Another feature of the observed values is reproduced by the calculated: the decrease of $d \ln \Lambda/dT$ with increasing concentration at a given temperature. At very low concentrations, where the curves are parallel, with a slope of minus $^1/_2$ on a log Λ–log c plot, the temperature coefficient is independent of concentration. But when the curves begin to flatten out toward the minimum, a decrease of the coefficient with increasing concentration appears. This is due to the shift of the minimum toward higher concentrations with increasing temperature, owing to increased dissociation of triple ions. The average differences between the observed temperature coefficients at 10^{-3} N and at 5×10^{-4} and 2×10^{-4} N are, respectively, 0.10 and 0.25%, while the calculated differences are 0.11 and 0.23% at 325° Abs. and 0.12 and 0.25% at 300°.

Using the average values of the parameters a and a_3 for tetra-n-butylammonium nitrate in anisole, together with various equations presented above, the conductance as a function of temperature may be calculated. The conductance minimum represents a characteristic point of the conductance curve; the influence of temperature on the location of the minimum is illustrated in Fig. 5, where Curve I is the calculated curve for the logarithm of the minimum equivalent conductance plotted against temperature and Curve II is the calculated curve for the logarithm of the corresponding concentration. The circles represent experimental values read directly from the curves of Fig. 2. Considering the simplicity of the assumed mechanism and the numerous assumptions and approximations made, not to mention possible experimental errors, the agreement between calculated and experimental values is quite as good as was to have been expected. For a temperature change of 128°, $\Lambda_{\text{min.}}$ varies approximately in the ratio 1:20 and $c_{\text{min.}}$ in the ratio 1–2; maximum deviations in $\Lambda_{\text{min.}}$ at the extreme temperatures amount to about 20% and maximum variations in $c_{\text{min.}}$ to about 10%.

Summary

1. The conductance of tetra-n-butylammonium nitrate and picrate in anisole, over the concentration range 0.00001 to 0.01 N and the temperature range -33 to $+95.1°$, are presented.

2. The experimental results at concentrations up to about 0.001 N are in numerical agreement with results calculated from previously derived equations which are based on the hypothesis of ion association.

PROVIDENCE, R. I. RECEIVED MAY 16, 1934

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

Dissociation Constants of Organic Boric Acids

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

In two previous papers[1] we reported the dissociation constants of the phenetyl, the chlorophenyl and some of the hydrocarbon boric acids. A discussion of the relative strengths of these acids based on resonance and negativity was given. The present paper is a continuation of this work and deals with the dissociation constants of some other substituted boric acids, all derived from phenylboric acid. With the exception of o-nitrophenylboric acid, all the results are in accord with the principles we have discussed in the previous articles. o-Nitrophenylboric acid is anomalously weak.

The dissociation constants were again obtained by measuring the P_H of a series of partially neutralized solutions with a hydrogen electrode. The constants we are using as a measure of acidic strength are actually a combination of activities and molalities, *i. e.*, $Ka = (\text{H}^+)\text{act.}\ (\text{A}^-)\ \text{mol.}/(\text{HA})\ \text{mol.}$ We are again assuming that the measured P_H is equal to the negative logarithm of the hydrogen-ion activity in the alcohol solutions, as well as in aqueous solution. The constants were again calculated by means of the equation

$$Ka = \frac{(\text{H}^+)\text{act.}\ (\text{Na}^+ + \text{H}^+ - Kw/\text{H}^+)}{M - (\text{Na}^+ + \text{H}^+ - Kw/\text{H}^+)}$$

M represents the total molality of the boric acid in the form of both acid and salt. Kw was again taken as 5×10^{-15} for 25% alcohol ($N_{\text{alc.}} = 0.0910$) and as 1.5×10^{-15} for 50% alcohol ($N_{\text{alc.}} = 0.225$). No other corrections were used

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[1] (a) Branch, Yabroff and Bettman, THIS JOURNAL, **56**, 937 (1934); (b) Yabroff, Branch and Bettman, *ibid.*, **56**, 1850 (1934).

except in the case of the second dissociation constants of the carboxyphenylboric acids. There it was necessary to extrapolate to infinite dilution. The method is described later.

Rapid reduction of the nitrophenylboric acids occurred with the hydrogen electrode, so these were measured with a glass electrode. The dissociation constants obtained for the nitro acids are probably less accurate than the others that we have measured since only one measurement was made on each acid. The order of strength of these isomers, however, is undoubtedly correct since it was checked with indicators and found to be the same as that obtained from the glass electrode.

A summary of the new constants obtained is given in Table I.

Table I

Dissociation Constants of Organic Boric Acids at 25°

Acid, boric	Solvent	*Ka*
m-Fluorophenyl-	25% EtOH	1.10×10^{-9}
m-Chlorophenyl-	25% EtOH	1.35
m-Bromophenyl-	25% EtOH	1.46
p-Fluorophenyl-	25% EtOH	3.66×10^{-10}
p-Chlorophenyl-	25% EtOH	6.30
p-Bromophenyl-	25% EtOH	7.26
o-Nitrophenyl-	25% EtOH	0.56×10^{-9}
m-Nitrophenyl-	25% EtOH	6.9
p-Nitrophenyl-	25% EtOH	9.8
m-Carboxyphenyl-	25% EtOH (1st *Ka*)	2.22×10^{-5}
p-Carboxyphenyl-	25% EtOH (1st *Ka*)	3.06
Benzoic acid	25% EtOH	2.29
m-Carboxyphenyl-	25% EtOH (2d *Ka*)	1.12×10^{-10}
p-Carboxyphenyl	25% EtOH (2d *Ka*)	1.90
Phenyl-	25% EtOH	1.97[1a]
p-Phenetyl-	50% EtOH	0.463×10^{-11}
p-Phenoxyphenyl-	50% EtOH	1.16
Phenyl-	50% EtOH	1.64[1b]

Experimental

Nitrophenylboric Acids.—These were prepared by the two nitration methods of Seaman and Johnson.[2] The acetic anhydride method for the ortho and para isomers gave an average yield of 0.9 g. of the para compound and 10 g. of the ortho compound from 10 g. of phenylboric acid. These averages are from ten such nitrations. Seaman and Johnson report 0.3 g. of the para isomer and 8 g. of the ortho isomer from 10 g. of phenylboric acid. Our increased yield may be due to the fact that we used samples of highly purified phenylboric acid for the nitrations. The other nitration method for the meta isomer gave about the same yield as previously reported. The ortho and meta isomers were purified by recrystallization from benzene and from water. The para isomer was recrystallized from water.

Isomer	Ortho	Meta	Para
B, % (direct titr.)[1a]	6.45	6.47	6.46
B, % calcd.	6.48	6.48	6.48
M. p., °C. corr. (instant immersion)	101, resolidifies to melt at 145–147	279–281 (dec.)	309
M. p., °C., of S. and J. in preheated bath	143.5–147.7 (anhydride)	275–276.5 (dec.)	305.5

m- and *p*-**Carboxyphenylboric Acids.**—These were prepared in 90 and 80% yields, respectively, by the oxidation of *m*- and *p*-tolylboric acids according to the method of Michaelis.[3] The meta isomer was purified by recrystallization from water, from which it separates in the form of fine needles, m. p. 253° (corr.). Koenig and Scharrnbeck[4] report the melting point as 240°. The para isomer was recrystallized from water, from which it separates as fine needles melting at 240° (corr.). The melting point has been reported[3,4] as 225°. Attempts to obtain the ortho isomer by the oxidation of *o*-tolylboric acid were unsuccessful.[5]

m- and *p*-**Fluorophenylboric Acids.**—These were both prepared by the interaction of the corresponding fluorophenylmagnesium bromide with *n*-butyl borate. *m*-Fluorobromobenzene was prepared by the thermal decomposition of *m*-bromobenzenediazonium fluoborate according to the method of Balz and Schiemann.[6] *p*-Fluorobromobenzene was available commercially. *m*-Fluorophenylboric acid was recrystallized from benzene and from water. The para isomer was recrystallized from benzene. Both compounds separate as fine needles; m. p., meta 220–221° (corr.), para 289–290° (corr.). *Analysis.*—B calcd., 7.74; B found (direct titration), meta 7.77; para 7.93. Neither compound has been reported previously.

m- and *p*-**Bromophenylboric Acids.**—These were both prepared by the interaction of the corresponding bromophenylmagnesium bromide with *n*-butyl borate. *m*-Dibromobenzene was prepared from *m*-bromoaniline by means of the Sandmeyer reaction. *m*-Bromophenylboric acid was purified by recrystallization from benzene and from water. It crystallizes from the latter solvent in the form of fine crystals melting at 170° (corr.). *p*-Bromophenylboric acid was recrystallized from 20% alcohol in the form of fine needles melting at 312–315° (corr.) upon instant immersion. Bean and Johnson[7] report the melting point of the anhydride as 301–302° on the Maquenne block. *Analysis.*—B calcd., 5.21; B found (direct titration), meta 5.26; para 5.14. The meta isomer has not been reported previously.

p-**Phenoxyphenylboric acid** was prepared by the interaction of *p*-phenoxyphenylmagnesium bromide and *n*-butyl borate. In order to obtain a satisfactory yield of the Grignard reagent it was necessary to reflux the reaction mixture with the magnesium for about five hours. *p*-Phenoxyphenylboric acid was recrystallized from benzene and from 25% alcohol. It crystallized from the latter solvent as short fine needles melting at 123–124° (corr.). *Analysis.*—B calcd., 5.07; B found (direct titration), 5.05. This compound has not been reported previously.

Miscellaneous.—Phenylboric acid, the three chloro-

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(2) Seaman and Johnson, This Journal, **53**, 711 (1931).

(3) Michaelis, *Ann.*, **315**, 19 (1901).

(4) Koenig and Scharrnbeck, *J. prakt. Chem.*, [2] **128**, 153 (1930).

(5) Bettman and Branch, This Journal, **56**, 1616 (1934).

(6) Balz and Schiemann, *Ber.*, **60**, 1188 (1927).

(7) Bean and Johnson, This Journal, **54**, 4415 (1932).

phenylboric acids, and *p*-phenetyl boric acid have been previously described.[1]

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

TABLE II

DISSOCIATION CONSTANTS AT 25°

Acid	Solvent, EtOH	Detns.	Molality range	Range of *Ka*	Mean *Ka*	Av. dev. from mean *Ka*, %
m-Fluorophenylboric	25%	9	0.06–0.02	1.08–1.12	1.10×10^{-9}	1.1
m-Chlorophenylboric	25%	9	.06– .02	1.32–1.38	1.35×10^{-9}	1.0
m-Bromophenylboric	25%	9	.03– .01	1.42–1.52	1.46×10^{-9}	1.8
p-Fluorophenylboric	25%	8	.06– .02	3.56–3.79	3.66×10^{-10}	2.3
p-Chlorophenylboric	25%	9	.06– .02	6.21–6.45	6.30×10^{-10}	1.2
p-Bromophenylboric	25%	9	.03– .01	7.09–7.38	7.26×10^{-10}	0.9
o-Nitrophenylboric	25%	1	.03		5.6×10^{-10}	
m-Nitrophenylboric	25%	1	.03		6.9×10^{-9}	
p-Nitrophenylboric	25%	1	.03		9.8×10^{-9}	
m-Carboxyphenylboric	25% (1st *Ka*)	12	.03– .005	2.15–2.30	2.22×10^{-5}	1.7
p-Carboxyphenylboric	25% (1st *Ka*)	8	.02– .005	3.00–3.11	3.06×10^{-5}	0.7
Benzoic acid	25%	11	.03– .005	2.20–2.36	2.29×10^{-5}	1.8
p-Phenetylboric	50%	9	.06– .02	4.56–4.76	4.63×10^{-12}	0.9
p-Phenoxyphenylborie	50%	9	.03– .01	1.13–1.18	1.16×10^{-11}	.9

It was found that the second *Ka* of the carboxyphenylboric acids varied with concentration. A value was obtained for infinite dilution by plotting $\mu^{1/2}$ against $-\frac{1}{4} \log Ka$ and fitting the resulting points to the theoretical Debye curve for activities.[8] There is a probable uncertainty of 10 to 20% in the extrapolation since the theoretical curve used was for aqueous solutions.

Three measurements were made at each concentration with the second acid group neutralized 40, 50 and 60%, respectively. The average of these three values at each concentration is given in Table III together with the maximum deviation.

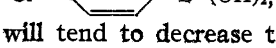
TABLE III

m- AND *p*-CARBOXYPHENYLBORIC ACIDS IN 25% ALCOHOL—SECOND *Ka*

Concn.	Meta $Ka \times 10^{10}$	Concn.	Para $Ka \times 10^{10}$
0.03	2.59 ± 0.01	0.03	4.32 ± 0.03
.02	2.38 ± .03	.02	4.00 ± .03
.01	2.14 ± .03	.01	3.63 ± .01
.005	1.97 ± .02	.005	3.37 ± .09
Extrapolated to 1.12×10^{-10}		Extrapolated to 1.90×10^{-10}	

Discussion of Results

Halogenophenylboric Acids.—The decreasing order of negativity of the halogens is F, Cl, Br, I. We have used[1b] Dericks α-factor for α-substituted acetic acids as a measure of negativity and this seems to confirm the above order. The dissociation constants of the α-fluoro, α-chloro, α-bromo and α-iodo acetic acids at 25° are given by Scudder[9] as 2.17, 1.55, 1.38 and 0.71×10^{-3}, respectively. The decreasing order of resonance interactions has been assumed to be I, Br, Cl and F. The experimental evidence for this order comes mainly from benzene substitution reactions,[10] but is not very definite: its existence has been derived mainly from theoretical deductions. The iodo group is much larger than the other halogeno groups and it has been assumed that its valency electrons would be more readily polarized than those of the smaller halogens. The fact that iodine, but not the other halogens, forms more than one bond to carbon in organic derivatives (iodinium compounds) has also been adduced as evidence for the resonance order.

In an earlier paper,[1a] the dissociation constants of the three chlorophenylboric acids were reported. It was assumed that resonance interactions of the chlorine atom were important in these derivatives since the ortho isomer was of about the same strength as the meta isomer. From the combination form,  it is seen that resonance will tend to decrease the strengths of the ortho and para acids. Negativity of course will increase the acidic strength in the order ortho > meta > para.

If we assume the negativity order F > Cl > Br > I and the old resonance order I > Br > Cl > F;

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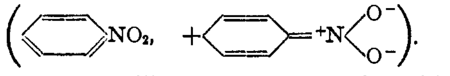
[8] Randall and Young, "Elementary Applications of Physical Chemistry," Chap. 28, pp. 7–8; book to be published.

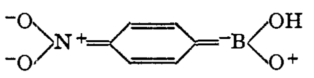
[9] Scudder, "Conductivity and Ionization Constants of Organic Compounds," Van Nostrand Co., New York, 1914, pp. 163, 99, 83, 189.

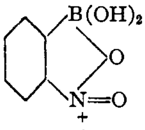
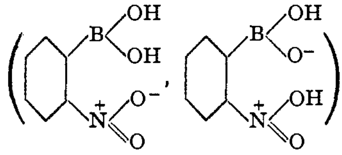
[10] See, for example, Ingold, *Rec. trav. chim.*, **48**, 797 (1929).

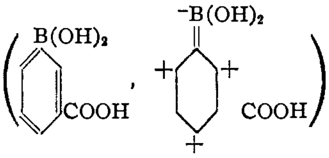
then the strength of the various halogeno phenylboric acids in a given position (*o*, *m* or *p*) must be F >Cl >Br >I. Actually the reverse order was found in both the para and meta positions. The experimental results obtained are of a comparative accuracy of about 5% since the three meta compounds were measured at the same time with the same electrode and the three para compounds were treated likewise. The new values for *m*- and *p*-chlorophenylboric acids agree fairly well with those obtained before. It will be noted in Table I that the differences between the halogeno acids are greater in the para than in the meta position. There is also a larger difference, in both the meta and para acids, between the fluoro and chloro acids than between the chloro and bromo acids.

Orders of strengths other than the normal negativity order, F >Cl >Br >I, have been obtained previously in the benzoic acid series.[11] This suggests some factor opposing the negativity effects in halogeno aromatic acids, but in the benzoic acids the differences in the strengths and the probable accuracy of the measurements are not such as to warrant any definite conclusions. In the halogenophenylboric acids the differences in the strengths seem to be definitely greater than the possible errors in the measurements. It seems reasonable to conclude that the assumed resonance order is in error and that the true order is F >Cl >Br. The fact that the meta acids show the same order as the para acids (although the differences are very small) is probably due to secondary resonance interactions between the halogen atom and the benzene ring.

Nitrophenylboric Acids.—*p*-Nitrophenylboric acid is stronger than its meta isomer. The para nitro derivatives of benzoic acid, phenol and anilinium ion are all stronger acids than their meta derivatives. In a previous paper we have attributed this order of strengths to the resonance . The latter structure will tend to stabilize the acid-strengthening resonance in the case of a boric acid derivative, and the combination form of the ion largely responsible for the great strength of *p*-nitrophenylboric acid is



o-Nitrophenylboric acid is weaker than *m*-nitrophenylboric acid, while in the other types of aromatic acids the ortho nitro compounds are stronger acids than their meta isomers. The negativity of the nitro group and its resonance interaction with the benzene ring would lead one to expect that *o*-nitrophenylboric acid should be considerably stronger than its meta isomer. It seems likely that ring formation has taken place giving rise to the structure . This form may be considered as either in equilibrium with the classical structure or as one of the forms whose combinations constitute the resonating molecule. In either case its existence tends to decrease the strength of the acid because of the negative charge imposed on the boron atom. The Referee of this paper suggests the possibility of hydrogen bond formation in *o*-nitrophenylboric acid as an alternative explanation of its weakness. In our method the molecule would then be represented as . We preferred to ascribe the ring formation to a boron bond, as *o*-nitrobenzoic acid is not anomalously weak, but this evidence is not conclusive.

Carboxyphenylboric Acids.—A comparison of the first dissociation constant of *m*-carboxyphenylboric acid with that of benzoic acid gives an approximate measure of the negativity of the $B(OH)_2$ group. In 25% alcohol the two acids have almost the same strength, $Ka = 2.22$ and 2.29×10^{-5}, respectively. From this it would appear that the $B(OH)_2$ group has nearly the same negativity as a hydrogen atom. However, the resonance  tends to increase the strength of *m*-carboxyphenylboric acid and the $B(OH)_2$ group should be rated as a slightly positive group, that is, the acid $(HO)_2B—CH_2COOH$ should be slightly weaker than acetic acid. That the $B(OH)_2$ group is not markedly negative can best be attributed to a negative charge imposed on the boron atom by

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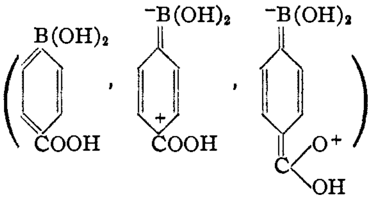
(11) Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 3, 31 (1928).

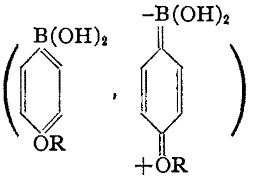
interaction of its sextet with donor atoms. Whether this interaction is with the attached hydroxyl groups or with solvent molecules is not shown by the measurements.

In *p*-carboxyphenylboric acid the resonance, brings the positive charge nearer to the dissociating proton than the resonance in the meta isomer. It is therefore not surprising to find that the para acid is stronger than either *m*-carboxyphenylboric acid or benzoic acid.



The second dissociation constant of *m*-carboxyphenylboric acid is less than that of phenylboric acid, just as the second *Ka* of isophthalic acid is less than that of benzoic acid. This agrees with the positivity of the carboxylate ion group. The second dissociation constant of *p*-carboxyphenylboric acid is greater than that of the meta isomer. This is in contrast with the phthalic acids, the second dissociation constant of terephthalic acid being less than that of isophthalic acid.

_p_-Phenoxyphenylboric Acid.—A comparison of the strengths of phenylboric, *p*-phenetylboric and *p*-phenoxyphenylboric acids is interesting. The last two acids are weaker than phenylboric acid. This may be attributed to the resonance which imposes a negative charge on the boron atom and so reduces the acidic strength. When R is a phenyl group this acid-weakening resonance is reduced because there is a competition for the unshared electrons of the oxygen atom between the group, —$C_6H_4B(OH)_2$ and the phenyl group. Consequently the substitution of a phenyl for an ethyl group increases the strength of the acid to a much greater extent than could be due to the relative negativities of the groups when they are so distant from the dissociation proton. The dissociation constants in 50% alcohol are phenylboric acid, $Ka = 1.64 \times 10^{-11}$; *p*-phenoxyphenylboric acid, $Ka = 1.16 \times 10^{-11}$ and *p*-phenetylboric acid, $Ka = 4.63 \times 10^{-12}$. The measurements were made in 50% alcohol because of the insolubility of *p*-phenoxyphenylboric acid in 25% alcohol and water.



***m*-Substituted Phenylboric and Benzoic Acids.**—The expression $\Delta pK = \log_{10} K_{\mathrm{HXH}} - \log_{10} K_{\mathrm{RXH}}$ in which RXH is the R derivative of the acid HXH, and K is a dissociation constant, has been used as a measure of the effect of the group, R, on the dissociation constant. ΔpK includes both negativity and resonance effects. Its magnitude and even its sign may vary with HXH. But it might be expected that the ΔpK values of a group are approximately the same when the acids are meta derivatives of benzoic and phenylboric acids. The classical structures of benzoic and phenylboric acids are very similar. The distances between the dissociating protons and the meta positions are the same in the two acids. A meta group has little or no resonance interaction with the acidic group, and so only minor differences can arise from this type of interaction. Resonance between the meta group and the benzene nucleus is approximately the same in a benzoic acid as in a phenylboric acid. However, this expectation is not borne out by the facts. This can be seen by inspection of Table IV in which ΔpK is shown for some meta groups in both benzoic and phenylboric acids.

TABLE IV

ΔpK VALUES[12] OF THE *m*-PHENYLBORIC ACID AND THE *m*-BENZOIC ACID SERIES

Group	ΔpK Phenylboric acid series	ΔpK Benzoic acid series
F	−0.75	−0.44
Cl	− .85	− .45
Br	− .87	− .42
OC_2H_5	− .19	− .14
NO_2	−1.55	− .72
COO^-	+0.24	+ .36
CH_3	+ .15	+ .07

The values of ΔpK for the benzoic and phenylboric acids are alike in that for both acids the order for the groups is nitro, halogeno, ethoxyl, methyl and carboxylate ion, and in that the first three are negative groups and the last two are positive. The magnitude of ΔpK for the group is larger, except for COO^-, in the meta substituted

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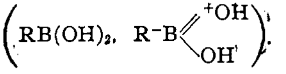
(12) All of the phenylboric acid values are from measurements in 25% alcohol. The constants of the halogenobenzoic acids and the second dissociation constant of isophthalic acid are taken from Kuhn and Wassermann[11] in 50% methyl alcohol and are referred to benzoic acid in the same solvent. The other values are from measurements in aqueous solution. The value for *m*-ethoxybenzoic acid is taken from Scudder, reference 9, p. 152; the other values are from Landolt and Börnstein, ed. 5, Vol. II, pp. 1143, 1148. ΔpK for COO^- in the benzoic acid series has been corrected for the equivalence of the COO^- groups in the divalent ion by subtracting $\log_{10} 2$.

phenylboric acid than in the corresponding benzoic acid derivative. The large ΔpK of groups in boric acid derivatives can also be seen in a comparison of the acid strengths of butyl, benzyl and β-phenylethylboric acids with those of the correspondingly substituted ammonium ions. ΔpK for benzyl minus butyl and for β-phenylethyl minus butyl are -1.63 and -0.73 in the first series and -1.27 and -0.78 in the second.[13] The negativity effects are thus at least as great in the boric acids as in the ammonium ions, though in the former series the dissociating protons are one atom further removed from the compared groups than in the latter. We have chosen the above groups for this comparison because they have no resonance interaction with the rest of the molecule.

The above observations may be explained by the theory of the boric acid resonance,  $\left(RB(OH)_2,\ R^{-}B\begin{matrix}\diagup\!\!\diagup\ {}^{+}OH \\ \diagdown\ OH\end{matrix}\right)$. The strength of a boric acid depends on the interaction of the unshared electron pairs of a hydroxyl group with the sextet boron atom. This process imposes a negative charge on the boron atom and is assisted by the negativity of the attached group. This effect is additional to the normal repulsion of the proton by a negative group and enhances the influence of the group. It may be noted that owing to the above resonance the action of a negative substituent is largely on the boron atom in a boric acid but on the hydroxyl group in a benzoic acid derivative, and so acts over a shorter distance in the former than in the latter case.

We wish to express our appreciation to Mr. C. E. Larson of the Biochemistry Department who carried out the glass electrode measurements on the nitrophenylboric acids.

Summary

The dissociation constants of some substituted phenylboric acid derivatives have been measured. These have been discussed and compared on the basis of negativity and resonance.

It is pointed out that the old resonance order assumed for the halogens is wrong and that the true order is F >Cl >Br.

o-Nitrophenylboric acid, unlike other *o*-nitro aromatic acids, is weaker than its meta and para isomers. An explanation for this has been given.

An enhanced effect of the negativity of substituted groups has been noted in boric acid derivatives.

BERKELEY, CALIF. RECEIVED MAY 21, 1934

[13] These values are calculated from dissociation constants given by Yabroff, Branch and Bettman, Reference 1b: and by Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

[CONTRIBUTION NO. 141 FROM THE EXPERIMENTAL STATION OF THE E. I. DU PONT DE NEMOURS & COMPANY]

Polymerization under High Pressure

BY HOWARD W. STARKWEATHER

Since polymerization reactions involve greater contractions in volume than most reactions in condensed systems, it seemed reasonable to suppose that polymerizations would be more sensitive to pressure than most reactions.

Strange and Bliss claimed[1] that the polymerization of hydrocarbons, such as butadiene, to rubber-like substances was greatly accelerated when they were subjected to high pressure.

Bridgman and Conant[2] reported the polymerization of isoprene, dimethyl-2,3-butadiene-1,3, styrene, indene, isobutyraldehyde and *n*-butyraldehyde at pressures up to 12,000 atmospheres. Conant and Tongberg[3] investigated the polymerization of isoprene, vinyl acetate and *n*-butyraldehyde in greater detail. They showed that the rate of polymerization of isoprene was accelerated by peroxides, was retarded by hydroquinone, and followed the rate for a first order reaction. Conant and Peterson[4] continued this investigation and concluded that peroxide catalysts were essential to the polymerization, and that the effect of increased pressure was only to accelerate the catalyzed reaction. Cyclohexene oxide was polymerized with great difficulty. Tammann and Pape[5] investigated in considerable detail the polymerization of styrene, isoprene, vinyl acetate, dimethylbutadiene and indene at pressures of 720 to 3100 atmospheres and temperatures of 140 to 160°.

[1] Strange and Bliss, British Patent 3045 (1913).

[2] Bridgman and Conant, *Proc. Nat. Acad. Sci.*, **15**, 680 (1929).

[3] Conant and Tongberg, THIS JOURNAL, **52**, 1659 (1930).

[4] Conant and Peterson, *ibid.*, **54**, 628 (1932).

[5] Tammann and Pape, *Z. anorg. allgem. Chem.*, **200**, 113 (1931).