tion reaction takes place upon evacuation of the $PCl_3Br_{5.7}$ aggregate and not before.

The X-ray evidence unambiguously indicates that the mixed halide $PCl_{4.67}Br_{0.33}$ is a true monophasic crystal and not a microcrystalline mixture of the respective phosphorus pentahalides.

Acknowledgment.—The authors are indebted to Drs. Thomas DeVries and W. W. Brandt of the Chemistry Department, Purdue University, for microphotometer traces of the X-ray diagrams.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

A Kinetic Study of the Reaction of Decaborane with Alcohols

BY H. C. BEACHELL AND T. R. MEEKER[1]

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The reaction of decaborane with low molecular weight alcohols to yield borate esters and hydrogen has been found to be consistent with the general concepts of the absolute and statistical kinetic theories. Specific bimolecular rate constants, energies of activation and Arrhenius frequency factors are given for several alcohols and relative rate constants are given for the reaction in several solvents of varying dielectric constant. For the reaction involving primary alcohols, the observed increase in rate constant as the number of carbon atoms increased from two to five and the effect of the dielectric constant of the medium, was found to be consistent with the application of Kirkwood's formula to the absolute theory of reaction rates. It is shown that a reasonable correlation between the observed heats of activation with the energy of the boron hydrogen bond and with the ionization energies of the alcohols is possible, thereby indicating that the boron hydrogen bond and the electrons on the alcohol are probably involved in the rate-determining step. The relative values of the entropies of activation are found to be in reasonable accord with the concept of a decrease in activation entropy with increasing complexity of the molecules concerned. The existence of intermediates in the alcoholysis reaction was not shown by the kinetic data, so that the point of attack of the alcohol on the decaborane was not determined. The results did not lead to any information concerning the nature of the reaction course involved in the formation of products from the activated complex.

The chemistry of the boron hydrides has been of increasing interest in the past few years.[2] This work is an attempt to add to the knowledge of these compounds by a kinetic study of the reaction of decaborane with several representative alcohols. Some of the properties of the activated complex were deduced from a study of the influence of solvent character and of the alcohol nature on the rate constant. Heats of activation and frequency factors were obtained for several alcohols. Application of the generally accepted theories of chemical kinetics to the observations yielded a consistent interpretation of the results of the experimental work. In analogy with the reaction of the lower boron hydrides with alcohols,[2-4] decaborane reacted with alcohols[5] to form alkyl borates and hydrogen according to equation 1

$$30ROH + B_{10}H_{14} \longrightarrow 10B(OR)_3 + 22H_2 \quad (1)$$

This reaction was studied with a specific effort to obtain any information on a kinetic basis for the presence of intermediates, either of a substituted decaborane nature or of a substituted borine nature,[3,4] but there was no indication in the kinetic pattern that any of these were formed.

Experimental

Materials.—In this study decaborane of 98% purity was further purified by vacuum sublimation and by recrystallization from pentane and subsequent removal of the pentane by storing in a vacuum desiccator over $CaCl_2$ to protect from moisture. The melting point of decaborane purified by either method (99.5°) was found to agree well with the value found by Stock for carefully purified samples.[6] Storage of this material in an unevacuated desiccator resulted in an unexplained increase in the observed rate constant after a few days, so the purified product was stored under vacuum. Stock also observed a similar phenomenon in his samples.[6]

The alcohols and solvents used in this study were dried either with metallic calcium or with calcium sulfate and distilled twice from a dry flamed all glass distilling flask equipped with a Vigreux column, and small middle fractions were taken for the kinetic experiments. The higher boiling branched alcohols were distilled under reduced pressure from the same apparatus. The boiling points and refractive indices agreed with those listed in the literature.[7] All materials were stored in a desiccator and repurified once more near the end of a set of experiments and the kinetics results remeasured and compared with the previous runs.

Method.—The reaction of decaborane with alcohols was found to yield hydrogen and the corresponding borate ester in good yield, even in two cases where the alcoholysis of BCl_3 or B_2O_3 gave no borate esters.[8] The following yields based on equation 1 were reported to us by Schar[9]: *n*-propyl, 95%; *n*-butyl, 98%; *sec*-butyl, 93%; *t*-butyl, 85–90%; *t*-amyl, 92%. These values showed that equation 1 was followed and that the reaction, under our experimental conditions, was subject to only minor side reactions, if any. A check of the hydrogen liberated under experimental conditions was found to yield 95–100% of the amount calculated by this equation.

The rates of alcoholysis were measured by studying the rate of hydrogen evolution according to equation I. Several runs were made for *n*-butyl alcohol and decaborane with the decaborane at a concentration of about 0.1 mole/liter and the alcohol concentration at about 0.1 mole/liter (equimolar quantity) and at about 3.0 mole/liter (equivalent quantity). Both alcohol concentrations gave analogous bimolecular relative rate constants except for the dielectric effect described later. Since no evidence for any intermediates was obtained, it was assumed that the rate of decaborane disappearance was −1/22 of the rate of appearance of the hydrogen gas evolved.

The increase in hydrogen pressure was measured with a Barcroft–Warburg[10] apparatus consisting of a small mercury

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(1) Taken in part from the thesis submitted by Thrygve R. Meeker to the University of Delaware in partial fulfillment of requirements for the degree of Doctor of Philosophy.

(2) H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).

(3) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4020 (1933).

(4) A. B. Burg and F. G. A. Stone, *ibid.*, **75**, 228 (1953).

(5) W. H. Hill and M. S. Johnston, *Anal. Chem.*, **27**, 1300 (1955).

(6) A. Stock, K. Friederici and O. Priess, *Ber.*, **46**, 3353 (1913).

(7) "Beilstein's Handbuch der Organischen Chemie," Vierte Auflage, Erster Band (1918), Erstes Ergänzungswerk (1928), Zweites Ergänzungswerk (1941), Springer, Berlin.

(8) L. H. Thomas, *J. Chem. Soc.*, 823 (1946).

(9) Unpublished work by W. C. Schar of this department.

(10) "Laboratory Apparatus and Reagents," Edition of 1950, A. H. Thomas Company, Cat. 3603, page 360.

manometer equipped with a mercury leveling device and attached to the reaction vessels with ground glass joints. The constant temperature bath was regulated to within ±0.03° by a mercury thermoregulator and the temperature read to the nearest 0.01° with a thermometer standardized to the nearest 0.5°. The alcohol solvent mixtures were prepared by weight and the decaborane was weighed by difference directly into the reaction vessel. At the beginning of a run, a known volume of alcohol solvent mixture at recorded room temperature (23.0 ± 1.0°) was added to the reaction vessel, which was attached to the manometer and placed in the bath. The leveling device was adjusted so that the volume of the system remained constant and readings of the pressure change in cm. were made at frequent time intervals. From these data slopes were obtained graphically and by the method of averages. Since only the first 5 or 10% of the reaction was being studied, the measured slopes are initial slopes. In conjunction with the known gas volume and the temperature, values of the initial change of decaborane concentration with time were calculated from these gas evolution slopes. From a study of the rates obtained by changing the decaborane and the alcohol concentrations, the reaction was found to be first order with respect to each reactant. Hence, the rate constants were calculated from the formula

$$k = -(\mathrm{d}\,C_{B_{10}H_{14}}/\mathrm{d}t)_0/(C_{ROH_0}C_{B_{10}H_{14}})_0$$

By this method specific bimolecular rate constants (Table I) were determined at four temperatures and from the data Arrhenius activation energies and frequency factors were determined for the reaction of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl and *sec*-butyl alcohols with decaborane in benzene solution and for *n*-butyl alcohol in nitrobenzene solution. Relative rate constants for the reaction of *n*-butyl alcohol with decaborane in various solvents at 298.36°K. are given in Table II. Some additional relative rate constants of interest are summarized in Table III.

TABLE I

KINETIC CONSTANTS FOR THE ALCOHOLYSIS OF DECABORANE IN BENZENE SOLUTION

$k = A \text{ exp. } E_a/RT)^c$

Alcohol[a]	Specific rate constant k. (10^{-7} l. mole^{-1} sec.$^{-1}$)	Heat of activation Ea, kcal./mole	Frequency factor A (l. mole^{-1} sec.$^{-1}$)
Methyl	7.27 ± 0.15	31.6 ± 0.5	1.04×10^{17}
Ethyl	5.20 ± .15	25.7 ± .5	3.35×10^{12}
n-Propyl	5.35 ± .15	24.5 ± .5	4.67×10^{11}
Isopropyl	2.01 ± .15	15.9 ± .5	8.53×10^{4}
n-Butyl	6.70 ± .15	25.5 ± .5	3.45×10^{12}
Isobutyl	4.79 ± .15	20.7 ± .5	7.77×10^{8}
sec-Butyl	3.80 ± .15	16.3 ± .5	3.17×10^{6}
t-Butyl	0.09 ± .15	....	....
n-Butyl[b]	3.72 ± .15	24.1 ± .5	1.51×10^{11}

[a] Calculated on the basis of equation 1. [b] In nitrobenzene solution. [c] The rate constants measured at 298.36, 300.50, 303.05 and 305.36°K. were reproduced by the values of E_a and A in this table to 0.5×10^{-7} l. mole^{-1} sec.$^{-1}$ in all cases.

TABLE II

RELATIVE RATE CONSTANTS FOR THE REACTION OF *n*-BUTYL ALCOHOL WITH DECABORANE AT 25.20°

Solvent	Effect of solvent, D Relative k	D^{12} Solvent
Benzene	1.0	2.27
Carbon tetrachloride	0.9	2.3
Carbon disulfide	0.8	2.65
n-Heptane	0.5	4.0
Dimethylcellosolve	0.4	..
Cyclohexane	0.9	2.1
Toluene	1.0	2.3
Ethyl acetate	0.4	6.4
Dioxane	0.8	3.0
Tri-*n*-butylborate	0.9	..

TABLE III

MISCELLANEOUS RELATIVE RATE CONSTANTS

Alcohol	Solvent	Relative k	R D solvent	V^{10} alc. (cc./mole)
Benzyl	Benzene	1.2	2.28	103
n-Amyl	Carbon tetrachloride	1.1	2.30	109
Phenol	Ethyl acetate	0.05	6.4	88
t-Amyl	Ethyl acetate	0.03	6.4	109
3-Pental	Carbon tetrachloride	0.03	2.30	108
Water[b]	Ethyl acetate	1.4[a]	6.4	18
Deuterium oxide[b]	Ethyl acetate	1.5[a]	6.4	20

[a] Same as footnote *c* of Table I. [b] The case of water is not a second-order reaction and hence cannot be compared with the other reactions. These values only included to demonstrate the deuterium effect in the alcohol.

Results

Frost and Pearson[11] discuss the application of a calculation by Kirkwood[12] to chemical kinetics. The results of the calculation are given by the equation

$$\ln k = \ln k_0 - \left(\frac{N}{RT}\right)\left(\frac{D-1}{2D+1}\right)\left(\frac{u_A^2}{r_A^3} + \frac{u_B^2}{r_B^3} - \frac{u^2}{r^3\ddagger}\right) \quad (2)$$

In order to show that the results of this study are consistent with this equation, values of log k_0 were calculated from the rate constants reported in Table I and the relative dependence of the rate constant on the molar volume of the alcohol and the dielectric constant of the medium was shown in Tables II and III. These values of log k_0 were calculated with the aid of the following assumptions. The molar volume of the activated complex is assumed to be the sum of the molar volumes of the alcohol and the decarborane[13] and the dipole moment of the activated complex is assumed to be the vector sum of the dipole moments of the two reactants. This latter assumption requires only a knowledge of the angle between the two moments in the activated complex. The required u_A's were taken from the literature.[14,15] The moment of decaborane, u_B, has been determined by Laubengayer and Bottei.[16] The r_A and r_B were calculated from the molecular weights and the densities.[6,17–19] Since the alcohols vary considerably in dielectric constant, this quantity was calculated for the solutions in the following way. It was found empirically from data in tables[20] that for ethyl alcohol in benzene solution the dielectric constant of the solution is nearly a linear function of the weight per cent. ethanol over the range 0–50% ethanol. Assuming

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[11] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 130.

[12] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

[13] S. Glasstone, K. J. Laidler, H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 422.

[14] Appendix, Table B(4), *Trans. Faraday Soc.*, 30 (1934).

[15] Landolt-Börnstein, "Zahlenwerte und Functionen, Atom- und Molekularphysik," Sechste Auflage, I Band, 3 Teil, Molekeln II, Springer-Verlag, Berlin, 1951, pp. 415–417.

[16] A. W. Laubengayer and R. Bottei, THIS JOURNAL, **74**, 1618 (1952).

[17] "Handbook of Chemistry and Physics," Thirty-third Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1951, pp. 644–1203.

[18] "International Critical Tables," Vol. III, First Edition, McGraw-Hill Book Co., New York, N. Y., 1928, p. 28.

[19] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," 5 Auflage, I Band, Springer-Verlag, Berlin, 1923, pp. 368–455.

[20] Reference 18, Vol. VI, p. 100.

this relationship to hold for the other alcohols and using the D values of Morgan and Yager[21] for benzene and the primary alcohols and tables[22] for the other required values, the dielectric constants of the alcohol–benzene media were calculated.

With these results it was found that the relative magnitudes of the values of log k_0 were rather insensitive to the value of θ, but the value 44.5° gave the best agreement between the two log k_0 values for the reaction of *n*-butyl alcohol with decaborane in benzene and in nitrobenzene solvent. Therefore, this value of θ was used to calculate the following log k_0's[23]: methyl alcohol in benzene (−4.80), ethyl alcohol in benzene (−5.21), *n*-propyl alcohol in benzene (−5.27), isopropyl alcohol in benzene (−5.58), *n*-butyl alcohol in benzene (−5.22), isobutyl alcohol in benzene (−5.27), *sec*-butyl alcohol in benzene (−5.45) and *n*-butyl alcohol in nitrobenzene (−5.19). Since equation 2 was derived for external non-specific electrostatic effects only, it is not surprising to find that the log k_0 values found for methyl alcohol and the branched alcohols differ from those found for the primary alcohols. This follows from a discussion of the general decrease of the rate constant with increasing number of degrees of freedom engaged in the distribution of the energy involved in the activated complex.[24] Hence, above ethyl or *n*-propyl, the bonds (and consequently the relative number of degrees of vibrational freedom involved in the activated complex), seem to remain fairly constant, so that this effect for the primary alcohols should cause the rate constant to remain constant or at least decrease slowly as the number of atoms increases. It is therefore seen that, with the evidence presented, the effect of changing alcohol or solvent in the primary series with the exception of methyl can be explained on the basis of electrostatic contributions to the rate constant alone. Table II lists some relative rates showing the approximate effect of solvent dielectric constant on the rate constant. Table III lists some relative rates showing solvent effect and also the effect of molar volume (proportional to r^3_{A}). It may be seen that equation 2 accounts for the observations in the case of these rates.

In an effort to determine which bonds are broken in the rate-determining step, the rate constant for deuterodecaborane[25] was measured and compared to that for decaborane. It was found that the observed decrease of about 50% in the rate constant[26] could be satisfactorily explained on the basis of a change in activation energy for the reaction equal to the change in the energy of the boron hydrogen bond, assuming that this change would be approximately the same for decaborane as for the boron hydrogen diatomic molecule. (0.04 e.v. is equal to 0.9 kcal./mole,[27] while with E_{a} equal 25 kcal./mole, an increase of 0.3 kcal./mole in this quantity reduces the rate by a factor of about one half, as observed, if the Arrhenius frequency factor remains constant for the deuterated form.)[28] In the case of the alcohols the relative rate constants of water and deuterium oxide were obtained (Table III), and although it is suspected that this reaction proceeds by a slightly different course, it is supposed that the reaction scheme is similar enough to warrant the assumption that the same effect would be observed upon deuteration of the alcohols. It was observed that the rate constant for deuterium oxide was actually a little larger than that for water showing that the OH bond probably was not broken in the rate-determining step. Some further results on the effect of bond energies on the rate constant may be afforded by a calculation due to Hirschfelder[29a] and outlined by Frost and Pearson[29b] who also give a table showing the relative validity of the calculation for the heats of activation of relatively complex reactions. Consequently, it was thought of interest to apply this calculation to the reaction under study. In this calculation the activation energy involved in a bimolecular gas phase reaction is given by 28% of the energy of the bonds broken in the rate determining step. The dissociation energy of the B–H bond in polyatomic molecules has not been published,[30] but this quantity can be estimated for decaborane from the observed near infrared spectrum, which contains two boron hydrogen overtone bands at 5190 and 7500 cm.$^{-1}$,[31] and the familiar diatomic molecule approximation[32] for dissociation energies. This calculation gives a value of 58.5 kcal./mole (no reliable estimate can be made of the error involved here due to the scope of the assumptions made, but we might compare this value with the C–H bond energy of about 98.5 kcal./mole[33] and with the measured B–H diatomic molecule dissociation energy of <82 kcal./mole.[27] Compare also Bauer's[34] statement that the bond energies in boron hydrides should be lower than that expected for normal covalent bonds.) According to Hirschfelder's calculation, then, if the boron hydrogen of the decaborane is the only bond which is broken in the rate-determining step, the heat of activation for the gas state reaction should be 28% of 58.5 or 16.4 kcal./mole, subject to several approximations, of course. Frost and Pearson[35] give the difference between the heat of activation in the gas phase and solution phase as

$$\Delta H_{\text{s}} - \Delta H_{\text{g}} - \Sigma\Delta H_{\text{vap}}$$

From tables it can be seen that ΔH_{Va} varies from 8 to 10 kcal./mole[36] for the alcohols studied and hence a value of 9 kcal./mole will be used for the calculation. The ΔH_{VB} (decaborane) has been re-

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[21] S. O. Morgan and W. V. Yager, *Ind. Eng. Chem.*, **32**, 1519 (1940).

[22] Reference 18, Vol. VI, pp. 83–93.

[23] Internally, these values are probably good to within 0.02 in the units presented, while the absolute values must vary somewhat more than this, due to the nature of the assumptions involved in the calculation.

[24] Reference 11, p. 61.

[25] Prepared by K. R. Lange of this department.

[26] K. B. Wiberg, *Chem. Revs.*, **55**, 734 (1955).

[27] G. Herzberg, "Spectra of Diatomic Molecules," Second Edition, Second Printing, D. Van Nostrand, New York, N. Y., 1951, p. 510.

[28] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

[29] (a) J. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941); (b) reference 11, pp. 101–103.

[30] T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954, p. 179.

[31] E. J. Levy, Doctoral Dissertation, University of Delaware, Newark, Delaware, 1955, p. 54.

[32] Reference 27, pp. 95–101.

[33] W. G. Palmer, "Valency," Cambridge University Press, 1948, p. 180.

[34] S. H. Bauer, *Chem. Revs.*, **31**, 43 (1942).

[35] Reference 11, p. 118.

[36] Reference 17, pp. 1921–1924.

ported by Furukawa and Park[37] to be 50759 abs. j./mole (12.4 kcal./mole). It should not therefore be an unreasonable assumption that the heat of vaporization of the complex is in the neighborhood of 9–12 kcal./mole, particularly if the complex resembles the reactants, as it should if only a boron hydrogen bond is broken in the rate-determining step. Consequently, the $\Sigma\Delta H_{\mathrm{vap}}$ (equal to $\Delta H_{\mathrm{v}}\ddagger - \Delta H_{\mathrm{vA}} - \Delta H_{\mathrm{vB}}$) is given by about 10 kcal./mole and the ΔH_{s} comes to about 26 kcal./mole, which may be compared with the observed value of 25–30 kcal./mole. The agreement may be fortuitous, but the most important contribution of this calculation is that if the alcohol bond were broken also (bond energy about 110 kcal./mole),[38] the calculated activation heat is in the neighborhood of 50 kcal./mole, thereby supporting the results of the deuteration studies in their indication that the O–H bond of the alcohol is not broken in the rate-determining step.

TABLE IV

RELATIVE RATES OF REACTION OF RELATED BORON HYDRIDES WITH *n*-BUTYL ALCOHOL

Boron hydride	Solvent	Relative rate constant
Decaborane	Carbon tetrachloride	0.9
Decaborane	Benzene	1.0
Deuterodecaborane	Carbon tetrachloride	0.5
Diiododecaborane	Carbon tetrachloride	2.7

If, however, the coördination[39] of the electrons from the alcohol is involved in the rate determining step, a correlation between the ionization energies of the alcohols and their heats of activation should be possible on a qualitative basis. Unfortunately, data for these quantities are rather scarce, so the corresponding data for the bromides and the radicals is also given in Table V[40,41] for comparison. It is seen from the table that the correlation is fair except for the butyl series, where alcohol work is lacking. Since the availability of the electrons on the oxygen of the alcohol should be related to the relative electron densities at this site, it might be reasonable to assume that the heats of activation fall off as the inductive effect of the attached alkyl group increases. This inductive effect is discussed by Ingold[42] and from the inductive series he presents, $-CH(CH_3)_2 > -CH_2(CH_3) > -CH_3$,[43] it might be concluded that the heats of activation vary in the inverse manner, since an increase in the electron density on the oxygen ought to increase the activation energy if the availability of the electrons is involved in its magnitude. This same variation of electric density on the oxygen atom with the structure of the alkyl group has been discussed by Ghosh[44] from a study of their dipole moments.

In addition to these facts concerning the heat of activation, we have listed in Table V entropies of activation calculated from the previously determined log k_0's and the observed heats of activation. The relative agreement in the values of log k_0 for the primary series of alcohols seems to indicate that specific solvent interactions are constant or zero in this series. If we assume that this also holds for the other alcohols, then the differences in the log k_0 values for methyl and the branched alcohols should be due to differences in the alcohol molecules or in the activated complexes. Hence a further test of the applicability of Kirkwood's equation to the data would be to use the log k_0's calculated from it with the observed heats of activation to obtain entropies of activation and then to compare the relative values of these entropies with the general relative magnitudes expected from the statement by Frost and Pearson[45] that the entropies of activation decrease as the molecular complexity increases. This means that the entropies of activation presented in Table V have been corrected for those electrostatic non-specific effects dealt with by the Kirkwood equation, and consequently may involve other effects not related to it. However, the relative magnitudes of these values seems to indicate that they are in the order expected from the discussion in the above text. It must also be kept in mind that these values contain rather large errors due to the methods of calculation, and thus they should be interpreted only as relative orders of magnitude.

TABLE V

ACTIVATION ENTROPIES AND COMPARISON OF ACTIVATION ENERGIES WITH IONIZATION ENERGIES FOR THE REACTION OF ALCOHOLS WITH DECABORANE

Alcohol	$\Delta S^{\ddagger\, b}$ (e.u.) $^{-20}$	Ea (kcal./mole)	Ionization energies[a] ROH[37]	RBr[37]	R[38]
Methyl	25.2	31.6	252	..	246
Ethyl	0.4	25.7	245	..	200
n-Propyl	− 2.2	24.5	241	237	180
Isopropyl	−32.7	15.9	..	234	179
n-Butyl	1.60	25.5	..	234	
Isobutyl	−14.7	20.7	..	236	
sec-Butyl	−28.6	16.3	..	234	

[a] Converted to kcal./mole from the original values in electron volts. [b] $k_0 = e(kT/h)\ \mathrm{exp.}\ [(T\Delta S\ddagger - E_{\mathrm{a}})/RT]$.

Experiment did not show the existence of any intermediates in the alcoholysis reaction, so that the actual point of attack of the alcohol on the decaborane molecule is still unknown. Also the nature of the steps following the formation of the activated complex and leading to the observed products was not indicated by any of the results obtained. It might be mentioned that the point of attack could be the same point attacked by the iodine molecule in the formation of diiododecaborane,[12] as evidenced by the study of Schaeffer[46] on the X-ray pattern.

Also an activated complex similar to the one described here was presented by Gerrard and Lap-

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(37) G. T. Furukawa and R. P. Park, National Bureau of Standards Report 3612 (July 25, 1954).

(38) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience Publ., Inc., New York, N. Y., 1950, p. 240.

(39) D. T. Hurd, "Introduction to the Chemistry of the Hydrides," Wiley, New York (1952), pp. 80–84.

(40) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

(41) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

(42) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter II.

(43) Ref. 42, p. 71.

(44) P. N. Ghosh, *Nature*, **123**, 413 (1929).

(45) Reference 11, p. 93.

(46) R. Schaeffer, The Molecular Structure of $B_{10}H_{12}I_2$, Division of Physical and Inorganic Chemistry of the American Chemical Society, Abstracts of Papers Presented at Cincinnati, Ohio, March 29, to April 7, 1955, p. 37Q.

pert[47] for the reaction of boron trichloride with alcohols to form the borate esters.

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[47] W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 2545 (1951).

[CONTRIBUTION FROM THE AMERICAN ELECTRO METAL CORPORATION]

Borides of Rare Earth Metals

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Until recently, hexaborides were the only binary compounds known to be formed between rare earth metals and boron. In this study, a series of tetragonal tetraborides of Pr, Sm, Gd and Yb isomorphous with CeB_4, ThB_4 and UB_4 were prepared and their lattice constants measured. The hexaborides of the above rare earth metals, as well as those of La and Th, were also prepared by carbon and boron reduction of their respective oxides. In addition, a group of isomorphous borides of a hitherto unreported structural type were found. The exact boron content of these compounds has not yet been determined.

I. Introduction

A wide variety of binary compounds are formed between boron and the transition metals of the 4th, 5th and 6th groups of the Periodic Table. These range in composition from M_2B to MB_{12}.[2] No such variety, however, characterizes the compounds formed between boron and the rare earth metals. Rare earth metal borides of the type MB_6 were prepared and described many years ago,[3,4] and, until recently, no other rare earth borides were known. Within the past few years, however, three compounds of the type MB_4 were prepared[5-8]; of these, one, CeB_4, is a rare earth metal boride and the other two (UB_4 and ThB_4) are closely related.

One of the objectives of the present investigation was the preparation and the study of hexaborides of various rare earth metals and of tetraborides of rare earth metals other than Ce. Efforts also have been made to prepare binary boride phases other than MB_6 or MB_4. In addition, procedures have been studied for the preparation of such binary borides by the direct reduction of the metal oxides by boron.

II. Raw Materials

Sm_2O_3, Gd_2O_3 and Yb_2O_3 were obtained from the Ames Laboratory of Iowa State College. The samarium and gadolinium oxides were of a purity greater than 99.9%, while the ytterbium oxide was 99.7% pure. The "Pr_4O_7" used was of a minimum purity of 93/94%, and contained about 5% La_2O_3. The La_2O_3 was of two grades, one of about 92% minimum purity, and the other approximately 99% pure. The boron powder used, purchased from Cooper Metallurgical Associates, was 96.3% pure, and contained 0.60% Fe and 0.26% C. The carbon used was Fisher carbon black "G" (gasblack).

III. Preparative Methods

Small amounts of rare earth oxide, boron and carbon black powders (totaling about 1 g.) were hand-mixed in the desired proportions until homogeneous and pressed at about 5 t.s.i. into thin wafers (1″ × 1/2″ × 1/16″). These were separately loaded into graphite crucibles about 1.5″ high by 5/8″ in diameter. The latter were in turn placed in larger graphite crucibles (4″ × 3″) and heated by induction in a hydrogen atmosphere; specimens were heated either for 2 hours at 1500° or for 1 hour at 1800°.

After heating, the sintered compacts were crushed to a fine powder and analyzed chemically and by X-ray diffraction methods to determine the reaction products.

There were strong indications that, especially in reactions carried out at 1800°, the boron, rather than the carbon, acted as the reducing agent. When no carbon was added to the reaction mixtures (enough excess boron was added to reduce the oxide by forming the volatile B_2O_3), the borides readily were formed both at 1500 and 1800°. In the latter case, although no carbon was added to the reaction mixture, about 1 to 2% was picked up from the graphite crucibles. It was found that the borides were formed equally well in the absence of carbon, *i.e.*, where ZrB_2 crucibles were used as containers.

IV. Experimental Results

a. Hexaborides (MB_6).—The MB_6 phase appears to be by far the most stable of the rare earth borides. In all instances, when the appropriate amounts of boron and metal were caused to react, the MB_6 phase was formed. It was also detectable on most X-ray diagrams when other compositions were employed.

The hexaborides of the rare earth metals have been investigated extensively. The structure is of the CsCl type, *i.e.*, the unit cell is primitive cubic, with boron octahedra at the corners and a metal

TABLE I

LATTICE CONSTANTS (IN Å.) OF THE CUBIC UNIT CELLS OF THE HEXABORIDES OF VARIOUS METALS

Metal	(1)[a]	(2)[b]	(3)[c]
Ba	4.29	4.268	
Sr	4.20	4.198	
Ca	4.153	4.145	
Y	4.08	4.113	
La	4.153	4.157	4.153
Ce	4.137	4.141	
Pr	4.129		4.130
Nd	4.126	4.128	
Sm			4.129
Eu			
Gd	4.13	4.112	4.110
Tb			
Dy			
Ho			
Er	4.11		
Tm			
Yb	4.14	4.144	4.140
Lu			
Th	4.16	4.113	4.110

[a] Various authors quoted in Kiessling.[2] [b] Blum and Bertaut.[6] [c] The present work.

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(1) To whom inquiries may be addressed.

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