87. *Some Reactions of Metal Borides.*

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The reactivity of the following metal borides towards a variety of reagents has been investigated: CaB_6, TiB_2, ZrB_2, VB_2, NbB_2, MoB, MoB_2, FeB_2, and NiB. Reaction occurred only with aqueous and non-aqueous acids. The products of these reactions are described, and the yields of reduction products from the acids discussed and compared with those obtained from similar reactions of some metal carbides.

The new compound dichlorodianilinenickel(II) was obtained from the reaction of nickel monoboride with anilinium chloride; the compound is a typical octahedral complex of nickel(II), being polymerized by means of chlorine bridges.

THE structures of metal borides are of considerable interest since they frequently contain boron atoms which are bound together in chains, sheets, or polyhedra, and metal atoms which are located in lattices similar to those of the parent metals. Despite these remarkable features, and their increasing industrial importance as refractory materials, comparatively little is known of their chemical reactions. Much of the work described in the older literature involves impure materials, and nearly all the later investigations concerned the production of boron hydrides by acid hydrolysis of the borides. The field has been reviewed.[1]

Metal borides are generally inert, but rapid reactions can be induced by three types of reagent: (i) concentrated oxidizing acids, particularly nitric and sulphuric acids; (ii) fused alkali salts of oxyacids, notably perchlorates and peroxides; (iii) the more electronegative elements such as fluorine or sulphur, but not oxygen. In the present work it was hoped to use metal borides as intermediates for the synthesis of novel polyboron compounds, and most of the reagents used were those which, on the basis of their known reactions with metals, might be expected to react with metal borides by removing the metal atoms. On this basis, aqueous mineral acids were an obvious choice, and the use of chlorosulphuric acid and fused amine hydrochlorides involved similar protonic systems in anhydrous conditions. An investigation of the reactions of some borides with glacial acetic acid will be described later.[2] Carbon monoxide, methyldichlorophosphine, phthalodinitrile, and *o*-cyanobenzamide were also employed in attempts to remove the metals as their zerovalent derivatives or as phthalocyanines. In addition, the action of aqueous and fused alkalies on borides was studied since this had been the subject of conflicting reports in the literature. Lastly, a report [3] of the recrystallization of calcium carbide from an alkali halide eutectic prompted an investigation of the behaviour of borides in similar media.

The reactivity of the borides towards these reagents is summarized in Table 1. The results exemplify the well-known inertness of metal borides, although some of the negative results are rather surprising. For instance, elemental nickel is very readily attacked by carbon monoxide or by methyldichlorophosphine, but nickel monoboride was completely unaffected by carbon monoxide at 20—350° or by methyldichlorophosphine in a sealed tube at 100°. Similarly, carbon monoxide did not react with chromium diboride at 250°/130 atm. or with iron diboride up to 350°. Again, many metals form phthalocyanines readily with phthalodinitrile or *o*-cyanobenzamide, but the only reaction observed with nickel monoboride or the diborides of vanadium, molybdenum, and iron was the formation of traces of metal-free phthalocyanine. This inertness is unexpected in view of the relatively low heats of formation of the borides (about 30 kcal./formula weight) [4] and must presumably be due to kinetic effects or the formation of protective layers.

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[1] Samsonov and Markovskii, *Uspekhi Khim.*, 1956, **25**, 190.

[2] Greenwood, Parish, and Thornton, to be published.

[3] Barber and Sloan, *J. Phys. Chem.*, 1961, **65**, 2026.

[4] Brewer and Haraldsen, *J. Electrochem. Soc.*, 1955, **102**, 399.

TABLE 1.

Reactivity of metal borides.

(+ = Reaction occurred; × = no reaction observed; — = reaction not attempted.)

Reagent	Boride									
	CaB_6	TiB_2	ZrB_2	VB_2	NbB_2	CrB_2	MoB	MoB_2	FeB_2	NiB
HNO_3 3M aq.	+	+	+	+	—	×	+	+	+	+
HCl 3M aq.	×	×	×	+	×	+	+	—	+	×
H_2SO_4 18M	+	+	+	+	—	+	+	+	+	+
H_2SO_4 2M aq.	×	×	×	+	—	+	×	+	+	×
$ClSO_3H$	+	—	×	+	+	+	+	—	—	—
$C_6H_5NH_3Cl$ anhydr.	—	—	—	—	—	—	+	+	+	+
C_5H_5NHCl anhydr.	—	—	—	—	—	+	—	—	—	+
CH_3PCl_2	—	—	—	—	—	—	—	—	—	×
CO	—	—	—	—	—	×	—	—	×	×
o-$C_6H_4(CN)_2$ or o-$C_6H_4(CN)\cdot CONH_2$	—	—	—	×	—	—	—	×	×	×
Alkali salts and hydroxides	×	×	×	×	—	×	×	×	—	×

Concentrated sulphuric acid was reduced to sulphur dioxide by all the borides; 2M-sulphuric acid reacted very slowly with the diborides of vanadium, chromium, molybdenum, and iron only. These reactions were not studied further. Ammonium hydroxide (*d* 0·880) had no effect on any of the borides, even at the boiling point, and sodium nitrate solution (2M) did not react with any of them. No reaction occurred when a concentrated aqueous solution of sodium hydroxide was heated with nickel monoboride or the diborides of titanium and chromium, and these borides did not react with or dissolve in the molten hydroxides of sodium and barium, or with fused alkali halides (NaCl, KCl, KF), cyanides (NaCN, KCN), or fused boric oxide.

The reactions of aqueous acids with the borides roughly parallel those with the corresponding metals. In no case were boron hydrides found, although 0·5—2% of diborane and tetraborane had been found[5] in hydrolyses with dilute hydrochloric acid. The products of those reactions with nitric and hydrochloric acids which were studied quantitatively are shown in Table 2, together with those from reactions with chlorosulphuric acid.

TABLE 2.

Products of the reactions of metal borides with acids.

Reagent	Boride	Major products			Minor products
HNO_3 (3M)	CaB_6	NO	Ca^{2+} aq.	$B(OH)_3$	N_2O, NO_2, CO
	TiB_2	NO, NO_2	TiO_2	$B(OH)_3$	
	ZrB_2	NO, NO_2	ZrO_2	$B(OH)_3$	
	VB_2	NO	VO^{2+} aq.	$B(OH)_3$	NO_2, H_2
	MoB	NO	Mo(V) aq.	$B(OH)_3$	NO_2
HCl (3M)	VB_2	H_2	VO^{2+} aq.	B	
	CrB_2	H_2	Cr^{3+} aq.	$B(OH)_3$	$B_2(OH)_4$?
	MoB	H_2	Mo(V) aq.	$B(OH)_3$	
$ClSO_3H$	CaB_6	SO_2, HCl, SO_2Cl_2	$CaSO_4$	$B(OH)_3$	
	VB_2	SO_2, HCl, Cl_2, SO_2Cl_2	VCl_4, SO_4^{2-}	$B(OH)_3$	V(IV)
	CrB_2	SO_2, HCl	Cr(III)	$B(OH)_3$	
	NbB_2	SO_2, HCl, Cl_2, SO_2Cl_2	Nb_2O_5	$B(OH)_3$	

The principal product of the reduction of nitric acid by metal borides is nitric oxide, which is accompanied by only small volumes of other nitrogen oxides and, in the reaction with vanadium diboride, hydrogen also. This behaviour contrasts with that of metal carbides in their reactions with 2M-nitric acid. Thus, the mono- and di-carbides of uranium each liberate nitric and nitrous oxides in the ratio 3·3 : 1,[6] and lanthanum sesqui- and di-carbides produce these gases in the ratios 0·68 : 1 and 0·21 : 1, respectively.[7] The

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[5] Markovskii and Bezruck, *Zhur. priklad. Khim.*, 1962, **35**, 491.

[6] Toogood, Thesis, Nottingham, 1962.

[7] Greenwood and Osborn, *J.*, 1961, 1775.

volumes of nitrogen oxides produced are almost always smaller than those calculated from the quantity of nitric acid required to oxidize the various borides. For example, the oxidation of one millimole of titanium diboride to titanium(IV) and boron(III) should produce 3·33 mmoles of nitric oxide, but only 1·93 mmoles were found. Similarly, 2·67 mmoles of nitric oxide should be produced by the oxidation of one millimole of molybdenum monoboride to molybdenum(V) and boron(III), but only 2·38 mmoles were found. Large deficiencies were also found in the yield of nitrogen oxides from the oxidation of the carbides of uranium.[6] The only exception to this pattern was the reaction of nitric acid with calcium hexaboride. Here, 10·5 mmoles of nitric oxide were evolved for each millimole of boride decomposed, but the formation of boron(III) from the B_6^{2-} ion should liberate only 6·67 mmoles. It is noteworthy that calcium carbide also behaves atypically in forming no nitrogen oxides when reacting with 2M-nitric acid, the C_2^{2-} ion being almost completely converted into acetylene.[7]

Dilute hydrochloric acid reacts with vanadium diboride, chromium diboride, and molybdenum monoboride to give hydrogen in each case, but there is an interesting variation in the actual amount of hydrogen evolved. Thus vanadium diboride yields vanadium(IV) and boron so that each millimole of boride should evolve 2 mmoles of hydrogen (observed 2·1 ± 0·1 mmoles). It is significant that no boric acid was detected in the products, since, if the boron had been oxidized to boron(III) in this way, 5 mmoles of hydrogen would have been expected. Molybdenum monoboride reacts slowly with dilute hydrochloric acid to give molybdenum(V), boric acid, and the stoicheiometric volume of hydrogen. Chromium diboride is oxidized completely by dilute hydrochloric acid to chromium(III) and a mixture of boric acid and a reducing boron species. The observed molar ratio of boron(III) to chromium(III) was 1·4 : 1, and if the lower oxidation state of boron is boron(II) then 1 mole of chromium diboride should liberate 4·2 mmoles of hydrogen (observed 4·0 ± 0·1 mmoles). Oxidation of all the boron, and also the chromium, to the oxidation state (III) would liberate 4·5 mmoles of hydrogen.

Attempts to isolate this lower-valent species failed. Similar observations had been made during the hydrolysis of magnesium diboride[8] and for some transition-element diborides.[9] The latter workers postulated the formation of boron monoxide (presumably present as diboronic acid) and were able to account for the deficiency in hydrogen evolution compared to that expected if boric acid had been formed.

Reaction between chlorosulphuric acid and metal borides yielded sulphur dioxide and hydrogen chloride as the principal gaseous products, together with appreciable quantities of chlorine and sulphuryl chloride, neither of which was formed in the reactions of chlorosulphuric acid with the carbides of calcium and lanthanum.[7] The reaction with chromium diboride liberated 1·96 mmoles of sulphur dioxide for each millimole of reacting boride, but oxidation to chromium(III) and boron(III) would be expected to produce 4·50 mmoles. In the other reactions which were studied, much more gas was evolved, and all the chlorosulphuric acid was decomposed.

The reaction of nickel monoboride and anilinium chloride produced the new, green compound dichlorodianilinenickel(II), identical with the compound produced by direct reaction between nickel(II) chloride and aniline. A brief report of an independent synthesis of this compound appeared during this investigation.[10] The colour of this material suggests that it contains octahedrally co-ordinated nickel, and this was confirmed by the diffuse-reflectance spectrum which showed bands at 23,400 cm.$^{-1}$ [$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$] and 13,900 cm.$^{-1}$ [$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$]; the third expected band [$^3A_{2g} \longrightarrow {}^3T_{2g}$], (about 8000 cm.$^{-1}$) was beyond the range of the instrument used. The magnetic moment of 3·43 B.M. at 20° also indicates octahedral co-ordination, which must be achieved by

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[8] Duhart, *Ann. Chim. (France)*, 1962, **7**, 369.

[9] Markovskii and Kaputovskaya, *Zhur. priklad. Khim.*, 1960, **33**, 569.

[10] Lumme and Peltonen, *Suomen Kem.*, 1963, **36**, *B*, 38, 43.

chlorine-bridging, as in dichlorodiaquonickel(II). This would account for the observed insolubility.

Similarly, pyridinium chloride reacted with chromium diboride and nickel monoboride, giving trichlorotripyridinechromium(III), dichlorotetrapyridinenickel(II), and pyridinium tetrachloronickelate(II), which were identified from their visible absorption spectra.

EXPERIMENTAL

Anilinium hydrochloride was prepared by the reaction of aniline and concentrated hydrochloric acid, and pyridinium hydrochloride by passing gaseous hydrogen chloride into a solution of pyridine in toluene. Chlorosulphuric acid was purified by distillation. The metal borides were generously supplied by Borax Consolidated Limited, London, and by the General Electric Company, Schenectady, New York.

Standard vacuum-line procedures were used. All gas volumes refer to s.t.p. Hydrogen was measured in a Töpler pump. Condensable gaseous products were identified by infrared spectroscopy, using Perkin-Elmer 137 Infracord spectrophotometers with sodium chloride and potassium bromide optics. Sulphuryl chloride and vanadium tetrachloride were also identified by their infrared specta.

Diffuse-reflectance spectra were recorded by the use of a standard attachment to a Unicam S.P. 500 spectrophotometer. Bulk magnetic susceptibility measurement was by the Gouy method. Elemental analyses were carried out by Mr. W. A. Campbell in this Department by means of standard procedures.

Reactions with Nitric Acid.—Nitric acid reacted with all the borides studied except chromium diboride, which was only slowly attacked by boiling 15M-acid. A quantitative study was made of the reactions of 3M-acid with calcium hexaboride, the diborides of titanium, zirconium, and vanadium, and with molybdenum monoboride.

Calcium hexaboride (0·2112 g., 2·01 mmoles) was treated *in vacuo* with 3M-nitric acid (10 ml., 30 mmoles). Reaction was slow at room temperature, but faster at 80°, this temperature being maintained for 24 hr., after which the reaction had apparently finished. Nitric oxide (276 ml., 12·1 mmoles) was evolved, together with small quantities of nitrous oxide, nitrogen dioxide, and carbon dioxide, the last presumably originating from some carbide impurity. The liquid fraction contained calcium and boron in the atomic ratio 1 : 6, all the boron being found as boric acid. Some calcium hexaboride (0·0908 g., 0·86 mmole) did not react.

Titanium diboride (0·1961 g., 2·84 mmoles) was treated *in vacuo* with 3M-nitric acid (7 ml., 21·0 mmoles). A vigorous exothermic reaction occurred at once, becoming increasingly violent until, after 30 min., all the boride had reacted. Nitric oxide (123 ml., 5·48 mmoles) and nitrogen dioxide (26 ml., 1·16 mmoles) were evolved. All the boron was present in the colourless liquid fraction as boric acid, and the white solid residue was identified as titanium dioxide from its *X*-ray powder pattern.

Zirconium diboride (0·3040 g., 2·70 mmoles) was treated *in vacuo* with 3M-nitric acid (7 ml., 21·0 mmoles). Only a feeble reaction occurred at 25°, and after 48 hr. evolution of gas stopped. Nitric oxide (74 ml., 3·30 mmoles) and nitrogen dioxide (19 ml., 0·85 mmole) had been evolved, and boric acid (0·2997 g., 4·84 mmoles) was found in the colourless liquid fraction. The grey residue was believed to consist of zirconium dioxide and unreacted zirconium diboride.

Vanadium diboride (0·1960 g., 2·68 mmoles) was treated *in vacuo* with 3M-nitric acid (7 ml., 21·0 mmoles) for 24 hr. at 25°. A mild reaction produced hydrogen (35 ml., 1·6 mmoles), nitric oxide (40 ml., 1·8 mmoles), a trace of nitrogen dioxide, and a blue solution containing vanadyl ion and boric acid in the ratio 1 : 2. Some vanadium diboride (0·0799 g., 1·09 mmoles) remained.

Molybdenum monoboride (0·0987 g., 0·843 mmole) was treated *in vacuo* with 3M-nitric acid (7 ml., 21·0 mmoles) for 24 hr. at 25°. A vigorous reaction produced nitric oxide (45 ml., 2·01 mmoles), nitrogen dioxide (1 ml., 0·04 mmole), and a yellow-brown solution containing molybdenum(V) and borate in the molar ratio 1 : 1. Only a little solid remained (0·0042 g.).

Reactions with Hydrochloric Acid.—3M-Hydrochloric acid reacted only with the diborides of vanadium, chromium, and iron, and with molybdenum monoboride.

Vanadium diboride (0·1105 g., 1·51 mmoles) was treated *in vacuo* with 3M-hydrochloric acid (7 ml., 21·0 mmoles) at 25° for 24 hr. A slow reaction produced hydrogen (11 ml., 0·49 mmole) and a blue solution containing vanadyl ion, but no boron could be detected as borate. Some vanadium diboride (0·0964 g., 1·28 mmoles) remained.

Chromium diboride (0·0824 g., 1·11 mmoles) was treated *in vacuo* with 3M-hydrochloric acid (5 ml., 15·0 mmoles) at 25° for 30 hr. All the boride dissolved, hydrogen was evolved (99 ml., 4·4 mmoles), and a green solution was obtained containing chromium(III) and borate in the ratio 1 : 1·4 only. The solution showed reducing properties ($KMnO_4$) which were retained after the precipitation of chromium by aqueous sodium hydroxide. Attempts to identify the reducing species by infrared spectroscopy or to isolate it from the solution failed.

Molybdenum monoboride (0·1931 g., 1·81 mmoles) was treated *in vacuo* with 3M-hydrochloric acid (7 ml., 21·0 mmoles) at 80°. After 48 hr. reaction was complete and only hydrogen (16 ml., 0·71 mmole) had been evolved. The yellow-brown solution contained molybdenum(V) and boron, all of which was present as borate in the ratio 1 : 1. Some molybdenum monoboride (0·1762 g., 1·64 mmoles) remained unreacted.

Reactions with Chlorosulphuric Acid.—All reactions were carried out in evacuated sealed tubes at 140° for 7 days. A control pyrolysis of the acid showed that it is not significantly decomposed by this treatment. Gaseous products were fractionated on a vacuum line before analysis.

Calcium hexaboride (0·1685 g., 1·60 mmoles) reacted with chlorosulphuric acid (3·744 g., 32·1 mmoles) to produce sulphur dioxide (394 ml., 17·6 mmoles), hydrogen chloride (140 ml., 6·23 mmoles), and sulphuryl chloride (1·759 g., 13·0 mmoles), together with calcium sulphate (0·2148 g., 1·58 mmoles) and boric acid (0·5845 g., 9·43 mmoles) in the molar ratio 1 : 6·0.

Vanadium diboride (0·0945 g., 1·29 mmoles) and chlorosulphuric acid (3·450 g., 29·6 mmoles) produced sulphur dioxide (372 ml., 16·6 mmoles), hydrogen chloride (185 ml., 8·26 mmoles), and chlorine (71 ml., 3·2 mmoles) as gaseous products. Distillation of the brown oily residue in an evacuated all-glass system produced sulphuryl chloride (0·9744 g., 7·23 mmoles) and vanadium tetrachloride (0·1862 g., 0·96 mmoles). A black tar remained undistilled, and extraction of this with hot water produced a pale blue acidic solution containing vanadyl and sulphate ions and boric acid.

Chromium diboride (0·1129 g., 1·53 mmoles) reacted with chlorosulphuric acid (3·532 g., 30·3 mmoles) to give, as gaseous products, hydrogen chloride (139 ml., 6·22 mmoles) and sulphur dioxide (67 ml., 3·0 mmoles). The liquid fraction was chlorosulphuric acid, and the brown solid residue, which was insoluble in benzene and carbon tetrachloride, was extracted with water to give a pale green solution containing chromium(III) (0·0806 g., 1·52 mmoles) and boric acid (0·0225 g., 0·38 mmole). After the hydrolysis there remained a brown putty-like material which contained 0·0224 g. of combined boron (2·04 mmoles).

Niobium diboride (0·0984 g., 0·86 mmole) and chlorosulphuric acid (3·027 g., 25·9 mmoles) produced sulphur dioxide (236 ml., 10·5 mmoles), hydrogen chloride (195 ml., 8·72 mmoles) and chlorine (39 ml., 1·7 mmoles). Sulphuryl chloride (0·935 g., 6·93 mmoles) was distilled from the yellow liquid fraction, leaving a little involatile brown oil. The white solid fraction (0·2188 g.) consisted of niobium pentoxide and boric acid in the molar ratio 1 : 3·6.

Reactions with Amine Hydrochlorides.—These reactions were all carried out under dry nitrogen at 200° for 48 hr.

Nickel monoboride (0·143 g., 2·06 mmoles) was heated with anilinium chloride (2·60 g., 18·9 mmoles) and aniline (2·5 ml., 38 mmoles). Extraction of the product with benzene gave diphenylamine (0·460 g., 2·73 mmoles) which was identified by mixed m. p. The remainder of the product was warmed with ethanol to remove the excess of anilinium chloride, and the residue was shaken with carbon tetrachloride. The resulting suspension of the complex was decanted from the excess of boride and filtered, yielding green crystals of *dichlorodianiline-nickel*(II) (0·236 g., 35% based on NiB) (Found: Cl, 21·1; Ni, 17·4. $NiCl_2,2PhNH_2$ requires Cl, 22·5%; Ni, 18·6). The appearance and spectrum of this material were identical with those of the compound obtained by direct reaction between alcoholic solutions of hexa-aquo-nickel(II) chloride and aniline (Found: Cl, 22·7%; Ni, 18·6). The diffuse-reflectance spectrum showed absorptions at 13,900 and 23,400 cm.$^{-1}$. The compound could be recrystallized only from aniline; in other solvents it either decomposed or was insoluble.

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