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The Reaction of Decaborane with Substituted Alcohols[1]

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Decaborane reacts with alcohols to yield the corresponding trialkyl borates and hydrogen in quantitative yield. The availability of the electrons on the oxygen of the alcohol has been varied with the use of substituents having different electron affinities. A more rapid degradation to products is observed as the electron availability increases. The kinetic data indicate that the reaction proceeds through a complex, which decomposes by the elimination of a hydrogen atom from the alcohol. Deuterium substituted alcohols show a decrease in reactivity, strengthening this observation.

Recently the kinetics of the oxidation of decaborane with alcohols[2] has been studied at this Laboratory (equation 1).

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

The present investigation is an extension of the data of these workers toward the establishment of a detailed mechanism for this process. A related purpose was to determine if an intermediate could be identified as a result of the degradation of the "cage-like" decaborane molecule.[3] Although Stock[4] claimed that an intermediate was formed in the hydrolysis of decaborane, this component was not isolated apparently due to its similarity to the hydride. Our attempts to find an intermediate having fewer than 10 boron atoms, using infrared techniques, partial reaction, freezing, etc., were not successful. However, a dialkoxyborane has been found in the reaction of pentaborane with alcohol.[5]

Hurd[6] and others[7,8] postulated that the coördination of a water molecule to form a complex with a hydride is the first step in the hydrolysis process.

Two methods of ionization of decaborane in aqueous-alcohol solutions have been proposed by Guter and Schaeffer,[9] either through ionization of a complex or self-ionization of the hydride. Beachell and Meeker[2] suggested that the completion of the boron octet by the electrons from the oxygen and the boron to hydrogen bond were involved in the alcoholysis rate.

The present study shifts the emphasis to the O–H bond cleavage as being rate determining. The position of attack on the hydride cannot be specified at present.

Experimental

Small quantities of aldehydes, ketones and halogens increase the velocity of the reaction markedly. The carbonyl contaminants were effectively removed by reducing them to the alcohols with a small quantity of decaborane and then redistilling the alcohols.

The deuterium containing alcohols were prepared by the deuterolysis of a sodium alcoholate and/or the corresponding boron ester. More enrichment was obtained with the high boiling alcohols when the boron compound was used, since the esters, unlike the higher alcoholates, were obtained pure and dry by distillation.

Decaborane was obtained as a research sample in 99% purity. This material, whether purified by sublimination or recrystallization from pentane, gave equivalent results. The kinetic studies were carried out on the recrystallized material. The reaction solvent used exclusively was benzene. This was carefully dried over lithium aluminum hydride and distilled.

Hydrogen evolution was followed by the manometric method described by Beachell and Meeker[2], using the Barcroft–Warburg apparatus. Solutions were made so that 0.5 ml. of benzene would contain approximately 8.0×10^{-5} mole of decaborane. After the addition of alcohol, the increase in hydrogen pressure was followed by adjusting the reaction to a constant volume. With the slower reacting phenols, it was necessary to increase the hydride concentration and the temperature of reaction to get a suitable hydrogen evolution; however, the larger amount of hydride greatly increased the induction period noticed in this reaction.[2,9] Unchanged decaborane could be recovered from all these systems.

All rate constants were determined by the method of initial slopes,[10] since no more than 5% of the hydride was allowed to react. The equation used was

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

The activation energies were calculated from the rate constants at three temperatures. The rates obtained for most alcohols were reproducible within ±6% and gave mean (reported) activation energies to ±0.7 kcal. Additional runs in the case of the deuteroalcohols and their normal alcohols reduced this error to ±0.5 kcal. The reproducibility of the rates for the slower acting alcohols ($k \cong 10^{-10}$ l./mole sec.) was not as good due to errors involved in reading small pressure changes.

Reaction of Decaborane with Alcohols (Pseudo First Order).—One-half milliliter of alcohol (*ca.* 5.0×10^{-3} mole) was added to a tared flask containing 8.0×10^{-5} mole of decaborane in 0.5 ml. of benzene. After reweighing, this was connected to the Barcroft–Warburg apparatus and brought to temperature with gentle agitation. After the 1–5 minute induction period, the system was adjusted to a volume of 6.25 ml. and closed. The change in pressure (corrected) *versus* time was recorded every 3 minutes for about 1 hr.

Reaction of Decaborane with Phenols.—One-half gram of decaborane (4.1×10^{-3} mole) was slurried with sufficient benzene to form 0.5 ml. of mixture. To this was added 0.5 ml. (*ca.* 5.0×10^{-3} mole) of the molten phenol. The temperature was adjusted to 48° and the system sealed as before. The reaction was followed every 15 minutes until a plot of pressure *versus* time became linear. The induction time in this case averaged 3–5 hr. The pressure (corrected) was then determined every half-hour for about 8 hr.

Results

Examination of the data of the 4 substituted butanols (*e.g.*, *n*-amyl, 4 chloro and 4 methoxy alcohols) indicated that substitution in this position has little influence on the rate (Table I).

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[1] Taken in part from the thesis submitted by Wayne C. Schar to the University of Delaware in partial fulfillment of requirements for the degree of Doctor of Philosophy.

[2] H. C. Beachell and T. R. Meeker, THIS JOURNAL, **78**, 1796 (1956).

[3] J. S. Casper, C. M. Lucht and D. Harker, *Ann. Rep. Prog. Chem.*, **48**, 84 (1949).

[4] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 84.

[5] A. F. Zhigach, E. B. Kazakova and R. A. Kigel, *Doklady Akad. Nauk S. S. S. R.*, **106**, 69 (1956).

[6] D. T. Hurd, "Introduction to the Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 83.

[7] B. V. Nekrasov, *J. Gen. Chem. (USSR)*, **10**, 1156 (1940).

[8] H. G. Weiss and I. Shapiro, THIS JOURNAL, **75**, 1221 (1953).

[9] G. A. Guter and G. W. Schaeffer, *ibid.*, **78**, 3546 (1956).

[10] S. L. Friess and A. Weissberger, "Rates and Mechanisms of Reactions, Technique of Organic Chemistry," Vol. VIII, Interscience Publishers, Inc., New York, N. Y., 1953, p. 182.

TABLE I

RATE CONSTANTS FOR THE ALCOHOLYSIS OF DECABORANE IN BENZENE SOLUTIONS AT 25.2°

Alcohol	Specific bimolecular rate constant (10^{-7} l./mole sec.)	Heat of activation, E_a (kcal./mole)
n-Butanol[a]	6.15	25.2
n-Butanol-*d*	2.76	27.2
2-Methyl-1-butanol[a]	9.47	17.9
3-Methyl-1-butanol	7.60	23.0
n-Amyl alcohol[b]	7.41	25.0
2-Chloro-1-butanol	1.78	18.0
3-Chloro-1-butanol	4.20	27.1
4-Chloro-1-butanol	8.20	25.0
2,4-Dichloro-1-butanol	1.68	..
4-Methoxy-1-butanol	7.56	23.5
Benzyl alcohol[b]	2.86	25.1
Benzyl alcohol-*d*	1.67	26.9
Cyclopentanol	3.36	27.1

[a] Eastman "White Label." [b] Matheson, Coleman and Bell.

The methyl substituted alcohols show a rate faster than butanol, and this rate increases as the methyl group is moved toward the hydroxyl. Converse to this are the chlorobutanol derivatives, which all react slower than butanol and which show that as the chloro group is moved toward the alcohol linkage, the rate is retarded.[11] A further example of this change in reactivity is noticed with the chlorinated ethanols (Table II). The di- and trichloroethanols react slowly.

TABLE II

Alcohol	Rate constant at 36.8°
2-Chloroethanol[a]	2.54×10^{-7}
2,2-Dichloroethanol	8.1×10^{-10}
2,2,2-Trichloroethanol	1.0×10^{-10}

[a] Eastman "White Label."

This is not explainable from steric considerations, since the more hindered tertiary butanol ($K = 0.09 \times 10^{-7}$ at 25°)[2] reacts more readily than either of these compounds. Similarly, if the bulk of the group attached to the hydroxyl were the major consideration in the rate process, then cyclopentanol and phenol should be of the same order of reactivity. Since they differ considerably, it is inferred that an inductive effect is responsible both in this case and the former example.

In general, the more acidic the hydrogen on the oxygen of the alcohol or phenol the slower the reaction. Other acidic compounds such as organic acids and mercaptans form substituted boric acid and demonstrate an exceedingly slow rate of reaction.

The phenols (Table III) were not run under the same conditions as those of the other alcohols. It was necessary to increase the decaborane concentration almost to the saturation point to get a measurable amount of gas evolved at 48°. Experimental difficulties at this temperature over a period of days makes these measurements less reliable, but they may be used for comparison within themselves. In these cases it is also possible to correlate the increased rate with the electron releasing methyl group and decreased rate with the electron attracting chloro substituents.

TABLE III

RATE OF REACTION OF PHENOLS WITH DECABORANE AT 48.0°[a]

Phenols	Specific rate constant $K \times 10^{-10}$
Phenol	7.0
p-Chlorophenol	2.0
m-Chlorophenol	5.0
o-Chlorophenol	3.0
p-Cresol	15.0
m-Cresol	19.0

[a] These rates are not comparable with the alcohols since a larger amount of decaborane had to be used to get appreciable reaction (see Experimental).

Of special interest are the β-halogenated alcohols (Table IV) which react in the opposite order predicted by the inductive effect, F > Cl > Br > I.[12] This reversal is not entirely unique and has been summarized[13,14] particularly for the substitution of halo benzenes. However, the over-all substitution of halogen appears to retard the rate of reaction when compared, with reservations, to ethanol.

TABLE IV

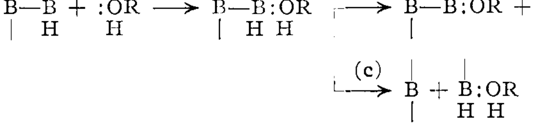
Alcohol	Rate constant $\times 10^{-7}$ at 25.2°	Heat of activation
Ethanol	5.20	25.7
2-Fluoroethanol[a,b]	4.00	..
2-Chloroethanol[a,c]	0.96	..
2-Chloroethanol[c]	.88	18.7
2-Bromoethanol	.80	..
2-Iodoethanol	.18	..

[a] No solvent. [b] Immiscible in benzene. [c] Eastman "White Label."

In the treatment of boron hydride with an alcohol the following properties are to be considered: (1) boron, being a strong electron acceptor can initially form a complex with a reactant such as alcohol; (2) the complex of alcohol and decaborane would be expected to have bond strengths differing from the original decaborane or alcohol.

Several possible processes have been considered for the path of alcoholysis; those which seem most likely are given below.

(1) If the rate-determining step for hydrogen evolution was the formation of an unstable complex which rapidly decomposed, then boron would attract the electron-rich hydroxyl in reaction (a) and would form the intermediate borinic ester and hydrogen in a rapid step (b) (equation 2).



$$\underset{|}{\overset{|}{B}}-\underset{H}{\overset{|}{B}} + :\underset{H}{OR} \xrightarrow{(a)} \underset{|}{\overset{|}{B}}-\underset{H}{\overset{|}{B}}:\underset{H}{OR} \begin{cases} \xrightarrow{(b)} \underset{|}{\overset{|}{B}}-\overset{|}{B}:OR + H_2 \\ \xrightarrow{(c)} \underset{|}{\overset{|}{B}} + \underset{H}{\overset{|}{B}}:\underset{H}{OR} \end{cases} \qquad (2)$$

(2) A second alternative is the rapid reaction (a) followed by the slow step (b). In this instance the

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[11] The E_a for most alcohols is about 25 kcal./mole; $\Delta S^{\ddagger}$ remains reasonably constant (ref. 2). Substitution in the 2-position of the alcohol lowers E_a to about 18-20 kcal./mole and changes $\Delta S^{\ddagger}$ considerably (Table I and ref. 2). Therefore, the interpretation of rates has its greatest reliability when the activation energies are equivalent.

[12] C. K. Ingold, *Chem. Revs.*, **15**, 237 (1934).

[13] J. W. Baker and H. B. Hopkins, *J. Chem. Soc.*, 1089 (1949).

[14] G. Baddeley, *ibid.*, 663 (1950).

substituted group on the alcohol affects the release of hydrogen. Step (b) has itself two possibilities; the rate step may be either the breaking of the oxygen to hydrogen bond of the associated alcohol or the parting of a boron to hydrogen bond.

(3) A rapid step (a) might be followed by a slow step (c) where the cleavage of the boron to boron bond would be important.

If either (a), (c) or the boron to hydrogen cleavage in (b) were rate determining, then isotopic alcohols should have no influence on the rate of reaction. However, if the alcoholic hydrogen is removed slowly, then an isotopic effect should be manifested. In order to determine this the deutero alcohols were prepared. The twofold difference between the heavy and normal alcohols indicates that the oxygen to hydrogen cleavage is rate-determining. Furthermore, the differences between the activation energies, corrected for experimental reproducibility, are +1000 to +3000 cal. The difference between the zero point energies of O–H and O–D is about +1000 cal.[15] These two observations are in the same direction and order of magnitude further supporting the O–H bond as the rate-determining cleavage site.

A mass spectrophotometric analysis of the first 5% of gas evolved when a large excess of decaborane reacted with deuterium oxide in dioxane gave these results in mole per cent.

Deuterium	61.10	Hydrogen	5.42
Hydrogen deuteride	32.73	Misc. gases	0.75

The total hydrogen released represents 21.78 mole % and the total deuterium represents 77.46%.

In the idealized equation (equation 3) the amount

$$B_{10}H_{14} + 30DOD \longrightarrow 10B(OD)_3 + 7H_2 + 15D_2 \quad (3)$$

of hydrogen obtained from a completely reacted system is 7/22 or 31.82 mole % of the total gas. Results of the partially reacted system yield a figure 10% lower. This could be accounted for either by: (1) an exchange reaction followed by the selective decomposition at the exchange site with more deuterium oxide, or (2) attack of deuterium oxide at a non-exchange site and preferential release of deuterium at the beginning of the reaction (*i.e.*, breaking of the O–D bond in step (b) of equation 2.) Although mass spectral data[16] show two hydrogens are rapidly exchanged for deuterium, this does not preclude the second alternative. The positions vulnerable to exchange have not been established.

A non-ionic mechanism is suggested by the fact that as the basicity of the hydride-hydrolytic system is increased, the hydrogen evolution becomes slower.[17] This is opposite the effect observed on the known ionic degradation of the silicon hydrides.[18] If the ionization of decaborane,[9] on the path leading to decomposition, was due to complex

$$\begin{tikzcd}
B_{10}H_{14} + ROH \arrow[r, shift left, leftarrow] \arrow[r, shift right] & \underset{H}{B_{10}H_{14}OR} \arrow[r, shift left, leftarrow] \arrow[r, shift right] \arrow[d] & {[B_{10}H_{14}OR]^- + H^+} \quad (4) \\
& \text{Non-ionic decomposition} &
\end{tikzcd}$$

formation (equation 4), then the decreased rate of hydrogen evolution caused by adding a base to the system would be due to the lowered concentration of the complex.

The addition of iodine accelerates the rate of alcoholysis (Table V). Smaller quantities of bromine have a similar effect. The resulting gas from these reactions contained the respective hydrogen halide. No other halogen containing material was found, and neither hydrogen iodide nor bromide was responsible for this acceleration. Since there is no reason to suspect the formation of hydrogen iodide from the elements at room temperature, it is inferred that the free halogens are intimately associated in the rate step of reaction. The halogens do not disintegrate the B–B bond in the decaborane molecule[19] but form substituted compounds. These react more rapidly than decaborane in alcoholysis but not as fast as the halogen initiated systems, consequently these are not intermediates. Furthermore, these compounds could not be produced under the conditions of the reaction.

TABLE V

CONCENTRATION OF IODINE AND ITS INFLUENCE ON THE RELATIVE RATE OF THE BUTANOL–DECABORANE REACTION

Moles of I_2 per mole $B_{10}H_{14}$	Relative rate	Moles of I_2 per mole $B_{10}H_{14}$	Relative rate
0	1	1.5	9.5
0.25	3	2.0	11.0
0.5	5.8	2.5	11.8
1.0	7.5	3.0	13.0

The addition of halogen does not change the cleavage site, since the use of deutero and normal alcohols indicated that an isotopic effect still existed. If the point of reaction had changed to the boron to hydrogen or boron to boron bonds, both reagents would react at the same rate. Consequently, it is felt that the role of the halogen is to aid in the removal of a hydrogen radical from the alcohol.

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(15) G. Hertzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand, New York, N. Y., 1951, p. 560.

(16) G. W. Schaeffer, private communication.

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

(18) N. V. Sidgwick, "The Electronic Theory of Valence," Oxford University Press, 1932, p. 155–160.

(19) Reference 4, p. 120.