

## ELECTROPHILIC DISPLACEMENT REACTIONS

### XV. KINETICS AND MECHANISM OF THE BASE-CATALYZED PROTODEBORONATION OF ARENEBORONIC ACIDS<sup>1</sup>

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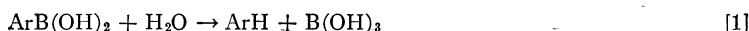
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Received June 7, 1963

#### ABSTRACT

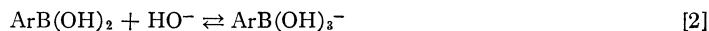
An investigation of the kinetics of the protodeboronation of benzenboronic acid in water in the pH range 2.0 to 6.7 is described. In addition to the acid-catalyzed reaction studied earlier a reaction whose rate is independent of pH and one whose rate increases linearly with hydroxide ion concentration have been observed. The effect of malonate buffer concentration at low pH confirms the earlier observations of general acid catalysis. Changes in buffer concentration at pH 6.70 have no effect on rate indicating specific hydroxide ion catalysis. Effect of substituents in the ortho, meta, and para position of the benzene ring on the rate of protodeboronation have been examined. Ortho-para ratios for this reaction are high; possible reasons for this are discussed. The Hammett equation using  $\sigma$  correlates the rates for meta and para substituents.

Among the reactions of areneboronic acids in which the dihydroxyboron group is subjected to electrophilic displacement the simple hydrolysis or protodeboronation (eq. [1]) is particularly interesting. Ainley and Challenger (1)



showed that the hydrolysis of boronic acid proceeds in water at 150°, and is catalyzed by concentrated sodium hydroxide, concentrated hydrochloric acid, as well as zinc and cadmium bromides. Ammoniacal silver nitrate has been shown to be an effective catalyst for the protodeboronation of benzenboronic acid and others of the arene series (2, 3, 4). An understanding of the mechanisms by which these catalysts function would be desirable, and we have embarked upon a series of kinetic investigations toward this end.

A fairly extensive and detailed study of the kinetics of acid-catalyzed protodeboronation has been described (5, 6, 7). Observation of the variation of rate constants in several acidic media, and in deuterium, as well as protium, solvents, along with determination of substituent effects led to the conclusion that the reaction is an electrophilic displacement in which the rate-determining step is the transfer of a proton from an acid to the boronic acid. In view of this an examination of the same reaction catalyzed by base was in order, especially because the strongest electrophile which might be present in significant concentration in aqueous base might well be water. The possibility that a SE1 type of reaction (eqs. [2-4]) might be involved also provided some attraction.



<sup>1</sup>Presented at the Symposium of Organometallic Compounds, sponsored by the Inorganic Chemistry Division of the Chemical Institute of Canada, and the University of British Columbia, in Vancouver, B.C., September 5, 1962. Preceding paper in this series: H. G. Kuivila, L. E. Benjamin, C. J. Murphy, A. D. Price, and J. H. Poley. *J. Org. Chem.* **27**, 825 (1962).

## RESULTS AND DISCUSSION

Exploratory kinetic experiments were carried out with *o*-methoxybenzeneboronic acid at 60° in aqueous borate buffers at pH 8.7. Several difficulties were encountered. First-order rate plots indicated very rapid initial reaction followed by a pronounced decrease to what appeared to be a linear plot. Rate plots could not be reproduced with satisfactory precision. In the presence of oxygen the expected product, anisole, was accompanied by guaiacol, formed by oxidative replacement of the dihydroxyboron group by hydroxyl. When the pH was decreased below 7, it was possible to eliminate these difficulties provided appropriate precautions described in the Experimental part were taken.

Most of the kinetic runs were conducted in aqueous malonate buffer solutions at pH 6.70 at 90°. At this temperature the buffers showed a detectable change in pH after about six days due, presumably, to decarboxylation of the malonic acid. Agreement of the ultraviolet spectrum of the product with that expected was taken as confirmation that the reaction took the expected course. In the cases of *o*-methoxy-, 2,6-dimethoxy-, and *p*-methoxybenzeneboronic acids a small amount of brown material appeared in the reaction mixture after several half-lives. It apparently functioned as a catalyst for the reaction, but generally made its presence felt in this way late enough in the course of the kinetic run so that satisfactory rate constants could be obtained from initial slopes. Figure 1 shows a typical first-order rate plot for 2,6-dimethoxybenzeneboronic acid;

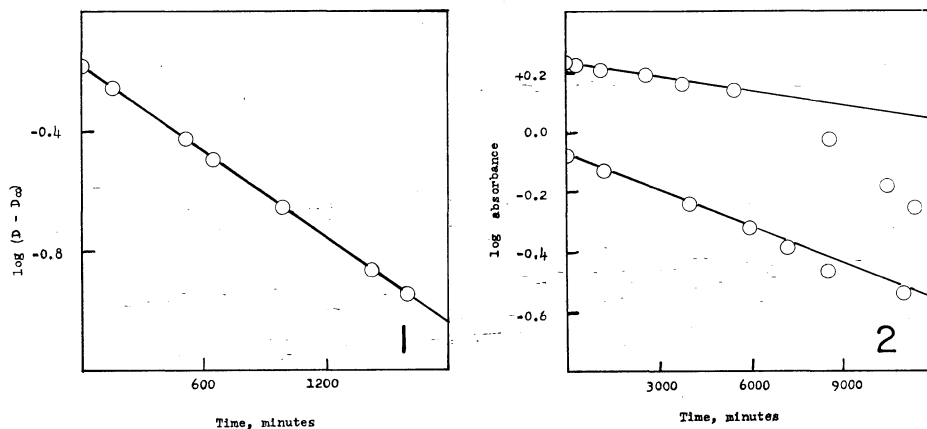


FIG. 1. Pseudo first-order rate plot for the base-catalyzed protodeboronation of 2,6-dimethoxybenzeneboronic acid at 90.0°, pH 6.70; ionic strength 0.14; malonate buffer.

FIG. 2. Pseudo first-order rate constants for base-catalyzed protodeboronation at 90.0°, pH 6.70; ionic strength 0.14; malonate buffer. Upper curve *p*-methoxybenzeneboronic acid. Lower curve *o*-methoxybenzeneboronic acid.

Fig. 2 shows a curved plot for *o*-methoxybenzeneboronic acid and the most extreme case of curvature observed with *p*-methoxybenzeneboronic acid. The other boronic acids gave good linear plots. As shown in Table I (runs 130 and 131), the first-order rate law is valid over at least a 10-fold variation in initial concentration of 2,6-dimethoxybenzeneboronic acid.

#### Effect of pH and Buffer Concentration

As a test of general base catalysis versus specific lyate ion catalysis the effects of variation of buffer concentration and pH on the rate coefficients were examined. Pertinent results are presented in Tables II and III. The data in Table II are at pH 6.70 and clearly

TABLE I  
Protodeboronation of 2,6-dimethoxybenzeneboronic acid

Run	Addend	Addend moles/l.	$k_{\text{obs}} \times 10^6$ sec <sup>-1</sup>
116*	—	—	17.4
117*	—	—	18.0
130†	—	—	18.2
131‡	—	—	18.3
139§	H <sub>3</sub> BO <sub>3</sub>	$3.45 \times 10^{-3}$	9.20
138	—	—	9.36

\*Run under "anaerobic" conditions.

†Initial concentration of 2,6-dimethoxybenzeneboronic acid =  $4.45 \times 10^{-3}$  M.‡Initial concentration of 2,6-dimethoxybenzeneboronic acid =  $5.25 \times 10^{-4}$  M.

§pH = 6.42; for all other runs in this table, pH = 6.70.

TABLE II

Run	10 <sup>3</sup> conc. malonate anion, moles/liter	Ionic strength	pH <sub>meas</sub>	10 <sup>6</sup> $k_{\text{calc}}^*$ sec <sup>-1</sup>	10 <sup>6</sup> $k_{\text{obs}}$ sec <sup>-1</sup>	10 <sup>6</sup> $k_{\text{corr}}^\dagger$ sec <sup>-1</sup>
—	0.543	0.14	6.70	18.1	18.1	18.1
93m	0.155	0.04	6.70	18.1	22.0	22.0
92m	0.764	0.20	6.70	18.1	20.2	18.8
91m	1.55	0.40	7.15	52.2	53.4	17.9

\*Rate of base-catalyzed reaction at pH indicated and  $\mu = 0.14$ , see Table V.

†Corrected to pH 6.70 and ionic strength 0.14, see Table V.

TABLE III

Variation of the rate of hydrolysis of 2,6-dimethoxybenzeneboronic acid with  
malonic acid concentration, 90°, ionic strength 0.14, corrected to pH 3.60;  
buffer ratio (H<sub>2</sub>A/HA<sup>-</sup>) = 0.155

Run	Conc. malonic acid 10 <sup>3</sup> moles/liter	pH <sub>meas</sub>	10 <sup>6</sup> $k_{\text{calc}}^*$ sec <sup>-1</sup>	10 <sup>6</sup> $k_{\text{obs}}$ sec <sup>-1</sup>	10 <sup>6</sup> $k_{\text{corr}}^\dagger$ sec <sup>-1</sup>
—	None	3.60	5.13	—	5.13
75m	0.27	3.70	4.37	5.11	5.87
74m	0.58	3.67	4.58	6.12	6.67
73m	1.17	3.67	4.58	8.60	9.15
70m	1.38	3.59	5.21	8.92	8.84
67m	1.90	3.54	5.66	9.64	9.11
71m	2.74	3.59	5.21	12.5	12.4
69m	3.16	3.72	4.24	7.25	8.14
68m	3.66	3.56	5.47	14.0	13.7
83m	3.90	3.76	3.94	9.27	10.5
72m	6.00	3.39	7.89	18.1	15.3
77m	6.00	3.55	5.56	12.9	12.5
85m	6.00	3.58	5.31	11.8	11.6
76m	11.7	3.61	5.05	21.9	22.0
86m	18.0	3.65	4.73	29.9	30.3
88m	47.4‡	3.62	5.01	55.7	54.2†
87m	50.4§	3.50	5.11	57.5	54.6†
84m	56.0	3.55	5.56	46.9	45.1†
89m	74.6¶	3.58	5.31	76.6	75.0†

\*Rate of H<sub>2</sub>O<sup>+</sup> catalyzed reaction at pH indicated.

†Corrected to pH 3.60 and ionic strength 0.14, see Table V.

‡Ionic strength 0.23.

§Ionic strength 0.26.

||Ionic strength 0.30.

¶Ionic strength 0.46.

indicate that there is no noticeable effect of malonate ion concentration on rate. Phosphate buffers, on the other hand, revealed an increase in rate with buffer concentration. This was attributed to the presence of catalytic impurities in the buffers because buffers of the same pH at the same concentration made from different reagents gave different rate coefficients.

The data presented in Table III were obtained with a buffer containing the malonate monoanion and malonic acid in a ratio of about 7, resulting in a pH of 3.60. A very pronounced increase in rate results as the buffer concentration is increased. This is a clear-cut indication of general acid catalysis, and confirms the results obtained earlier in the study of the acid-catalyzed reaction. A plot of the data is shown in Fig. 3. A linear relationship between rate and buffer concentration would be expected. The reason for the non-linear plot is not clear at this time.

The effect of pH on the rate of reaction was examined, providing the data presented in Table IV and plotted in Fig. 4. Above pH 6.0 the plot has unit slope as would be

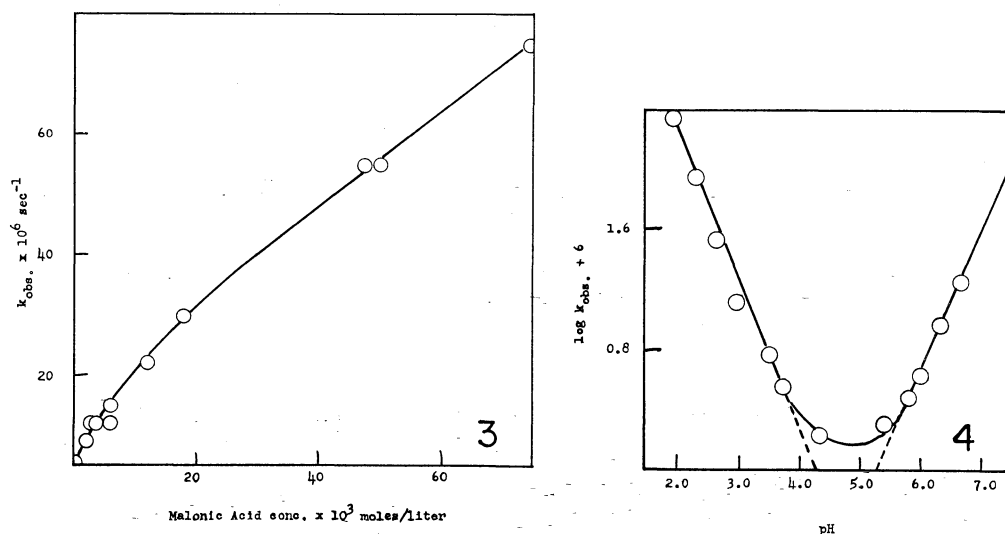


FIG. 3. Test of Brönsted catalysis law for 2,6-dimethoxybenzeneboronic acid at 90.0° with malonate buffers; pH 3.60; ionic strength 0.14.

FIG. 4. pH -  $\log k$  profile for protodeboronation of 2,6-dimethoxybenzeneboronic acid at 90.0°; ionic strength 0.14.

required for a reaction whose rate is directly dependent upon hydroxide ion concentration. Below this value the slope drops to a minimum near pH 4.85 and then rises again to a negative unit slope below pH 3.5 as the acid-catalyzed reaction comes into prominence. In the pH region around the minimum the rate constants are larger than the sum of the expected contributions from the base- and acid-catalyzed reactions. This means that there is also a pH-independent reaction which predominates in this region. The value of the uncatalyzed rate constant is  $0.630 \times 10^{-6} \text{ sec}^{-1}$ . This value has been used in constructing the solid line between pH 3.8 and 5.8.

In the pH range between about 6.0 and 6.7 the linear relationship between pH and  $\log k_{\text{obs}}$  suggests the following two-step mechanism as a reasonable working hypothesis.

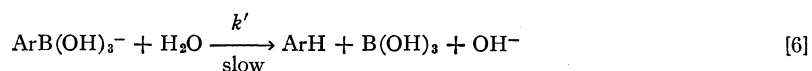
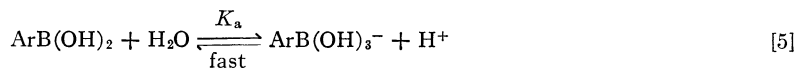


TABLE IV

Effect of pH on the hydrolysis of 2,6-dimethoxybenzene-boronic acid in aqueous malonic acid-sodium malonate buffer at 90.0° C, ionic strength 0.14

Run	pH	$k_{\text{obs}} \times 10^6$ sec <sup>-1</sup>	log $k_{\text{obs}} + 6$
118, 119	6.70	18.1	1.258
138	6.42	9.36	0.971
137	6.05	4.25	0.628
136	5.85	3.05	0.484
140	5.45	2.04	0.310
141	4.42	1.78	0.250
82m	3.81	3.66	0.563
78m	3.55	5.96	0.775
20m, 22m	3.00*	20.7	1.316
26m	2.70*	34.5	1.538
24m, 21m	2.40*	90.2	1.955
23m	2.00*	230	2.362

\*These runs were carried out in the absence of buffer; perchloric acid was used to adjust acidity.

Now,

$$[7] \quad K_a = \frac{[\text{BA}^-][\text{H}^+]}{[\text{BAH}]} = \frac{[\text{BA}^-][\text{H}^+]}{[\text{BAH}]_s - [\text{BA}^-]}$$

where  $[\text{BA}^-]$  is the concentration of boronate anion,  $[\text{BAH}]$  and  $[\text{BAH}]_s$  are the actual and stoichiometric concentrations of boronic acid. Solving for  $[\text{BA}^-]$ ,

$$[8] \quad [\text{BA}^-] = \frac{K_a[\text{BAH}]_s}{[\text{H}^+] + K_a} = \frac{K_a[\text{BAH}]_s}{[\text{H}^+]}$$

if  $K_a$  is much smaller than the hydronium ion concentration. This is true, since pH in these experiments is below 6.8 and the  $\text{p}K_a$  values for the boronic acids are greater than 8.25. The expression for the overall reaction velocity is given by

$$[9] \quad V = k_{\text{obs}}[\text{BAH}]_s = k'[\text{BA}^-][\text{H}_2\text{O}] = k'[\text{H}_2\text{O}] \frac{K_a}{[\text{H}^+]} [\text{BAH}]_s.$$

Whence

$$[10] \quad k_{\text{obs}} = 55.5 k' \frac{K_a}{[\text{H}^+]} \text{ or } \log k_{\text{obs}} = \text{pH} + \text{const.}$$

and

$$[11] \quad k' = k_{\text{obs}}[\text{H}^+]/55.5 K_a.$$

The logarithmic form of eq. [10] describes the linear portion of the rate profile in Fig. 4, indicating that this analysis is reasonable. If the mechanism is correct, knowledge of the pH and the value of  $\text{p}K_a$  in conjunction with the experimentally determined rate coefficient,  $k_{\text{obs}}$ , permits evaluation of the specific rate constant  $k'$  for reaction [6].

#### Effect of Ionic Strength

When the ionic strength is increased beyond 0.140 by the addition of sodium perchlorate, the specific rate constant decreases as can be seen from the last column in Table V. This would imply a negative salt effect. However, addition of the salt has the effect of decreasing the  $\text{p}K_a$  of the acid; the rate constant expected as a result of the change in

TABLE V

Effect of ionic strength on the base-catalyzed hydrolysis of  
2,6-dimethoxybenzeneboronic acid in aqueous malonic acid - sodium  
malonate buffer (pH 6.70) at 90.0° C

Run	NaClO <sub>4</sub> moles/l.	Total $\mu$	pH <sub>meas</sub>	$k_{calc} \times 10^{6*}$ sec <sup>-1</sup>	$k_{obs} \times 10^6$ sec <sup>-1</sup>
118, 119	0.0	0.140	6.70	(18.1)	18.1
128	0.036	0.176	6.67	17.0	18.7
127	0.076	0.216	6.63	15.5	17.1
124	0.120	0.260	6.57	13.5	14.9
126	0.240	0.380	6.54	12.6	14.1
123	0.360	0.500	5.49	11.1	13.8

\*Calculated by assuming that  $k_{obs} = 18.1 \times 10^{-6}$  at pH 6.70 and that the reaction is first order in hydroxide ion.

pH is shown in the penultimate column. Comparison of the values in the two columns shows that the primary kinetic salt effect is actually positive since the observed rate constants are larger than those calculated at each pH.

#### Effect of Added Boric Acid

The possibility that boric acid formed in the reaction might have an effect on the rate was tested. The result of run 139 in Table I reveals that no effect is observed when the acid is present in concentration of the order of magnitude of the initial boronic acid.

#### Effect of Oxygen

In view of the difficulties encountered in preliminary work at high pH values when oxygen was in contact with reaction solutions, its effect was tested at the lower pH. The reaction solutions of runs 116 and 117, Table I, were thoroughly degassed by alternate freezing and thawing at reduced pressure and sealed *in vacuo* before being placed in the constant temperature bath. Oxygen clearly has no effect on the reaction under these conditions.

#### Effects of Substituents

Rates of protodeboronation of several meta- and para-substituted benzeneboronic acids were measured at pH 6.70. In order to ascertain whether the reaction followed was only the one whose rate coefficient increases linearly with hydrogen ion concentration the rates were also measured at pH 6.42 in several cases. The values found at these two pH values are shown in Table VI, second and third columns. In the fourth column are shown the values which would be expected at the lower pH assuming linear dependence of rate coefficient on hydroxide ion concentration. The agreement between the expected and observed values is satisfactory, and assures that the rate of the same reaction is being measured in each case. Because of the very slow reactions in the case of meta substituents it was not practical to make the same check, but it is probably safe to assume that the result would be the same.

Examination of the values in the second column of Table VI reveals that all substituents increase the value of  $k_{obs}$ . Obviously no simple linear free energy relationship will correlate these data with other electrophilic aromatic substitutions. However, if values of  $k'$  of equation [11] are estimated, the pattern changes, as seen below.

It is not feasible to determine  $pK_a$  values of many boronic acids in water because of their limited solubility. However, values in 25% methanol have been determined by Polevy (8). Another limitation is that the  $pK_a$  values were determined at 25° while the

TABLE VI

Effect of substituents on the rate of hydrolysis of benzenboronic acid in aqueous malonic acid - sodium malonate buffer at 90.0° C, ionic strength 0.14

Substituent	$10^6 k_{\text{obs}}$ pH 6.70	(sec <sup>-1</sup> ) pH 6.42	$10^6 k_{\text{calc}}$ pH 6.42	$10^{10} K_a$	$10^6 k'$ (l./mole sec)	$\log (k'/k'_0)$
H	0.145	0.08	0.076	7.59	0.688	0
<i>p</i> -CH <sub>3</sub> O	0.610	0.322	0.320	2.57	8.54	1.09
<i>p</i> -CH <sub>3</sub>	0.260	0.145	0.137	3.02	3.10	0.654
<i>p</i> -Cl	0.187	0.10	0.098	20.9	0.322	-0.330
<i>p</i> -F	0.250	0.141	0.131	9.33	0.966	0.149
<i>o</i> -CH <sub>3</sub> O	1.53	0.772	0.803	2.14	25.8	1.58
<i>o</i> -CH <sub>3</sub>	0.360	0.208	0.189	1.02	12.6	1.27
<i>o</i> -Cl	8.60	4.76	4.52	26.9	12.0	1.24
<i>o</i> -F	11.1	—	—	56.2	7.14	1.02
<i>m</i> -CH <sub>3</sub> O	0.343	—	—	16.6	0.744	0.034
<i>m</i> -CH <sub>3</sub>	0.294	—	—	7.08	1.50	0.338
<i>m</i> -Cl	0.217	—	—	51.3	0.152	-0.656
<i>m</i> -F	0.332	—	—	57.5	0.208	-0.520
2,6-diCH <sub>3</sub> O	18.1	9.36	9.47	0.295	2200	3.51

kinetic experiments were conducted at 90°. Thus, absolute values of  $k'$  cannot be accurately obtained with the data at hand, but relative values should be significant, and sufficient for our purposes. The last three columns in Table VI contain, respectively, values of  $K_a$ ,  $k'$ , calculated according to equation [11], and  $\log (k'/k'_0)$ . Inspection of these values shows that the normal pattern for electrophilic aromatic substitution emerges. When these are plotted against Brown's  $\sigma^+$  values (9) the point for *p*-methoxy falls considerably below the line; when they are plotted against  $\sigma + 0.5$  ( $\sigma^+ - \sigma$ ) (10) the plot is improved somewhat, but considerable scatter results. On the other hand, when the ordinary  $\sigma$  values are used in the plot a good line with a slope of  $-2.32$  results as can be seen in Fig. 5.

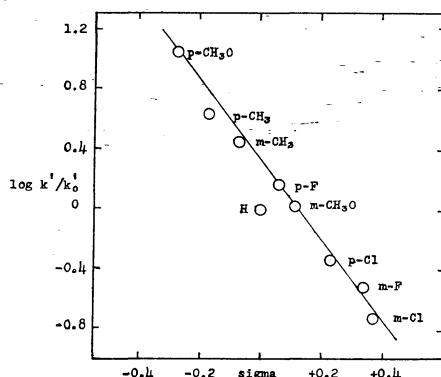


FIG. 5. Hammett plot for protodeboronation of benzenboronate anions at 90.0°; ionic strength 0.14.

Interestingly enough, the only pronounced deviation from the line is the point for benzenboronic acid. The negative value of rho indicates that a positive charge develops in the benzene ring in the transition state. The magnitude of the charge is a relatively small one for electrophilic aromatic substitutions which generally have rho values larger than four (11). Displacements of silicon, germanium, tin, and lead from the benzene ring by the proton have rho values of  $-5.0$ ,  $-4.6$ ,  $-3.8$ , and  $-2.5$ , respectively (12-15). Proto-deboronation of benzenboronic acid in 6.3 *N* sulphuric acid at 60° has a rho value of

-5.0, and the rates are correlated best by  $\sigma^+$  (7). The decrease in  $\rho$  when the more reactive boronate anion is the substrate would be expected because the negative charge on the boronate anion decreases the electron demand at the seat of reaction.

The Taft equation for ortho-substituted benzenes (16) can be used as a device for detecting influences on reactivity other than inductive and resonance effects. A plot of  $k'$  for the ortho-substituted benzenboronic acids is not linear; therefore, other factors do indeed play a role in this series.

The methyl and chloro substituents, which have similar steric but opposite electronic effects, produce about the same rate acceleration. Although *o*-fluoro usually has a larger partial factor than *o*-chloro in electrophilic aromatic substitution the reverse is true in the present case.

The ortho-para ratios shown in Table VII are striking in that no simple trend is dis-

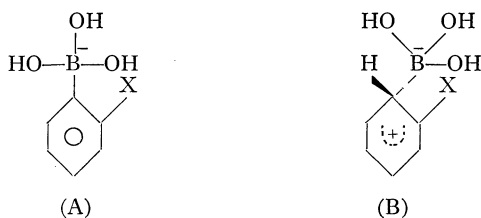
TABLE VII

Ortho-para ratios ( $k'_{\text{ortho}}/k'_{\text{para}}$ ) for protodeboronation of areneboronic acids in aqueous malonic acid-sodium malonate buffers (pH 6.70) at 90.0° C

Substituent	$k'_{\text{ortho}}/k'_{\text{para}}$
CH <sub>3</sub> O	3.02
CH <sub>3</sub>	4.06
F	7.34
Cl	37.3

cernible. In each case the value is greater than the statistical value of two, in marked contrast to acid-catalyzed protodeboronation in which case only *o*-methyl has a value greater than two (8). Furthermore, methyl and chloro have different values although they have similar bulk; chloro and fluoro have different values although they have similar electronic effects.

These observations may be interpreted as resulting from a combination of steric effects, hydrogen bonding, and electrostatic interactions and will be discussed in terms of the transition state for the formation of a pentadienate intermediate (B) by the attack of a water molecule on a boronate anion (A). Thus the carbon to which the proton becomes



attached is in the process of changing hybridization from  $sp^2$  to  $sp^3$ . Since the C—X and C—B bonds are eclipsed in (A), but staggered in (B), release of strain accompanying this change in dihedral angle in the order methyl > chloro > methoxy  $\approx$  fluoro would be expected. This may be a major factor for all substituents but the fluoro. The distance between the negative charge and the C—X dipole will increase in going from (A) to (B), with a resultant decrease in electrostatic repulsion. The introduction of a positive charge into the ring will decrease the magnitude of the C—X dipoles involving chlorine and fluorine, because the negative end is toward the halogen in the ground state. This will



lead to further decrease in electrostatic repulsion. The carbon bonded to boron decreases in electronegativity due to decreasing *s* character in the orbital involved, but increases in electronegativity due to the positive charge developing in the ring. The net result is probably a negligible change in the magnitude of charge on boron, and the electrostatic effect is very probably rate-enhancing for chloro and fluoro.

The oxygen in the methoxy group has a relatively high electron density and is at the the negative end of two dipoles. The electrostatic effect should be similar to that for chloro and fluoro. It is to be noted that the introduction of one methoxy group ortho to the boronic acid function increases the rate of reaction by a factor of 38.7 and the introduction of second methoxy increases the rate by a factor of 85.3 beyond that of the first. This kind of enhancement is frequently encountered in steric effects.

The methyl group is at the positive end of the X—C dipole in the boronic acid. As a result the electrostatic repulsion due to change in the bond moment will increase in going to the transition state. This will be counteracted by the change in dihedral angle and leads to the conclusion that the deactivating effect of the methyl group due to electrostatic factors will be smaller than the activating effect of fluoro and chloro.

The effects of hydrogen bonding are difficult to evaluate. Polevy (8) has shown that intramolecular hydrogen bonding occurs to ortho-methoxy, -chloro, and -fluoro in the free boronic acids. Loss of conjugation between substituent and boron, and development of the negative charge on boron in conversion to the anion must diminish the strength of the hydrogen bonds substantially. Whatever remains can be expected to be decreased further due to the electrostatic and geometric changes occurring in going to the transition state.

The resultant of these effects for the four substituents may be summarized as follows. Fluoro activates because of the electrostatic effect; methyl activates mainly because of the relief of steric strain; chloro and methoxy activate because of both effects. In the case of methoxy the reason for activation is not quite clear, since only the steric effect would seem to activate and this should be little larger than that for fluoro.

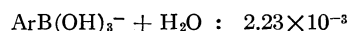
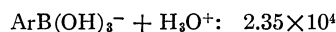
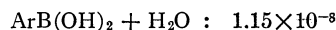
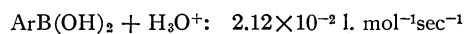
### *Mechanism*

In the earlier papers of this series on acid-catalyzed protodeboronation it was established that the reaction involves a rate-determining proton transfer from acid to boronic acid. This conclusion was based primarily on the observation of a kinetic isotope effect and general acid catalysis. The base-catalyzed reaction, on the other hand, appears not to be subject to general base catalysis. The mechanism represented by equations [5] and [6] with reaction [6] rate-determining is consistent with this observation. An increase in base concentration results in an increase in rate only when it leads to an increase in the concentration of the boronate anion through an increase in pH. Reaction [6] might very well be subject to general acid catalysis, but this possibility has not yet been examined explicitly. Satisfactory correlation of the rate constants by the "normal" sigma constants and the small value of rho suggests that the positive charge in the benzene ring is not highly developed.

The SE1 type of mechanism (equations [2-4]) can be eliminated as a possibility because it would be expected to have a positive value of rho, whereas a negative value is actually observed.

The uncatalyzed reaction must have a transition state which is neutral overall. This could result from attack on a boronic acid molecule by water, or from attack on a boronate anion by hydronium ion. Rate constants for 2,6-dimethoxybenzeneboronic acid at 90° have

been calculated assuming these two possibilities, and these are given below along with those for the acid- and base-catalyzed reactions. Perhaps the only conclusions which can



be drawn from these data with any confidence are that the boronate anion is about a million times as reactive as the boronic acid molecule and the hydronium ion is about a million times as powerful an electrophile as water in aromatic protodeboronation.

## EXPERIMENTAL

### Materials

All of the boronic acids used in this investigation have been described previously, and the wavelength at which the analytical determinations were made have also been reported (5-8). In view of the sensitivity of the reaction to adventitious materials dissolved in ordinary distilled water all of the water used was redistilled. Recrystallization of the boronic acids and of the buffer substituents were from redistilled water. All pH measurements were made at 25° and are reported as measured.

### Kinetics

(A) *Base-catalyzed hydrolysis*.—An appropriate amount of areneboronic acid was transferred to a 100-ml volumetric flask. The malonate buffer solution was added and the solution diluted to the mark with redistilled water. After all of the areneboronic acid was dissolved, aliquots were transferred to ampoules, which were sealed and placed in the constant-temperature bath at  $90.0 \pm 0.02^\circ$  for appropriate intervals. The ampoules were removed from the bath and chilled in ice water, the contents were transferred to a volumetric flask containing sufficient hydrochloric acid to neutralize the buffer base and analyzed spectrophotometrically.

(B) *Acid-catalyzed hydrolysis*.—The procedure was substantially the same with the exception that sodium acetate was used in the final dilution procedure to neutralize the perchloric acid.

## ACKNOWLEDGMENT

It is a pleasure to express our appreciation for support of this research by the U.S. Air Force Office of Scientific Research (Contract AF 49(638)-312).

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