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Electrophilic Displacement Reactions. XIII. The Kinetics of the Phenylmercurideboronation of Benzeneboronic Acid[1-3]

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The kinetics of the reaction between benzeneboronic acid and basic phenylmercuric perchlorate in aqueous ethanol have been studied. The rate was found to be first order in each reactant. Investigations in buffer systems showed a retardation in the rate by phosphoric acid, acetic acid and dihydrogen phosphate ion. The reaction rate is *p*H-independent in the range *p*H 4–8. Above *p*H 10 the rate decreases with increasing *p*H. The bearing of these and other observations on the mechanism of the reaction is discussed.

Previous investigations in this Laboratory have sought elucidation of mechanisms of displacement of the boronic acid group from an aromatic ring.[4] Electrophilic displacement by bromine or iodine is thought to involve attack by free halogen upon a quadricovalent boronate intermediate in the rate-determining step.[4a,b] The reaction of benzeneboronic acid with hydrogen peroxide involves hydroxylation of the aromatic ring with the production of phenol. The kinetics of this reaction reveal that any of five kinetically distinct mechanisms may be operative under given conditions.[4c]

Areneboronic acids react readily with mercuric chloride in aqueous solution to produce the corresponding arylmercuric chloride and boric acid.[5] Although the reaction is reported to take place with

$$ArB(OH)_2 + HgCl_2 \xrightarrow{H_2O} ArHgCl + B(OH)_3 + HCl \quad (1)$$

phenylmethaneboronic acid, other alkyl derivatives are unreactive toward mercuric salts.[6]

When two equivalents of benzeneboronic acid are heated with one equivalent of mercuric oxide for one hour, diphenylmercury and boric acid are the only products.[7] Moreover, if equimolar quantities of benzeneboronic acid and phenylmercuric hydroxide are allowed to react under the same conditions, the products are identical.[8] It seems most probable that diphenylmercury is produced in the former instance by way of intermediate formation of phenylmercuric hydroxide.

$$ArB(OH)_2 + HgO + H_2O \longrightarrow ArHgOH + B(OH)_3 \quad (2)$$

$$ArHgOH + ArB(OH)_2 \longrightarrow Ar_2Hg + B(OH)_3 \quad (3)$$

Previous mechanistic studies on aromatic mercuration reactions have concerned replacement of hydrogen and have been confined to non-polar or highly aqueous media.[9,10] Westheimer[10] proposed that the mercuration of benzene in aqueous solution in the presence of perchloric acid proceeds by attack of a tetrahedrally coördinated mercuric ion upon benzene in the rate-controlling step.

$$C_6H_6 + Hg(H_2O)_3(ClO_4)^+ \longrightarrow C_6H_5Hg(H_2O)_3^+ + H^+ + ClO_4^- \quad (4)$$

Mercuration of benzene in glacial acetic acid is catalyzed by perchloric acid.[9]

This paper describes an attempt to gain a more intimate understanding of electrophilic aromatic substitution by mercury. It was hoped that this could be done by means of a detailed study of the reaction of eq. 3 which permits, among other things, a study of the effect of relatively subtle changes not only in the substrate, but also in the electrophile.

Results

The ultraviolet absorption spectra of reactants and products differed sufficiently so that the reaction could be followed accurately by a spectrophotometric procedure. Aqueous ethanol was chosen as a solvent since it satisfied the necessary condition of transparency in the ultraviolet region and permitted studies to be made with several buffers over a considerable *p*H range. The insolubility of mercury compounds in aqueous media has proved to be a serious limitation in previous kinetic investigations. In the present system the rate of reaction was sufficiently rapid so that the low concentrations needed to ensure the dissolution of all components could be used. Preliminary experiments with phenylmercuric chloride revealed kinetics which did not follow any simple rate law. When basic phenylmercuric perchlorate was used, on the other hand, good second-order kinetics, first order in each reactant, were observed. The order did not change with variation of solvent from "30%" to "60%" aqueous ethanol, a change which led to a decrease in the rate constant by more than 75%. Data which indicate the reproducibility of the results and the variation of rate constant with solvent composition are displayed in Table I.

Addition of boric acid had no appreciable effect upon the observed rate constant (Table II). The rate was also relatively insensitive to changes in ionic strength (Table III). A fourfold variation in ionic strength, both in the presence (runs 12, 13, 26) and absence (runs 61, 62) of a phosphate buffer, failed to alter the observed rate constant. This behavior suggests that the enhancement of

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(1) Preceding paper in this series, K. V. Nahabedian and H. G. Kuivila, *J. Am. Chem. Soc.*, **83**, 2167 (1961).

(2) Partial support of this work by the Office of Naval Research and by the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-312, is acknowledged. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(3) Taken from the Ph.D. dissertation of T. C. Muller, May, 1960. Presented at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March 21, 1961; Abstracts p. 29-R.

(4) (a) H. G. Kuivila and A. R. Hendrickson, *J. Am. Chem. Soc.*, **74**, 5068 (1952); (b) H. G. Kuivila and R. M. Williams, *ibid.*, **76**, 2679 (1954); (c) H. G. Kuivila, *ibid.*, **76**, 870 (1954).

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

(6) E. Khotinsky and M. Melamed, *ibid.*, **42**, 3090 (1909).

(7) F. Challenger and O. V. Richards, *J. Chem. Soc.*, 405 (1934).

(8) R. Freidlina, A. N. Nesmejanow and K. A. Kozeschkow, *Ber.*, **68**, 565 (1935).

(9) H. C. Brown and C. W. McGary, Jr., *J. Am. Chem. Soc.*, **77**, 2300 (1955).

(10) R. M. Schramm, W. Klapproth and F. H. Westheimer, *J. Phys. and Coll. Chem.*, **55**, 843 (1951).

TABLE I

SECOND-ORDER RATE CONSTANTS, k_{obs} IN AQUEOUS ETHANOL 0.003 M NaH_2PO_4, 0.003 M Na_2HPO_4, $\mu = 0.01$

Run	Solvent	$[C_6H_5B(OH)_2]$, moles/l. × 10^5	$[C_6H_5HgOH \cdot C_6H_5HgClO_4]_0$, moles/l. × 10^5	$k_{obs.}$, l. sec.$^{-1}$ mole^{-1}
1	"60%" EtOH	5.015	12.15	2.80
2	"60%" EtOH	5.015	6.075	2.84
3	"60%" EtOH	5.015	3.098	2.90
4	"60%" EtOH	9.027	7.592	3.16
5	"60%" EtOH	6.018	7.592	3.41
7	"60%" EtOH	10.97	7.440	3.03
8	"60%" EtOH	6.580	7.440	2.88
10	"50%" EtOH	4.860	10.470	5.17
11	"50%" EtOH	4.860	6.955	5.24
12	"40%" EtOH	5.075	7.160	8.85
13	"40%" EtOH	5.075	5.372	8.28
14	"30%" EtOH	4.918	6.225	13.1
15	"30%" EtOH	4.918	3.112	13.6
16	"30%" EtOH	2.447	3.105	13.5
17	"30%" EtOH	2.447	6.210	13.1

rate with increasing water content of the solvent may be ascribed to a specific role of water in the rate-determining step rather than to a change in the dielectric constant of the medium.

TABLE II

SECOND-ORDER RATE CONSTANTS, k_{obs} IN PRESENCE OF ADDED BORIC ACID

Run	Solvent	$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_0$, moles/l. × 10^5	$[C_6H_5B(OH)_2]_0$, moles/l. × 10^5	$[B(OH)_3]_0$, moles/l. × 10^5	k_{obs}
21	"40%" EtOH	5.105	7.410	8.38	7.70
22	"40%" EtOH	10.21	7.410	8.38	7.86
23	"40%" EtOH	2.042	7.410	8.38	7.93
24	"60%" EtOH	5.060	7.220	9.95	3.06
25	"60%" EtOH	10.12	7.220	9.95	3.01

TABLE III

EFFECT OF IONIC STRENGTH IN "40%" AQUEOUS ETHANOL

Run	$[NaH_2PO_4]$, moles/l. × 10^3	$[Na_2HPO_4]$, moles/l. × 10^3	μ	k_{obs}
12	3.00	3.00	0.01	8.85
13	3.00	3.00	.01	8.28
26	3.00	3.00	.04	8.22
61	0	0	.04	18.4
62	0	0	.16	17.9

TABLE IV

SECOND-ORDER RATE CONSTANTS, k_{obs}, FOR PHOSPHATE BUFFERS IN "40%" AQUEOUS ETHANOL, $\mu = 0.04$

Run	$[NaH_2PO_4]$, moles/l. × 10^3	$[Na_2HPO_4]$, moles/l. × 10^3	"pH"	k_{obs}, l. mole^{-1} sec.$^{-1}$	$1/k_{obs}$
42	10.0	2.50	6.99	3.69	0.287
27	6.00	6.00	7.57	6.53	.153
37	6.00	12.0	7.88	5.62	.178
26	3.00	3.00	7.57	8.23	.122
38	3.00	6.00	7.88	8.92	.112
39	3.00	12.0	8.14	8.45	.118
34	2.00	2.00	7.57	9.89	.101
35	1.20	4.80	8.14	12.8	.0785
29	1.00	1.00	7.57	13.6	.0739
40	0.600	2.40	8.14	15.2	.0658
30	0.500	0.500	7.57	15.0	.0667

TABLE V

VALUES OF k_{obs} FOR ACETATE BUFFERS IN "40%" AQUEOUS ETHANOL, $\mu = 0.04$

Run	[HOAc], moles/l. × 10^3	[NaOAc], moles/l. × 10^3	"pH"	k_{obs}	$1/k_{obs}$
44	10.0	10.0	5.37	1.38	0.724
46	7.50	7.50	5.37	1.86	.538
45	5.00	5.00	5.37	2.46	.407
47	2.50	2.50	5.37	4.36	229

TABLE VI

VALUES OF k_{obs} FOR PHOSPHORIC ACID–DIHYDROGEN PHOSPHATE BUFFERS IN "40%" AQUEOUS ETHANOL, $\mu = 0.04$

Run	$[H_3PO_4]$, moles/l. × 10^3	$[NaH_2PO_4]$, moles/l. × 10^3	"pH"	k_{obs}	$1/k_{obs}$
53	1.50	9.00	3.76	1.01	0.990
54	1.25	7.50	3.76	1.37	.730
49	1.00	4.00	3.60	1.55	.645
50	1.00	8.00	3.93	1.59	.628
51	0.500	2.00	3.60	3.13	.319
52	0.500	4.00	3.93	2.68	.373

In a dihydrogen phosphate–monohydrogen phosphate buffer system, a significant decrease in rate was observed with increasing buffer concentration when the pH was maintained constant (Table IV, (Runs 26, 27; 34, 29). When the monohydrogen phosphate ion concentration was varied, the rate did not change (runs 27, 37; 26, 38, 39). Therefore, the rate is dependent only upon the concentration of dihydrogen phosphate ion (runs 27, 38; 37, 39). Similarly, in acetic acid–acetate and phosphoric acid–dihydrogen phosphate buffers, the lowering of the second-order rate constants was a function of the molecular acid concentration (Tables V and VI). The magnitude of this effect increased as the ionization constant of the acid component of the buffer system became larger.

When phosphoric acid–dihydrogen phosphate buffers were used, the rate plots displayed a pronounced downward curvature after about 50% reaction. The rate constants for these runs were determined by measuring initial slopes. At a phosphoric acid concentration of 1.25 × 10^{-3} M, the change in slope became noticeable after 33% reaction (1.5 hours). It was thought that this change in slope might be due to acid cleavage of diphenylmercury, which would have an effect on the rate of change in absorbance which would lead to rate plots of the type observed. In order to test this possibility the absorbance of a solution 1.25 × 10^{-3} M in phosphoric acid and 3.22 × 10^{-5} M in diphenylmercury was measured as a function of time; the results indicated about 2.5% cleavage in three hours. Thus, it appears that this cleavage cannot be the major cause of the nonlinear rate plots.

In carbonate buffers the rate was independent of buffer concentration but decreased with increasing pH above pH 10 (Table VII). The disappearance of a rate dependence upon molecular acid concentration in this case is not surprising since the magnitude of this effect has been shown to be a function of the pK_a of the acid (Tables IV, V and VI). Bicarbonate ion is apparently too weak an acid to produce a significant decrease in the reaction rate.

TABLE VII

VALUES OF k_{obs} FOR CARBONATE BUFFERS IN "40%" AQUEOUS ETHANOL, $\mu = 0.15$

Run	[NaHCO$_3$], moles/l. × 10^2	[Na$_2$CO$_3$], moles/l. × 10^2	"pH"	k_{obs}	log k_{obs}	log $\left(\frac{k'}{k_{obs}} - 1\right)$
63	3.00	1.00	10.10	5.76	0.760	0.330
64	3.00	3.00	10.53	2.36	.373	.824
59[a]	2.50	0.50	10.25	5.29	.723	.380
65	1.00	3.00	10.96	1.13	.0531	1.18
66	1.00	4.50	11.15	0.726	− .139	1.38
60[a]	0.60	0.12	10.25	5.20	.716	0.391

[a] Ionic strength, 0.04.

Discussion

Organomercuric salts are known to hydrolyze in aqueous solution with the formation of the corresponding weakly ionized organomercuric hydroxides.[11] This hydrolysis causes aqueous solutions of these salts to be somewhat acidic. The various equilibria which result when phenylmercuric salts are dissolved in aqueous solvents are represented

$$\mathrm{PhHgX} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{PhHg^+ + X^-}$$

$$K_1 = \frac{[\mathrm{PhHg^+}][\mathrm{X^-}]}{\mathrm{PhHgX}} \tag{5}$$

$$\mathrm{PhHg^+ + 2H_2O} \overset{K_2}{\rightleftharpoons} \mathrm{PhHgOH + H_3O^+}$$

$$K_2 = [\mathrm{PhHgOH}][\mathrm{H_3O^+}]/[\mathrm{PhHg^+}] \tag{6}$$

$$\mathrm{HX + H_2O} \overset{K_3}{\rightleftharpoons} \mathrm{H_3O^+ + X^-}$$

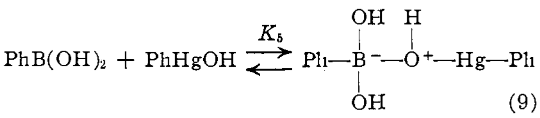
$$K_3 = [\mathrm{H_3O^+}][\mathrm{X^-}]/[\mathrm{HX}] \tag{7}$$

The equilibrium which involves formation of benzeneboronate anion is represented in eq. 8

$$\mathrm{PhB(OH)_2 + 2H_2O} \overset{K_4}{\rightleftharpoons} \mathrm{PhB(OH)_3^- + H_3O^+}$$

$$K_4 = [\mathrm{PhB(OH)_3^-}][\mathrm{H_3O^+}]/[\mathrm{PhB(OH)_2}] \tag{8}$$

Interaction between benzeneboronic acid and phenylmercuric hydroxide may also give rise to the following equilibrium:



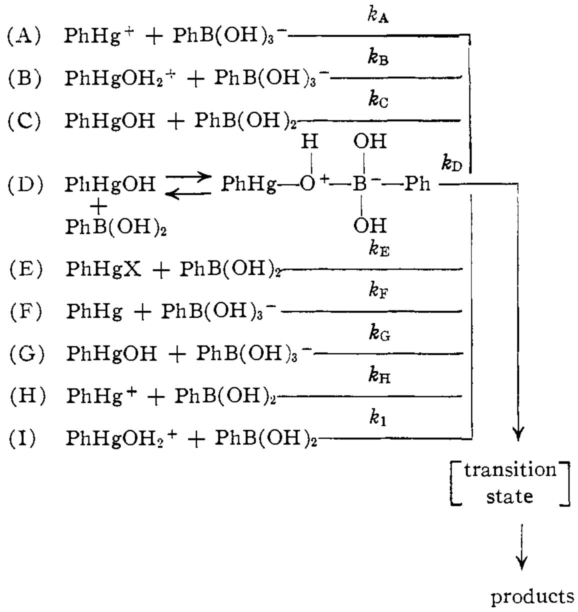
$$\mathrm{PhB(OH)_2 + PhHgOH} \overset{K_5}{\rightleftharpoons} \mathrm{Ph{-}\overset{OH}{\underset{OH}{B^-}}{-}\overset{H}{O^+}{-}Hg{-}Ph} \tag{9}$$

$$K_5 = \frac{[\mathrm{Ph{-}B^-(OH)_2{-}O^+(H){-}Hg{-}Ph}]}{[\mathrm{PhB(OH)_2}][\mathrm{PhHgOH}]}$$

Consideration of the above equilibria permits a designation of PhHgX, PhHg$^+$, PhHgOH$_2^+$ and PhHgOH as possible electrophilic agents and PhB(OH)$_2$ and PhB(OH)$_3^-$ as possible substrates.

The transition state might arise from any of the combinations listed (mechanisms A through I).

Mechanisms A and B differ only because a molecule of water is attached to the mercurial in B. The same can be said for mechanisms H and I. Since water is in constant active mass, each of these pairs of mechanisms is kinetically indistinguishable.

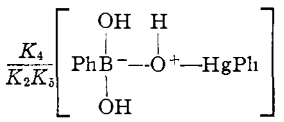


The rate expression for mechanism A is expressed in eq. 10

$$v = k_A[\mathrm{PhHg^+}][\mathrm{PhB(OH_3)^-}] \tag{10}$$

It can be shown from eq. 6, 8 and 9 that

$$[\mathrm{PhHg^+}][\mathrm{PhB(OH)_3^-}] = \frac{K_4}{K_2}[\mathrm{PhHgOH}][\mathrm{PhB(OH)_2}] =$$



$$\frac{K_4}{K_2K_5}\left[\mathrm{Ph\overset{OH}{\underset{OH}{B^-}}{-}\overset{H}{O^+}{-}HgPh}\right] \tag{11}$$

Therefore mechanisms A through D are kinetically equivalent.

The purpose of the following analysis is to differentiate among Mechanisms A, E, F, G and H and to determine which is most consistent with the data. Symbols to be used include (brackets indicate concentration)

$[\mathrm{PhHgX}]_s$ = stoichiometric mercurial
$[\mathrm{PhHgX}]$ = phenylmercuric salt
$[\mathrm{BBA}]_s$ = stoichiometric benzeneboronic acid
$[\mathrm{BBA}]$ = free benzeneboronic acid
$[\mathrm{BA^-}]$ = benzeneboronate anion, $[\mathrm{PhB(OH)_3^-}]$
$[\mathrm{HX}]$ = molecular acid
k_{obs} = observed rate constant

The stoichiometric concentrations of benzeneboronic acid and mercurial can be expressed in terms of the individual species:

$$[\mathrm{PhHgX}]_s = [\mathrm{PhHgX}] + [\mathrm{PhHgOH}] + [\mathrm{PhHg^+}] \tag{12}$$

$$[\mathrm{BBA}]_s = [\mathrm{BBA}] + [\mathrm{BA^-}] \tag{13}$$

Since the reaction has been shown to be first order in stoichiometric benzeneboronic acid and stoichiometric mercurial, eq. 14 may be written

$$v = k_{obs}[\mathrm{PhHgX}]_s[\mathrm{BBA}]_s \tag{14}$$

In mechanism A phenylmercuric ion attacks benzeneboronate anion in the rate-determining step. Thus

$$v = k_A[\mathrm{PhHg^+}][\mathrm{BA^-}] \tag{15}$$

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[11] T. D. Waugh, H. F. Walton and J. A. Laswick, *J. Phys. Chem.*, **59**, 395 (1955).

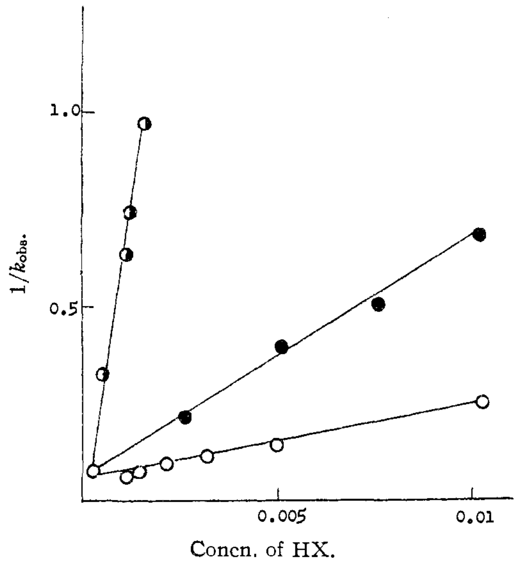

Fig. 1.—Effect of buffer acid concentration on rates of phenylmercuride boronation of benzeneboronic acid in "40%" aqueous ethanol at 25°; open circles, NaH_2PO_4; filled circles, HOAc–NaOAc; half-filled circles, H_3PO_4–NaH_2PO_4.

We can express eq. 12 and 13 in terms of the appropriate equilibrium constants

$$[\mathrm{PhHgX}]_s = \left(\frac{[\mathrm{X^-}]}{K_1} + \frac{K_2}{[\mathrm{H_3O^+}]} + 1\right) [\mathrm{PhHg^+}] \quad (16)$$

$$[\mathrm{BBA}]_s = \left(\frac{[\mathrm{H_3O^+}]}{K_4} + 1\right) [\mathrm{BA^-}] \quad (17)$$

Combining eq. 14, 16 and 17

$$v = k_{obs}\left(\frac{[\mathrm{H_3O^+}][\mathrm{X^-}]}{K_1K_4} + \frac{K_2}{K_4} + \frac{[\mathrm{H_3O^+}]}{K_4} + \frac{[\mathrm{X^-}]}{K_1} + \frac{K_2}{[\mathrm{H_3O^+}]} + 1\right) [\mathrm{BA^-}][\mathrm{PhHg^+}] \quad (18)$$

Substitution of eq. 7 leads to

$$v = k_{obs}\left(\frac{K_3}{K_1K_4}[\mathrm{HX}] + \frac{K_2}{K_4} + \frac{[\mathrm{H_3O^+}]}{K_4} + \frac{K_3[\mathrm{HX}]}{K_1[\mathrm{H_3O^+}]} + \frac{K_2}{[\mathrm{H_3O^+}]} + 1\right) [\mathrm{BA^-}][\mathrm{PhHg^+}] \quad (19)$$

If K_6 = [PhHg$^+$] [HO$^-$]/[PhHgOH] and K_w = [H_3O^+] [HO$^-$], then eq. 19 becomes

$$v = k_{obs}\left(\frac{K_3}{K_1K_4}[\mathrm{HX}] + \frac{K_w}{K_4K_6} + \frac{[\mathrm{H_3O^+}]}{K_4} + \frac{K_3[\mathrm{HX}]}{K_1[\mathrm{H_3O^+}]} + \frac{K_w}{K_6[\mathrm{H_3O^+}]} + 1\right) [\mathrm{PhHg^+}][\mathrm{BA^-}] \quad (20)$$

Since K_w, K_4 and K_6 have been measured in water, it becomes possible to estimate the relative magnitudes of the terms in eq. 20. The values of pK_4 and pK_6 in water are 8.7 and 10, respectively.[4c,12] Thus the magnitude of the fraction K_w/K_4K_6 must be greater than 10^4 since the value of this fraction should be somewhat larger in aqueous ethanol than in pure water. Then below pH 8, $K_w/K_4K_6 > K_w/K_6[H_3O^+] + 1$. Furthermore, above pH 4, $K_w/K_4K_6 = K_2/K_4 > [H_3O^+]/K_4$. Finally, $K_3[HX]/K_1K_4 > K_3[HX]/K_1[H_3O^+]$ when $[H_3O^+] > K_4$, that is below pH 10.

Applying these approximations in the pH range 4 to 8, eq. 20 reduces to the expression

$$v = k_{obs}\left(\frac{K_3}{K_1K_4}[\mathrm{HX}] + \frac{K_w}{K_4K_6}\right) [\mathrm{PhHg^+}][\mathrm{BA^-}] \quad (21)$$

Combining eq. 15 and 21 and rearranging we have

$$\frac{1}{k_{obs}} = \frac{1}{k_A}\left(\frac{K_3}{K_1K_4}[\mathrm{HX}] + \frac{K_w}{K_4K_6}\right) \quad (22)$$

Equation 22 predicts that a plot of $1/k_{obs}$ *versus* [HX] should give a straight line of slope $K_3/k_AK_1K_4$ and intercept $K_w/k_AK_4K_6$. Such a plot was made for each buffer system used. Figure 1 demonstrates that linearity is observed over a tenfold change in molecular acid concentration for dihydrogen phosphate ion, acetic acid and phosphoric acid. The common intercept of the lines is consistent with eq. 22.

If we assume that the value of the fraction K_w/K_6 does not change appreciably with variation of solvent from water to "40%" aqueous ethanol, it becomes possible to calculate the values of K_3K_1 from the slopes and intercept of the lines in Fig. 1. The calculated values of the ratios of ionization constants are listed in Table VIII. A significant decrease in K_3/K_1 can be observed as pK_3 of the buffer acid increases. A comparison of $-\log (K_3/K_1)$ and pK_3 is made in Table VIII for each buffer system. There appears to be a roughly linear correlation between the dissociation constant of an acid HX and the dissociation constant of the corresponding mercuric salt, PhHgX. A study of a wider variety of buffers would be required, however, in order to substantiate this point.

TABLE VIII

VALUES OF $K_3/k_AK_1K_4$ AND K_3/K_1 FOR VARIOUS BUFFER SYSTEMS

Buffer acid	$K_3/k_A\ K_1K_4$	K_3/K_1	$-\log$ (K_3/K_1)	pKa[a]
H_3PO_4	578	0.96	0.020	2.12
HOAc	67.1	.12	0.92	4.76
$H_2PO_4^-$	17.80	.031	1.50	7.21

[a] pK_a values of buffer acids in aqueous solution.

It is significant that the intercept for the phosphoric acid runs in Fig. 1 coincides with those for the two other buffer systems. This implies, according to eq. 20, that $K_w/K_4K_6 > [H_3O^+]/K_4$ even slightly below pH 4 (see Table VI). If this were not true, pH dependence at zero buffer concentration would be manifested in a change in the intercept for phosphoric acid. It is not improbable that the value of K_w/K_6 which is reported to be 10^{-4} in water becomes larger in "40%" aqueous ethanol. This point must remain a speculative one, however, because of the uncertainty of the absolute hydronium ion concentration in water–alcohol mixtures.

As the concentration of hydronium ion is decreased, the term $K_w/K_6[H_3O^+]$ increases in magnitude; eq. 20 predicts that the molecular acid dependence should disappear in favor of a dependence upon hydronium ion when $K_w/K_6[H_3O^+] > K_3[HX]/K_1K_4$, since $K_1 >> K_6$. The results with carbonate buffers substantiate this prediction (Table VII). Above pH 10, the rate is independent of molecular acid concentration, but decreases with increasing pH. Applying this assumption at high pH values, eq. 20 may be transformed into 24

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[12] R. M. Schramm, *J. Am. Chem. Soc.*, **69**, 1831 (1947).

$$v = \frac{k_{obs}K_w}{K_4K_6}\left(1 + \frac{K_4}{[H_3O^+]}\right)[PhHg^+][BA^-] \quad (23)$$

Combining eq. 15 and 23 we have

$$k_A = \frac{k_{obs}K_w}{K_4K_6}\left(1 + \frac{K_4}{[H_3O^+]}\right) \quad (24)$$

$$\frac{k_AK_4K_6}{k_{obs}K_w} - 1 = \frac{K_4}{[H_3O^+]} \quad (25)$$

Taking the log of both sides

$$\log\left(\frac{k_AK_4K_6}{k_{obs}K_w} - 1\right) = pH - pK_4 = \log\left(\frac{k'}{k_{obs}} - 1\right) \quad (26)$$

Referring to eq. 25, note that the fraction $k_AK_4K_6/K_w$ is the reciprocal of the common intercept of the lines in Fig. 1, and is called k'.

The applicability of eq. 26 to our data was tested by plotting $\log\left(\frac{k'}{k_{obs}} - 1\right)$ *versus* pH. Inspection of Fig. 2 reveals that the points fall near a line which is drawn with the required unit slope. Furthermore, according to eq. 26, $K_4/[H_3O^+]$ should be unity when $k' = 2k_{obs}$. This occurs in Fig. 2 at pH 9.8 giving a value for the pK_a of benzeneboronic acid of 9.8. Excellent agreement exists between this value and the values obtained by two other methods described below.

The ionization constant, K_4, for benzeneboronic acid was determined potentiometrically in "40%" aqueous ethanol at ionic strength 0.15. The pH value at the half-equivalence point was 9.82. In order to check this value, a spectrophotometric determination of K_4 was made. The value calculated from the spectrophotometric method was 9.85 ± 0.02.

The above treatment demonstrates that mechanism A is compatible with the experimental data throughout the entire pH region studied. The composite expression for k_{obs} over this region is

$$1/k_{obs} = A[HX] + B(1 + (K_4/[H_3O^+])) \quad (27)$$

where

$$A = K_2/k_AK_1K_4 \text{ and } B = K_w/k_AK_4K_6 = 1/k'$$

It is important to consider that the rates of brominolysis, iodinolysis and the reactions with hydrogen peroxide with areneboronic acids are independent of the nature of the buffer component.[4] It is therefore reasonable to conclude that the specific inhibiting effects of the buffer acids which have been observed do not involve interaction between buffer acid and benzeneboronic acid.

Rate expressions for mechanisms E, F, G and H can be developed similarly and are listed in the following chart:

Mechanism	Rate expression
E	$\frac{1}{k_{obs}} = \frac{K_6}{k_EK_1K_w} + \frac{1}{k_E[H_3O^+][X^-]} + \frac{K_4}{k_E[H_3O^+][X^-]}$
F	$\frac{1}{k_{obs}} = \frac{K_6}{k_FK_1K_wK_4}[H_3O^+] + \frac{1}{k_FK_4[X^-]} + \frac{1}{k_F[H_3O^+][X^-]}$
G	$\frac{1}{k_{obs}} = \frac{K_6}{k_GK_1K_wK_4}[H_3O^+]^2[X^-] + \frac{[H_3O^+]}{k_GK_4} + \frac{1}{k_G}$
H	$\frac{1}{k_{obs}} = \frac{K_2K_6}{k_HK_1K_w}[X^-] + \frac{K_2}{k_H[H_3O^+]} + \frac{K_4K_2}{k_H[H_3O^+]^2}$

Mechanism E requires that the rate increase with increasing HX concentration, an effect opposite to that which is observed (see Fig. 1). If mechanism F were correct there could be no inhibition of the rate by HX. Furthermore, a decrease in rate with increasing hydronium ion concentration would be expected when $[H_3O^+] >> K_4$. The hydronium ion dependence can also be used to eliminate mechanism G, because an increase in hydroxide ion concentration would enhance the observed rate constant in the region where $pK_4 = p$H. Mechanisms G and H can be eliminated because extrapolations to zero anion concentration in Fig. 1 would result in intercepts which would be dependent upon pH. Figure 1 clearly shows a common intercept for the various buffer systems.

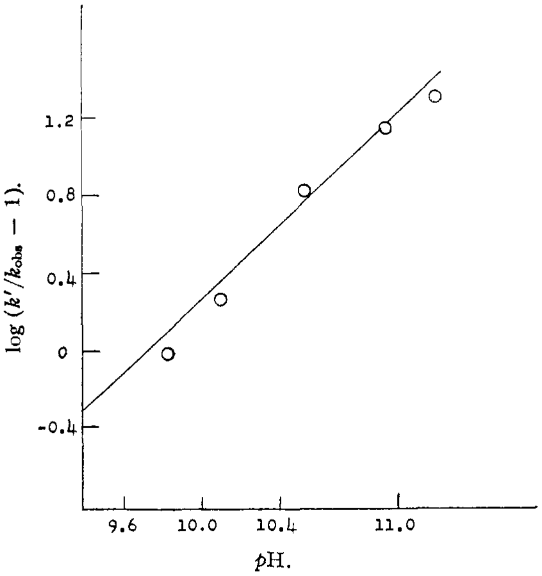
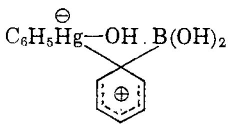
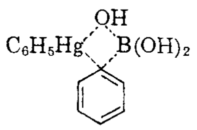


Fig. 2.—Test of eq. 26.

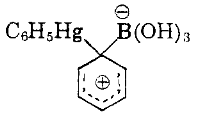
Possible transition states for the reaction are



I



II



III

If the analysis above, suggesting that $C_6H_5HgH_2PO_4$, C_6H_5HgOAc and $C_6H_5HgHPO_4^-$ are ineffective as mercurating agents, is correct, structure I can be eliminated because the first two of these species, at least, should be more effective electrophiles than C_6H_5HgOH. A distinction between II and III might be made on the basis of substituent effects on the boronic acid. The completely concerted reaction implied by II, which is unlikely,

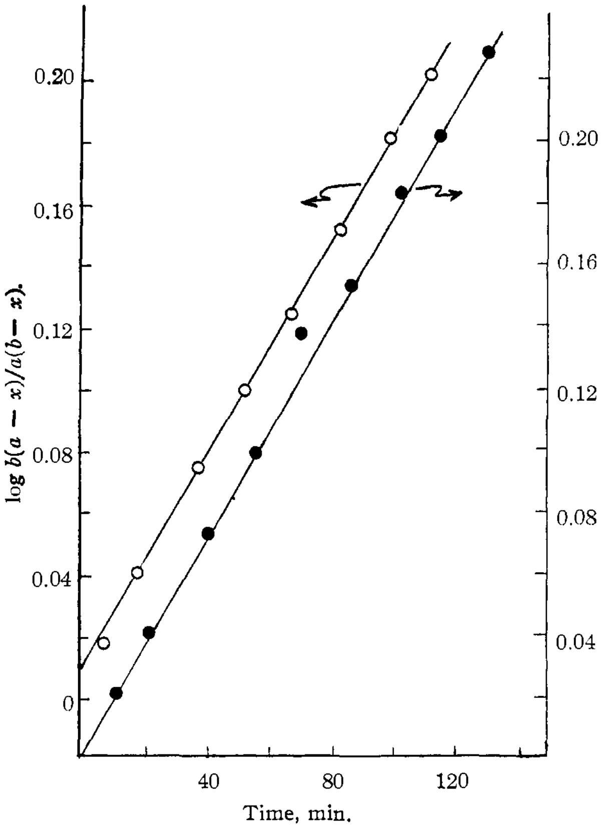


Fig. 3.—Typical rate plots for the phenylmercuride boronation of benzeneboronic acid in "40%" aqueous ethanol at 25°: open circles, run 60, HCO_3^- 0.0060 *M*, $CO_3^=$ 0.0012 *M*, "pH" 10.25, ionic strength 0.04; closed circles, run 58; HCO_3^- 0.025 *M*, $CO_3^=$ 0.005 *M*, "*p*H" 10.25, ionic strength 0.04.

would show no electronic effect of substituents; a more likely alternative would be a four-center transition state in which some separation of charge exists. The alternative III would be expected to have a negative rho in spite of its over-all electroneutrality, because the positive charge is distributed in the ring. Furthermore, correlation of rates by the simple Hammett equation should fail while use of Brown's σ-values might give a linear correlation.

Experimental

Materials.—Benzeneboronic acid was prepared as described by Bean and Johnson[13] and stored as the anhydride.

Basic Phenylmercuric Perchlorate.—A solution containing 5 g. (0.048 mole) of benzeneboronic acid in 200 ml. of water was added slowly to a solution containing 11 g. (0.05 mole) of mercuric oxide in 100 ml. of aqueous 2 *N* perchloric acid. The white crystalline precipitate which formed was filtered and washed several times with 20-ml. portions of water. The yield before recrystallization was 90%. The product was recrystallized from "50%" aqueous ethanol which was 0.1 *N* in perchloric acid. The compound melted at 199–200° and immediately resolidified.

Anal. Calcd. for $C_{12}H_{11}Hg_2ClO_5$: C, 21.45; H, 1.64; Hg, 59.71. Found: C, 21.48; H, 1.92; Hg, 59.81.

Kinetic Procedure.—All runs were carried out at 25.0 ± 0.02°. The solvent mixtures were made up by adding water to known volumes of 95% ethanol. For example, "30%" aqueous ethanol refers to a solution which resulted from the addition of water to 300 ml. of 95% ethanol until the total volume of the solution was one liter.

Stock solutions of each reactant were made up by weighing out 100-mg. samples in paraffin cups which were emptied into volumetric flasks. Successive dilutions were made until the proper concentration range was attained. Appropriate aliquots from standard buffer solutions were added when required. The flasks were then placed in the bath and allowed to come to reaction temperature. To the reaction flask was added 25-ml. aliquots of each reactant. Small aliquots were removed at measured time intervals and the optical density was read in a Beckman DU spectrophotometer.

The optical densities of each reactant were measured before each run. No deviation from Beer's law was detected in the concentration range studied. The concentrations of product at any given time were calculated using the formula

$$x = \frac{[\text{O.D.}]_t - A\epsilon_A - B\epsilon_B}{\epsilon_C - \epsilon_B - \epsilon_A}$$

where

A = init. concn. of benzeneboronic acid
B = init. concn. of mercurial
x = concn. of product at time t
ϵ_A = extinction of benzeneboronic acid
ϵ_B = extinction coefficient of mercurial
ϵ_C = extinction coefficient of product
$[\text{O. D.}]_t$ = optical density at time t of the reaction mixture
log ϵ_A = 3.36 (below *p*H 8, log ϵ_B = 3.38, log ϵ_C = 4.38 at 227.5 mμ

The concentration of phenylmercurial was taken as twice the molar concentration of basic phenylmercuric perchlorate in calculation of rate constants. Typical rate plots, calculated on assumption of the following stoichiometry, are shown in Fig. 3.

$$PhHgOH{\cdot}PhHgClO_4 + 2PhB(OH)_2 + H_2O \longrightarrow 2Ph_2Hg + 2B(OH)_3 + HClO_4$$

Determination of *p*K$_a$ for Benzeneboronic Acid.—A solution containing 0.1099 g. (0.001058 mole) of benzeneboronic acid in 100 ml. of "40%" aqueous ethanol was titrated potentiometrically at ionic strength 0.15 with 0.1086 *N* NaOH using a Cambridge model R *p*H meter with a high alkalinity glass electrode for the *p*H measurements. The *p*H value at the half-equivalence point was recorded as the pK_a.

A spectrophotometric determination of the pK_a was made by measuring the optical densities of 1.432×10^{-4} *M* benzeneboronic acid solutions in a series of eight carbonate buffers in the *p*H region 9.45 to 11.35 at ionic strength 0.15. The following equation was used to calculate values for the pK_a

$$pH = pK_a + \log \frac{\epsilon\lambda - \epsilon\lambda'}{\epsilon\lambda'' - \epsilon\lambda}$$

where $\epsilon_{\lambda'}$ and $\epsilon_{\lambda''}$ refer to the molar extinctions of benzeneboronic acid and benzeneboronate anion, respectively, and ϵ_λ is the molar extinction of the solution.

log $\epsilon_{\lambda'}$ = 3.68, log $\epsilon_{\lambda''}$ = 3.02 at 225 mμ

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(13) F. R. Bean and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 4415 (1932).