

were designed, however, for a different purpose, and are not as well adapted for extrapolation,

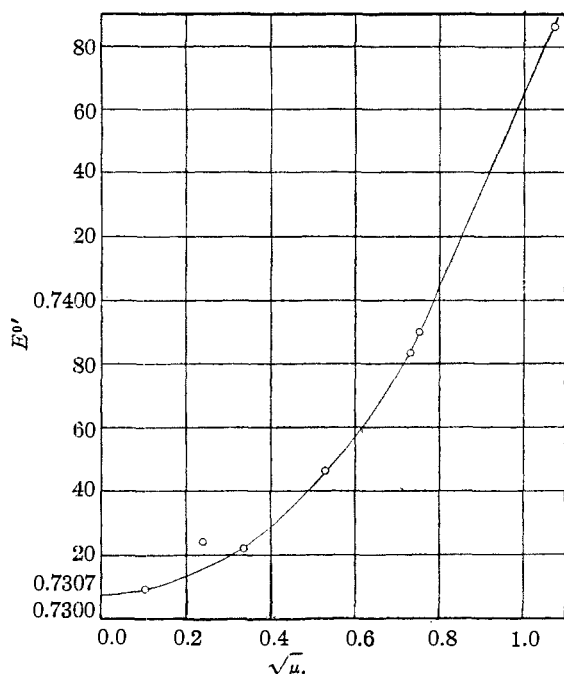


Fig. 2.—Extrapolation of  $E^\circ$ .

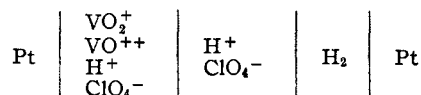
which requires systematic dilution from cell to cell of all solutes present, whereas in these,

vanadium concentrations were held constant. The value given above is therefore the better.

I wish to express my appreciation to Professor William C. Bray, to whom I am indebted for suggesting the problem and for valuable assistance from time to time during its completion.

### Summary

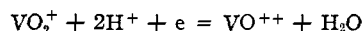
1. By observation of the variation of the electromotive force of the cell



with acid concentration and with concentration of pentavalent vanadium, the formula of the pentavalent vanadium ion has been shown to be  $\text{VO}_2^+$  in acid solution.

2. The data of Coryell and Yost<sup>2</sup> for a similar cell have been recalculated, correcting for a small error in acid molality, and shown to be in complete agreement with this result.

3. From the recalculated data of Coryell and Yost, the standard electrode potential for the reaction



has been determined as 0.9996 volt.

BERKELEY, CALIF.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## The Relative Strengths of Some Hydrocarbon Derivatives of Boric Acid

BY DAVID L. YABROFF, G. E. K. BRANCH AND BERNARD BETTMAN

### Introduction

**Resonance.**—If the group X may act as a donor of electrons in an acid of the type  $\text{XB}(\text{OH})_2$ , then the structure  $\text{X}^+=\text{B}^-(\text{OH})_2$  will be in resonance with the forms  $\text{XB}(\text{OH})_2$ ,  $\text{XB} \begin{array}{l} \text{OH} \\ \diagdown \\ \text{O}^+\text{H} \end{array}$ , and  $\text{XB} \begin{array}{l} \text{O}^+\text{H} \\ \diagup \\ \text{OH} \end{array}$ . Since the negative part of the dipole in the structure  $\text{X}^+=\text{B}^-(\text{OH})_2$  is nearer the dissociating hydrogen atom than is the positive pole, the effect of this structure is to decrease the strength of the acid. The extent of the contribution of  $\text{X}^+=\text{B}^-(\text{OH})_2$  to the structure of the molecule depends on its stability with respect to  $\text{XB}(\text{OH})_2$  and on the number of structures represented by  $\text{X}^+=\text{B}^-(\text{OH})_2$  relative to the number represented by  $\text{XB}(\text{OH})_2$ . The impor-

tance of  $\text{X}^+=\text{B}^-(\text{OH})_2$  becomes greater, then, as its stability increases relative to  $\text{XB}(\text{OH})_2$  and as the number of forms represented by  $\text{X}^+=\text{B}^-(\text{OH})_2$  increases relative to the number of structures represented by  $\text{XB}(\text{OH})_2$ .

There is another type of molecular resonance introduced when X has a double bond so situated that it forms a conjugate system with the double bond in  $\text{X}-\text{B} \begin{array}{l} \text{O}^+\text{H} \\ \diagdown \\ \text{OH} \end{array}$ . An example is  $\text{CR}_2=\text{CH}-\text{B} \begin{array}{l} \text{O}^+\text{H} \\ \diagdown \\ \text{OH} \end{array}$ . In general, a conjugate system may have two internally ionized resonating forms. In this case they would be  $\text{C}^+\text{R}_2-\text{CH}=\text{B}^-(\text{OH})_2$  and  $\text{C}^-\text{R}_2-\text{CH}=\text{B} \begin{array}{l} \text{O}^+\text{H} \\ \diagdown \\ \text{OH} \end{array}$ . The first of these forms is of the type  $\text{X}^+=\text{B}^-(\text{OH})_2$  which has

been described in the preceding paragraph. The resonance arising from the second form is acid-strengthening because of the two positive charges on the oxygen atom. The formula of this second resonating form of the acid obviously shows that it is practically non-existent and the resulting resonance small, but the corresponding form of

the ion,  $C^-R_2-CH=B-\begin{matrix} O^+ \\ \diagdown \\ OH \end{matrix}$ , is a more reasonable structure. For this reason one must not assume that this type of resonance is entirely negligible. In general, then, the acid-weakening resonance due to forms of the type  $X^+=B-(OH)_2$  is much more important than the acid-strengthening resonance due to forms of the type  $X^-=B-\begin{matrix} O^+H \\ \diagdown \\ OH \end{matrix}$ .<sup>1</sup>

We have used the adjectives acid-strengthening and acid-weakening to qualify, respectively, the resonances that tend to make acids stronger or weaker than would be expected from classical structures. We have decided on the acid-strengthening or acid-weakening character of a resonance by considering the direction of the dipole imposed on the classical structure by the internally ionized form to which the resonance is due. A resonance may also be recognized as acid-strengthening when it reduces the energy of the ion more than it does that of the undissociated acid, both reductions being relative to the classical structures. The calculation of resonance energies by the method used by Pauling and Wheland<sup>2</sup> for free radicals has not been achieved for acids and ions, as it involves internally ionized forms and bonds between different kinds of atoms. However, the relative energy reductions in acids and their ions can be estimated from the ease of formation of alternative forms from the corresponding classical structures. Thus the process  $XB(OH)_2 \rightarrow X^+=B^-(OH)_2$  requires less energy than the corresponding change for the ion,

(1) One of the Referees of this paper has suggested that the form of the ion,  $C^-R_2-CH=B-\begin{matrix} OH \\ \diagdown \\ O^+ \end{matrix}$ , and that of the acid,  $C^+R_2-$

$CH=B^-(OH)_2$ , may be considered as belonging to the same type, and that they might contribute equally but oppositely to the strength of the acid. Resonance in the ion, however, is much less than in the undissociated acid because the form  $CR_2=CH-B-\begin{matrix} OH \\ \diagdown \\ O \end{matrix}$  is much more stable than any other configuration, and so the contribution of  $C^-R_2-CH=B-\begin{matrix} OH \\ \diagdown \\ O^+ \end{matrix}$  to the structure of the ion is less than that of  $C^+R_2-CH=B^-(OH)_2$  to the undissociated acid.

(2) Pauling and Wheland, *J. Chem. Physics*, **1**, 362 (1933).

$X-B-\begin{matrix} OH \\ \diagdown \\ O^- \end{matrix} \rightarrow X^+=B-\begin{matrix} OH \\ \diagdown \\ O^- \end{matrix}$ , because of the re-

pulsion of negative charges and the greater interaction of the boron sextet with  $O^-$  than with  $OH$ . Hence this resonance reduces the energy of the acid more than it does that of the ion, and is acid-weakening. It may be noted that in simple cases this method must give the same result as the one we have used, for when the alternative form has an electric dipole, its formation is easier in the ion than in the acid when the dipole repels the dissociating proton.

In complicated cases it is not always possible to decide whether the total resonance is acid-strengthening or the reverse from chemical analogies. Thus in the case of  $CR_2=CH-B(OH)_2$ , quoted above, there is little doubt that the resonance due to the "vinyl" group is chiefly acid-weakening. It might be quite erroneous, however, to assume the same thing if a nitro group were substituted for the "vinyl" group. In our present state of knowledge decisions based on chemical analogies must be constantly revised by the findings of experiment.

**Negativity.**—A substituted group affects the strength of an acid apart from any resonance interactions. Unlike resonance, the existence and sign of this effect is not dependent on a particular spatial relationship between the group and some other part of the molecule. The magnitude of the effect increases with decreasing number of atoms intervening between the group and the dissociating hydrogen atom. The rate of this increase of magnitude depends on the nature of the intervening groups. This type of effect we shall attribute to a group property which we shall call the negativity. In acids of the type  $XCH_2COOH$ , the group  $X$  is relatively free from any resonance interaction with the rest of the molecule, and the relative strengths of such acids is chiefly governed by the negativities of the  $X$  groups. We may therefore use Derick's  $\alpha$ -factor<sup>3</sup> ( $\alpha = (\log K_{CH_3COOH} / \log K_{XCH_2COOH}) - 1$ ) for  $\alpha$ -substituted acetic acids as a measure of the negativities. However, since negativity and resonance are not the only factors that govern acidic strength, even this is not a truly quantitative definition. Indeed, negativity is probably not capable of exact mathematical formulation. Negativity (which we are using in a much more restricted sense than is

(3) Derick, *THIS JOURNAL*, **33**, 1153 (1911); **34**, 74 (1912); **40**, 537 (1918).

generally used in chemistry) is the ability of a group to exert a pull on the electrons in the molecule. There must be no chemical interaction between the group and the rest of the molecule, neither by resonance nor by simple chemical reaction, like that between the amino and carboxyl groups in an amino acid. High negativities are associated with positively charged atoms, high kernel charges, and double and triple bonds. The hydrogen atom is a convenient arbitrary zero of negativity. It is more negative than a saturated alkyl group, but less negative than an aryl group.  $R_3^+N-$ ,  $NO_2-$ ,  $N\equiv C-$ ,  $Cl-$  and  $R-C\equiv O$  are examples of strongly negative groups.

Even in a partial analysis of the order of strengths of a series of acids of the type  $X'B(OH)_2$ ,  $X''B(OH)_2$ , etc., it is necessary to take into account both the relative negativities of the X groups, and their relative resonance interactions with the  $B(OH)_2$  group. The acid tends to be stronger the greater the negativity of the X group and the less the resonance interaction of X with the  $B(OH)_2$  group, neglecting for the moment the less important acid-strengthening resonance. One expects the strength of the acid to depend more upon the negativity of the X group than on its resonance interaction, since the lack of electrons on the boron atom (upon which resonance depends) is to a large extent counterbalanced by the two hydroxyl groups which also tend to supply the boron atom with electrons.

**Measure of Acidic Strength.**—To test the above ideas we have compared the strengths of several acids of the type  $XB(OH)_2$ , in which X is a hydrocarbon radical. These acids are very weak and often only sparingly soluble in water. Consequently dissociation constants obtained from conductivity measurements could not be used as a measure of acidic strengths. Nor can a comparison of the strengths of many of the acids be obtained in aqueous solution. We have therefore used mixtures of water and alcohol as well as water for the solvent.

As a measure of acidic strength we have used the hydrogen ion activity of a solution containing equal molal concentrations of the undissociated acid and its negative ion. This quantity is not identical with the true or thermodynamic dissociation constant. It is, however, independent of the concentration in fairly dilute solutions and can be calculated from the hydrogen-ion activities of solutions of any degree of neutralization. For

each substance we have obtained very concordant values over a range of concentrations and degrees of neutralization. We have called this quantity<sup>4</sup> the dissociation constant, to which it is very closely related.

A numerical value for an activity implies some arbitrary standard. We have used the same standard for all solvents, *i. e.*, activity equals molal concentration in an infinitely dilute aqueous solution. This introduces a further deviation between the constants we are using and the true dissociation constants when the solvent contains alcohol. This variation could be expressed as a common factor for all the acids, and it does not interfere with a comparison of the strengths in any one solvent.

### Results and Discussion

We have compared the strengths of some of the acids in water, some in 25% alcohol by volume and some in 50% alcohol by volume. We shall not discuss the first of these three sets of measurements as all of the acids measured in water were also measured in 25% alcohol. The necessity for the measurements in 50% alcohol arose from the insolubility of the diphenyl boronic acids in 25% alcohol. As the measurements in one solvent are not comparable with those in another, the strengths of the three diphenyl boronic acids are only compared with themselves and with that of phenylboronic acid whose dissociation constant was measured in all three solvents. A summary of the dissociation constants measured is given in Table I. The starred values are taken from an earlier paper.<sup>5</sup>

TABLE I  
DISSOCIATION CONSTANTS IN WATER, 25 AND 50%  
ALCOHOL

Acid	Water	$K_a \times 10^{11}$	
		25% EtOH	50% EtOH
Boric	65.3*	13.4*	
Phenylboric	137*	19.7*	1.64
<i>o</i> -Tolylboric	18.1	2.61	
<i>m</i> -Tolylboric		14.0	
<i>p</i> -Tolylboric		10.0	
$\alpha$ -Naphthylboric		8.88	
$\beta$ -Naphthylboric		26.0	
Benzylboric	75.5	14.9	
$\beta$ -Phenylethylboric	10.0	1.81	
<i>n</i> -Butylboric	1.82	0.344	
<i>o</i> -Diphenylboric			0.0984
<i>m</i> -Diphenylboric			1.85
<i>p</i> -Diphenylboric			1.58

(4) Brønsted, *Chem. Rev.*, **5**, 293 (1928), calls this the "acidity constant." This constant has been used by other investigators as a measure of acidic strength.

(5) Branch, Yabroff and Bettman, *This Journal*, **56**, 937 (1934).

The negativity of the hydroxyl group is greater than that of the hydrocarbon radicals. The phenyl group is more negative and the methyl group less negative than a hydrogen atom. With the additional fact in mind that the influence of a group is greater the nearer it is to the dissociating hydrogen atom, we may set up a theoretical order of decreasing negativities as follows: hydroxyl,  $\alpha$ -naphthyl,  $\beta$ -naphthyl, phenyl, *p*-tolyl, *m*-tolyl, *o*-tolyl, benzyl,  $\beta$ -phenylethyl and *n*-butyl. This is the decreasing order of strengths of the corresponding  $\alpha$ -substituted fatty acids in so far as their dissociation constants are known. There is some slight doubt whether the  $\alpha$ -naphthyl is more negative than the  $\beta$ -naphthyl group. If we had used the reverse order our results would be more easily explained. We believe, however, that the order given is the correct one.

The resonance interactions of the hydroxyl group are greater than those of hydrocarbon groups. The form  $\text{HO}^+=\text{B}^-(\text{OH})_2$  has no atom with a sextet of electrons and is therefore much more stable than forms of the type  $\text{X}^+=\text{B}^-(\text{OH})_2$  in which  $\text{X}^+$  contains a positively charged carbon atom with only a sextet of electrons.  $\text{X}^+=$

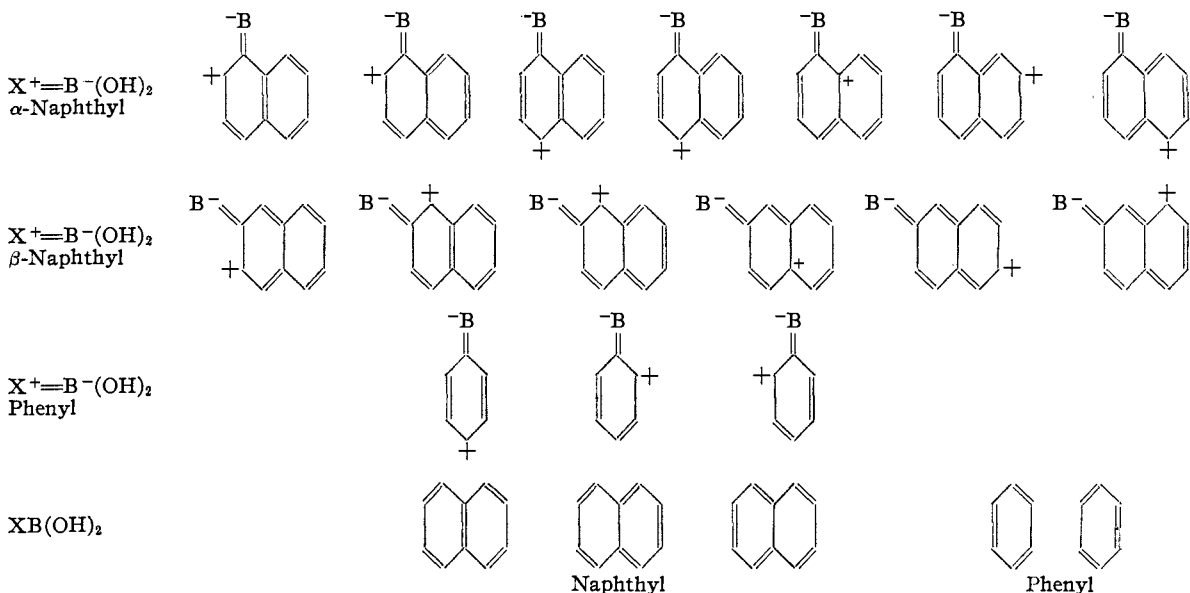
we have ignored para bonded and the more internally ionized forms. The structures enumerated are as shown herewith.

This order of group resonances is the same as that given by Pauling and Wheland<sup>6</sup> for free radicals. There are factors that tend to make the resonance effects of the phenyl and naphthyl groups (especially the  $\beta$ -naphthyl) more nearly the same in the arylboric acids than they are in the arylmethylys. These are mentioned in the discussion of the diphenyl groups.

The resonance of the phenyl group depends on the forms  $\text{C}_6\text{H}_5=\text{B}^-(\text{OH})_2$  and  $\text{C}_6\text{H}_5^+=\text{B}^-(\text{OH})_2$ .

As the methyl group is less negative than a hydrogen atom, an ortho or para methyl group stabilizes one of these forms and increases the resonance interaction. The effect of a meta methyl group is very small and the resonances of the meta tolyl and phenyl groups are approximately equal. The decreasing order of resonances is therefore *o*- and *p*-tolyl (approximately equal) and *m*-tolyl and phenyl (approximately equal).

The benzyl,  $\beta$ -phenylethyl and *n*-butyl groups have no double bonds so situated that they can



$\text{B}^-(\text{OH})_2$  represents seven forms when  $\text{X}$  is  $\alpha$ -naphthyl, six when  $\text{X}$  is  $\beta$ -naphthyl and three when  $\text{X}$  is phenyl. In  $\text{XB}(\text{OH})_2$   $\text{X}$  has three forms when it is either of the naphthyl groups and two when it is the phenyl group. The decreasing order of resonances is therefore  $\alpha$ -naphthyl,  $\beta$ -naphthyl and phenyl. In enumerating the forms

supply the boron atom with electrons, and so produce no resonance effects on the acidic strength. The decreasing order of resonances of all the above groups is hydroxyl,  $\alpha$ -naphthyl,  $\beta$ -naphthyl, *o*- and *p*-tolyl (approximately equal),

(6) Pauling and Wheland, *loc. cit.*; see also Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1, 421 (1929).

*m*-tolyl and phenyl (approximately equal) and benzyl,  $\beta$ -phenylethyl and *n*-butyl (the last three being approximately equal).

The influence of negativity and resonance on the strength of the boric acids discussed above is shown in the following table, which contains the order of strength expected from negativity alone, that expected from resonance alone and the actual order found. It is seen from this table that the actual order is a combination of the negativity and resonance orders, but more nearly follows the order of negativity. All inversions from the negativity order can be explained by the resonance order; those groups equal in resonance (1-2-3, 4-5, 6-7) follow the negativity order. In no case is there an inversion from both the resonance and negativity order.

TABLE II

Comparison of expected and actual orders of strengths of some boric acids measured in 25% ethyl alcohol. The orders are indicated by numbers, 1 representing the strongest acid and 10 the weakest.

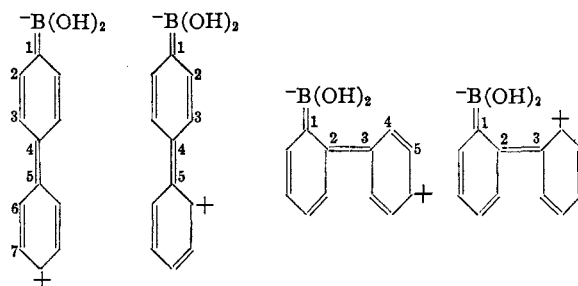
Acid	Expected order from negativity	Expected order from resonance	Actual order
HOB(OH) <sub>2</sub>	1	10	5
$\alpha$ -C <sub>10</sub> H <sub>7</sub> B(OH) <sub>2</sub>	2	9	7
$\beta$ -C <sub>10</sub> H <sub>7</sub> B(OH) <sub>2</sub>	3	8	1
C <sub>6</sub> H <sub>5</sub> B(OH) <sub>2</sub>	4	4-5	2
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> B(OH) <sub>2</sub>	5	6-7	6
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> B(OH) <sub>2</sub>	6	4-5	4
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> B(OH) <sub>2</sub>	7	6-7	8
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> B(OH) <sub>2</sub>	8	1-2-3	3
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> B(OH) <sub>2</sub>	9	1-2-3	9
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> B(OH) <sub>2</sub>	10	1-2-3	10

In the actual order found in 25% alcohol, 3, 4 and 5 are nearly equal and 6 and 7 are nearly equal.

The order of the negativities of the phenyl and three diphenyl groups is determined by the greater negativity of the phenyl group than of a hydrogen atom, and by the rule that negativity effects decrease with the number of intervening atoms. The decreasing order hence becomes *o*-diphenyl, *m*-diphenyl, *p*-diphenyl and phenyl.

The ortho and para diphenylboric acids have nine major forms of the type X<sup>+</sup>=B<sup>-</sup>(OH)<sub>2</sub> and four of the type XB(OH)<sub>2</sub>. The nine forms arise from the six positions for the positive charge, which may be on the ortho or para position of both benzene nuclei, and the fact that there are two configurations of the second nucleus for each position of the charge on the first nucleus. The four forms of XB(OH)<sub>2</sub> arise from the two configurations of each of the nuclei and the fact that they

may be combined in any way. Hence the *o*- and *p*-diphenyl groups are capable of more resonance than the phenyl group. However, when the charge is on the second ring in the forms X<sup>+</sup>=B<sup>-</sup>(OH)<sub>2</sub>, the number of atoms separating the positively and negatively charged atoms is greater in the *p*-diphenyl compounds than in the ortho compounds. This can be seen by inspection of the formulas



The energy required for the separation of opposite charges is therefore greater in the para compound than in the ortho, and resonance is smaller in *p*-diphenyl than in the *o*-diphenyl group. Similarly the separation of like charges is greater in *p*-diphenyl than in *o*-diphenyl forms of the type X<sup>-</sup>=B<sup>+</sup>(OH)<sub>2</sub>. Hence *p*-diphenyl forms

of this type are more stable than the *o*-diphenyl forms. This follows since it requires energy to bring like charges closer together. Hence the acid-strengthening resonance is greater and more important in *p*-diphenylboric acid than in the ortho acid. The expectation from resonance is that the *p*-diphenylboric acid is stronger than the ortho isomer. It may be noted that the above factors tend to make  $\beta$ -naphthylboric acid stronger than the alpha compound. It also tends to make the net resonance effects of the naphthyl and diphenyl groups smaller with respect to those of the phenyl group than would be expected from the mere enumeration of the forms.

In *m*-diphenylboric acid the second phenyl nucleus has very little influence on the resonance as it is only involved in very unstable forms having bonds between distant atoms or more internal ionization than is shown by the formula X<sup>+</sup>=B<sup>-</sup>(OH)<sub>2</sub>. The resonance effect of the *m*-diphenyl group is obviously less than that of the other diphenyl groups and is approximately the same as that of the phenyl group. We shall take *o*-diphenyl, *p*-diphenyl, *m*-diphenyl and phenyl (the last two being approximately equal) as

the decreasing order of the resonances of these groups.

The orders of acidic strength predicted from negativity, from resonance, and the actual order found are shown in the following table. Unlike the previous table it shows resonance as the predominant factor. This is probably due to the very small range of negativities of the included groups.

TABLE III

Comparison of expected and actual orders of strengths of some boric acids measured in 50% ethyl alcohol. The orders are indicated by numbers, 1 representing the strongest acid and 4 the weakest.

Acid	Expected order from negativity	Expected order from resonance	Actual order
$C_6H_5B(OH)_2$	4	1-2	2
$o-C_6H_5C_6H_4B(OH)_2$	1	4	4
$m-C_6H_5C_6H_4B(OH)_2$	2	1-2	1
$p-C_6H_5C_6H_4B(OH)_2$	3	3	3

In the actual order found in 50% alcohol, 1, 2 and 3 are very nearly the same.

### Experimental Section

**Materials.**—All of our compounds were prepared by the interaction of the corresponding Grignard reagent with *n*-butyl borate<sup>7</sup> except the *m*- and *p*-tolylboric acids, which were prepared with boron trifluoride.<sup>8</sup> The compounds listed in Table IV have been previously reported.

TABLE IV  
SUBSTITUTED BORIC ACIDS (PREVIOUSLY REPORTED)

Boric acid	Recrystallized from	Boron, %		M. p., °C.	
		Calcd.	(direct titration)	(instant immersion)	reported
<i>o</i> -Tolyl	Bz-water	7.96	7.73	171	168 <sup>9</sup>
<i>m</i> -Tolyl	Water			165	157 <sup>9</sup>
<i>p</i> -Tolyl	Water			253-254	245 <sup>9</sup>
					258-259 <sup>7</sup>
$\alpha$ -Naphthyl	Bz, pptn. of alc. soln.				202 <sup>9</sup>
	with water	6.29	6.31	219	259 <sup>13</sup>
$\beta$ -Naphthyl	Same as $\alpha$ -naphthyl	6.29	6.28	280	
				2 cryst. forms	{ 248 <sup>9,10</sup> 266 <sup>9,10</sup>
Benzyl	Bz-water	7.96	7.91	102-acid	161 <sup>11,12</sup>
				140-anhydride	(acid)

**Special Observations.**— $\alpha$ -Naphthylboric acid cannot be recrystallized from hot water without decomposition. A white odorless sample from benzene was recrystallized from hot water and the resulting product was yellow and had a distinct odor of naphthalene.

(7) Bean and Johnson, *THIS JOURNAL*, **54**, 4415 (1932).

(8) Krause and Nitsche, *Ber.*, **55**, 1261 (1922).

(9) Koenig and Scharrnbeck, *J. prakt. Chem.*, [2] **125**, 153 (1930).

(10) Michaelis, *Ber.*, **27**, 244 (1894).

(11) Krause, German Patent 371,467; *Chem. Abst.*, **18**, 992 (1924).

(12) Khotinsky and Melamed, *Ber.*, **42**, 3090 (1909-1910).

$\beta$ -Naphthylboric acid, like the  $\alpha$ -isomer, is partially decomposed by recrystallization from hot water. This probably accounts for the difference in the melting points of the two crystalline forms previously reported since the lower melting form was recrystallized from water. We have found<sup>13</sup> that the crystalline form of several organic boric acids depends not only on the solvent, but on the concentrations and the rate of cooling, as well.

Benzylboric acid is readily oxidized by the air to boric acid and benzaldehyde, but the rate is markedly accelerated by the presence of unknown impurities. Benzyl boric acid prepared from impure benzyl chloride could not be air-dried without decomposition into boric acid and benzaldehyde. When prepared from chemically pure benzyl chloride, however, it could be air-dried without appreciable decomposition. Upon standing it developed an odor of benzaldehyde and some boric acid was formed. Even when prepared from pure benzyl chloride the product sometimes underwent rapid autoxidation. In one case, a sample upon drying suddenly became warm, gave off white fumes, partially melted, and shrank to an amorphous mass which consisted almost entirely of boric acid. Other samples did not behave in this manner. Measurements were taken on benzylboric acid immediately after it was dry.

$\beta$ -Phenylethylboric acid crystallizes from water in the form of needles melting at 88° (corr.). It is comparatively stable to oxidation by air, developing a faint odor of phenylethyl alcohol only after about a month. This compound has not been previously reported. *Analysis* (direct titration): B found, 7.03; calcd., 7.23.

*n*-Butylboric acid was purified by recrystallization from water and from benzene. It crystallizes from water in very long flat needle-like sheets, and from benzene in light camphor-like crystals. It melts at 93-94° (corr.). *n*-Butylboric acid has not been previously reported. *Analysis* (Carius): B found, 10.67, 10.47; calcd., 10.62. Krause and Nitsche<sup>14</sup> report that the aliphatic boric acids have spicy, terpene-like odors. After recrystallization from benzene, *n*-butylboric acid was obtained entirely odorless. It may be air-dried without decomposition, but after about fifteen hours it develops an odor and small amounts of boric acid are present in the resulting product. This is probably due to oxidation by the air.

*o*-Diphenylboric acid was prepared by the interaction of *o*-diphenylmagnesium iodide with *n*-butyl borate. The Grignard reagent tends to solidify if it is too near the carbon dioxide-acetone bath, so it was added to the *n*-butyl borate in small portions through the neck of the flask, rather than through a dropping funnel. Upon hydrolysis of the reaction mixture there was considerable effervescence (boiling of ether) indicating that the Grignard reagent had not reacted completely with the *n*-butyl borate. Only a 5% yield of the compound was obtained. It was purified by recrystallization from benzene and from water. It separates from both solvents in long needles which melt at 129° (corr.) with effervescence on instant immersion and then resolidify. The new solid (the anhydride) melts at

(13) Reference 5, see *p*-chlorophenylboric acid. *o*-Tolylboric acid crystallizes from water in the form of needles, but yields plates if the solution is stirred or cooled somewhat rapidly.

(14) Krause and Nitsche, *Ber.*, **54**, 2784 (1921).

195° (corr.). This compound has not been previously reported. *Analysis* (Carius): B found, 5.46, 5.32; calcd., 5.47.

*m*-Diphenylboric acid was prepared in 25% yield by the interaction of *m*-diphenylmagnesium bromide with *n*-butyl borate. The *m*-bromodiphenyl was prepared by the coupling of diazotized *m*-bromoaniline with benzene in the presence of alkali according to the method of Gomberg and Bachmann.<sup>15</sup> *m*-Diphenylboric acid was purified by recrystallization from benzene and by the precipitation of an alcoholic solution with water. It forms plates melting at 207–208° (corr.). This compound has not been previously reported. *Analysis* (direct titration): B found, 5.49; calcd., 5.47.

*p*-Diphenylboric acid was prepared by the interaction of *p*-diphenylmagnesium bromide and *n*-butyl borate in 20% yield. There seems to be no reference in the literature to the preparation of this particular Grignard reagent, although difficulty has been experienced<sup>16</sup> with similar compounds. Our Grignard reagent was prepared through the use of magnesium activated with ethyl bromide and iodine, and by the long refluxing of the reaction mixture with the addition of an excess of magnesium powder from time to time. This type of procedure is necessary since the surface of the magnesium becomes coated over during the course of the reaction. *p*-Diphenylboric acid was purified by recrystallization from benzene and from 50% alcohol. It forms fine crystals melting at 232–234° (corr.). It has not been previously reported. *Analysis* (Carius): B found, 5.30; calcd., 5.47.

**Mole Fractions of the Alcohol Solutions.**—The 25 and 50% solutions of alcohol by volume were prepared to contain 25 and 50 cc., respectively, of absolute alcohol in a total volume of 100 cc. The mole fraction of alcohol

## Results

The dissociation constants were obtained as before<sup>5</sup> by measuring the *P<sub>H</sub>* of a series of partially neutralized solutions with a hydrogen electrode. The reference cell was a saturated calomel electrode. Its half-cell value at 25° as determined by the acetate and phthalate buffers was 0.2454 volt, corresponding to hydrogen gas at one atmosphere. The value recommended by Clark is 0.2458; that used by the Danish investigators is 0.2448.

The constants were again<sup>5</sup> calculated by means of the equation

$$K_a = \frac{[H^+][Na^+ + H^+ - Kw/H^+]}{M - [Na^+ + H^+ - Kw/H^+]}$$

*M* represents the total concentration of the boric acid in the form of both acid and salt. In the case of a very weak acid the calculated value of *K<sub>a</sub>* depends considerably upon the value of *K<sub>w</sub>*. We have used values for *K<sub>w</sub>* in the 25 and 50% alcohol which remove the trends in the weakest acids measured in these solvents, *i. e.*, *n*-butylboric acid in 25% alcohol and *o*-diphenylboric acid in 50% alcohol. The *K<sub>w</sub>*'s so obtained for 25 and 50% alcohol are 5 and  $1.5 \times 10^{-15}$ , respectively. *K<sub>w</sub>* in water was taken as  $10^{-14}$ . The value of *K<sub>w</sub>* obtained for 25% alcohol is the same as that used in our previous paper.<sup>5</sup>

TABLE V  
DISSOCIATION CONSTANTS AT 25°

Acid	Solvent	Detns.	Molality range		Range of <i>K<sub>a</sub></i>	Mean <i>K<sub>a</sub></i>	Av. dev. from mean <i>K<sub>a</sub></i> , %
<i>o</i> -Tolylboric	Water	8	0.03	–0.01	1.72 –1.93	$1.81 \times 10^{-10}$	3.5
Benzylboric	Water	9	.03	–.01	7.20 –7.80	$7.55 \times 10^{-10}$	2.8
$\beta$ -Phenylethylboric	Water	9	.03	–.01	0.961–1.03	$1.00 \times 10^{-10}$	1.4
<i>n</i> -Butylboric	Water	9	.03	–.01	1.79 –1.85	$1.82 \times 10^{-11}$	1.0
<i>o</i> -Tolylboric	25% EtOH	8	.03	–.01	2.53 –2.72	$2.61 \times 10^{-11}$	2.3
<i>m</i> -Tolylboric	25% EtOH	12	.06	–.01	1.36 –1.47	$1.40 \times 10^{-10}$	1.7
<i>p</i> -Tolylboric	25% EtOH	11	.06	–.01	0.974–1.05	$1.00 \times 10^{-10}$	2.1
$\alpha$ -Naphthylboric	25% EtOH	6	.01333–	.00667	8.36 –9.21	$8.88 \times 10^{-11}$	3.0
$\beta$ -Naphthylboric	25% EtOH	7	.03	–.01	2.54 –2.66	$2.60 \times 10^{-10}$	1.5
Benzylboric	25% EtOH	9	.06	–.02	1.46 –1.52	$1.49 \times 10^{-10}$	1.1
$\beta$ -Phenylethylboric	25% EtOH	9	.06	–.02	1.78 –1.85	$1.81 \times 10^{-11}$	0.9
<i>n</i> -Butylboric	25% EtOH	9	.06	–.02	3.35 –3.53	$3.44 \times 10^{-12}$	1.5
Phenylboric	50% EtOH	9	.06	–.02	1.58 –1.72	$1.64 \times 10^{-11}$	2.4
<i>o</i> -Diphenylboric	50% EtOH	9	.03	–.01	9.53 –10.25	$9.84 \times 10^{-13}$	1.4
<i>m</i> -Diphenylboric	50% EtOH	9	.03	–.01	1.80 –1.89	$1.85 \times 10^{-11}$	1.4
<i>p</i> -Diphenylboric	50% EtOH	5	.015	–.0075	1.56 –1.59	$1.58 \times 10^{-11}$	0.8

calculated from the amount of water and alcohol necessary for each solution was 0.0910 for 25% alcohol and 0.225 for 50% alcohol.

(15) Gomberg and Bachmann, *THIS JOURNAL*, **46**, 2339 (1924).

(16) Gomberg and Pernert, *ibid.*, **48**, 1382 (1926); Schlenk, *Ann.*, **368**, 298 (1909).

The experimental results are summarized in the table above. Measurements were usually taken at three concentrations, and at each concentration the molal ratio of added sodium hydroxide to the total acid was 0.4, 0.5 and 0.6, respectively.

### Summary

The dissociation constants of some hydrocarbon derivatives of boric acid have been determined. These constants have been com-

pared and discussed on the basis of the resonances and negativities of the various groups involved.

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## Properties of Electrolytic Solutions. XI. The Temperature Coefficient of Conductance

BY RAYMOND M. FUOSS

### I. Introduction

It has been shown<sup>1</sup> that the conductance of many electrolytes up to concentrations corresponding to the minimum in conductance can be described in terms of the hypothesis that free ions, ion pairs and ion triples are present. The constants describing the equilibria have been calculated as functions of ion size,<sup>2</sup> dielectric constant and temperature. It should therefore be possible to calculate the temperature coefficient of conductance in the above range of concentration. In this paper we shall derive for the case of weakly dissociated electrolytes an explicit expression for the following function

$$\frac{1}{\Lambda} \frac{d\Lambda}{dT} = f(a, D, T, c, \eta)$$

where  $\Lambda$  = equivalent conductance,  $T$  = temperature,  $a$  = ion size,  $D$  = dielectric constant,  $c$  = concentration and  $\eta$  = solvent viscosity.

### II. Calculation of the Temperature Coefficient

For the case of binary electrolytes in solvents of dielectric constant under 10, the conductance over a considerable concentration range is given by the following limiting form of the general conductance equation

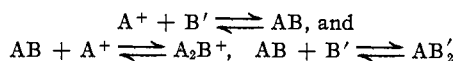
$$\Lambda g(c) = \Lambda_0 \sqrt{K}/\sqrt{c} + (\lambda_0 \sqrt{K}/k) \sqrt{c} \quad (1)$$

Here  $\Lambda_0$  and  $\lambda_0$  are limiting conductances for the electrolytes ( $A^+$ ) ( $B'$ ) and ( $A_2B^+$ ) ( $AB'_2$ ), respec-

(1) Fuoss and Kraus, *THIS JOURNAL*, **55**, 476, 1019, 2387 (1933).

(2) The "ion size" is an arbitrary constant calculated from experimentally determined dissociation constants. It gives the radius of an imaginary particle whose properties duplicate more or less quantitatively those of the real solute. While the dependence of  $a$  on the solvent and solute is gradually becoming clearer as more data are obtained, at present it is only possible to predict the order of magnitude and sometimes the sequence of  $a$ -values for different solvents or solutes from independent data. The parameter includes both the size of the lattice ion and the apparent increase of size of the latter due to solvation. (By solvation, we mean either actual compound formation or simply orientation of solvent dipoles in the ionic field, or both.)

tively, and  $K$  and  $k$  are the equilibrium constants<sup>3</sup> for the reactions



The function  $g(c)$  takes into account the average effects of the free ions on mobility and thermodynamic potential, and reduces to unity in the case of small free ion concentrations. It has a very small temperature coefficient; for tetrabutylammonium nitrate in anisole ( $D = 4.29$  at  $25^\circ$ ), for example, at  $10^{-3} N$ , it varied from 0.942 at  $95^\circ$  to 0.951 at  $-33^\circ$  or by less than 0.01% per degree. We shall therefore neglect its change with temperature.

Writing (1) in the form

$$\Lambda = \Lambda(\Lambda_0, \lambda_0, K, k, c)$$

we obtain the total differential

$$\frac{d \ln \Lambda}{dT} = \frac{1}{\Lambda} \left( \frac{\partial \Lambda}{\partial \Lambda_0} \frac{d\Lambda_0}{dT} + \frac{\partial \Lambda}{\partial \lambda_0} \frac{d\lambda_0}{dT} + \frac{\partial \Lambda}{\partial K} \frac{dK}{dT} + \frac{\partial \Lambda}{\partial k} \frac{dk}{dT} + \frac{\partial \Lambda}{\partial c} \frac{dc}{dT} \right) \quad (2)$$

The last term in the parentheses is negligible; it furnishes in the final result a term of the order of the coefficient of cubical expansion of the solvent (about 0.1%), multiplied by ( $d \ln \Lambda / d \ln c$ ) and the latter varies from  $(-1/2)$  through zero to about  $(+1/2)$  in the concentration range considered.

For the partial derivatives we obtain from (1)

$$\frac{\partial \Lambda}{\partial \Lambda_0} = \sqrt{K}/g \sqrt{c} \quad \frac{\partial \Lambda}{\partial \lambda_0} = \sqrt{K}c/k g \\ \frac{\partial \Lambda}{\partial K} = \Lambda/2K \quad \frac{\partial \Lambda}{\partial k} = -\lambda_0 \sqrt{K}c/k^2 g$$

In order to evaluate  $d\Lambda_0/dT$  and  $d\lambda_0/dT$ , we shall assume that the products  $\Lambda_0\eta$  and  $\lambda_0\eta$  are independent of temperature,<sup>4</sup> which leads to the result that

$$\frac{\partial \Lambda}{\partial \Lambda_0} \frac{d\Lambda_0}{dT} + \frac{\partial \Lambda}{\partial \lambda_0} \frac{d\lambda_0}{dT} = -\Lambda \frac{d \ln \eta}{dT} = \Lambda \frac{d \ln \varphi}{dT} \quad (3)$$

(3) For simplicity, we are retaining our earlier assumption that  $[A_2B^+] = [AB'_2]$ .

(4) Walden, *Z. physik. Chem.*, **78**, 257 (1912).