Acknowledgment.—This work was carried out for the Armstrong Cork Company, Lancaster, Pennsylvania, to whom we are indebted for long-term financial support.

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A New Method for the Preparation of B_6H_{10}

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Received August 4, 1964

The study of the chemistry of B_6H_{10} has been largely hampered by a lack of a suitable method of preparation, which we now report from reaction of $B_9H_{14}^-$ ion[1,2] with polyphosphoric acid.[3] The yield is only 2.5% based upon $B_9H_{14}^-$, and 14 mole % of the volatile hydrides. Nevertheless, $B_9H_{14}^-$ can be made available in large quantities, the volatile materials are easily separated by use of standard vacuum line techniques, and the reaction is very easily carried out.

The starting material, $(C_2H_5)_3NHB_9H_{14}$, prepared by reaction[2] of $B_{10}H_{14}$ with KOH, was allowed to react at room temperature with polyphosphoric acid in an evacuated flask. The volatile boranes, B_2H_6 (40 mole % yield), B_4H_{10} (37%), B_5H_{11} and B_5H_9 (10%), B_6H_{10} (14%), and traces of B_8H_{12} and $B_{10}H_{14}$, were caught in a series of traps at $-196°$ and then separated in a small number of fractional condensations. Only B_8H_{12} remained with the B_6H_{10}, but it decomposed quantitatively[4] when the B_6H_{10} was warmed to 0° for vapor pressure measurements. Separation of the B_6H_{10}–B_8H_{12} mixture below $-20°$ may also yield reasonable amounts of B_8H_{12} for further study. All hydrides were identified by mass spectrometric methods,[5] and, in addition, the B_6H_{10} was shown to have a vapor pressure of 7.2 mm. at 0°.

We believe that this method of preparation is more convenient, in spite of the low yield, than boride hydrolysis,[6,7] discharge methods,[8,9] or base-catalyzed conversion[10,11] from other hydrides.

Experimental

The $(C_2H_5)_3NHB_9H_{14}$ was prepared according to the procedure of Benjamin, Stafiej, and Takacs.[2] Solid $(C_2H_5)_3NHB_9H_{14}$ (1 g., 4.7 mmoles) was then added slowly *in vacuo* to polyphosphoric acid. This mixture was continuously evacuated and stirred with the use of an Asco Laboratory gland stirrer (Arthur F. Smith Co.) which was lubricated with No. 90 Kel-F grease. Volatile products were trapped in three successive U-tubes cooled to $-196°$ with liquid nitrogen. After 3 days the effervescence had stopped, and the gas pressure measured with a McLeod gauge had been constant for 1 day. The $B_{10}H_{14}$ was then separated from more volatile hydrides by passage of the mixture through a U-tube cooled to $-23°$. Three quick passes through a $-63°$ trap then retained B_6H_{10} and B_8H_{12}, but allowed the B_2H_6, B_4H_{10}, B_5H_{11}, and B_5H_9 to pass through. After the B_6H_{10}–B_8H_{12} mixture was raised to 0° for measurement of its vapor pressure, a considerable pressure of H_2 remained upon recooling to $-196°$. Since the remaining liquid was pure B_6H_{10}, we concluded that the B_8H_{12} had decomposed. The presence of B_8H_{12} before the sample was warmed to 0° was proved by the observation of its characteristic pattern[4] in the mass spectrum, including, in particular, the maximum peak at 93 and the parent peak at 100 mass units. After the sample had been warmed to 0° this pattern disappeared, leaving only the B_6H_{10} peaks in the mass spectrum. About 0.12 mole of B_6H_{10} remained. Yields of B_2H_6 (0.33 mmole), B_4H_{10} (0.31 mmole), and B_5H_{11} and B_5H_9 (0.08 mmole) were also determined after separation by fractional condensation. The vapor pressure of B_6H_{10} at 0° (7.2 mm.) is in agreement with the value given by Stock,[6] and the mass spectrum was found to be exactly like the published spectrum.[5]

Acknowledgment.—We acknowledge support of this research by the Office of Naval Research, the U. S. Army Research Office (Durham), and the Advanced Research Projects Agency.

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CONTRIBUTION FROM THE BUREAU OF MINES,
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The Nature of the Nickel Boride Formed by the Action of Sodium Borohydride on Nickel Salts

BY L. J. E. HOFER, J. F. SHULTZ, R. D. PANSON, AND R. B. ANDERSON

Received May 15, 1964

Investigations indicate that finely divided nickel boride is useful in catalysts[1,2] and fuel cell electrodes.[3] The action of solutions of sodium or potassium borohydride on solutions of nickel salts has been described as resulting in nickel boride, Ni_2B.[4,5] Though nickel boride formed by the action of sodium borohydride on nickel salts has received considerable attention as a catalyst, no structure study of this nickel boride has

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been reported. X-Ray powder diffraction analysis of the nickel boride is therefore indicated and is the subject of the present note.

Experimental

The nickel borides were made using analytical reagent nickel acetate and nickel chloride. A 2.5 *M* solution of sodium borohydride (0.1 l.) was added slowly with stirring to 1 l. of a 0.5 *M* solution of nickel salt. A black precipitate appeared immediately upon the first addition of the sodium borohydride solution. The precipitate was filtered and washed extensively with distilled water. Prolonged contact with water results in the formation of nickel hydroxide, $Ni(OH)_2$. The precipitate is therefore stored under alcohol. In some experiments as indicated in Table I the washing was performed with distilled water at 90°.

Specimens to be heat treated were placed in a tube furnace and protected by a stream of helium. When free of alcohol the specimens were heated to the indicated temperature (Table I) and maintained there for 18 hr. For chemical analysis the preparation was dried similarly at 100°.

TABLE I

PREPARATION OF NICKEL BORIDE[a] FROM NICKEL SALTS[b] AND SODIUM BOROHYDRIDE[c]

Nickel chloride		Nickel acetate	
Thermal treatment,[d] °C.	X-Ray powder diffraction anal.	Thermal treatment,[d] °C.	X-Ray powder diffraction anal.
None	Amorphous[e]	None	Amorphous[e]
250	Ni,[f] Ni_3B[g,h]	100	Amorphous[e]
500	Ni,[f] Ni_3B[g]	200	Amorphous[e]
750	Ni,[f] Ni_3B[g]	260	Ni_3B,[g] Ni[f,h]
None[i]	Ni,[f] amorphous[e]	350	Ni,[f] Ni_3B[g]
250[i]	Ni_3B,[g] Ni[f]		

[a] All preparations in this table represent duplicates or triplicates. [b] Aqueous 0.5 *M*. [c] Aqueous 2.5 *M*. [d] 18 hr. under helium stream at indicated temperature. [e] Broad reflection at ~2.03 Å. [f] Face-centered cubic nickel (O_h^5). [g] Isomorphous with cementite (D_{2h}^{16}) (see Table II). [h] Sample was hydrolyzed with 6 *N* HCl forming only hydrogen gas as determined by a mass spectrometer. [i] Sample was washed in water at 90° instead of 25°.

The X-ray powder diffraction patterns were taken in a 114.6-mm. diameter Debye–Scherrer camera using Fe Kα radiation as obtained from a sealed-off commercial X-ray tube equipped with an iron anode, beryllium windows, and manganese dioxide filters. The samples were mixed with a commercial nitrocellulose cement and extruded from a 0.4-mm. inside diameter stainless steel tube.

Two preparations formed from the nickel chloride were analyzed for nickel gravimetrically by the dimethylglyoxime method and for boron by alkalimetric titration of boric acid complexed with mannitol. The same two preparations were also analyzed by emission spectroscopy.

Results and Discussion

The nickel:boron ratio suggests the formula $Ni_{2.501}B$ but the nickel and boron content accounts for only 89.0% of the precipitate. The remaining 11.0% is probably water, in spite of drying at 100° for 24 hr., and sodium carbonate, as suggested by semiquantitative emission spectroscopy. The analyses of Paul, Buisson, and Joseph[5] leave up to 9% by weight of their preparations unreported and they suggest that this quantity may be the result of slight oxidation. As indicated in Table I, all the precipitates analyzable by X-ray powder diffraction analysis contained some metallic nickel so that the formula of the nickel boride phase should be lower than the indicated analysis and closer to the formula Ni_3B.

TABLE II

COMPARISON OF X-RAY POWDER DIFFRACTION DATA FOR ORTHORHOMBIC Ni_3B OF THE CEMENTITE TYPE

	Prepd. by sintering of elements at 900° (Fruchart)		Prepd. by pptn. from aq. soln. of $Ni(C_2H_3O_2)_2$ and $NaBH_4$ followed by tempering at 250° (present study)	
Indices	I/I_0	*d*, Å.[a]	I/I_0[b]	*d*, Å.[c]
002	10	3.307[d]	10	3.32
111	10	2.997[d]	10	3.00
020	10	2.611[d]	25	2.60
021	50	2.428	25	2.42
112	100	2.358	50	2.36
120	50	2.245	50	2.24 (b)
200	25	2.195	25	2.18 (b)
121	100	2.125	50	2.12
022	100	2.050	100	2.05
210	100	2.024	100	2.03
103	100	1.971	50	1.97
211	100	1.936	50	1.94
122	100	1.857	50	1.85 (b)
113	100	1.843		
202	10	1.829[d]		
212	50	1.727	35	1.73
023	50	1.685	25	1.68
004	25	1.654	10	1.658
130	75	1.618	35	1.615
131	25	1.572[d]		
222	10	1.498[d]	10	1.491
114	25	1.484[d]		
024	25	1.397[d]	10	1.401
311	25	1.379[d]		
223	10	1.337[d]		
124	10	1.331[d]		
312	100	1.297[d]	50	1.297
105	10	1.267[d]	50	1.247 (b)
232		1.261[d]		
140	100	1.252[d]		
115	50	1.231[d]	10	1.220
141		1.230[d]		
042	50	1.214[d]		
313	100	1.188[d]		
025	50	1.180[d]	25	1.178
224		1.179[d]		
142	25	1.171[d]		
233	100	1.160[d]	57	1.157
134		1.157[d]		
125	100	1.140[d]	50	1.138
330	100	1.120[d]	50	1.118
215	100	1.107[d]	25	1.107 (b)
331	50	1.105[d]	25	1.101 (b)
006		1.102[d]		
400	50	1.098[d]		
410	50	1.074[d]	25	1.074
411	100	1.061[d]	50	1.062 (b)
			10	1.039
			50	1.022 (b)
			25	0.999

[a] Fruchart's values are reduced to four significant figures. [b] Estimated intensities. Diffraction pattern was made on a 0.4-mm. diameter extruded specimen in a 114.6-mm. diameter Debye–Scherrer camera using Fe Kα radiation. [c] b indicates broad line. [d] Calculated interplanar spacings based on lattice parameters (Fruchart: $a_0 = 4.392$, $b_0 = 5.223$, $c_0 = 6.615$ Å.).

Excessive exposure of the precipitate to water leads to the formation of green nickel hydroxide, $Ni(OH)_2$, as identified by X-ray powder diffraction analysis. Less extensive washing leaves the precipitate associated with sodium carbonate or sodium hydroxide. This dilemma prevents the establishment of the composition of the boride by direct chemical means either at the stage of metal precipitation or at any successive stage.

X-Ray powder diffraction analyses proved that the initial precipitate as washed in cold water is amorphous. The diffraction pattern showed only a broad halo with a maximum corresponding to an interplanar spacing of ~2.03 Å. (see Table I). The breadth of the halo indicates a crystallite size of about 15 Å. diameter, a value which corresponds to a surface area of about 1200 m.^{2}/g.

Thermal treatment of the precipitate at 250° causes recrystallization to the Rundquist[6] and Fruchart[7] structure and metallic nickel (Table I).

X-Ray powder diffraction analysis gave the pattern reported in Table II, where it is compared with that of the Ni_3B of Fruchart.[7] The correspondence is so close even in the back reflection region that not only must the structures be the same but also the lattice parameters must correspond to within ±0.002 Å.

The recrystallization to the Rundquist[6] Ni_3B and metallic nickel also occurred at temperatures as high as 750°, and this confirms both Anderson and Kiessling's[8] and Rundquist's[6] observations that Ni_3B is stable at this temperature.

Diffraction analysis of the precipitate after washing at 80° shows the presence of metallic nickel in the face-centered cubic form as indicated by 111, 200, 220, 311, and 222 reflections. The broad halo at 203 Å. was still present. The precipitate at this stage must be regarded as metallic nickel accompanied by amorphous material.

Attempts to recrystallize the precipitate as prepared from the acetate at 200° and below failed.

Although the diffraction pattern of Bjurstrom's[9] Ni_2B with lattice parameters $a_0 = 4.980$ and $c_0 = 4.236$ Å. and space group $D_{4h}{}^{18}$ was sought, no trace was found in any of the present preparations.

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CONTRIBUTION FROM GOODRICH-GULF CHEMICALS, INC.,
AND THE B. F. GOODRICH RESEARCH CENTER,
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Preparation and X-Ray Data of Compounds Formed in Divalent Metal Chloride–Aluminum Chloride Fused Salt Systems

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Received May 25, 1964

The first compounds of $AlCl_3$ combined with divalent metallic chlorides (MCl_2) were apparently prepared by Baud[2] and characterized by thermal data. A more thorough study of fused salt systems of $AlCl_3$ with metallic chlorides was made by Kendall, Crittenden, and Miller,[3] who attempted to enumerate the main factors which governed compound formation and solubility behavior. Further general work seems to have been abandoned except for single systems. The $CdCl_2$–$AlCl_3$ system has been examined with X-ray techniques and a powder pattern listed.[4] Recently a complete structure determination of the compound $Co(AlCl_4)_2$ was reported.[5] The present work covers in detail the preparation, X-ray powder data, and a discussion of compounds in many additional systems.

TABLE I

FUSION RESULTS OF MIXED SYSTEMS

Divalent chloride fused with $AlCl_3$	Color of product	Type of compd.[c]
$MgCl_2$	White	1–2[a]
$CaCl_2$	White	Unknown
VCl_2	Violet	1–2[b]
$CrCl_2$	Violet	1–2[b]
$MnCl_2$	Pink	1–2[b]
$FeCl_2$	Yellow-green	1–2[b]
$CoCl_2$	Blue	1–2[a]
$NiCl_2$	Green	Unknown
$CuCl_2$	Yellow-brown	Unknown
$SrCl_2$	White	Unknown
$CdCl_2$	White	Probably 1–2
$BaCl_2$	White	Unknown
$SnCl_2$	White	Unknown
$PbCl_2$	White	Unknown
$PdCl_2$	Red	Unknown

[a] By chemical analysis. [b] From similarity of powder patterns. [c] Experiments with the chlorides of Be, Zn, Ti, Hg, and Pt showed no compound formation.

Experimental

Anhydrous salts were used for all preparations and commercial reagent grades were utilized when available Several compounds were prepared by thermal decomposition of hydrates. The X-ray powder diffraction pattern of each substance was taken, and the lines were compared with standard patterns. If any unexplained lines were present, the material was rejected or purified further. The aluminum chloride was not purified even though it was evident from thermal discoloration that small amounts of $FeCl_3$ (*ca.* 0.01%) or other decomposable salts were present. These slight impurities could in no manner affect the reported results.

Compounds were prepared by weighing out the initial reactants and inserting them in heavy-walled Pyrex glass tubes. All operations were performed in a glove box purged with dry nitrogen and dried with P_2O_5. The tubes were sealed and reaction was effected by heating over a flame or in a capped metal tube. Temperatures were always above the melting point of $AlCl_3$. In cases where compounds were formed, a clear solution was usually obtained but not always. Initial experiments were confined to compositions involving molar ratios of 1:2 for MCl_2:$AlCl_3$. Additional samples over the composition range of 1:3 to 3:1 were then chosen for each system. The X-ray results showed the same *d* spacings independent of the charged composition. However, they do not preclude other compounds in narrow composition ranges bordering the pure components.

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