by the reaction of $LiAlH_4$ with $(C_2H_5)_2Zn$[9] and $(CH_3)_2Zn$.[10] The latter two patterns differ from one another, as well as from the pattern of ZnH_2 prepared in this study. However, the X-ray powder patterns of ZnH_2 prepared by the reaction of LiH with $ZnBr_2$ and NaH with ZnI_2 are identical. It has been our experience that ZnH_2 prepared by the reaction of $LiAlH_4$ with a dialkylzinc compound is usually amorphous, yielding an X-ray powder pattern with only two broad, diffuse lines, one at a *d* spacing of about 4.0 and the other at 2.5. Indeed, two reports in the recent literature[9,10] claim different X-ray powder patterns for ZnH_2 prepared by the latter method. In addition, ZnH_2 prepared by the Schlesinger method ($LiAlH_4 + R_2Zn$) turns black after a few days at room temperature and hydrolyzes slowly with water. The ZnH_2 prepared in the present study remains white for several weeks and hydrolyzes rapidly with water at room temperature, in addition to giving a distinct, reproducible powder pattern. However, it does decompose thermally at 90° to produce zinc metal and hydrogen.

The reactions of KH with $ZnCl_2$ in 1:2, 1:1, 2:1, and 3:1 molar ratios proceed according to eq 8–11. In the reaction

$$KH + 2ZnCl_2 \rightarrow {}^1/_3KZn_2Cl_5 + {}^1/_2ZnCl_2 + {}^1/_3K_2ZnCl_4\downarrow + {}^1/_2ZnH_2\downarrow \qquad (8)$$

$$2KH + ZnCl_2 \rightarrow {}^1/_6KZn_2Cl_5 + {}^1/_6K_2ZnCl_4\downarrow + {}^1/_2KCl\downarrow + {}^1/_2ZnH_2\downarrow \qquad (9)$$

$$2KH + ZnCl_2 \rightarrow 2KCl\downarrow + ZnH_2\downarrow \qquad (10)$$

$$3KH + ZnCl_2 \rightarrow KH\downarrow + 2KCl\downarrow + ZnH_2\downarrow \qquad (11)$$

of KH with $ZnCl_2$ in a 1:2 molar ratio, KZn_2Cl_5 remains in solution, while K_2ZnCl_4 and ZnH_2 precipitate from solution. This statement is supported by the fact that the filtrate from this reaction mixture contained K, Zn, Cl, and H in molar ratios of 0.29:1.00:2.27:0.00 and 58.6% of the starting zinc. A mixture of ${}^1/_3KZn_2Cl_5 + {}^1/_2ZnCl_2$ will have K, Zn, and Cl in molar ratios of 0.282:1.00:2.28 and will contain $(({}^3/_2 + {}^1/_2)/2)100 + 58.5\%$ of the starting zinc. The solid from the reaction mixture contained K, Zn, Cl, and H in molar ratios of 0.82:1.00:1.62:1.19. A mixture of ${}^1/_3K_2ZnCl_4 + {}^1/_2ZnH_2$ will have K, Zn, Cl, and H in molar ratios of 0.80:1.00:1.60:1.21. The X-ray powder diffraction pattern of the solid (shown in Table I) corresponds to a mixture of K_2ZnCl_4 and ZnH_2. The pattern for ZnH_2 in the mixture is the same as that for ZnH_2 produced by the reactions of LiH with $ZnBr_2$ and NaH with ZnI_2.

At this stage it might be interesting to consider the origin of the KZn_2Cl_5 found in the filtrate and the K_2ZnCl_4 found in the precipitate. The reaction between KCl and $ZnCl_2$ in a 1:1 molar ratio is shown in eq 12. The filtrate from this

$$KCl + ZnCl_2 \rightarrow {}^1/_3KZn_2Cl_5 + {}^1/_3K_2ZnCl_4 \qquad (12)$$

reaction mixture contains K, Zn, and Cl in molar ratios of 0.06:2.00:4.94 and two-thirds of the starting zinc. The solid contains K, Zn, and Cl in molar ratios of 1.96:1.00:3.94 and one-third of the starting zinc. The analytical data are consistent with the proposed reaction products. The solid product is not a physical mixture of KCl and $ZnCl_2$ in 2:1 ratio since the X-ray powder diffraction pattern (shown in Table I) of the product contains no lines common to either KCl or $ZnCl_2$. Thus, the solid product is presumed to be a true coordination compound (K_2ZnCl_4). The compound in the filtrate is represented as KZn_2Cl_5 for two reasons. First, KCl is not soluble in THF; therefore if it is in solution, it should be present as a complex. Second, if the remaining KCl is not complexed to $ZnCl_2$ as KZn_2Cl_5, one would expect to see all of the KCl react with half of the $ZnCl_2$ to give ${}^1/_2$ equiv of K_2ZnCl_4, instead of ${}^1/_3$ equiv. In the latter case, one would expect to find half the starting zinc in the filtrate and half in the solid. This is not what is observed and therefore KZn_2Cl_5 must be a true coordination complex.[11]

An opportunity was given for KZn_2Cl_5 to react with AlH_3 to form KZn_2H_5. The reaction of KZn_2Cl_5 with AlH_3 yielded a white solid containing K, Zn, Cl, H in molar ratios of 0.46:1.00:0.52:2.00. The X-ray powder pattern of the solid (shown in Table I) contains lines for KCl, and therefore it must be a mixture of KCl and ZnH_2. The ZnH_2 formed in this reaction did not show any distinct lines; therefore, it must be amorphous, as is the ZnH_2 that sometimes is produced from the reaction of $LiAlH_4$ with a dialkylzinc compound. The complex KZn_2Cl_5 evidently is not completely reduced to KZn_2H_5, but instead KCl and ZnH_2 are formed.

With this information, one can write a reasonable sequence (eq 13 and 14) for the reaction of KH with $ZnCl_2$ in 1:2

$$KH + 2ZnCl_2 \rightarrow KCl + {}^1/_2ZnH_2 + {}^3/_2ZnCl_2 \qquad (13)$$

$$KCl + ZnCl_2 \rightarrow {}^1/_3KZn_2Cl_5 + {}^1/_3K_2ZnCl_4 \qquad (14)$$

molar ratio. First, KH reacts with 2 equiv of $ZnCl_2$ to give 1 equiv of KCl, ${}^1/_2$ equiv of ZnH_2, and ${}^3/_2$ equiv of $ZnCl_2$. After this, the KCl reacts with 1 equiv of $ZnCl_2$ to give ${}^1/_3$ equiv each of KZn_2Cl_5 and K_2ZnCl_4.

The reactions of KH with $ZnCl_2$ in 1:1, 2:1, and 3:1 molar ratios are similar to the reaction just discussed. The first step is the maximum conversion of KH into KCl with the simultaneous formation of ZnH_2. Then, if any $ZnCl_2$ remains, KCl reacts with it to give KZn_2Cl_5 and K_2ZnCl_4. The total reactions as written in eq 9–11 are supported by analytical and X-ray powder diffraction data (Table I). It

---

(9) E. C. Ashby and R. G. Beach, *Inorg. Chem.*, 10, 2486 (1971).

(10) D. J. Shriver, G. J. Kubas, and J. A. Marshall, *J. Amer. Chem. Soc.*, 93, 5067 (1971).

(11) One of the reviewers suggested that K_2ZnCl_4 and KZn_2Cl_5 might be cocrystallates of KCl and $ZnCl_2$. In order to be able to establish the authenticity of $Zn_2Cl_5^-$ and $ZnCl_4^-$ anions, one would need the corresponding interatomic distances to support such a claim. These interatomic distances are not available at the present time. However, X-ray powder diffraction patterns are available and these powder patterns do show that the above compounds are not simple physical mixtures of KCl and $ZnCl_2$. Thus, if these compound are cocrystallates of KCl and $ZnCl_2$, it does seem more than just fortuitous that the analytical data would turn out as it did. For KZn_2Cl_5, the molar ratios of K, Zn, and Cl were 1.06:2.00:4.94. For K_2ZnCl_4, the molar ratios of K, Zn, Cl were 1.96:1.00:3.94.

is important to note that the ZnH_2 formed in all these reactions of KH with $ZnCl_2$ gives the same powder pattern as the ZnH_2 prepared by the reaction of LiH with $ZnBr_2$ and NaH with ZnI_2.

The reaction of NaH with $ZnCl_2$ in 1:1 molar ratio proceeds according to eq 15. The filtrate from this reaction

$$NaH + ZnCl_2 \rightarrow {}^1/_2ZnCl_2 + NaCl + {}^1/_2ZnH_2 \qquad (15)$$

contained Na, Zn, Cl, and H in molar ratios of 0.00:1.00:1.96:0.00 and half the starting zinc. The solid contained Na, Zn, Cl, and H in molar ratios of 1.94:1.00:1.97:1.27. The analytical data support the reaction as written and the X-ray powder pattern of the solid (Table I) contained lines only for NaCl and zinc metal. The powder pattern for ZnH_2 seen in the other cases was not observed. Also, this was the only reaction between an alkali metal hydride and zinc halide where the ZnH_2 produced turned black after just a few days. Why the ZnH_2 from this reaction behaved thus is unknown at present.

Several salient points about ZnH_2 are worth noting at this point. First, ZnH_2 is an isolable species which has moderate stability at or below room temperature. Second, ZnH_2 is the most thermally stable of the group IIb hydrides. Cadmium hydride[12,13] and mercury hydride[12] decompose rapidly even below 0°. Third, ZnH_2 exhibits ready reactivity in situations where the product is soluble.[12,14] The ZnH_2 prepared in this study remains stable longer and is more reactive than ZnH_2 prepared by the Schlesinger method. In view of point 3 we are presently studying ZnH_2 as a reducing agent toward organic substrates.[15]

Acknowledgment. We are indebted to the Office of Naval Research, under Contract No. N-14-67-A-0159-005, for support of this research.

Registry No. KH, 7693-26-7; KCl, 7447-40-7; AlH_3, 7784-21-6; NaH, 7646-69-7; LiH, 7580-67-8; ZnH_2, 14018-82-7; $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8; ZnI_2, 10139-47-6; KZn_2Cl_5, 52002-83-2.

(12) G. D. Barbaras, C. Dillard, A. E. Finholt, J. Wartick, K. E. Wilzbach, and H. F. Schlesinger, *J. Amer. Chem. Soc.*, 73, 4584 (1951).

(13) E. Wiberg and W. Henle, *Z. Naturforsch. B*, 6, 461 (1951).

(14) J. J. Watkins and E. C. Ashby, in press.

(15) Note Added in Proof. The reaction of NaH with ZnI_2 in 2:1 molar ratio in THF produces ZnH_2 in essentially quantitative yield when the reaction mixture is allowed to stir for 24–48 hr. It has been suggested that the reaction time might be reduced by using triethylaluminum as a catalyst to solubilize the NaH as $NaAl(C_2H_5)_3H$. This idea was tested by repeating the above reaction in the presence of a catalytic amount of triethylaluminum. The reaction time was reduced considerably in the initial stages of the reaction; however, at least 24 hr was required for complete reaction and the final product turned black during the reaction period unlike the uncatalyzed reaction.

Contribution from the Department of Chemistry,
University of North Dakota, Grand Forks, North Dakota 58201

A Study of the Products of the Reactions of Thiocyanate with Chromium(III) Ion in Water–Methanol Solvent Mixtures[1,2]

RICHARD J. BALTISBERGER,* CURTIS L. KNUDSON, and MARY F. ANDERSON[3]

Received July 11, 1973 AIC30512L

The thiocyanate anation of hexaaquochromium(III) and pentaaquomethanolchromium(III) ions in a water–methanol mixed solvent of 0.308 mol of methanol gives three products, isothiocyanatopentaaquochromium(III), and *cis*- and *trans*-isothiocyanatotetraaquomethanolchromium(III). The rate law was found to be: rate = $\{[Cr(OH_2)_6{}^{3+}]k_1 + (k_2 + k_3 + k_4)[Cr(OH_2)_5(CH_3OH)^{3+}]\}[SCN^-]$ where k_1 and k_2 correspond to pathways involving the formation of isothiocyanatopentaaquochromium(III) while k_3 and k_4 involve the formation of *trans*- and *cis*-isothiocyanatotetraaquomethanolchromium(III). The methanol and the trans water replacement accelerate the thiocyanate reaction in mixed solvents. Single site reactivities relative to the replacement of a single water on hexaaquochromium(III) at 30° in 0.1 *M* $HClO_4$ and 0.42 *M* ionic strength were found to be $k_2^*{:}k_1^* = 3.0$, $k_3^*{:}k_1^* = 2.0$, and $k_4^*{:}k_1^* = 1.0$. Solvent exchange equilibrium quotients and rate coefficients were measured for the products. The fluoride anation of hexaaquochromium(III) and pentaaquomethanolchromium(III) ion in 0.308 mol of methanol are also reported. In this case the products were not separated and analyzed.

Introduction

Previous kinetic studies of methanol-catalyzed association of chromium(III) with thiocyanate[4] and chloride[5] ions in water–methanol solvents have been limited to the measurement of the total concentration of products, CrX^{2+}. The slowness of the solvent exchange reaction[5]

$$CrO_6{}^{3+} + M \rightarrow CrO_5M^{3+} + O \qquad (1)$$

(O = H_2O, M = methanol)

makes it possible to identify two reactants, pentaaquomethanolchromium(III) and hexaaquochromium(III) ions, for the association reactions with various nucleophiles. In this work the thiocyanate–chromium(III) association was further studied in order to separate and measure the three possible products of the reactions

$$CrO_6{}^{3+} + N^- \xrightarrow{k_1} CrO_5N^{2+} + O \qquad (2)$$

$$CrO_5M^{3+} + N^- \xrightarrow{k_2} CrO_5N^{2+} + M \qquad (3)$$

$$CrO_5M^{3+} + N^- \xrightarrow{k_3} trans\text{-}CrO_4MN^{2+} + O \qquad (4)$$

$$CrO_5M^{3+} + N^- \xrightarrow{k_4} cis\text{-}CrO_4MN^{2+} + O \qquad (5)$$

(N^- = SCN^- coordinated through nitrogen, M = CH_3OH)

The interchange of solvent on the products of the thiocy-

---

(1) Based upon the M.S. Thesis of C. L. Knudson, University of North Dakota, May 1972.

(2) Part of this work was supported by a National Science Foundation Undergraduate Research Participation (U.R.P.) program and a Faculty Research Grant of the University of North Dakota.

(3) Undergraduate research participant from College of Saint Teresa, Winona, Minn.

(4) R. J. Baltisberger and J. V. Hanson, *Inorg. Chem.*, 9, 1573 (1970).

(5) R. J. Baltisberger and E. L. King, *J. Amer. Chem. Soc.*, 86, 795 (1964).