

Electron Spin Resonance Spectra.—The second derivatives of the observed electron spin resonance absorption spectra are shown in Fig. 1 and 2. Because of the length of the spectra, only the low-field half is given. The spectra have been reconstructed using the coupling constants in Table I and assuming the phenoxy structure. The reconstructions match the experimental spectra in all details. Special care was

TABLE I
COUPLING CONSTANTS FOR THE DIALKYLAMINOPHENOXY

RADICALS IN AQUEOUS SOLUTION (GAUSS)			
	R = CH ₃		R = C ₂ H ₅
N	7.45	N	7.45
CH	2.14	CH	2.08
CH ₃	7.08	CH ₂	4.16

taken to obtain the tails of the spectra in order to measure the smaller ring proton coupling constants. In the case of the diethyl radical, one cannot distinguish between the ring proton and the CH₂ proton coupling constants. The analogy with the dimethyl radical, however, suggests the order given in Table I, since the nitrogen and ring proton coupling constants should not be much different in the two radicals. Some interesting properties of the spectra of these radicals may be mentioned. In the first place, one observes (Table I) a much smaller spin density at the ethyl CH₂ proton in the *p*-diethylaminophenoxy than at the methyl CH₃ protons in the *p*-dimethylaminophenoxy. This discrepancy can be explained in terms of hyperconjugation. A discussion of hyperconjugation of the (CH₃)₂-C- and (CH₃)₂-N- groups using the valence bond model was given by McLachlan.¹⁴ In this model, steric hin-

(14) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); J. R. Bolton, A. Carington, and A. D. McLachlan, *ibid.*, **5**, 31 (1962).

drance with respect to free rotation of the alkyl group can lead to a lower average spin density on the alkyl. The present results give a direct measure of the average exchange integral between the nitrogen p_z and the C-H orbital. Any inductive effect on the spin distribution has to be very small since in both radicals the nitrogen and ring coupling constants remain the same. In the diethylaminophenoxy radical the hyperfine lines are broadened, presumably due to the small unresolved hyperfine splitting of the CH₃ protons. Secondly, it was found that the spectra are solvent dependent.

Although a more detailed discussion on the solvent effects will be given at a later date, some results will be mentioned presently. In water solutions, the four ring-proton coupling constants are the same, a somewhat accidental result in view of the symmetry of these radicals. It is interesting that addition of dimethyl sulfoxide (DMSO) leads to a change in coupling constants. The ring-proton coupling constants are no longer the same and occur in two pairs in DMSO solution (see Table II). Preliminary calculations have shown that the spectral changes can be explained in the same fashion as was done by Gendell, Freed, and Fraenkel for semiquinones.¹ The electron cloud is polarized by the solvent, leading to these effects.

TABLE II
SOLVENT EFFECT ON COUPLING CONSTANTS OF
p-DIMETHYLAMINOPHENOXY RADICAL

Solvent composition, %	Dimethyl sulfoxide	Coupling constants (gauss)			
		N	CH(2x)	CH(2x)	CH ₃
100	0	7.45	2.14	2.14	7.08
50	50	7.05	2.52	1.65	6.64
0	100	6.29	3.53	0.81	5.90

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Electrophilic Displacement Reactions. XVI. Metal Ion Catalysis in the Protodeboronation of Areneboronic Acids¹⁻³

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A kinetic investigation has been made of the protodeboronation of benzeneboronic acids, and the effects of pH and of substituents in the *o*-, *m*-, and *p*-positions on rate. The pH-rate profile shows a base-catalyzed and an "uncatalyzed" reaction, each of which is catalyzed by cadmium ion in turn. The *ortho-para* ratios generally parallel those observed earlier for the reaction in the absence of cadmium ion, but the *meta*- and *para*-substituted acids show different linear free energy relationships for the two kinds of reaction. Salts of magnesium, zinc, copper(II), lead(II), nickel(II), cobalt(II), and silver also catalyze the protodeboronation. The mechanism of the metal ion catalyzed protodeboronation is discussed in the light of the experimental results.

Previous investigations on protodeboronation of benzeneboronic acids have revealed the existence of three mechanisms which can be distinguished on the

(1) (a) Presented in part at the Symposium on Organometallic Compounds, sponsored by the Inorganic Chemistry Division of the Chemical Institute of Canada and the University of British Columbia, Vancouver, B. C., Sept. 5, 1962; (b) preceding paper in this series: H. G. Kuivila, J. F. Reuwer, Jr., and J. A. Mangravite, *Can. J. Chem.*, **41**, 3081 (1963).

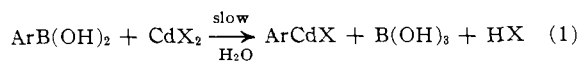
(2) Taken in part from the Ph.D. Dissertation of J. F. R., Jr., University of New Hampshire, June, 1962.

(3) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Contract AF 49 (638)-312 and by the Atomic Energy Commission under contract AT (30-1)-2970.

basis of kinetics. One of these is a general acid catalyzed reaction in which the rate-determining step involves proton transfer from an acid to the carbon of the benzene ring bearing the dihydroxyboron group.⁴ The rates for *m*- and *p*-substituted benzeneboronic acids are correlated by σ^+ with a ρ -value of -5.0 . A second mechanism displays specific hydroxide ion catalysis below pH 6.8 and is believed to involve proton transfer from a water molecule to the benzeneboronate

(4) H. G. Kuivila and K. V. Nahabedian, *J. Am. Chem. Soc.*, **83**, 2159, 2164 (1961); K. V. Nahabedian and H. G. Kuivila, *ibid.*, **83**, 2167 (1961).

anion.^{1b} Rates for *m*- and *p*-substituted benzenboronic acids are correlated by σ with a ρ -value of -2.32 . The third mechanism may be described as a "solvent" reaction, whose rate is independent of pH. It may have a rate-determining step in which hydronium ion reacts with a boronate anion. Substituent effects have not been examined. The long known fact that metallic salts such as those of cadmium, zinc, and silver also function as catalysts for protodeboronation of areneboronic acids⁵⁻⁸ suggests that other mechanisms may also exist. In view of the fact that mercuric salts react with areneboronic acids to form arylmercurials, Ainley and Challenger⁵ suggested that the other metallic salts react in an analogous manner forming easily hydrolyzed organometallic intermediates as shown in eq. 1 and 2.



In this paper we report the results of an investigation in some detail of the kinetics of the protodeboronation of areneboronic acids catalyzed by cadmium ion, and a survey of the effects of several metal ions on the rate of protodeboronation of 2,6-dimethoxybenzenboronic acid.

Results and Discussion

Our examination of the cadmium ion catalyzed reaction was designed to parallel the earlier work on the base-catalyzed reaction.^{1b} The kinetic experiments were carried out at 90° in aqueous solution in the presence of perchloric acid or a malonic acid-sodium malonate buffer using the spectrophotometric method described previously.^{1b}

Since the pH does not change during the reaction, and cadmium ion is not consumed, pseudo first-order kinetics are obeyed. The occasional deviations from linearity of the plot shown in the previous work (ref. 1b, Fig. 2) either were not observed, or appeared only after at least 65% reaction.

Effect of Cadmium Ion Concentration.—With *o*-methoxybenzenboronic acid at pH 6.70, addition of 1.0×10^{-4} and 5.0×10^{-4} M cadmium ion increased the pseudo-first-order rate coefficient from 1.53×10^{-6} to 42.4×10^{-6} and 203×10^{-6} sec.⁻¹, respectively, corresponding to a 4.87-fold increase in cadmium ion concentration. Data for 2,6-dimethoxybenzenboronic acid are shown in Table I. Comparison of the data for reactions carried out in the presence of 10^{-3} M perchloric acid suggests that dependence of rate coefficient on cadmium ion concentration is probably linear at very low concentrations, but falls off at higher concentrations. This is reflected in the values of k_b^{Cd} shown in the last column. This coefficient represents the difference between the experimental pseudo-first-order rate coefficient, $k_{\text{exp}}^{\text{Cd}}$, and that which would be observed in the absence of cadmium ion, k_{exp}^0 , and thus is that part of the total rate due to the presence of the ion.

Effect of pH.—The first ten entries in Table I show the effect of pH in the range 2.20–6.70. A

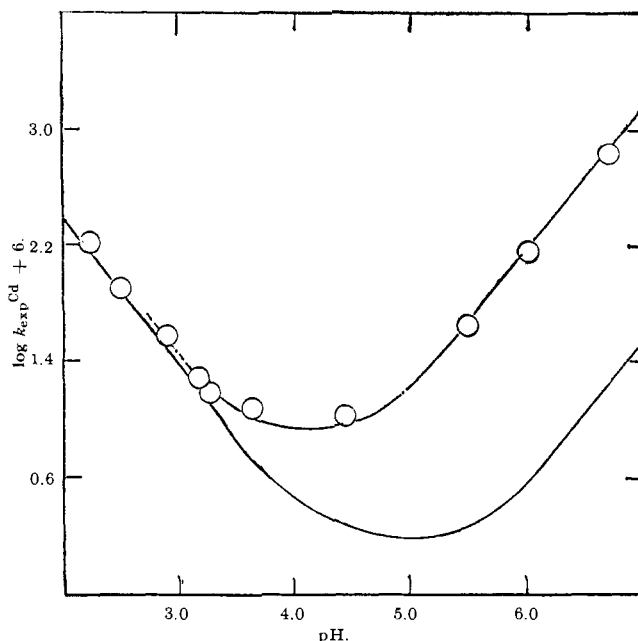


Fig. 1.— $\log k_{\text{exp}}^{\text{Cd}}$ vs. pH for the cadmium ion catalyzed protodeboronation of 2,6-dimethoxybenzenboronic acid at 90°.

semilogarithmic plot of the figures in the third column vs. pH is shown in the upper curve of Fig. 1. The linear portions are drawn with the theoretical positive and negative slopes for specific hydroxide and hydro-

TABLE I
EFFECT OF CADMIUM ION ON THE RATE OF PROTODEBORONATION OF 2,6-DIMETHOXYBENZENEBOONIC ACID AT 90°

$10^3[\text{Cd}^{2+}]$, M	pH	$10^6 k_{\text{exp}}^{\text{Cd}, b}$, sec. ⁻¹	$10^6 k_{\text{exp}}^0, c$ sec. ⁻¹	$10^3 k_b^{\text{Cd}, d}$ l. mole ⁻¹ sec. ⁻¹
0.10	2.20	176	151	250
.10	2.47	82.4	67.4	150
.10	2.91	42.1	35.1	70
.10	3.10	19.5	18.2	13
.10	3.18	15.4	10.4	50
.10	3.62	13.4	5.10	83
.10	4.42	11.8	1.78	100
.10	5.45 ^e	47.5	2.04	455
.10	6.05 ^e	140	4.25	1360
.10	6.70 ^e	698	18.1	6800
1.00	2.24 ^e	190	168	22
1.00	3.18	32.2	10.4	22
5.00	3.19	66.2	10.3	11
10.0	3.13	98.4	13.6	8.5
50.0	3.17	312	17.2	6.0
100	3.16	442	16.1	4.3
10.0	2.05	214	200	1.4
1.0	2.01	240	223	17
0.10	1.91	246	245	..

^a Ionic strength 0.14; initial boronic acid concentration 4.45×10^{-3} M. ^b Experimental rate coefficient. ^c Rate coefficient observed at given pH in absence of added Cd^{2+} . ^d Rate coefficient due to added $\text{Cd}^{2+} = (k_{\text{exp}}^{\text{Cd}} - k_{\text{exp}}^0)/[\text{Cd}^{2+}]$. ^e Malonic acid-sodium malonate buffer; in all other experiments only perchloric acid was used.

nium ion catalysis, respectively. The curved portion around the minimum was drawn by assuming the presence of an "uncatalyzed" reaction with a specific rate coefficient of 6×10^{-6} sec.⁻¹ in addition to the catalyzed reaction. The lower curve in the figure is the pH-rate profile for the reaction in the absence of added metal ion.^{1b} At any pH the difference in the vertical direction between the two curves represents the rate due to the presence of 10^{-4} M cadmium ion. A plot of

(5) A. D. Ainley and F. Challenger, *J. Chem. Soc.*, 2171 (1930).

(6) A. Michaelis and P. Becker, *Chem. Ber.*, **15**, 180 (1882).

(7) A. Michaelis and M. Behrens, *ibid.*, **27**, 244 (1894).

(8) J. R. Johnson, M. G. van Campen, Jr., and O. Grummitt, *J. Am. Chem. Soc.*, **60**, 111 (1938).

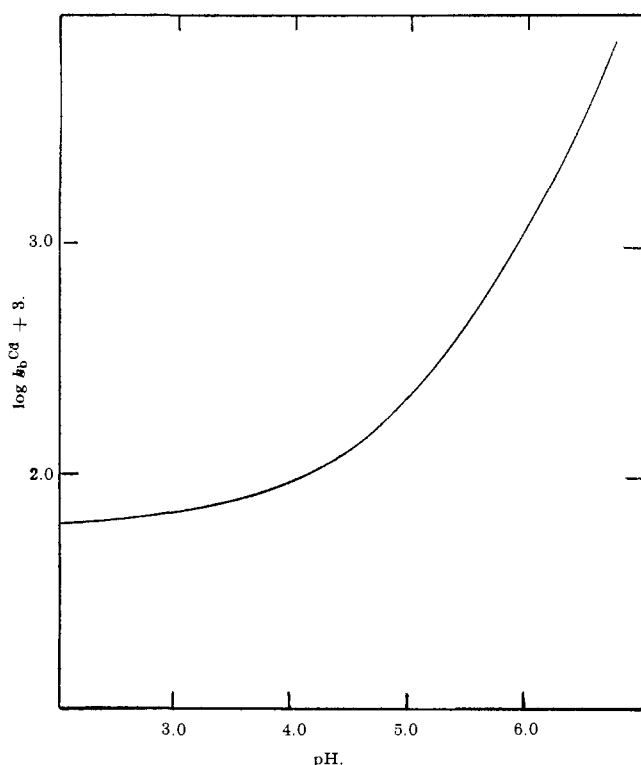


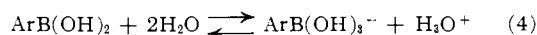
Fig. 2.—pH-rate profile for the cadmium ion catalyzed protodeboronation of 2,6-dimethoxybenzeneboronic acid at 90° (schematic).

these differences results in the pH-rate profile shown in Fig. 2 in which the ordinate is k_b^{Cd} , the analytic specific rate constant for catalysis by cadmium ion. In this plot the values at high pH should be reasonably accurate, representing, as they do, data from reactions in which the cadmium ion catalysis dominates the overall rates. In the region of the minimum, and at lower values of pH, the data are less accurate because relatively small differences between larger numbers are involved.

The most obvious conclusion to be drawn from the pH-rate profile is that the base-catalyzed and the uncatalyzed protodeboronations are in turn catalyzed by cadmium ion, but that this is probably not true for the acid-catalyzed reaction. Therefore, the measured rate coefficient in any given experiment will be given by eq. 3, or a kinetic equivalent, in which the group of terms in the first set of braces represents k_{exp}^0 and that in the second set represents k_b^{Cd} in Table I. It has been suggested that the reaction may occur by any of four

$$k_{exp} = \{k_H^0(H^+) + k_{HO}^0(HO^-) + k_{H_2O}^0(H_2O)\} + (Cd^{2+})\{k_{HO}^{Cd}(HO^-) + k_{H_2O}^{Cd}(H_2O)\} \quad (3)$$

mechanisms in the absence of cadmium ion^{1b,4}: (a) attack by an acid on the benzeneboronic acid molecule, which provides the first kinetic term; (b) formation of the boronate anion in the rapidly established equilibrium of eq. 4, whose equilibrium constant is designated by K_a , followed by attack by a water molecule in



the rate-determining step whose specific rate constant is given by $(k_{HO}^0)(H_3O)/55.5K_a$; (c) a rate-determining reaction between a water molecule and a boronic acid molecule, in which case the specific rate constant

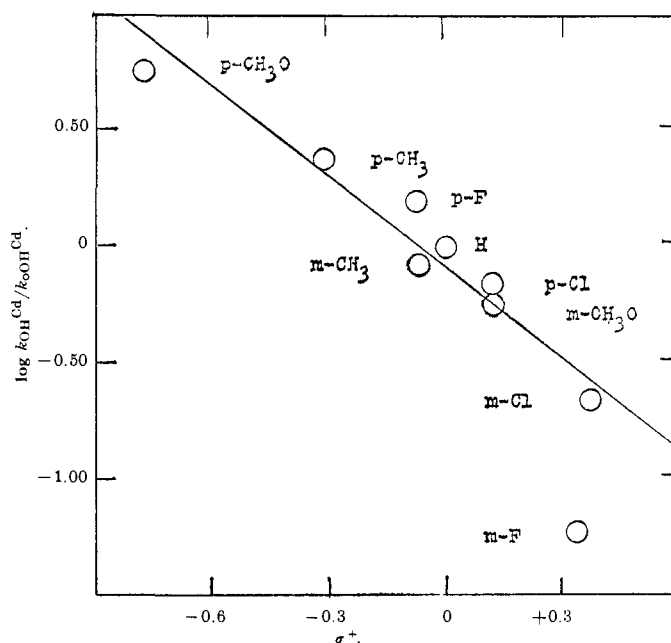


Fig. 3.—Hammett plot for cadmium ion catalyzed protodeboronation of substituted benzeneboronic acids at 90°.

is $k_{H_2O}^0$. (d) Mechanism (c) is indistinguishable on simple kinetic grounds from one in which a hydronium ion reacts with a boronate anion in the rate-determining step in which case the specific rate constant is $k_{H_3O}^0/55.5K_a$. The presence of corresponding terms for the last three cases in the cadmium-catalyzed set suggests transition states of the same compositions with a cadmium ion added in each case. Specific rate constants can be estimated for each case^{1b} and are listed in Table II, along with the ratios k^{Cd}/k^0 .

TABLE II
RELATIVE SPECIFIC RATE CONSTANTS IN PROTOBORONATION OF 2,6-DIMETHOXYBENZENEBORONIC ACID AT 90°, pH 6.70^a

Reactants	k^0 , 1. mole ⁻¹ sec. ⁻¹	k^{Cd} , 1. ² mole ⁻² sec. ⁻¹	k^{Cd}/k^0 , 1. mole ⁻¹
(a) $ArB(OH)_2 + H_3O^+$	2.12×10^{-2}		
(b) $ArB(OH)_2^- + H_2O$	2.24×10^{-8}	7.6×10^2	3.4×10^6
(c) $ArB(OH)_2 + H_2O$	1.15×10^{-8}	6×10^{-2}	5×10^6
(d) $ArB(OH)_3^- + H_3O^+$	7.0^b	4×10^7	5×10^6

^a The absolute magnitudes of these rate constants have no significance inasmuch as pH measurements were made at 25° and the values of K_a used in the computations were obtained in 25% aqueous ethanol at 25°, whereas the kinetic measurements were made in water at 90°. ^b The value given for this constant in ref. 1b was in error.

Substituent Effects.—The rates of protodeboronation at 90° and pH 6.70 of fourteen benzeneboronic acids catalyzed by cadmium ion were measured. Substituents chosen were methyl, methoxy, fluoro, and chloro, each in the *o*-, *m*-, and *p*-position. The unsubstituted acid and the 2,6-dimethoxy derivative were also used. Results are presented in Table III. Examination of the values in the fifth column, headed k_b^{Cd} , reveals that most of the substituents increase the over-all rate of the reaction catalyzed by cadmium ion. This is also true of the reaction in the absence of the metal ion.^{1b} If we assume that the rate-determining step involves reaction between a boronate anion and a cadmium ion, the specific rate constant is given by $k_{HO}^{Cd} = k_b^{Cd}(H_3O^+)/55.5K_a$ in 1.² mole⁻² sec.⁻¹. These values are shown in the penultimate column and the

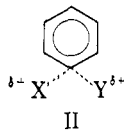
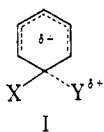
TABLE III
 SUBSTITUENT EFFECTS IN THE CADMIUM ION CATALYZED PROTODEBORONATION OF BENZENEBOONIC ACID^a

Substituent	$10^4[\text{Cd}^{2+}]$, M	$10^4 k_{\text{exp}}^{\text{Cd}}$, sec. ⁻¹	$10^4 k_{\text{exp}}^0$, ^b sec. ⁻¹	$10^3 k_{\text{b}}^{\text{Cd}}$, ^c l. mole ⁻¹ sec. ⁻¹	$10^{10} K_{\text{a}}^{\text{d}}$	$k_{\text{HO}^- \text{Cd}}^{\text{e}}$, l. mole ⁻² sec. ⁻¹	$\log \left(\frac{k_{\text{OH}^- \text{Cd}}}{k_{\text{HO}^- \text{Cd}}} \right)$
H	1.00	2.39	0.145	22.4	7.59	0.121	0
<i>p</i> -CH ₃ O	1.00	5.46	.610	48.5	2.57	.680	0.750
<i>p</i> -CH ₃	10.0	50.3	.610	49.7	2.57	.699	.762
<i>p</i> -CH ₃	1.00	2.66	.260	24.0	3.02	.286	.373
<i>p</i> -CH ₃	10.0	25.3	.260	25.0	3.02	.297	.389
<i>p</i> -Cl	1.00	5.19	.187	50.0	20.9	.086	-.148
<i>p</i> -Cl	10.0	48.3	.187	48.2	20.9	.083	-.164
<i>p</i> -F	1.00	4.86	.250	46.1	9.33	.178	.167
<i>p</i> -F	10.0	50.0	.250	49.7	9.33	.196	.210
<i>m</i> -CH ₃ O	5.00	14.5	.343	28.4	16.6	.062	-.291
<i>m</i> -CH ₃ O	10.0	32.2	.343	31.9	16.6	.069	-.244
<i>m</i> -CH ₃	5.00	10.1	.294	19.6	7.08	.100	-.083
<i>m</i> -CH ₃	10.0	20.8	.294	20.5	7.08 ^f	.104	-.066
<i>m</i> -Cl	5.00	19.8	.217	39.4	51.3 ^f	.027	-.652
<i>m</i> -Cl	10.0	35.2	.217	35.0	51.3 ^f	.025	-.684
<i>m</i> -F	5.00	6.49	.322	12.3	57.5 ^f	.0076	-1.20
<i>m</i> -F	10.0	11.3	.322	11.0	57.5	.0070	-1.24
<i>o</i> -CH ₃ O	1.0	42.5	1.53	410	2.14	6.89	1.76
<i>o</i> -CH ₃	1.0	5.81	0.360	54.5	1.02	1.93	1.20
<i>o</i> -Cl	1.0	83.8	8.60	752	26.9	1.00	0.917
<i>o</i> -F	1.0	204	11.1	1930	56.2	1.23	1.01
2,6-Di-CH ₃ O	1.0	698	18.1	6800	0.295	800	3.82

^a At 90.0°, pH 6.70, ionic strength 0.14. ^b Rate coefficient in absence of cadmium ion. ^c Rate coefficient due to added cadmium ion = $(k_{\text{exp}}^{\text{Cd}} - k_{\text{exp}}^0)/[\text{Cd}^{2+}]$. ^d Ionization constant of the boronic acid in 25% ethanol at 25.0°; see ref. 13. ^e $k_{\text{b}}^{\text{Cd}}(\text{H}_3\text{O}^+)/55.5K_{\text{a}}$; cf. eq. 3. ^f Interpolated from Hammett plot; $K_{\text{a}} = 7.59 \times 10^{-10}$, $\rho = -2.95$.

logarithms of the ratios of these to the value for benzeneboronic acid are shown in the last column. A simple Hammett plot of the data for *m*- and *p*-substituents gives considerable scatter with the points for all *p*-substituents falling above the line for *m*-substituents. If σ^+ is used⁹ the plot is improved, and is shown in Fig. 3. There remains some scatter, but it seems unlikely that the plot could be improved significantly by modifications of the type suggested by Yukawa and Tsuno.¹⁰ We have no explanation for the very low rate constant observed for *m*-fluorobenzeneboronic acid.

The ρ -value of -1.2 observed for this reaction is the lowest one of which we are aware in which a σ^+ correlation is observed for an electrophilic substitution in the benzene ring.¹¹ Comparison with the reaction in the absence of cadmium ion under the same conditions reveals another striking fact. The ρ -value in that case is -2.32 , indicating a more discriminating electrophile, but the best correlation is given by σ , and not σ^+ . It may be concluded that the cadmium ion catalyzed reaction proceeds by a mechanism approaching S^{*}E2 in which localization of π -electrons occurs in passage to the transition state I, which has considerable penta-dienate character¹² and may well pass over into a



σ -complex intermediate. The simple base-catalyzed reaction, on the other hand, appears to proceed by the

SE2 mechanism¹² with a transition state, II, in which there is little disturbance of the π -electron system and the positive charge is borne largely by the attacking species, Y, and the departing species, X. This transition state passes over into products directly. Since the boronate anion is the substrate in each of the two reactions under consideration, it appears likely that the difference in type of mechanism is due to a difference in the nature of the electrophile. If this inference is correct, the transition state for the rate-determining step of the cadmium ion catalyzed reaction does not involve a proton transfer.

The change from an S^{*}E2 mechanism for the reaction between the boronic acid molecule and a hydronium ion to an SE2 mechanism for the reaction between the boronate anion and a water molecule is consistent with the idea that the more polar the carbon-metal bond the more likely the latter mechanism is to be observed.¹² Our results indicate that a similar change in mechanism can be realized with a given aromatic substrate by an appropriate change in the nature of the electrophile.

ortho-para ratios for the two base-catalyzed reactions and for the acid-catalyzed protodeboronation¹³ are presented in Table IV. The values for the acid-catalyzed reaction are of magnitudes normally found for electrophilic aromatic substitutions, whereas the values for the two base-catalyzed reactions are unusually large and are roughly parallel. The large values for the cadmium ion catalyzed reaction can be attributed in general to the same factors previously invoked for the base-catalyzed reaction^{1b}: a combination of release of strain and electrostatic repulsions in the transition state in which the boron-bearing carbon is changing from trigonal to approximately tetrahedral geometry.

(9) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957).

(10) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 965, 971 (1959).

(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 208.

(12) Use of the terms S^{*}E2 and SE2 to distinguish between the two types of transition state have been suggested by H. Minato, J. C. Ware, and T. G. Traylor (*J. Am. Chem. Soc.*, **85**, 3024 (1963)).

(13) J. H. Poley, Ph.D. Dissertation, University of New Hampshire, 1960.

TABLE IV
ortho-para RATIOS FOR PROTODEBORONATION OF
 ARENEBORONIC ACIDS

Substituent	<i>ortho-para</i> ratio		
	Acid catalysis ^a	Base catalysis ^b	Cd ²⁺ catalysis ^c
CH ₃ O	0.23	3.02	10.2
CH ₃	1.12	4.06	6.74
F	0.12-0.19	7.34	6.95
Cl	0.20	37.3	12.1

^a In aqueous sulfuric acid at 60°; ref. 13. ^b At 90°, pH 6.70; ref. 1b. ^c At 90°, pH 6.70, ionic strength 0.14.

Effects of Other Metal Ions.—The effects of a number of metal ions on the rate of protodeboronation of 2,6-dimethoxybenzeneboronic acid were examined with the results shown in Table V. Nitrates or perchlorates were used in order to minimize complications which might result from the presence of several different complex ions in the solutions. This precaution was not always essential inasmuch as copper(II) chloride and nitrate gave the same rate constant within the experimental error. The order of effectiveness of the cations listed in the table is copper(II) > lead(II) > silver > cadmium > zinc > cobalt(II) > magnesium > nickel(II). No specific rate constant is given for silver ion because of difficulties in measuring the rate due to the formation of precipitate, but the very rough value obtained was of the same magnitude as that for cadmium ion.

TABLE V

EFFECT OF METAL IONS ON THE RATE OF PROTODEBORONATION OF 2,6-DIMETHOXYBENZENEBORONIC ACID AT 90°, $\mu = 0.14$, pH 6.70

Metal ion	Metal ion concn., moles/liter	10 ³ k _{exp} , ^a sec. ⁻¹	k _{cat} , ^b 1. mole ⁻¹ sec. ⁻¹
Ni ²⁺	1.0 × 10 ⁻³	23.0	0.0049
Mg ²⁺	1.0 × 10 ⁻³	30.6	.0130
Co ²⁺	1.0 × 10 ⁻³	51.3	.0332
Zn ²⁺	1.0 × 10 ⁻⁵	35.2	1.67
Cd ²⁺	1.0 × 10 ⁻⁵	70.3	5.22
Pb ²⁺	1.0 × 10 ⁻⁵	236	21.8
Cu ²⁺	1.0 × 10 ⁻⁵	416	39.8
Cu ²⁺ ^c	1.0 × 10 ⁻⁵	421	40.3

^a Average of values from four experiments, initial boronic acid concentration 4.45 × 10⁻³ M. ^b k_{cat} = k_{exp}M²⁺ - 18.1 × 10⁻⁶/metal ion concentration. ^c As chloride; average of values from two experiments.

As described in the Experimental section, kinetic data could not be obtained with gold(II) chloride, palladium(II) chloride, iron(III) nitrate, or manganese(II) sulfate. No catalysis was observed when the following addends were used: NaNO₃, KNO₃, LiNO₃, Al(NO₃)₃, Cr(NO₃)₃, and H₂PtCl₆.

Mechanism.—An alternative to the kind of mechanism shown in eq. 1 and 2 is one in which the protodeboronation product is formed directly as a result of proton transfer to the substrate from one of the ligand water molecules of the metal ion; *i.e.*, the hydrated ion functions as a Brønsted acid. The similarity in *ortho-para* ratios for the two types of reaction shown in Table IV would suggest a similarity in mechanism. On the other hand, the difference in the nature of the linear free energy correlations argues for a difference in mechanism. We tend to favor the Ainley-Challenger picture for this reason and on the basis of analogy. It is known that mercury(II), silver, and thallium(III) salts react with areneboronic acids to form arylmetals, and it would appear to be unlikely that other members of the same groups in the periodic table would function by different mechanisms.

The case of copper(II) is novel. Cupric chloride and bromide react very rapidly with areneboronic acids to form halobenzenes and cuprous salts. In our experiments this type of reaction could consume only 1% of the boronic acid because of the low initial concentration of copper(II) used. Thus it is likely that the actual catalyst in this case is copper(I) rather than copper(II).

Experimental

Materials.—All of the boronic acids used in this investigation have been described previously, and the wave lengths at which analytical determinations were made were those used in our earlier work.^{1b,4} Because of the sensitivity of the rate of protodeboronation to the presence of catalytic amounts of impurities, redistilled water was used as the solvent in the recrystallization of the boronic acids and salts used, and as the solvent for kinetic runs. pH measurements were made at 25°, and are reported as such although the kinetic experiments were carried out at 90°.

Kinetics.—Usually 1 mmole of boronic acid was placed in a 100-ml. volumetric flask and dissolved in malonic acid-malonate buffer solution. An aliquot of the metal ion solution was added and the resulting solution diluted to the mark; aliquots were sealed in carefully cleaned ampoules and placed in the bath maintained at 90.0 ± 0.02°. Ampoules were removed at intervals, chilled in ice-water, the contents neutralized, and analyzed using a Beckman Model DU spectrophotometer. The specific compounds used as addends were sodium perchlorate, copper(II) chloride, and the nitrates of potassium, sodium, lithium, magnesium, chromium, zinc, lead, and copper.

Kinetic data could not be obtained with ferric nitrate because its absorption masked that of the boronic acid. When manganese sulfate was used the reaction solution turned an increasingly deep brown color with time.

When chloroauric acid (1 × 10⁻³ M) was added to 2,6-dimethoxybenzeneboronic acid (4.45 × 10⁻³ M) at room temperature a blue dispersion of metallic gold appeared immediately, and the odor of resorcinol dimethyl ether could be detected. When the concentration of the gold compound was decreased to 1 × 10⁻⁵ M and the kinetics examined, the initial rate was about the same as the uncatalyzed rate, but increased with time after about 20% reaction.

Upon mixing a solution of palladium(II) chloride and the boronic acid a precipitate appeared and turned silvery upon standing.