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KINETICS OF THE ARYLMERCURATION OF ARENEBORONIC ACIDS

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THESIS

KINETICS OF THE ARYLMERCURATION OF ARENEBORONIC ACIDS

Submitted by
Thomas C. Muller

to the
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in partial fulfillment
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This thesis has been examined and approved.

Paul R. Jones

H. A. Iddles

Date

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To Skipper

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INTRODUCTION

$$ArB(OH)_2 + HgCl_2 \longrightarrow ArHgCl + B(OH)_3 + HCl \qquad (1)$$

Although the reaction is reported to take place with phenylmethaneboronic acid, other alkyl derivatives do not react with mercuric salts.[18]

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.[5] However, if equimolar quantities of benzeneboronic acid and phenylmercuric hydroxide are allowed to react under the same conditions, the products are identical.[9] It seems most probable that diphenylmercury is produced in the former instance by way of the intermediate formation of phenylmercuric hydroxide.

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

$$ArHgOH + ArB(OH)_2 \longrightarrow ArHgAr + B(OH)_3 \qquad (3)$$

A wide variety of mixed diarylmercury compounds can be synthesized by varying the aromatic groups on boron and mercury in reaction (3).

Recent studies on the mercuration (mercurideprotonation) of benzene by mercuric perchlorate in strong acid have revealed that the substitution is truly electrophilic. In this medium, mercuric ion, which is complexed with a catalyzing anion, is the attacking reagent.[29]

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

Brown has proposed that the isomer distribution in aromatic electrophilic substitution reactions is correlated by the activity of the attacking reagent. Consequently, when the log of the relative toluene/benzene reactivities is plotted against the log of the toluene para/meta ratios, a simple linear relationship is observed. In his study of the mercuration of benzene in glacial acetic acid, he found that both the un-catalyzed and perchloric acid-catalyzed reactions obeyed this proposed linear relationship. It was concluded that the attacking species in the un-catalyzed reaction was less selective than that in the perchloric acid-catalyzed reaction.[3]

The reaction of arylmercuric salts [equation (3)] with benzeneboronic acid constitutes an intriguing area of study. The mechanistic status of aromatic mercuration in glacial acetic acid has been elucidated, but the picture in aqueous media is somewhat obscure. The aromatic electrophile in this instance provides a means of changing the electrophilicity of mercury by varying substituents in the ring. Thus a correlation of selectivity of the reagent and substituent constants becomes possible in principle. The purpose of this work is to formulate a mechanism for this reaction and to test the applicability of linear free-energy relationships to electrophile and substrate in the light of this mechanism.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

I. Analytical Procedure.

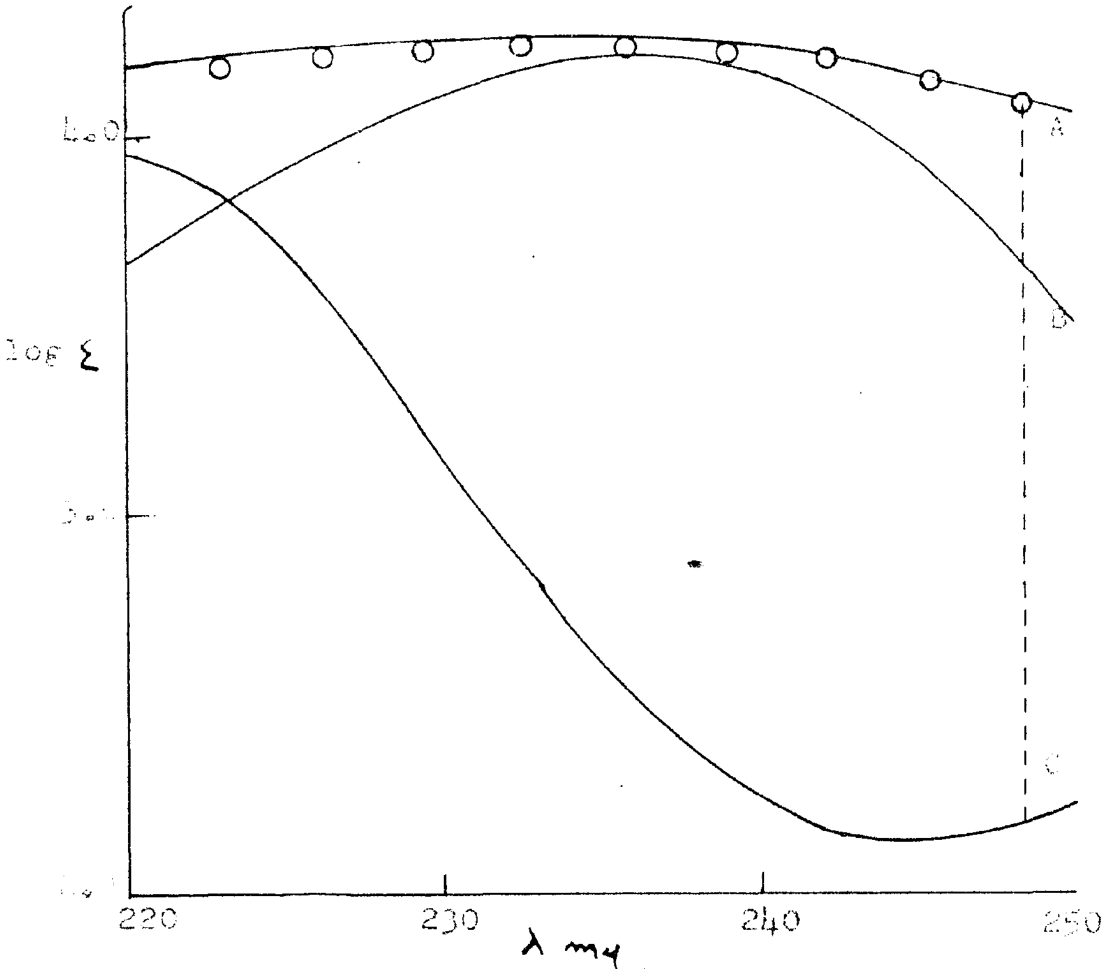
The ultraviolet absorption spectra of reactants and products differed sufficiently so that the reaction could be followed accurately by a spectrophotometric procedure. The smallest change in optical density during the course of a reaction was observed with p-methoxybenzeneboronic acid and phenylmercuric hydroxide as reactants. The absorption curves for this system are shown in Figure 1. Points defining the spectrum of the system when reaction was complete coincide well with the spectrum of the expected product.

II. Choice of Reaction System.

Organomercury compounds are, in general, insoluble in aqueous media. Consequently, most previous studies have been conducted in non-aqueous systems. The choice of aqueous ethanol as a solvent for this investigation was made on the basis of the extremely small concentrations of reactants which were required to follow this unusually rapid reaction. Also, this solvent satisfied the necessary condition of transparency in the ultraviolet region.

Although mercuric ion complexes readily with halide ions by assuming a quadricovalent state, no such complexes have been reported with organometallic compounds of mercury.[25]

Figure 1. Spectra of p-methoxybenzeneboronic acid, phenylmercuric hydroxide and (p-methoxyphenyl) phenyl mercury. Solvent: "50%" aqueous ethanol.



A - (p-methoxyphenyl) phenyl mercury.
B - p-methoxybenzeneboronic acid.
C - phenylmercuric hydroxide.

*Circles represent points obtained at "infinite time" in a rate experiment.

Preliminary experiments with phenylmercuric chloride revealed that the kinetics did not follow any simple rate law. When basic phenylmercuric perchlorate was used, good second order behavior was observed. Therefore, this salt was employed throughout the investigation.

III. Kinetics of Reaction.

A. Reaction order. The reaction between benzeneboronic acid and basic phenylmercuric perchlorate was found to be first order in each reactant. The order does not change with variations of solvent from "60%" to "30%" aqueous ethanol. (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.) The consistency of the second order rate constants with variations in the concentrations of each reactant at constant ionic strength is indicated in Table I.

A typical second order rate plot is shown in Figure 2A. The reaction in this case was followed through 90% completion. The rate of the reaction in a phosphate buffered system increases with increasing water content of the solvent when the buffer concentration is maintained constant as can be seen from the data in Table I.

B. The effect of added boric acid. Since boric acid is a product of the reaction, its effect on the rate was tested. The results are tabulated in Table II. The

TABLE I

SECOND ORDER RATE CONSTANTS, $k_{obs.}$ IN AQUEOUS ETHANOL, .003M NaH_2PO_4, .003M Na_2HPO_4, μ = .01.

Run	Solvent	Initial Benzeneboronic Acid (m/l. X 10^5)	Initial Basic Phenylmercuric Perchlorate (m/l. X 10^5)	k_{obs}, (l. $sec^{-1}mol^{-1}$)
1	"60%" EtOH	5.015	12.15	2.80
2	"	5.015	6.075	2.84
3	"	5.015	3.098	2.90
4	"	9.027	7.592	3.16
5	"	6.018	7.592	3.41
7	"	10.97	7.440	3.03
8	"	6.580	7.440	2.88
10	"50%" EtOH	4.860	10.470	5.17
11	"	4.860	6.955	5.24
12	"40%" EtOH	5.075	7.160	8.85
13	"	5.075	5.372	8.28
14	"30%" EtOH	4.918	6.225	13.1
15	"	4.918	3.112	13.6
16	"	2.447	3.105	13.5
17	"	2.447	6.210	13.1

data indicate that the boric acid which is produced in the reaction must have no effect upon the reaction rate.

C. The effect of ionic strength. Possible influences of ionic strength upon the rate constant were investigated in the presence and absence of a phosphate buffer. Inspection of Table III reveals that variations of ionic strength have

TABLE II

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

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

TABLE III

EFFECT OF IONIC STRENGTH IN "40%" AQUEOUS ETHANOL.

Run	$[NaH_2PO_4]$ moles/l. $\times 10^3$	$[Na_2HPO_4]$ moles/l. $\times 10^3$	μ	$k_{obs.}$
12	3.0	3.0	0.01	8.85
13	3.0	3.0	0.01	8.28
26	3.0	3.0	0.04	8.22
61	0	0	0.04	18.4
62	0	0	0.16	17.9

a negligible effect upon the reaction rate. Therefore, the rate increase with increasing water content of the solvent is not to be identified with a dielectric constant effect.

D. The effect of buffer concentration. In a dihydrogen phosphate - monohydrogen phosphate system, a significant decrease in rate was observed with increasing buffer concentration when the pH was maintained constant (Table IV) (Runs 26, 27, 34). When the monohydrogen phosphate concentration was varied, the rate did not change (Runs 26, 37; 27, 38, 39). Therefore, the rate is dependent only upon the concentration of dihydrogen phosphate ion. 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 curvature after 50% reaction. Figure 2B shows a run at a phosphoric acid concentration of 0.00125 moles/l. The slope becomes noticeable after 1 1/2 hours. Thus, rate constants were calculated from initial slopes in these runs. This curvature could possibly be due to cleavage of diphenylmercury by molecular phosphoric acid. Corwin and Kaufman[14] have measured the rate of cleavage of diphenylmercury with acetic acid in dioxane at 42° C.

TABLE IV

SECOND ORDER RATE CONSTANTS, $k_{obs.}$ IN AQUEOUS ETHANOL,

$\mu = .04.$

Run	NaH_2PO_4	Na_2HPO_4	"pH"	$k_{obs.}$	$1/k_{obs.}$
42	0.0100	0.0025	6.99	3.69	0.287
27	0.006	0.006	7.57	5.53	0.153
37A	0.006	0.012	7.88	5.52	0.181
37B	0.006	0.012	7.88	5.71	0.175
26A	0.003	0.003	7.57	8.22	0.122
26B	0.003	0.003	7.57	8.42	0.119
26C	0.003	0.003	7.57	8.04	0.124
38A	0.003	0.006	7.88	9.10	0.109
38B	0.003	0.006	7.38	8.74	0.114
39A	0.003	0.012	8.14	8.52	0.117
39B	0.003	0.012	8.14	8.37	0.119
34A	0.002	0.002	7.57	10.2	0.0980
34B	0.002	0.002	7.57	9.59	0.104
35A	0.0012	0.0048	8.14	12.2	0.0819
35B	0.0012	0.0048	8.14	13.3	0.0751
29A	0.001	0.001	7.57	14.0	0.0714
29B	0.001	0.001	7.57	13.1	0.0763
40	0.0006	0.0024	8.14	15.2	0.0658
30	0.0005	0.0005	7.57	15.0	0.0667

TABLE V

VALUES OF $k_{obs.}$ FOR ACETATE BUFFERS IN "40%" AQUEOUS ETHANOL,

μ = .04.

Run	$[HOAc] \times 10^3$ moles/l.	$[NaOAc] \times 10^3$ moles/l.	"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	0.538
45	5.00	5.00	5.37	2.46	0.407
47	2.50	2.50	5.37	4.36	0.229

TABLE VI

VALUES OF $k_{obs.}$

FOR PHOSPHORIC ACID - DIHYDROGEN PHOSPHATE BUFFERS,

μ = .04.

Run	$[H_3PO_4] \times 10^3$ moles/l.	$[NaH_2PO_4] \times 10^3$ moles/l.	"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	0.730
49	1.00	4.00	3.60	1.55	0.645
50	1.00	8.00	3.93	1.59	0.628
51	0.50	2.00	3.60	3.13	0.319
52	0.50	4.00	3.93	2.68	0.373

The reported rate constant is 2.05 X $10^{-4}sec^{-1}$. In order to test this hypothesis the optical density of a solution of diphenylmercury in the presence of phosphoric acid was measured as a function of time. The results are tabulated in Table VII. The progressive decrease in optical density with time indicates that acid cleavage of the product is probably the cause of the sloping rate plots.

TABLE VII

RATE OF CHANGE OF OPTICAL DENSITY OF DIPHENYLMERCURY IN THE PRESENCE OF PHOSPHORIC ACID IN "40%" AQUEOUS ETHANOL.

Diphenylmercury $3.217X10^{-5}$M., phosphoric acid $1X10^{-3}$M., sodium dihydrogen phosphate $4X10^{-3}$M.

Time (hours)	Optical Density
0	0.802
3	0.780
6	0.762
22	0.667

Diphenylmercury $3.217X10^{-5}$M., phosphoric acid $1X10^{-3}$M., sodium dihydrogen phosphate $8X10^{-3}$M.

Time (hours)	Optical Density
0	0.780
3	0.760
6	0.750
22	0.650

E. The effect of pH. In carbonate buffers the rate was independent of buffer concentration but decreased with increasing pH above pH 10. 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). Carbonic acid is apparently too weak to produce a significant inhibition of the reaction rate. The pH effect suggests that a term which involves benzeneboronate anion, $\phi B(OH)_3^-$, may make an important contribution to the rate expression at high pH values. These results are summarized in Table VIII.

TABLE VIII

VALUES OF $k_{obs.}$ FOR CARBONATE BUFFERS IN "40%" AQUEOUS ETHANOL, $\mu = .15$.

Run	$[NaHCO_3]X10^2$ moles/l.	$[Na_2CO_3]X10^2$ moles/l.	"pH"	$k_{obs.}$	log $k_{obs.}$	log $\frac{k'}{k_{obs.}} - 1$*
63	0.03	0.01	10.10	5.76	0.760	0.330
64	0.03	0.03	10.53	2.36	0.373	0.824
65	0.01	0.03	10.96	1.13	0.0531	1.18
66	0.01	0.045	11.15	0.726	-.139	1.38

*See page 24 for definition of k'.

F. Development of the rate expression. Organomercuric salts are known to hydrolyze in aqueous solution with the formation of the corresponding weakly ionized organomercuric hydroxides.[33] 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 below:

$$\Phi HgX \xrightleftharpoons{K_1} \Phi Hg^+ + X^- \tag{1}$$

$$\Phi Hg^+ + 2H_2O \xrightleftharpoons{K_2} \Phi HgOH + H_3O^+ \tag{2}$$

$$HX + H_2O \xrightleftharpoons{K_3} H_3O^+ + X^- \tag{3}$$

The equilibrium constants may be expressed as follows, assuming that water is in constant active mass and may be neglected:

$$K_1 = \frac{[\Phi Hg^+][X^-]}{[\Phi HgX]} \tag{4}$$

$$K_2 = \frac{[\Phi HgOH][H_3O^+]}{[\Phi Hg^+]} \tag{5}$$

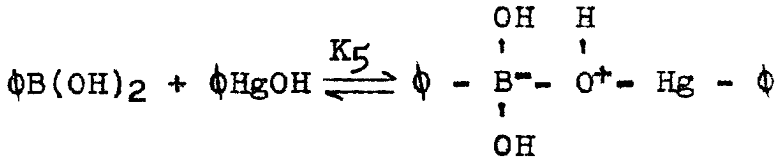
$$K_3 = \frac{[H_3O^+][X^-]}{[HX]} \tag{6}$$

The equilibrium which involves formation of benzeneboronate anion is represented in equations (7) and (8):

$$\Phi B(OH)_2 + 2H_2O \xrightleftharpoons{K_4} \Phi B(OH)_3^- + H_3O^+ \tag{7}$$

$$K_4 = \frac{[\Phi B(OH)_3^-][H_3O^+]}{[\Phi B(OH)_2]} \tag{8}$$

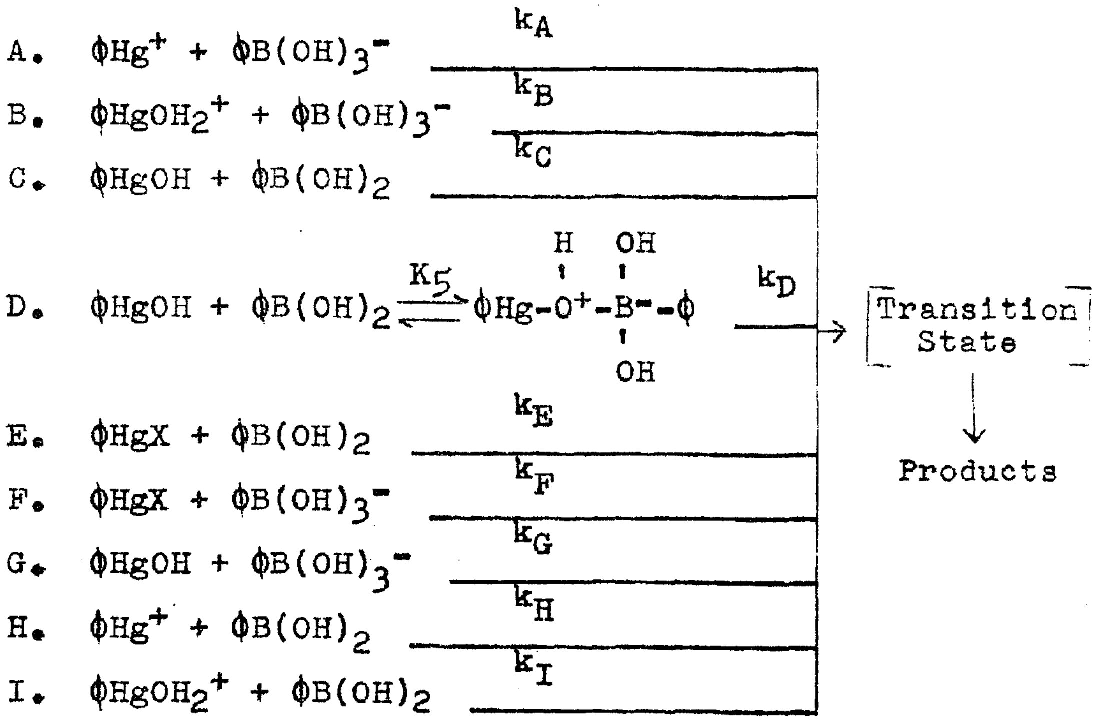
Interaction between benzeneboronic acid and phenylmercuric hydroxide may also give rise to the following equilibrium:



$$\phi B(OH)_2 + \phi HgOH \overset{K_5}{\rightleftharpoons} \phi - \overset{OH}{\underset{OH}{B^-}} - \overset{H}{O^+} - Hg - \phi \qquad (9)$$

Consideration of the above equilibria permits a designation of ϕHgX, ϕHg^+, $\phi HgOH_2^+$ and $\phi HgOH$ as the possible electrophilic agents and $\phi B(OH)_2$ or $\phi B(OH)_3^-$ as the possible substrates. In order to distinguish among the potential pairs of reactants it becomes necessary to develop a rate expression which will incorporate all of the equilibria and to determine whether the expression is consistent with the experimental data.

The transition state may arise from any of the combinations listed below (Mechanisms A through I):



In the following analysis, each of the possible mechanisms is considered separately. Symbols to be used include the following:

$[\phi\text{HgX}]_s$ = stoichiometric mercurial

$[\phi\text{HgX}]$ = phenylmercuric salt

$[\text{BBA}]_s$ = stoichiometric benzeneboronic acid

$[\text{BBA}]$ = free benzeneboronic acid

$[\text{BA}]$ = benzeneboronate anion, $[\phi\text{B(OH)}_3^-]$

$[\text{HX}]$ = molecular acid

$k_{obs.}$ = observed rate constant

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

$$[\phi\text{HgX}]_s = [\phi\text{HgX}] + [\phi\text{HgOH}] + [\phi\text{Hg}^+] \qquad (10)$$

$$[\text{BBA}]_s = [\text{BBA}] + [\text{BA}] \qquad (11)$$

Since the reaction has been shown to be first order in stoichiometric benzeneboronic acid and stoichiometric mercurial, equation (12) may be written:

$$v = k_{obs.}[\phi\text{HgX}]_s[\text{BBA}]_s \qquad (12)$$

According to Mechanism A, phenylmercuric ion attacks benzeneboronate anion in the rate determining step. Thus:

$$v = k_A[\phi\text{Hg}^+][\text{BA}] \qquad (13)$$

We can express equations (10) and (11) in terms of the appropriate equilibrium constants:

$$[\phi\text{HgX}]_s = \frac{[\phi\text{Hg}^+][\text{X}^-]}{K_1} + \frac{K_2[\phi\text{Hg}^+]}{[\text{H}_3\text{O}^+]} + [\phi\text{Hg}^+] \qquad (14)$$

$$[\phi\text{HgX}]_s = \left(\frac{[\text{X}^-]}{K_1} + \frac{K_2}{[\text{H}_3\text{O}^+]} + 1\right)[\phi\text{Hg}^+] \qquad (15)$$

$$[BBA]_s = \frac{[BA][H_3O^+]}{K_4} + [BA] \qquad (16)$$

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

Combining equations (12), (15) and (17):

$$v = k_{obs.}\left(\frac{[H_3O^+][X^-]}{K_1K_4} + \frac{K_2}{K_4} + \frac{[H_3O^+]}{K_4} + \frac{[X^-]}{K_1} + \frac{K_2}{[H_3O^+]} + 1\right)[BA][\phi Hg^+] \qquad (18)$$

Substituting from equation (6) into the first term in brackets of (18):

$$v = k_{obs.}\left(\frac{K_3}{K_1K_4}[HX] + \frac{K_2}{K_4} + \frac{[H_3O^+]}{K_4} + \frac{[X^-]}{K_1} + \frac{K_2}{[H_3O^+]} + 1\right)[BA][\phi Hg^+] \qquad (19)$$

The ionization constant of $\phi HgOH$, K_6, is

$$K_6 = \frac{[\phi Hg^+][OH^-]}{[\phi HgOH]} \qquad (20)$$

Equation (5) can be represented in terms of K_6:

$$K_2 = \frac{K_w}{K_6} \qquad (21)$$

Equation (19) now becomes:

$$v = k_{obs.}\left(\frac{K_3}{K_1K_4}[HX] + \frac{K_w}{K_4K_6} + \frac{[H_3O^+]}{K_4} + \frac{[X^-]}{K_1} + \frac{K_w}{K_6[H_3O^+]} + 1\right)[\phi Hg^+][BA] \qquad (22)$$

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 equation (22). The values of pK_4 and pK_6 in water are 8.7 and 10 respectively.[21,28] 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, $K_3[HX]/K_1K_4 = [H_3O^+][X^-]/K_1K_4 > [X^-]/K_1$ when $[H_3O^+] > K_4$, that is below pH 10.

Applying these assumptions in the pH range 4 to 8, equation (22) reduces to the expression which is illustrated below.

$$v = k_{obs.}\left(\frac{K_3}{K_1K_4}[HX] + \frac{K_w}{K_4K_6}\right)[\phi Hg^+][BA] \qquad (23)$$

Combining equations (13) and (23) we have:

$$k_{obs.}\left(\frac{K_3}{K_1K_4}[HX] + \frac{K_w}{K_4K_6}\right) = k_A \qquad (24)$$

or

$$\frac{1}{k_{obs.}} = \frac{1}{k_A}\left(\frac{K_3}{K_1K_4}[HX] + \frac{K_w}{K_4K_6}\right) = \frac{K_w}{k_AK_4K_6} + \frac{K_3[HX]}{k_AK_1K_4} \qquad (25)$$

Equation (25) 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 $K_w/k_AK_4K_6$. In order to test the validity of equation (25), plots of $1/k_{obs.}$ versus [HX] were made for each buffer system which was used. Figure 3 demonstrates that linearity is observed over a ten-fold change in molecular acid concentration for dihydrogen phosphate ion, acetic acid and phosphoric acid. The common intercept of the three lines is consistent with equation (25). The slopes of the lines in Figure 3 increase as the ionization constant of the acid in the buffer system increases. In terms of equation (25) this would indicate that the fraction K_3/K_1 increased as K_3 became larger. The values of the slopes of the lines in Figure 3 are listed in Table IX.

TABLE IX

VALUES OF THE SLOPES FOR PLOTS OF $1/k_{obs.}$ vs. $[HX]$.

Acid	Slope
$H_2PO_4^-$	17.8
HOAc	67.1
H_3PO_4	578.0

It is interesting to note that the intercept for the phosphoric acid runs in Figure 3 coincides with those for the two other buffer systems. This implies, according to equation (22), that $K_w/K_4K_6 > [H_3O^+]/K_4$ even slightly below pH 4 (see Table VI). If this were not true, a pH dependence at zero buffer concentration would be demonstrated by 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. Therefore, equation (22) predicts that the molecular acid dependence should disappear in favor of a dependence upon hydronium ion when $K_w/K_6[H_3O^+] > K_3[HX]/K_1K_4$. The results with carbonate buffers substantiate this prediction (Table VIII). Above pH 10, the rate is independent of molecular acid concentration, but decreases with increasing pH. Applying this assumption at high pH values, equation (22) may be transformed into (28):

$$v = k_{obs.}\left(\frac{K_w}{K_4K_6} + \frac{K_w}{K_6[H_3O^+]}\right)[\Phi Hg^+][BA] \tag{26}$$

$$v = k_{obs.}\left(\frac{K_w}{K_4K_6} + \frac{K_wK_4}{K_4K_6[H_3O^+]}\right)[\Phi Hg^+][BA] \tag{27}$$

$$v = \frac{k_{obs.}K_w}{K_4K_6}\left(1 + \frac{K_4}{[H_3O^+]}\right)[\Phi Hg^+][BA] \tag{28}$$

Combining equations (13) and (28) we have:

$$k_A = \frac{k_{obs.}K_w}{K_4K_6}\left(1 + \frac{K_4}{[H_3O^+]}\right) \tag{29}$$

$$\frac{k_AK_4K_6}{k_{obs.}K_w} - 1 = \frac{K_4}{[H_3O^+]} \tag{30}$$

Taking the log of both sides:

$$\log\left(\frac{k_AK_4K_6}{k_{obs.}K_w} - 1\right) = \log K_4 - \log [H_3O^+] \tag{31}$$

$$\log\left(\frac{k_AK_4K_6}{k_{obs.}K_w} - 1\right) = pH - pK_4 \tag{32}$$

Referring to equation (25), note that the fraction $k_A K_4 K_6/K_w$ is the reciprocal of the common intercept of the lines in Figure 3. If this fraction is called k', for the purpose of simplicity, equation (32) becomes:

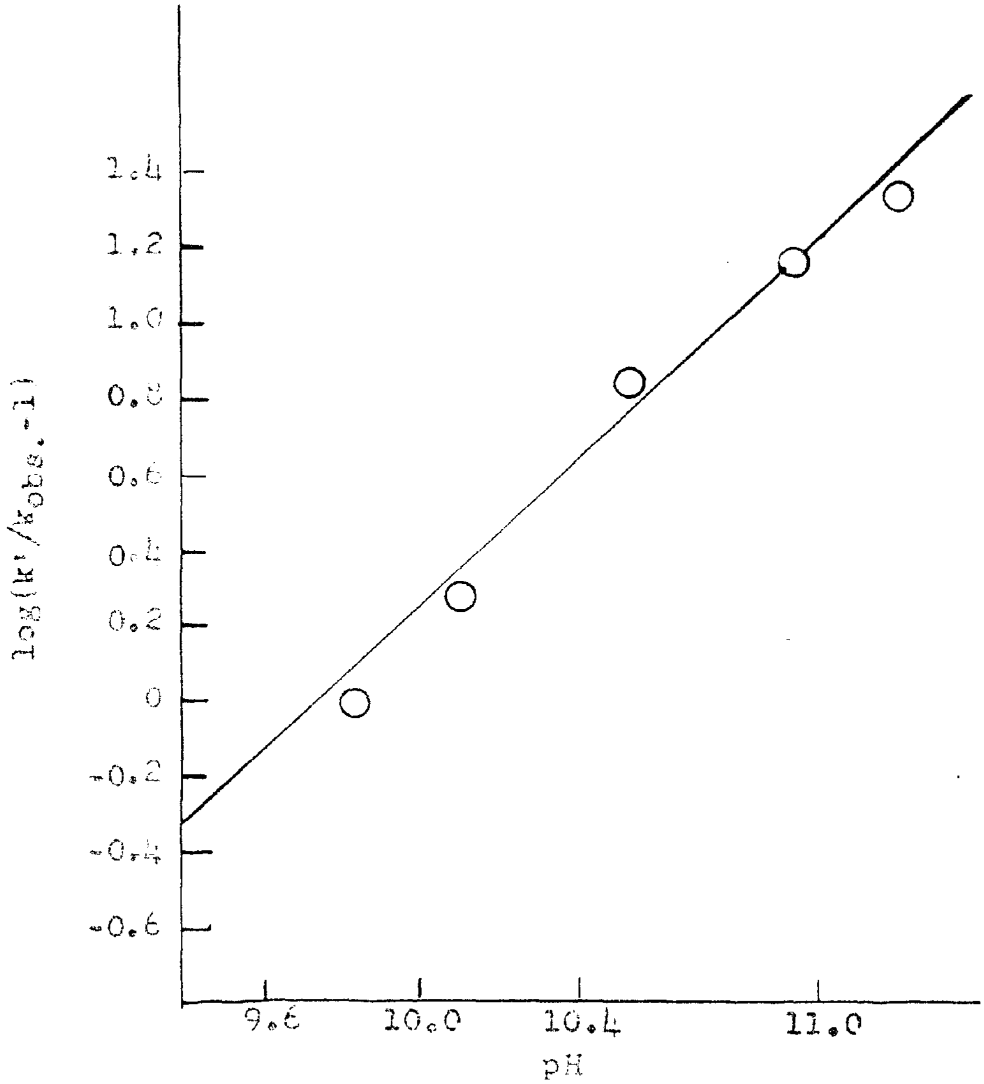
$$\log\left(\frac{k'}{k_{obs.}} - 1\right) = pH - pK_4 \qquad (33)$$

The validity of equation (33) was examined by plotting $\log(k'/k_{obs.} - 1)$ versus pH. Inspection of Figure 4 reveals that the points fall on a line which is drawn with the required unit slope. Equation (33) predicts that $k_{obs.}$ will be essentially independent of pH when the concentration of hydronium ion greatly exceeds the value of K_4, in other words, when $pK_4 \gg pH$. As the fraction $K_4/[H_3O^+]$ approaches zero, $k_{obs.}$ approaches k' as a limit. Thus the absence of a pH effect below pH 8 becomes reasonable. Furthermore, according to equation (33), $K_4/[H_3O^+]$ should be unity when $k' = 2\ k_{obs.}$ This occurs in Figure 4, at pH 9.80 giving a value for the pK_a of benzeneboronic acid of 9.80. 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 (Figure 5). 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 variation in the molar

Figure 4. $\log(k'/k_{obs.}-1)$ versus pH above pH 9.5.



extinction of benzeneboronic acid with pH is shown in Figure 6. Equation (34) was used to calculate K_4, where $\varepsilon\lambda'$ and $\varepsilon\lambda''$ refer to the molar extinctions of benzeneboronic acid and benzeneboronate anion respectively:

$$pH = pK_a + \log \frac{\varepsilon\lambda - \varepsilon\lambda'}{\varepsilon\lambda'' - \varepsilon\lambda} \qquad (34)$$

The agreement among the calculated values of K_4 is demonstrated in Table X. The mean value of K_4 as determined by this method is 9.85±0.02.

TABLE X

SPECTROPHOTOMETRIC DETERMINATION OF K_a FOR BENZENEBORONIC ACID IN "40%" AQUEOUS ETHANOL, μ = .15, λ = 225mu.

"pH"	log ε	pK_a
3.95	3.685	———
9.45	3.580	9.88
9.69	3.534	9.91
9.82	3.468	9.83
10.10	3.389	9.87
10.53	3.168	9.63
10.96	3.107	9.80
11.35	3.071	9.86
11.80	3.020	———

The above treatment demonstrates that Mechanism A is compatible with the experimental data throughout the entire pH region which was studied. The composite expression for $k_{obs.}$ over this region is illustrated below:

$$\frac{1}{k_{obs.}} = A[HX] + B\left(1 + \frac{K_4}{[H_3O^+]}\right) \tag{35}$$

$$\text{where } A = \frac{K_3}{k_A K_1 K_4} \text{ and } B = \frac{K_w}{k_A K_4 K_6} = \frac{1}{k'}$$

It now becomes necessary to apply a similar treatment to the other possible mechanisms in order to determine which are kinetically indistinguishable from Mechanism A.

Mechanism B differs from A only by the presence of a molecule of water attached to mercury in the transition state. This hydration of phenylmercuric ion can be expressed simply by equation (36):

$$K_7 = \frac{[\phi HgOH_2^+]}{[\phi Hg^+]} \tag{36}$$

The rate expression for Mechanism B is:

$$v = k_B[\phi HgOH_2^+][BA] \tag{37}$$

Combining equations (23) and (36) and omitting the terms which have been shown to be negligible:

$$v = k_{obs.}\left(\frac{K_3}{K_1K_4K_7}[HX] + \frac{K_w}{K_4K_6K_7} + \frac{K_w}{K_6K_7[H_3O^+]}\right)[\phi HgOH_2^+][BA] \tag{38}$$

$$\frac{1}{k_{obs.}} = \frac{K_3}{k_BK_1K_4K_7}[HX] + \frac{K_w}{k_BK_4K_6K_7} + \frac{K_w}{k_BK_6K_7[H_3O^+]} \tag{39}$$

Equation (39) has the general form of equation (35)

where $A = \frac{K_3}{k_B K_1 K_4 K_7}$ and $B = \frac{K_w}{k_B K_4 K_6 K_7}$

Therefore, Mechanisms A and B are indistinguishable.

Mechanism C describes a rate-determining attack of phenylmercuric hydroxide upon benzeneboronic acid. Therefore,

$$v = k_C[\phi HgOH][\phi B(OH)_2] \tag{40}$$

If we divide equation (8) by (5), we obtain:

$$\frac{K_2}{K_4} = \frac{[\phi HgOH][\phi B(OH)_2]}{[\phi Hg^+][BA]} = \frac{K_w}{K_4 K_6} \tag{41}$$

Substitution in equation (22) gives:

$$v = k_{obs.}\left(\frac{K_3K_6[HX]}{K_1K_w} + 1 + \frac{K_6[H_3O^+]}{K_w} + \frac{K_4K_6[X^-]}{K_1K_w} + \frac{K_4}{[H_3O^+]} + \frac{K_4K_6}{K_w}\right) X \; [\phi HgOH][\phi B(OH)_2] \tag{42}$$

Since equation (42) resulted from multiplication of each term in equation (22) by a constant, K_4K_6/K_w, the same inequalities as were applicable to Mechanism A will hold and equation (42) becomes:

$$v = k_{obs.}\left(\frac{K_3K_6[HX]}{K_1K_w} + 1 + \frac{K_4}{[H_3O^+]}\right)[\phi HgOH][\phi B(OH)_2] \tag{43}$$

We can now substitute equation (40) and obtain:

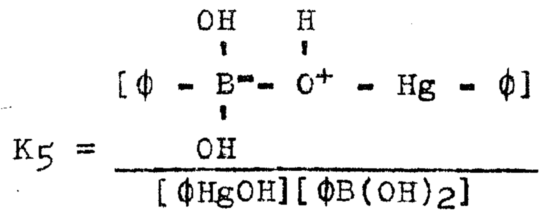
$$\frac{1}{k_{obs.}} = \frac{K_3K_6}{k_CK_1K_w}[HX] + \frac{1}{k_C} + \frac{K_4}{k_C[H_3O^+]} \tag{44}$$

Again the requirements of equation (35) are fulfilled

where $A = \dfrac{K_3K_6}{k_CK_1K_W}$ and $B = \dfrac{1}{k_C}$

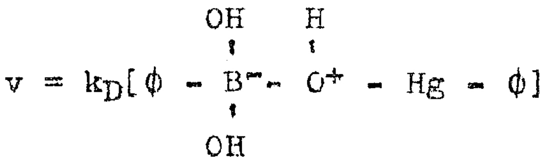
and Mechanism C becomes acceptable.

In Mechanism D there is a pre-equilibrium involving phenylmercuric hydroxide and benzeneboronic acid followed by a slow intramolecular reaction to give products. The transitory intermediate which is presented may exist in the form of an ion-pair. The equilibrium constant, K_5, is shown below:



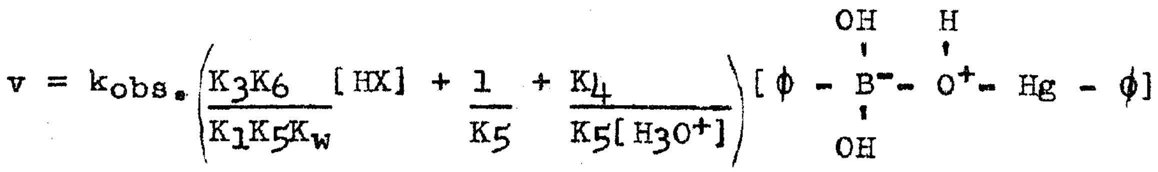
$$K_5 = \frac{[\phi - \underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{B}^-}} - \overset{\mathrm{H}}{\mathrm{O}^+} - \mathrm{Hg} - \phi]}{[\phi\mathrm{HgOH}][\phi\mathrm{B(OH)_2}]} \qquad (45)$$

The rate expression is:



$$v = k_D[\phi - \underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{B}^-}} - \overset{\mathrm{H}}{\mathrm{O}^+} - \mathrm{Hg} - \phi] \qquad (46)$$

Substitution of equation (45) into equation (43) produces:



$$v = k_{obs.}\left(\frac{K_3K_6}{K_1K_5K_W}[HX] + \frac{1}{K_5} + \frac{K_4}{K_5[H_3O^+]}\right)[\phi - \underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{B}^-}} - \overset{\mathrm{H}}{\mathrm{O}^+} - \mathrm{Hg} - \phi] \qquad (47)$$

and further substitution of equation (46):

$$\frac{1}{k_{obs.}} = \frac{K_3K_6}{k_DK_1K_5K_W}[HX] + \frac{1}{k_DK_5} + \frac{K_4}{k_DK_5[H_3O^+]} \qquad (48)$$

Reference to equation (35) shows

$$A = \frac{K_3K_6}{k_DK_1K_5K_w} \quad \text{and} \quad B = \frac{1}{k_DK_5}$$

We now have four mechanisms (A through D) which fit the experimental data according to the rate expression which has been derived.

Mechanisms E and F denote the phenylmercuric salt as the electrophilic species in a reaction with free benzeneboronic acid and benzeneboronate anion respectively.

Equation (49) is derived by multiplication of equations (4) and (5):

$$K_1K_2 = \frac{[\phi HgOH][H_3O^+][X^-]}{[\phi HgX]} \qquad (49)$$

Solving for [ϕHgOH] and substituting in equation (43):

$$v = k_{obs.}\left(\frac{K_6[H_3O^+][X^-]}{K_1K_w} + 1 + \frac{K_4}{[H_3O^+]}\right)\frac{[\phi HgX][\phi B(OH)_2]}{[H_3O^+][X^-]} \qquad (50)$$

or:

$$v = k_{obs.}\left(\frac{K_6}{K_1K_w} + \frac{1}{[H_3O^+][X^-]} + \frac{K_4}{[H_3O^+]^2[X^-]}\right)[\phi HgX][\phi B(OH)_2] \qquad (51)$$

Since:

$$v = k_E[\phi HgX][\phi B(OH)_2] \qquad (52)$$

Then:

$$\frac{1}{k_{obs.}} = \frac{K_6}{k_EK_1K_w} + \frac{1}{k_E[H_3O^+][X^-]} + \frac{K_4}{k_E[H_3O^+]\ [X^-]} \qquad (53)$$

This mechanism can be rejected since equation (53) predicts a rate increase with increasing molecular acid concentration, an effect opposite to that which is observed. It also predicts an increase in rate with increasing H_3O^+ (last term) which is not observed.

A similar derivation follows for Mechanism F, employing equations (8) and (51):

$$v = k_{obs.}\left(\frac{K_6}{K_1K_w} + \frac{1}{[H_3O^+][X^-]} + \frac{K_4}{[H_3O^+]^2[X^-]}\right)[\phi HgX][\phi B(OH)_3^-]\frac{[H_3O^+]}{K_4} \tag{54}$$

$$v = k_{obs.}\left(\frac{K_6[H_3O^+]}{K_1K_wK_4} + \frac{1}{K_4[X^-]} + \frac{1}{[H_3O^+][X^-]}\right) \tag{55}$$

$$v = k_F[\phi HgX][\phi B(OH)_3^-] \tag{56}$$

$$\frac{1}{k_{obs.}} = \frac{K_6}{k_FK_1K_wK_4}[H_3O^+] + \frac{1}{k_FK_4[X^-]} + \frac{1}{k_F[H_3O^+][X^-]} \tag{57}$$

According to equation (57) there can be no inhibition by molecular acid. Furthermore, a decrease in rate with increasing hydronium ion concentration is to be expected when $[H_3O^+] \gg K_4$. This behavior is not observed, and Mechanism F becomes unacceptable.

For Mechanism G:

$$v = k_G[\phi HgOH][\phi B(OH)_3^-] \tag{58}$$

Combination of equations (43) and (8) yields:

$$v = k_{obs.}\left(\frac{K_6[H_3O^+][X^-]}{K_1K_w} + 1 + \frac{K_4}{[H_3O^+]}\right)\frac{[H_3O^+][\phi B(OH)_3^-][\phi HgOH]}{K_4} \tag{59}$$

Inspection of equation (65) reveals that a dependence upon $[X^-]$ should be observed at constant pH below pH 8. Also, at zero anion concentration the reaction should be accelerated by hydronium ion concentration. This is clearly not the case. Thus, Mechanisms H and I are ruled out.

3. Effect of substituents on benzeneboronic acid. Preliminary experiments indicated that several substituted diarylmercurials were insoluble in "40%" aqueous ethanol to the extent of less than 10^{-5} molar. Therefore, the solvent was changed to "50%" aqueous ethanol for the substituent runs.

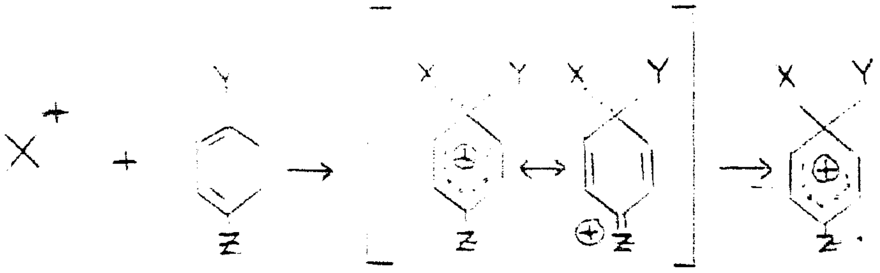
TABLE XI

VALUES OF $k_{obs.}$ FOR THE REACTION OF BASIC PHENYLMERCURIC PERCHLORATE WITH SUBSTITUTED BENZENEBORONIC ACIDS IN "50%" AQUEOUS ETHANOL AT 25.0° C.

Run	Substituent	$k_{obs.}$ $l.mol^{-1}sec^{-1}$	$\log k/k_o$
70	H	7.97	0
72	*p*-OCH_3	103.3	1.06
71	*p*-CH_3	28.7	0.448
75	*p*-F	8.32	0.019
79	*p*-Cl	2.94	-0.433
78	*m*-F	2.70	-0.470
74	*m*-NO_2	0.429	-1.27

Inspection of Table XI reveals that electron-releasing substituents on the boronic acid component increase the reaction rate. These results are consistent with an electrophilic attack on the boronic acid by mercury since such an attack will be favored by a high electron density on the ring carbon. The small magnitude of this effect is somewhat surprising; electrophilic aromatic substitution reactions are usually much more sensitive to electronic effects transmitted to the reaction center.

A plot of log k/k_o vs. Hammett's sigma constants[10] is shown in Figure 7. Lack of a good correlation is apparent since both the <u>p</u>-methoxy and <u>p</u>-tolyl points lie above the line. Electron-releasing groups often exhibit this behavior when located in a position <u>para</u> to the seat of electrophilic substitution. The effect has been attributed to resonance stabilization of an electron deficient transition state leading to a sigma complex [equation (66)].



(66)

TRANSITION STATE

Brown and Okamoto[4] have corrected the Hammett substituent constants for this added resonance stabilization and have given them the designation, σ^+, hereafter called "sigma-plus." In Figure 8 log k/k_o is plotted

Figure 7. log k/k$_o$ versus σ for the reaction of substituted benzeneboronic acids with phenylmercuric hydroxide in "50%" aqueous ethanol.

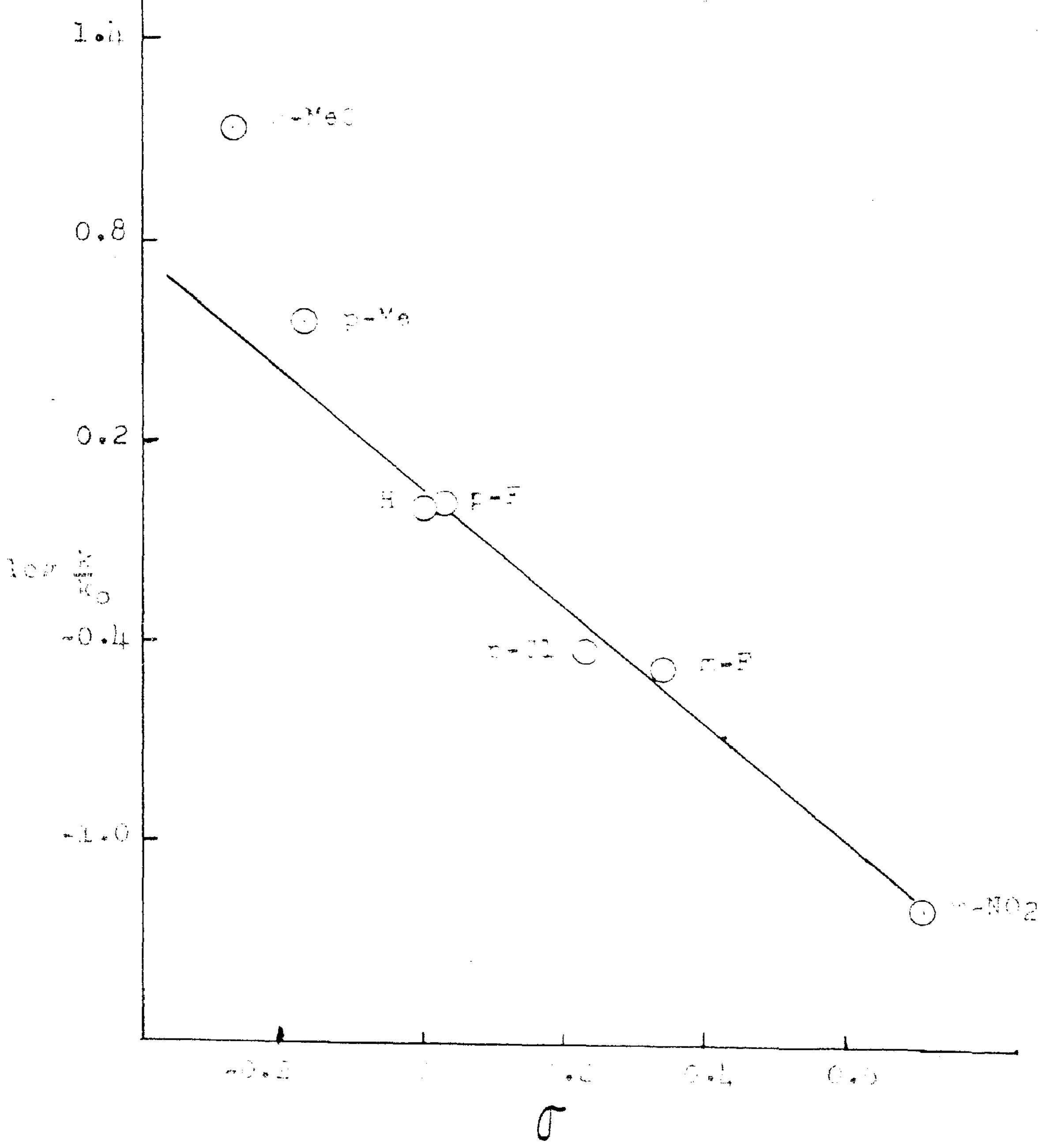
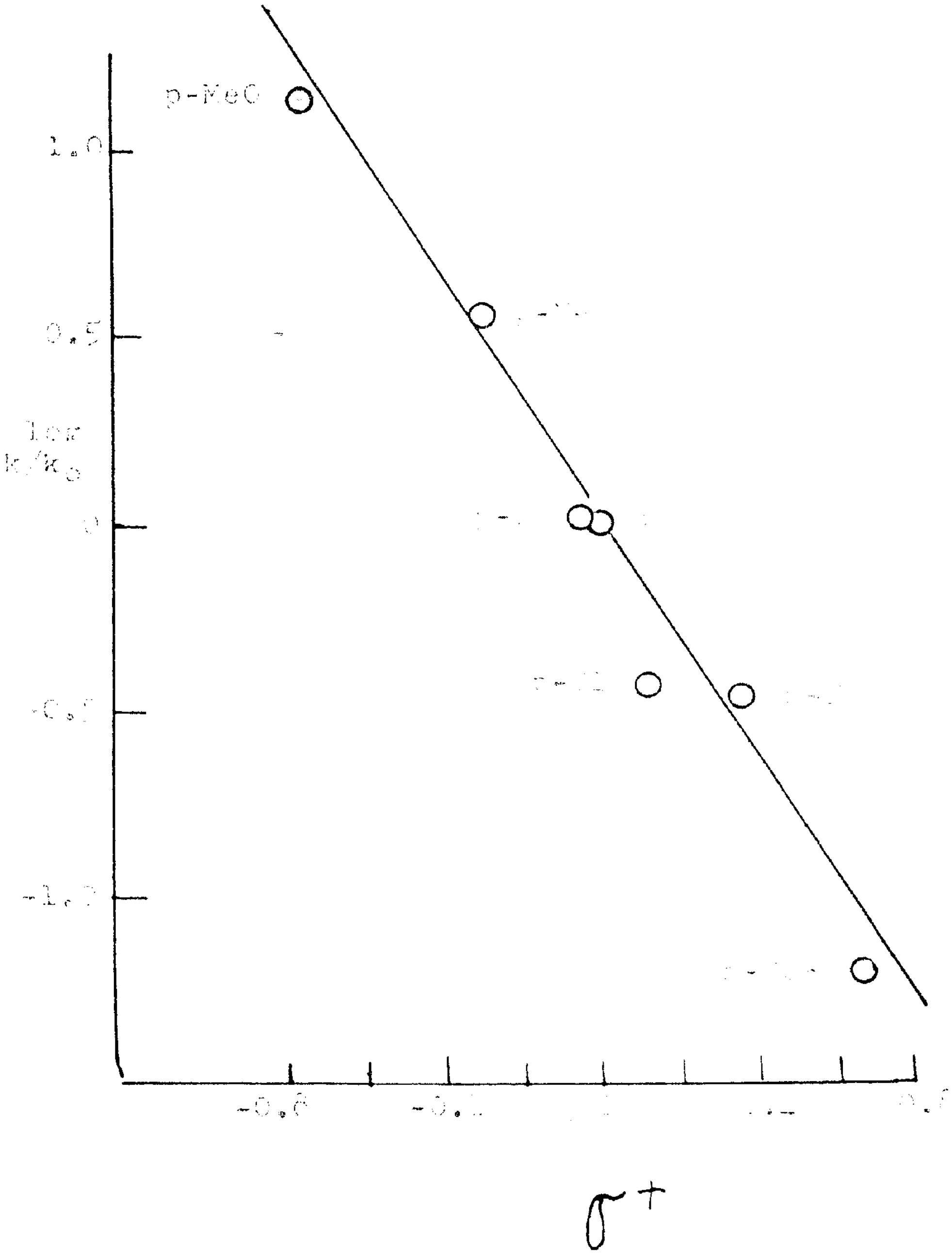


Figure 8. log k/k_0 versus σ^+ for the reactions of substituted benzeneboronic acids with phenylmercuric hydroxide in "95%" aqueous ethanol.



against Brown's sigma-plus constants. The points approximate a linear relationship although a possible curved trend is discernible for the para groups ($\rho = -1.62$, $s = 0.147$, $r = 0.983$). The small value of ρ suggests that a pre-equilibrium may be involved before the rate-determining step in the reaction with opposite electron demands.

Recently, Yukawa and Tsuno[32,35,36] have investigated the general applicability of the sigma-plus constants. Their study of the decomposition of substituted ω-diazoacetophenones in acetic acid at 40° C. revealed that a better linear correlation was observed by using sigma-plus than sigma. However, they noted that all of the points for the para substituents in the sigma-plus plot fell below the "meta" line. This was attributed to the possible lesser availability of transition state resonance of this reaction than of that described on the basis of sigma-plus. Further examples were cited in which the resonance effect appeared to be less effective than described by Brown and Okamoto's sigma-plus. Among those are the solvolysis of neophyl brosylates,[12] the Beckmann rearrangement of acetophenone oxime picryl ethers,[13] the Beckmann rearrangement of acetophenonoximes,[27] Diels-Alder reaction of 1-phenyl-1,3-butadienes with maleic anhydride[8] and acid-catalyzed rearrangement of phenylpropenylcarbinols.[2] On the other hand, in the brominolysis of benzeneboronic acids[23] the contribution of transition state resonance appears greater than predicted by sigma-plus. On the basis of this evidence Yukawa and Tsuno proposed that a unique set of sigma-plus values was not sufficient to correlate all reactions which involve electron deficient transition states where resonance stabilization is possible. Furthermore, a modified Hammett equation was developed which might correlate electrophilic reactions in general:

$$\text{"}\log k/k_o = \rho(\sigma + r\Delta\bar{\sigma}_R{}^+) \tag{67}$$

where *r* is a reaction constant describing the degree of transition state resonance or measuring the magnitude of positive charge to be necessarily stabilized at the transition state, and $\Delta\bar{\sigma}_R{}^+$ which corresponds to a proper set of $\sigma^+ - \sigma$ is a substituent constant suggesting the resonating capacity of substituent."[35] The value of *r* remains constant in a reaction series, but is a variable of reactions.

Thirty-five reactions have been correlated by the relationship expressed in equation (67). According to the results, "*r*" varies over a wide range from 0.2 to 2.3 with respect to the change in reaction, and rho ranges from -12.0 to 0.6. The authors explain the success of Brown and Okamoto's equation by indicating that most of the reactions in the literature have "*r*" values of 0.7 to 1.3.

In Figure 8A the data for the reaction of basic phenylmercuric perchlorate with substituted benzeneboronic acids is plotted against $\sigma + 0.608\Delta\bar{\sigma}_R{}^+$. The value of "*r*", 0.608, was calculated from the p-methoxy, p-tolyl, p-fluoro and p-chloro points, using the rho value for the "meta" line of -2.04. A better correlation is obtained than when the sigma-plus constants are used ($\rho = -1.81$, $s = 0.10$, $r = 0.992$).

According to Yukawa and Tsuno's postulation, this may mean that there is a lesser degree of resonance stabilization in the transition state for this reaction than for Brown's reference reaction. If this line of reasoning were correct, use of the sigma-plus constants would result in an over-compensation for the resonance effect.

E. Effect of substituents on the mercurial. The absence of a pH effect below pH 8 has been shown in Figure 3. A further substantiation of this fact was obtained by comparing the rates of phenylmercuric hydroxide and basic phenylmercuric perchlorate with benzeneboronic acid in "50%" aqueous ethanol (Table XII). Therefore, arylmercuric

TABLE XII

VALUES OF $k_{obs.}$ FOR THE REACTION OF BENZENEBORONIC ACID WITH BASIC PHENYLMERCURIC PERCHLORATE AND PHENYLMERCURIC HYDROXIDE IN "50%" AQUEOUS ETHANOL.

Run	Mercurial	$k_{obs.}$
70A	basic perchlorate	7.72
70B	basic perchlorate	8.22
77A	hydroxide	8.30
77B	hydroxide	8.10

hydroxides were employed in the substituent work. A study of the reaction was made with various substituted arylmercuric hydroxides and acetates to determine the effect of changing the electrophilicity of the attacking reagent by variation of substituents. Wherever possible, rates were measured as a function of molecular acetic acid concentration and values of the slopes from plots of $1/k_{obs.}$ vs. [HOAc] were determined.

Values of $k_{obs.}$ for the reaction of phenylmercuric acetate with benzeneboronic acid at various acetic acid concentrations are given in Table XIII. A similar set of runs using p-tolylmercuric acetate and benzeneboronic acid are listed in Table XIV. A comparison of the plots of $1/k_{obs.}$ vs. [HOAc] is made in Figure 9. Linearity is observed in each plot throughout the region studied. It is interesting to note that the two lines have a common intercept and show only a slight variation in slope. Table XV shows a set of runs with p-tolylmercuric acetate and p-tolueneboronic acid at various acetic acid concentrations. A plot of the data is shown in Figure 10. These results are summarized in Table XVI where the slopes and intercepts of the lines in Figures 9 and 10 are listed for each set of runs.

Rate constants at zero acetic acid concentration were obtained from extrapolation of the plots in Figures 9

TABLE XIII

VALUES OF $k_{obs.}$ FOR THE REACTION OF PHENYLMERCURIC ACETATE WITH BENZENEBORONIC ACID IN "50%" AQUEOUS ETHANOL IN THE PRESENCE OF ACETIC ACID.

Run	[HOAc]X10^4 moles/l.	$k_{obs.}$ l.mol^{-1}sec^{-1}	1/$k_{obs.}$
80	7.17	3.65	0.274
81	14.34	2.20	0.455
82	21.51	1.49	0.671
83	28.68	1.20	0.833

TABLE XIV

VALUES OF $k_{obs.}$ FOR THE REACTION OF p-TOLYLMERCURIC ACETATE WITH BENZENEBORONIC ACID IN "50%" AQUEOUS ETHANOL IN THE PRESENCE OF ACETIC ACID.

Run	[HOAc]X10^4 moles/l.	$k_{obs.}$ l.mol^{-1}sec^{-1}	1/$k_{obs.}$
84	2.39	6.08	0.164
85	8.34	3.56	0.281
86	9.56	3.34	0.299
87	16.73	2.51	0.399
88	23.90	2.20	0.455
89	25.02	1.84	0.543
90	33.36	1.62	0.617

TABLE XV

VALUES OF $k_{obs.}$ FOR THE REACTION OF p-TOLYLMERCURIC ACETATE WITH p-TOLUENEBORONIC ACID IN "50" AQUEOUS ETHANOL IN THE PRESENCE OF ACETIC ACID.

Run	[HOAc]X10^4 moles/l.	$k_{obs.}$ $l.mol^{-1}sec^{-1}$	$1/k_{obs.}$
92	2.78	25.9	0.0386
93	11.12	13.4	0.0746
94	19.46	9.97	0.102
95	27.80	7.02	0.142

TABLE XVI

THE EFFECT OF A p-CH_3 SUBSTITUENT UPON A AND B FOR THE REACTION OF PHENYLMERCURIC ACETATE WITH BENZENEBORONIC ACID IN THE PRESENCE OF EXCESS ACETIC ACID IN "50%" AQUEOUS ETHANOL AT 25.0°.

$$1/k_{obs.} = A[HX] + B$$

Substituent on Boronic Acid	Substituent on Mercurial	A	B
H	p-CH_3	183	0.130
H	H	209	0.130
p-CH_3	p-CH_3	27.7	0.025

and 10. These rate constants are $k_{obs.}$ for the substituted arylmercuric hydroxides assuming complete hydrolysis of the arylmercuric acetates at infinite dilution. The extrapolated rate constant for the reaction of phenylmercuric acetate with benzeneboronic acid is 8.00. This value is in excellent agreement with those obtained by using the hydroxide or basic perchlorate in the absence of acetic acid (Table XII, p. 42). The value of $k_{obs.}$ for the reaction of p-tolylmercuric hydroxide with m-nitrobenzeneboronic acid was obtained by using the free hydroxide.

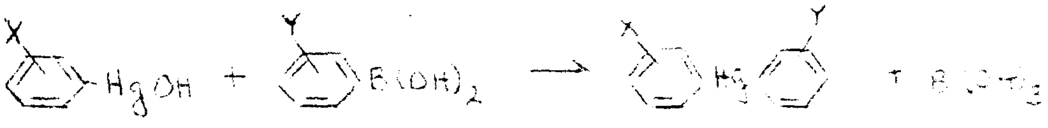
Table XVI indicates that a p-CH_3 substituent on the mercurial has virtually no effect upon the value of the slope (A) or intercept (B) in equation (35). Furthermore, a p-CH_3 substituent on the boronic acid lowers both the slope and intercept by the same degree.

In terms of the rate expression which applies to Mechanisms A through D, this implies that a substituent on the mercurial has a similar effect upon K_1 and K_6 [equations (25), (39), (44) and (48); pp. 20, 29, 30, 31]. Also, this effect must be similar in magnitude and opposite in direction to the effect upon $\bar{k}$, the specific reaction rate constant. Consequently, a p-CH_3 group on the mercurial produces no noticeable effect upon the observed rate constant. Substitution of a p-CH_3 group into the substrate should tend to diminish K_4 but increase the specific reaction rate constants k_A and k_B in reference to Mechanisms A and B. The results suggest that the latter effect must be greater than the former. Nevertheless, these opposing influences could explain the small value of ρ which is observed in Figure 8. A similar explanation can be used in reference to Mechanism D by a consideration of the opposite electronic demands of K_5 and k_D. The rate expression for Mechanism C [equation (44), p. 30] implies that $k_C = k_{obs.}$ at zero buffer concentration. Since phenylmercuric hydroxide should be a weak electrophile and quite selective, a simple transition state which involved bond formation between mercury and carbon would be improbable in view of the small value of rho. However, a simultaneous attack by oxygen on boron and mercury on carbon could explain the low selectivity which is observed.

A comparison of the effect of substituent variation on benzeneboronic acid with several substituted phenylmercuric hydroxides is made in Table XVII. It is noteworthy that a change in substituent on the mercurial from p-CH_3 to m-NO_2 produces no variation in the observed rate constant when the substrate is benzeneboronic acid. This strengthens the argument which has been proposed previously. The electronic demand of a pre-equilibrium involving the mercurial is opposite to that of the rate determining step. These opposing effects tend to cancel one another. On the other hand, when the substrate is p-tolylboronic acid, electron-withdrawing groups on the electrophile serve to produce a slight decrease in reaction rate. Most likely the unique behavior of this substrate can be attributed

TABLE XVII

VALUE OF $k_{obs.}$ FOR THE REACTION OF SUBSTITUTED BENZENEBORONIC ACIDS WITH SUBSTITUTED PHENYLMERCURIC HYDROXIDES IN "50%" AQUEOUS ETHANOL AT 25.0° C.



Y	X = *p*-CH$_3$		X = H		X = *m*-NO$_2$	
	$k_{obs.}$ l.mol^{-1} sec^{-1}	log k/k_o	$k_{obs.}$ l.mol^{-1} sec^{-1}	log k/k_o	$k_{obs.}$ l.mol^{-1} sec^{-1}	log k/k_o
H	8.00	0	7.97	0	8.89	0
p-CH$_3$	38.5	0.682	28.7	0.557	20.1	0.354
m-F	—	—	2.70	-0.433	1.48	-0.780
m-NO$_2$	0.392	-1.31	0.429	-1.27	—	—

to varying degrees of resonance stabilization in the transition state. Because of the small rate differences which were observed with *p*-tolueneboronic acid, it would be interesting to study the reactivity of *p*-methoxybenzeneboronic acid with different mercurials. The insolubility of (*p*-methoxyphenyl) *m*-nitrophenyl mercury and di-*p*-methoxyphenyl mercury in "50%" aqueous ethanol made this extension impossible in this solvent.

The rate plots involving *m*-nitrophenylmercuric hydroxide sloped downward toward the end of the reaction.

An example of this slope is shown in Figure 11 with benzeneboronic acid. The rate constants in these runs were calculated from initial slopes.

A study was made of the effect of acetic acid upon the rates of reaction of m-nitrophenylmercuric acetate with substituted benzeneboronic acids. Again it was necessary to determine initial slopes because of the fall-off in rate toward the end of the reaction. The data in Table XVIII suggest that the rates are relatively independent of acetic acid concentration below 10^{-3} molar acetic acid. At higher concentrations of acetic acid the extent of curvature in the rate plots increased so that it was impossible to determine rate constants.

TABLE XVIII

VALUES OF $k_{obs.}$ FOR THE REACTION OF m-NITROPHENYLMERCURIC HYDROXIDES WITH BENZENEBORONIC ACIDS IN "50%" AQUEOUS ETHANOL IN THE PRESENCE OF ACETIC ACID.

Run	Substituent	[HOAc]X10^4 moles/l.	$k_{obs.}$ l.mol^{-1}sec^{-1}	$1/k_{obs.}$
97	H	0	8.89	0.112
98	H	2.840	8.23	0.121
99	H	5.680	8.19	0.122
100	m-F	0	1.48	0.676
101	m-F	2.840	0.629	1.59
102	m-F	5.680	0.553	1.81

Figure 11. Second order rate plot of reaction between benzeneboronic acid and m-nitrophenylmercuric chloride in "50%" aqueous ethanol.

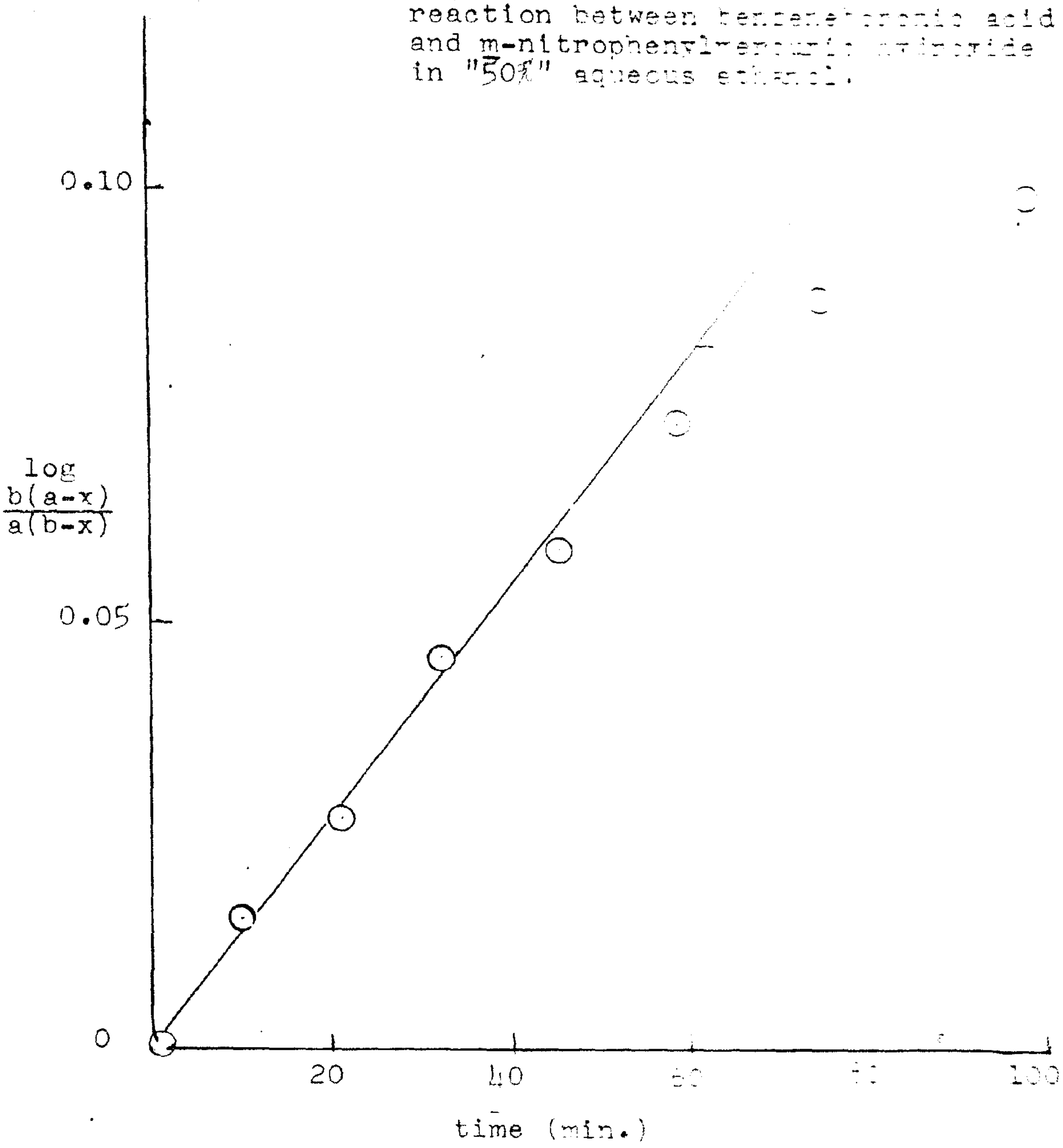
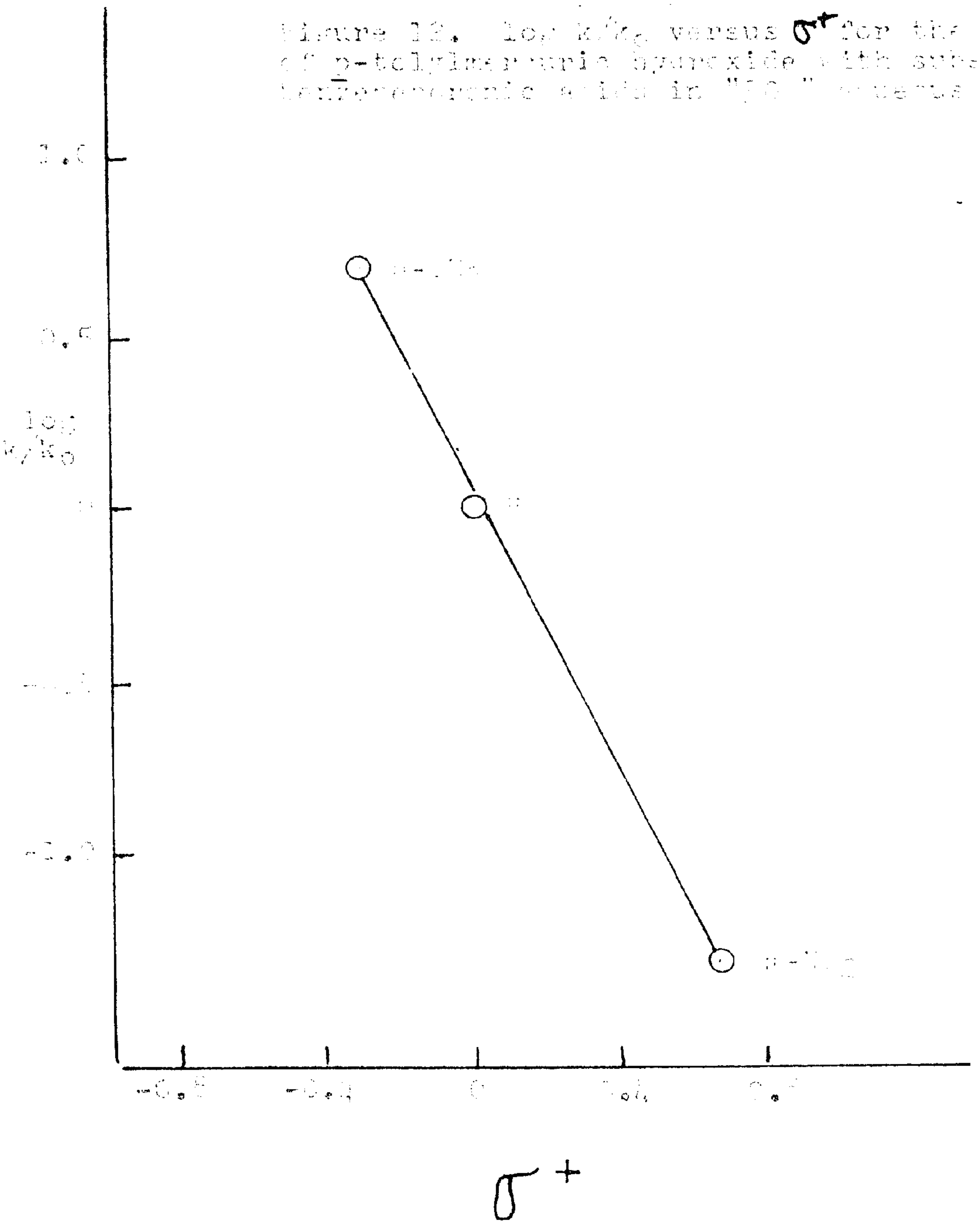


Figure 12. log k/k_0 versus σ^+ for the reaction of p-tolylmercuric hydroxide with substituted benzeneboronic acids in "50 %" aqueous ethanol.

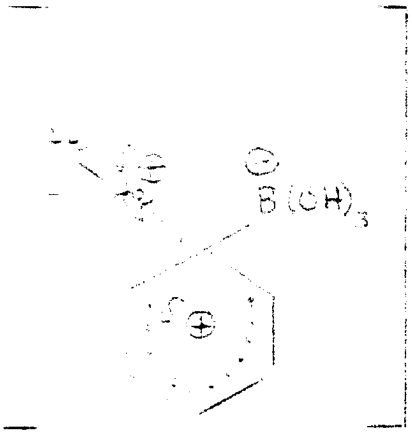


IV. Mechanism.

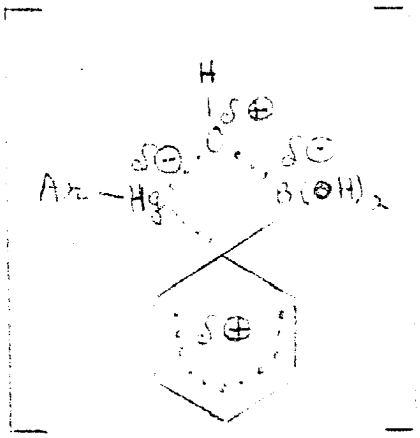
Although it does not appear possible to distinguish on purely kinetic evidence among the pairs of reactants listed in Mechanisms A through D (page 17), substituent effects can provide valuable information concerning the transition state. Equation (66)(page 36) describes a positively charged transition state and the stabilization produced by substituents which can interact with the pi electron system in the ring and aid in the delocalization of this charge. Reactions which proceed through such a transition state will not be correlated by the Hammett equation since this relationship does not account for this added resonance stabilization. The present work reveals that two sets of data fail to give a Hammett correlation, namely, the reactions of p-tolylmercuric hydroxide and phenylmercuric hydroxide. Although the data for p-tolylmercuric hydroxide is correlated by the sigma-plus constants proposed by Brown (Figure 12), the points for phenylmercuric hydroxide show a possible deviation from linearity in a sigma-plus plot (Figure 8). A better correlation is realized for phenylmercuric hydroxide (Figure 8A) when the modified Hammett equation developed by Yukawa is used.

The results indicate three outstanding features of the reaction: (1) the small negative value of rho which remains reasonably constant over a wide range of substituent changes in the mercurial, (2) the insensitivity of reaction rate to substituent variation in the electrophile and (3) the inability of one set of substituent constants to correlate all of the data. It may be possible to rationalize this apparently unusual behavior by using an argument which has been proposed by Dewar[7] in a theoretical discussion of the nature of the transition state in electrophilic aromatic substitution.

The transition state may involve a simple electrophilic attack by arylmercuric ion upon benzeneboronate ion (I) or a simultaneous electrophilic attack upon carbon and nucleophilic attack upon boron (II). For purposes of discussion let us assume that the transfer of hydroxide ion occurs prior to a rate-determining carbon-mercury bond formation.

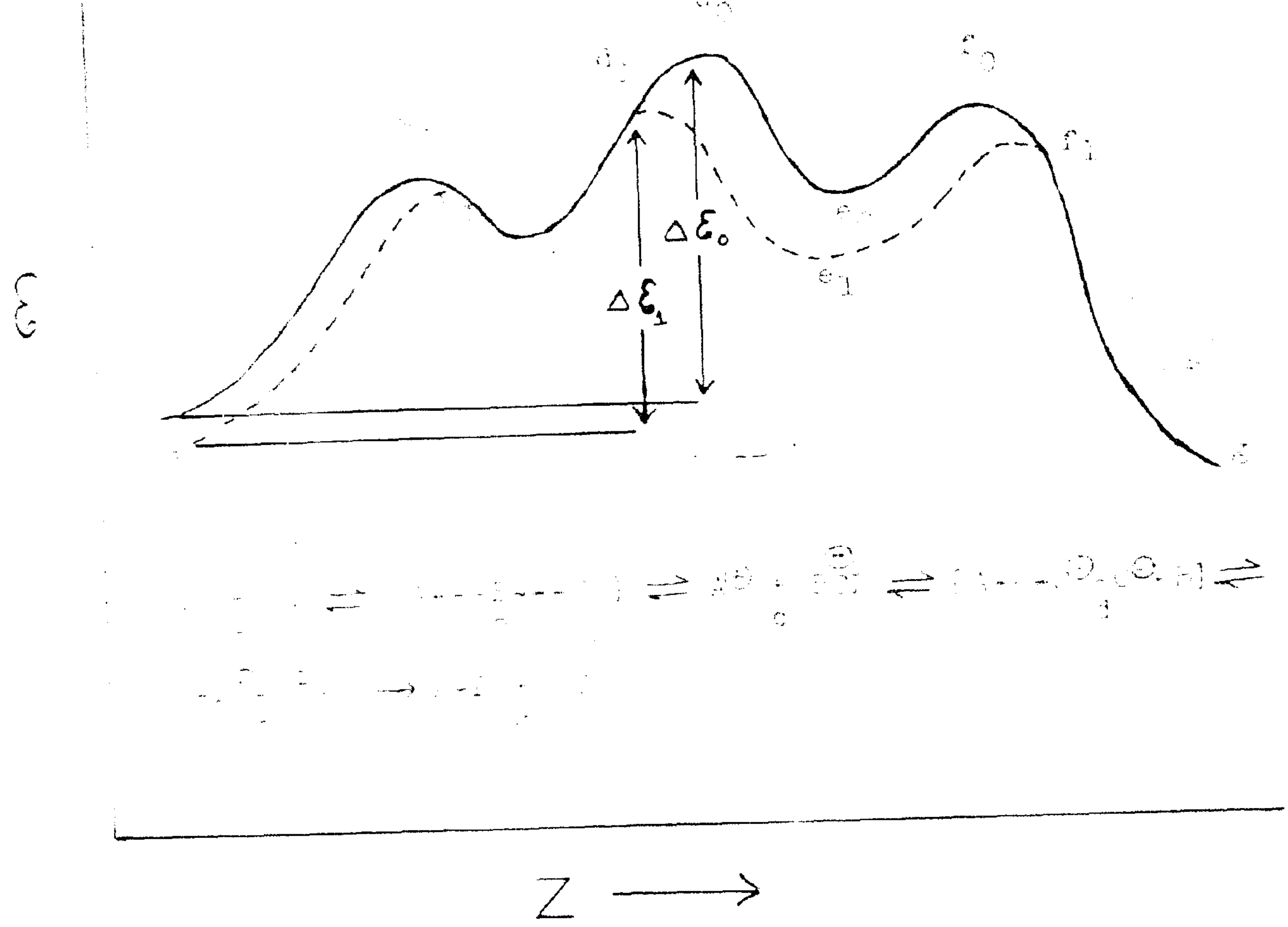


I



II

Let us consider a hypothetical potential energy diagram for the reaction (Figure 14). The curve represents the change in potential energy in passing along the reaction coordinate "Z" for each of the species involved in the [illegible] Potential energy diagram for reaction of [illegible] hydroxide with substituted benzene[illegible] acids.



reaction. Minima in the curve correspond to the potential energies of reactants, intermediates and products (a, c, e and g). Transition states are shown as maxima along the reaction coordinate (b, d and f). The highest point in the curve refers to the transition state in the rate-determining step of the reaction. Since the reaction rate is facilitated by electron-releasing substituents on the substrate, it seems likely that "d" is the higher-energy transition state. The difference between the potential energy of this transition state and that of the zero-point energy of reactants is the energy of activation, $\Delta\mathcal{E}$.

This is indeed an oversimplified picture of the potential energy changes during the course of a reaction. More correctly the diagram should be in three dimensions with the transition states designated as saddle points between two valleys. The reactants could then approach the transition state in any number of ways along the floors of these valleys. However, for our purposes it will suffice to consider access to the transition state in a two coordinate system. Furthermore, the shape of each curve as we have drawn them is arbitrary and is not intended to portray the actual situation. We will be concerned only with relative positions of minimum and maximum potential energy and assume that the changes in entropy which determine the shape of the curves will either be constant or negligible for small structure changes in the molecule.

In Figure 14 the first step is an acid base reaction, a simple transfer of hydroxide ion from mercury to boron. The zero-point energies of the free acid and base are designated by "a" and those of the ions (or ion-pair) by "b".

If "a_0" represents the system benzeneboronic acid plus phenylmercuric hydroxide, then a change to para-methyl benzeneboronic acid will lower the curve to "a_1". A para-methyl substituent should increase the stability of the free acid relative to the anion and therefore lower "a_0" relative to "c_0" without changing the shape of the curve. This change in structure will also lower "e_0" relative to "c_0" because of the parallel effect of increasing the stability of the A-D bond. One would predict on purely electronic grounds--since a carbon atom in the ring is in closer proximity to the substituent--that the latter effect would be greater than the former; therefore, we have given a greater displacement to "e_0" than to "a_0". The resultant $\Delta\varepsilon_1$ is smaller than $\Delta\varepsilon_0$, but the difference is not as great as would be anticipated if there were no displacement of "a_0". This illustration can serve to explain how the present reaction system displays such a small dependence upon substituent variation in the substrate ring.

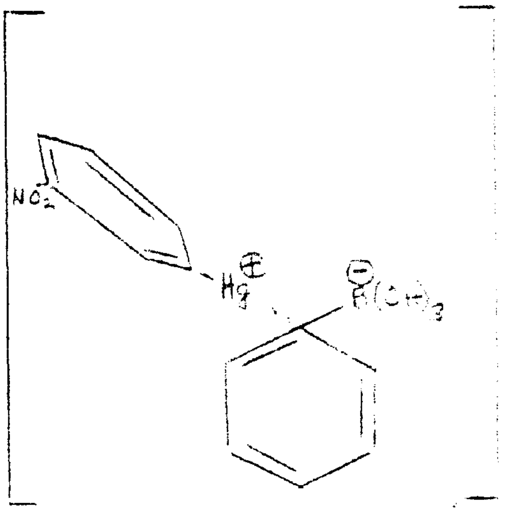
Similar considerations are applied to substituent changes in the electrophile in Figure 14A. Introduction of a p-methyl substituent into the mercurial will increase the reactivity of the free base in the first step. This is shown in the diagram by raising "a_0" relative to "c_0". It will also decrease reactivity of A^+ in the second step. One would expect that these opposing effects would be nearly equal in magnitude. Resonance stabilization of the arylmercuric ion would seem unlikely because of the large size of mercury. "a_0" therefore becomes "a_2". The diagram reveals that $\Delta\varepsilon_0$ is equal to $\Delta\varepsilon_2$. Neglecting entropy effects, the rate for the *p*-tolyl mercurial will equal that of the unsubstituted mercurial with any given substrate. This type of reasoning can explain similar rates of various mercurials with benzeneboronic acid.

It is important to note that, although there is no change in the activation energy, $\Delta\varepsilon$, with this structure variation, the transition state "d" moves closer to the intermediate, "e", by an amount which we will call "ΔZ". A *m*-nitro group on the mercurial would transfer the transition state closer to reactants in like manner. We might therefore conclude that the substitution in the boronic acid component from *m*-nitro to *p*-methoxy will cause a change in the position of the transition state from "d_0" to "d_1" for a given mercurial. The term "d_0" will refer to the unsubstituted acid. Electron-releasing groups on the mercurial will make this shift in the transition state, $d_1 - d_0 + \Delta z_j$, where Δz_j is the change in position of the transition state when a substituent "j" is placed in the ring of the electrophile. Electron-releasing substituents in the mercurial would cause Δz_j to be positive and electron-withdrawing substituents would produce a negative Δz_j. It follows that the more positive Δz_j, the more the transition state will resemble the pentadienate intermediate, "e".

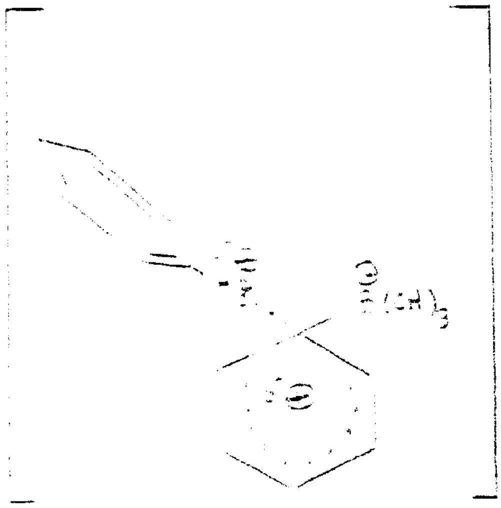
If the picture which we have presented is correct, for electrophilic aromatic substitution the degree of resonance stabilization provided by a substituent in the transition state will depend upon the similarity of this transition state to the pentadienate intermediate. The concept concerning the position of the transition state in relation to reactants and products was originally proposed by Hammond and is commonly referred to as the "Hammond postulate."[11]

It appears likely that the parameter "r" which has been introduced by Yukawa to determine substituent constants is analagous to Δz_j and tells us where the transition state lies along the reaction coordinate. When "r" is equal to unity, the transition state model may resemble that of the solvolysis of aryldimethylcarbinyl chlorides. The reaction would then be correlated by sigma-plus. If "r" is less than unity, the transition state can be said to resemble reactants more closely. When "r" becomes zero, it is possible that no significant bond formation occurs between the electrophile and ring carbon in the transition state.

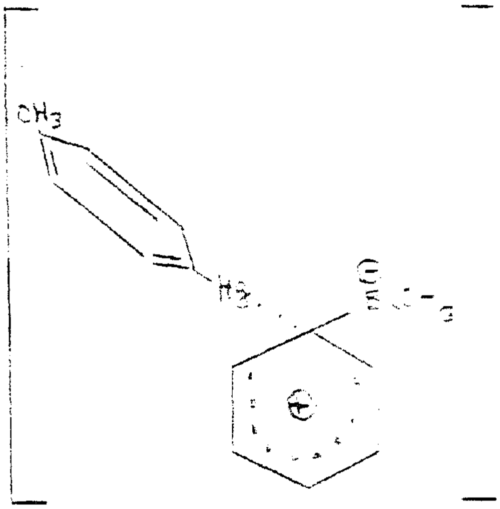
The present investigation reveals that three different sets of substituent constants may be necessary to correlate all of the data (pp. 39-42). On the basis of the above arguments transition states III, IV and V may be postulated for the different reaction series.



III



IV



V

Supporting evidence for this view comes from a recent study by Dessy[6] which described the cleavage of symmetrically substituted diarylmercuries. The reactions with HgI_2 were shown to be an electrophilic displacement which was correlated by sigma. He concluded that the transition state resembled reactants. The cleavage with HCl was correlated by a set of substituent constants which correspond to $0.5(\sigma^+ + \sigma)$.

Further studies upon similar reaction systems may be instrumental in establishing the significance of the transition state model in linear free energy relationships.

EXPERIMENTAL

I. Materials.

A. Benzeneboronic acids. All of the boronic acids which were used, with the exception of the m-nitrobenzeneboronic acid, were prepared according to the method of Bean and Johnson.[1] The procedure described by Seaman and Johnson[30] was used to prepare m-nitrobenzeneboronic acid.

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

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

C. Arylmercuric hydroxides. To 2 g. of the appropriate arylmercuric acetate in "50%" dioxane water was added drop by drop a 10% sodium hydroxide solution until the resulting solution was decidedly basic. The sodium hydroxide was made carbonate-free by dissolving it in an equal weight of water and filtering through a sintered glass funnel.[31]

TABLE XX

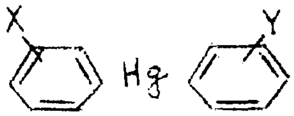
SUBSTITUTED PHENYLMERCURIC ACETATES.

Substituent	M.P.	M.P. Lit.	% Hg Calc.	% Hg Found	Ref.
H	149	149	59.58	59.53	34
p-CH_3	153-155	153	57.15	57.38	34
m-NO_2	167-169	—	52.56	52.20	—

B. Diaryl mercurials. To a solution containing 0.0045 moles of the arylmercuric acetate in 200 ml. of 70% aqueous ethanol was added drop by drop a solution of 10% carbonate-free sodium hydroxide until the solution was slightly basic. This solution was then added to a solution which contained 0.005 moles of the appropriate boronic acid in the same solvent. The solvent was cooled, filtered and washed with cold 95% ethanol. The yields were quantitative. Mercury analyses indicated that no recrystallization was necessary. The compounds are tabulated in Table XXI.

TABLE XXI

SUBSTITUTED DIARYL MERCURIALS.



Substituents X	Y	M. P.	M. P. Lit.	% Hg Calc.	% Hg Found	Ref.
H	H	124-125	125.5	56.54	56.50	34
H	*p*-CH_3O	110-140d.	____	52.13	52.70	__
H	*p*-CH_3	140-185d.	120-155d.	54.31	54.31	16
H	*p*-F	110-115	111-115	53.81	53.86	17
H	*p*-Cl	162-200	160-205	51.55	51.72	15
H	*m*-F	107-111	107-111	53.81	54.18	17
H	*m*-NO_2	220-240d.[a]	113-115	50.18	50.05	9
CH_3	*m*-NO_2	210-235d.	____	48.48	48.11	__
m-F	*m*-NO_2	160-233d.	____	48.01	47.64	__
CH_3	CH_3	230-231	238	52.46	52.80	34

[a] This compound softens at 113 but does not melt until 220.

II. Method of Mercury Analysis.

A modification of the method of Koten and Adams[20] was used in the analyses for mercury. An 0.1 g. sample of the mercury compound was weighed out in a 125 ml. Erlenmeyer flask. The sample was decomposed by 10 ml. of 7% fuming sulfuric acid and 5 ml. of fuming nitric acid. The flask was then heated on a hot plate for two hours in order to insure decomposition. If this heating was omitted, the results were invariably low. After cooling, 10 ml. of water was added to the flask in small portions. A solution of potassium permanganate was then added drop by drop until its color persisted for five minutes. The excess permanganate was destroyed by adding ferrous sulfate. To the clear solution was added one ml. of a saturated ferric ammonium alum solution. The flask was then cooled to 5°[19] and titrated with a standard potassium thiocyanate solution. The potassium thiocyanate was standardized against reagent grade mercury. The precision was good to within 0.3%.

III. Kinetic Procedure.

All runs were carried out at 25.0 ± 0.02° C. An NBS thermometer was used for calibration.

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. The flask was shaken to insure complete mixing. Small aliquots were removed at measured time intervals and transferred to quartz cuvettes. The cuvettes were then placed in a Beckman DU Spectrophotometer and the optical densities of the reaction mixture was recorded. A blank containing solvent was used for each run.

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

$$(A-X)\varepsilon_A + (B-X)\varepsilon_B + X\varepsilon_C = [O.D.]_t$$

$$A\varepsilon_A - X\varepsilon_A + B\varepsilon_B - X\varepsilon_B + X\varepsilon_C = [O.D.]_t$$

$$(\varepsilon_C - \varepsilon_B - \varepsilon_A)X = [O.D.]_t - A\varepsilon_A - B\varepsilon_B$$

$$X = \frac{[O.D.]_t - A\varepsilon_A - B\varepsilon_B}{\varepsilon_C - \varepsilon_B - \varepsilon_A}$$

where

A = initial concentration of boronic acid.

B = initial concentration of mercurial.

X = concentration of product at time t.

ε_A = extinction of boronic acid.

ε_B = extinction of mercurial.

ε_C = extinction of product.

$[O.D.]_t$ = optical density at time t of reaction mixture.

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RUN #1

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 12.15 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.015 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3510

$[C_6H_5B(OH)_2]$ = 3.3789

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "60%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 8.31 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.392	0	12.15	5.02	0
20	0.720	1.71	10.44	3.31	0.115
35	0.870	2.49	9.63	2.53	0.198
54	0.985	3.09	9.07	1.93	0.288
94	1.151	3.95	8.20	1.07	0.498
164	1.273	4.58	7.57	0.431	0.860
253	1.339	4.93	7.22	0.088	1.53

$k_{obs.}$ = 2.80 l.mol^{-1}sec^{-1}

RUN #2

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.075 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.015 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3510

$[C_6H_5B(OH)_2]$ = 3.3789

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "60%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 8.31 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.256	0	6.08	5.02	0
16	0.378	0.630	5.45	4.39	0.0108
31	0.473	1.13	4.95	3.89	0.0215
50	0.580	1.69	4.39	3.33	0.0368
91	0.743	2.53	3.54	2.48	0.0712
160	0.870	3.19	2.88	1.82	0.1259
249	0.985	3.79	2.28	1.22	0.1880
386	1.06	4.19	1.89	0.827	0.2750

$k_{obs.}$ = 2.84 $l.mol^{-1}sec^{-1}$

RUN #3

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 3.038 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 5.015 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3510$

$[C_6H_5B(OH)_2] = 3.3789$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "60%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 8.31 $\qquad$ u = 0.01 $\qquad$ λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.188	0	5.02	3.04	0
14	0.231	0.224	4.79	2.81	0.0134
29	0.312	0.645	4.37	2.39	0.0439
50	0.376	0.978	4.04	2.06	0.0745
89	0.442	1.32	3.69	1.72	0.115
158	0.565	1.96	3.05	1.08	0.235

$k_{obs.} = 2.90\ l.mol^{-1}sec^{-1}$

RUN #5

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_0 = 7.592 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_0 = 6.018 \times 10^{-5}$ moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3510$

$[C_6H_5B(OH)_2] = 3.3789$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "60%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 8.31　　u = 0.01　　λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.314	0	7.59	6.02	0
18	0.630	1.64	5.95	4.37	0.0326
32	0.714	2.08	5.51	3.94	0.0452
54	0.880	2.95	4.65	3.07	0.0787
88	1.012	3.63	3.96	2.39	0.119
117	1.111	4.15	3.45	1.87	0.164
212	1.284	5.05	2.55	0.971	0.318

$k_{obs.} = 3.41$ l.mol^{-1}sec^{-1}

RUN #8

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.440 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 6.580 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3897

$[C_6H_5B(OH)_2]$ = 3.3748

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "60%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 8.27 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.338	0	7.44	6.58	0
15	0.580	1.27	6.17	5.31	0.0119
30	0.703	1.92	5.52	4.66	0.0202
49	0.835	2.61	4.83	3.97	0.0318
71	0.940	3.16	4.28	3.42	0.0441
89	1.027	3.62	3.82	2.96	0.0574
110	1.127	4.15	3.29	2.43	0.0782
141	1.180	4.42	3.02	2.16	0.0922
164	1.244	4.76	2.68	1.82	0.115

$k_{obs.}$ = 2.88 $l.mol^{-1}sec^{-1}$

RUN #10

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 10.43 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.86 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3510

$[C_6H_5B(OH)_2]$ = 3.3448

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "50%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 8.04 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.341	0	10.43	4.86	0
17	0.750	2.11	8.32	2.75	0.149
31	0.900	2.84	7.59	2.02	0.243
47	1.004	3.42	7.01	1.44	0.356
64	1.091	3.87	6.56	0.99	0.500
84	1.146	4.15	6.28	0.71	0.615
101	1.204	4.45	5.98	0.41	0.832

$k_{obs.}$ = 5.17 l.mol^{-1}sec^{-1}

RUN #11

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_0$ = 6.955 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_0$ = 4.860 X 10^{-5} moles/l.

log ϵ

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3510

$[C_6H_5B(OH)_2]$ = 3.3448

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "50%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 8.04 u = o.ol λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.263	0	6.96	4.86	0
13	0.510	1.27	5.69	3.59	0.0444
29	0.650	1.99	4.97	2.87	0.0828
43	0.767	2.60	4.36	2.26	0.130
61	0.850	3.02	3.94	1.84	0.175
83	0.935	3.46	3.50	1.40	0.242
98	0.960	3.59	3.37	1.27	0.268
113	0.995	3.77	3.19	1.09	0.311
145	1.062	4.12	2.84	0.74	0.428

$k_{obs.}$ = 5.24 l.mol^{-1}sec^{-1}

RUN #12

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.160 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.075 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3510

$[C_6H_5B(OH)_2]$ = 3.3717

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 7.82 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.281	0	7.16	5.08	0
11	0.583	1.57	5.59	3.51	0.0526
21	0.721	2.29	4.87	2.79	0.0925
31	0.850	2.96	4.20	2.12	0.147
43	0.915	3.30	3.86	1.78	0.187
55	0.995	3.72	3.44	1.36	0.254
69	1.055	4.03	3.13	1.05	0.325
84	1.102	4.27	2.89	0.81	0.403
99	1.134	4.44	2.72	0.64	0.479
121	1.169	4.62	2.54	0.46	0.593
137	1.184	4.70	2.46	0.38	0.662

$k_{obs.}$ = 8.85 $l.mol^{-1}sec^{-1}$

RUN #13

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 5.372 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 5.075 \times 10^{-5}$ moles/l.

log ϵ

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3510$

$[C_6H_5B(OH)_2] = 3.3717$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 7.82 $\qquad$ u = 0.01 $\qquad$ λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.241	0	5.37	5.08	0
8	0.431	0.993	4.38	4.08	0.0058
18	0.544	1.58	3.79	3.50	0.00987
28	0.676	2.27	3.10	2.81	0.0180
40	0.757	2.69	2.68	2.39	0.0250
53	0.819	3.01	2.36	2.07	0.0322
66	0.885	3.35	2.02	1.73	0.0426
81	0.925	3.56	1.81	1.52	0.0511
96	0.968	3.78	1.59	1.30	0.0628
119	1.002	3.96	1.41	1.12	0.0753
150	1.038	4.15	1.22	0.93	0.0932

$k_{obs.} = 8.28$ l.mol^{-1}sec^{-1}

RUN #14

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.225 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.918 X 10^{-5} moles/l.

log $\mathcal{E}$

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3510

$[C_6H_5B(OH)_2]$ = 3.3717

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "30%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.
$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 7.66 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.256	0	6.23	4.92	0
5	0.461	1.07	5.15	3.85	0.0240
9	0.576	1.67	4.55	3.25	0.0438
14	0.660	2.10	4.12	2.82	0.0623
19	0.744	2.54	3.68	2.38	0.0869
25	0.802	2.84	3.38	2.08	0.112
30	0.855	3.12	3.10	1.80	0.134

$k_{obs.}$ = 13.1 $l.mol^{-1}sec^{-1}$

RUN #16

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 3.105 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 2.447 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3311

$[C_6H_5B(OH)_2]$ = 3.3438

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "30%" EtOH

Buffer = $[Na_2HPO_4]$ 0.00305 moles/l.

$[KH_2PO_4]$ 0.00314 moles/l.

"pH" = 7.58 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.121	0	3.11	2.45	0
13	0.246	0.646	2.47	1.81	0.0313
22	0.318	1.02	2.09	1.44	0.0583
30	0.340	1.13	1.98	1.33	0.0697
36	0.365	1.26	1.85	1.20	0.0846
60	0.429	1.59	1.52	0.87	0.139
91	0.484	1.87	1.24	0.59	0.219
114	0.502	1.96	1.15	0.50	0.258

$k_{obs.}$ = 13.5 l.mol^{-1}sec^{-1}

RUN #18

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 3.189 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 2.862 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3377

$[C_6H_5B(OH)_2]$ = 3.2972

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "30%" EtOH

Buffer = $[Na_2HPO_4]$ 0.01 moles/l.

$[KH_2PO_4]$ 0.01 moles/l.

"pH" = 7.37 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.126	0	3.19	2.86	0
10	0.140	0.071	3.12	2.79	0.0011
23	0.177	0.259	2.93	2.60	0.0044
36	0.223	0.493	2.70	2.37	0.0092
56	0.255	0.655	2.53	2.21	0.0129
80	0.296	0.863	2.33	2.00	0.0188
109	0.332	1.05	2.14	1.81	0.0258
141	0.369	1.23	1.96	1.63	0.0331
190	0.413	1.46	1.73	1.40	0.0449

$k_{obs.}$ = 2.77 l.mol^{-1}sec^{-1}

RUN #19

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 2.930 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 2.422 \times 10^{-5}$ moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3726$

$[C_6H_5B(OH)_2] = 3.3829$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.01 moles/l.

$[NaH_2PO_4]$ 0.01 moles/l.

"pH" = 7.60 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.127	0	2.93	2.42	0
12	0.172	0.236	2.68	2.19	0.0064
31	0.190	0.332	2.60	2.11	0.0077
58	0.221	0.499	2.43	1.92	0.0191
105	0.273	0.778	2.15	1.64	0.0342
152	0.331	1.09	1.84	1.33	0.0583
223	0.351	1.20	1.73	1.22	0.0690
294	0.374	1.32	1.61	1.10	0.0827
361	0.410	1.51	1.42	0.91	0.111

$k_{obs.} = 2.28$ l.mol^{-1}sec^{-1}

RUN #20

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 2.930 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.845 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3377

$[C_6H_5B(OH)_2]$ = 3.2972

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.01 moles/l.

$[NaH_2PO_4]$ 0.01 moles/l.

"pH" = 7.60 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$ x 10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.186	0	4.85	2.93	0
7	0.213	0.142	4.70	2.79	0.0087
13	0.232	0.241	4.60	2.69	0.0151
22	0.247	0.320	4.53	2.61	0.0206
32	0.284	0.514	4.33	2.42	0.0351
51	0.322	0.713	4.13	2.22	0.0520
81	0.363	0.928	3.92	2.00	0.0731
147	0.474	1.51	3.34	1.42	0.153
235	0.554	1.93	2.92	1.00	0.247

$k_{obs.}$ = 2.06 $l.mol^{-1}sec^{-1}$

RUN #21

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.410 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.105 X 10^{-5} moles/l.

$[B(OH)_3]_o$ = 8.380 X 10-5 moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3594

$[C_6H_5B(OH)_2]$ = 3.3730

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 7.82 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b\,(a-x)}{a\,(b-x)}$
0	0.290	0	7.41	5.11	0
3	0.420	0.677	6.73	4.43	0.0202
8	0.526	1.23	6.18	3.87	0.0415
14	0.627	1.76	5.65	3.34	0.0665
23	0.761	2.45	4.96	2.65	0.110
31	0.835	2.84	4.57	2.26	0.144
42	0.920	3.28	4.13	1.82	0.194
56	0.995	3.67	3.74	1.43	0.256
70	1.055	3.98	3.43	1.12	0.324
87	1.109	4.26	3.15	0.84	0.412

$k_{obs.}$ = 7.70 $l.mol^{-1}sec^{-1}$

RUN #23

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.410 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 2.042 X 10^{-5} moles/l.

$[B(OH)_3]_o$ = 8.380 X 10^{-5} moles/l.

<u>log $\mathcal{E}$</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3594

$[C_6H_5B(OH)_2]$ = 3.3730

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[KH_2PO_4]$ 0.003 moles/l.

"pH" = 7.82 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.218	0	7.41	2.04	0
4	0.286	0.354	7.06	1.69	0.0514
11	0.350	0.688	6.72	1.35	0.126
19	0.404	0.969	6.44	1.07	0.209
30	0.466	1.29	6.12	0.752	0.341
37	0.491	1.42	5.99	0.622	0.414
45	0.525	1.60	5.81	0.442	0.549

$k_{obs.}$ = 7.93 $l.mol^{-1}sec^{-1}$

RUN #24

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 7.22 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 5.06 \times 10^{-5}$ moles/l.

$[B(OH)_3]_o = 9.95 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.4728$

$[C_6H_5B(OH)_2] = 3.3840$

$[(C_6H_5)_2\,Hg] = 4.3774$

Solvent = "60%" EtOH

Buffer = $[NaH_2PO_4]$ 0.003 moles/l.

$[Na_2HPO_4]$ 0.003 moles/l.

"pH" = 8.31 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.344	0	7.22	5.06	0
18	0.516	1.01	6.22	4.06	0.0311
29	0.594	1.43	5.80	3.64	0.0482
40	0.661	1.79	5.44	3.28	0.0656
52	0.733	2.17	5.05	2.89	0.0881
65	0.780	2.43	4.80	2.64	0.1056
85	0.870	2.91	4.31	2.15	0.148
106	0.915	3.15	4.07	1.91	0.174

$k_{obs.} = 3.06$ $l.mol^{-1}sec^{-1}$

RUN #25

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.22 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 10.12 X 10^{-5} moles/l.

$[B(OH)_3]_o$ = 9.95 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4728

$[C_6H_5B(OH)_2]$ = 3.3840

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "60%" EtOH

Buffer = $[NaH_2PO_4]$ 0.003 moles/l.

$[Na_2HPO_4]$ 0.003 moles/l.

"pH" = 8.31 u = 0.01 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.469	0	10.12	7.22	0
8	0.650	1.01	9.12	6.22	0.0196
16	0.772	1.67	8.45	5.55	0.0359
27	0.916	2.45	7.67	4.77	0.0596
38	1.038	3.11	7.01	4.11	0.0852
50	1.143	3.69	6.44	3.54	0.113
73	1.287	4.47	5.65	2.75	0.166
83	1.346	4.79	5.33	2.43	0.194
92	1.387	5.00	5.12	2.22	0.216
111	1.432	5.26	4.86	1.96	0.248

$k_{obs.}$ = 3.01 $l.mol^{-1}sec^{-1}$

RUN #26A

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.505 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.095 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4091

$[C_6H_5B(OH)_2]$ = 3.3323

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[NaH_2PO_4]$ 0.003 moles/l.

$[Na_2HPO_4]$ 0.003 moles/l.

"pH" = 7.57 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.301	0	7.51	5.10	0
4	0.464	0.852	6.65	4.24	0.0271
8	0.530	1.20	6.30	3.90	0.0400
13	0.636	1.75	5.75	3.35	0.0664
18	0.711	2.14	5.36	2.96	0.0897
24	0.794	2.58	4.92	2.52	0.122
34	0.888	3.07	4.43	2.03	0.171
45	0.960	3.44	4.06	1.66	0.220
58	1.040	3.86	3.64	1.24	0.299
71	1.094	4.14	3.36	0.96	0.376

$k_{obs.}$ = 8.22 $l.mol^{-1}sec^{-1}$

RUN #26B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.46 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.82 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3956

$[C_6H_5B(OH)_2]$ = 3.3737

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.
$[NaH_2PO_4]$ 0.003 moles/l.

"pH" = 7.57   u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X 10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.242	0	7.46	4.82	0
5	0.460	0.842	6.62	3.98	0.0313
9	0.561	1.37	6.09	3.45	0.0573
19	0.723	2.23	5.23	2.59	0.116
30	0.848	2.88	4.58	1.94	0.184
39	0.906	3.19	4.27	1.63	0.229
49	0.962	3.48	3.98	1.34	0.283
59	1.012	3.75	3.71	1.07	0.350
69	1.054	3.97	3.49	0.85	0.414

$k_{obs.}$ = 8.42 $l.mol^{-1}sec^{-1}$

RUN #26C

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 7.46 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 4.82 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3956$

$[C_6H_5B(OH)_2] = 3.3737$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.003 moles/l.

$[NaH_2PO_4]$ 0.003 moles/l.

"pH" = 7.57 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.242	0	7.46	4.82	0
7	0.526	1.19	6.27	3.63	0.0478
18	0.710	2.16	5.30	2.66	0.110
27	0.793	2.60	4.86	2.22	0.151
37	0.888	3.10	4.36	1.72	0.214
48	0.974	3.55	3.91	1.27	0.299
66	1.030	3.84	3.62	0.98	0.378
72	1.041	3.90	3.56	0.92	0.398

$k_{obs.} = 8.04$ l.mol^{-1}sec^{-1}

RUN #27

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 7.29 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 4.87 \times 10^{-5}$ moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.4240$

$[C_6H_5B(OH)_2] = 3.3863$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.006 moles/l.

$[NaH_2PO_4]$ 0.006 moles/l.

"pH" = 7.57 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.312	0	7.29	4.87	0
4	0.420	0.581	6.71	4.29	0.0191
8	0.508	1.05	6.24	3.82	0.0378
15	0.597	1.52	5.77	3.35	0.0608
23	0.693	2.04	5.25	2.83	0.0931
33	0.784	2.52	4.77	2.35	0.132
47	0.892	3.10	4.19	1.77	0.199
60	0.956	3.44	3.85	1.43	0.255

$k_{obs.} = 6.53$ l.mol^{-1}sec^{-1}

RUN #29A

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 7.29 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 4.87 \times 10^{-5}$ moles/l.

log $\mathcal{E}$

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3816$

$[C_6H_5B(OH)_2] = 3.3770$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.001 moles/l.

$[NaH_2PO_4]$ 0.001 moles/l.

"pH" = 7.57 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.292	0	7.29	4.87	0
3	0.445	0.821	6.37	4.05	0.0215
6	0.559	1.43	5.86	3.44	0.0560
10	0.652	1.93	5.36	2.94	0.0855
14	0.770	2.57	4.72	2.30	0.137
19	0.816	2.81	4.48	2.06	0.162
30	0.936	3.46	3.56	1.14	0.319
36	0.984	3.72	3.31	0.89	0.395
42	1.019	3.91	3.12	0.70	0.474
48	1.038	4.01	3.02	0.60	0.527

$k_{obs.} = 14.0$ $l.mol^{-1}sec^{-1}$

RUN #29B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.46 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.82 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3861

$[C_6H_5B(OH)_2]$ = 3.3621

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.001 moles/l.

$[NaH_2PO_4]$ 0.001 moles/l.

"pH" = 7.57 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.292	0	7.46	4.82	0
4	0.490	1.03	6.43	3.79	0.0401
8	0.601	1.61	5.85	3.21	0.0711
12	0.722	2.24	5.22	2.58	0.116
19	0.804	2.67	4.79	2.15	0.158
25	0.874	3.04	4.42	1.78	0.205
30	0.914	3.25	4.21	1.57	0.234
36	0.954	3.46	4.00	1.36	0.279
41	0.998	3.69	3.77	1.13	0.334

$k_{obs.}$ = 13.1 $l.mol^{-1}sec^{-1}$

RUN #30

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 7.29 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 4.87 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.4010$

$[C_6H_5B(OH)_2] = 3.3826$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.0005 moles/l.

$[NaH_2PO_4]$ 0.0005 moles/l.

"pH" = 7.57 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.301	0	7.29	4.87	0
3	0.483	0.962	6.33	3.91	0.0341
7	0.631	1.74	5.55	3.13	0.0735
10	0.712	2.17	5.12	2.70	0.103
14	0.782	2.54	4.75	2.33	0.134
19	0.872	3.01	4.28	1.86	0.187
24	0.940	3.38	3.91	1.49	0.244
30	0.986	3.62	3.67	1.25	0.292
36	1.020	3.80	3.49	1.07	0.338
43	1.057	4.00	3.29	0.87	0.402

$k_{obs.} = 15.0$ l.mol^{-1}sec^{-1}

RUN #31A

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 7.425 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 4.836 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3636$

$[C_6H_5B(OH)_2] = 3.3326$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer $[Na_2HPO_4]$ 0.004 moles/l.

$[NaH_2PO_4]$ 0.002 moles/l.

"pH" = 7.88 $\quad$ u = 0.04 $\quad$ λ = 227.5 mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.275	0	7.43	4.84	0
8	0.532	1.32	6.10	3.52	0.0526
17	0.670	2.03	5.39	2.81	0.0967
26	0.778	2.59	4.83	2.25	0.146
37	0.854	2.98	4.44	1.86	0.192
47	0.920	3.32	4.10	1.52	0.245
58	0.972	3.59	3.83	1.25	0.300

$k_{obs.} = 7.45$ l.mol^{-1}sec^{-1}

RUN 31B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 7.425 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 4.836 \times 10^{-5}$ moles/l.

<u>log ϵ</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3636$

$[C_6H_5B(OH)_2] = 3.3326$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.004 moles/l.

$[NaH_2PO_4]$ 0.002 moles/l.

"pH" = 7.88 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.275	0	7.43	4.84	0
6	0.473	1.02	6.40	3.82	0.0379
23	0.748	2.43	4.99	2.41	0.130
35	0.846	2.94	4.48	1.90	0.186
45	0.904	3.24	4.18	1.60	0.231
56	0.960	3.53	3.89	1.31	0.286

$k_{obs.} = 7.34$ l.mol^{-1}sec^{-1}

RUN #34B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_0 = 7.46 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_0 = 4.82 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3956$

$[C_6H_5B(OH)_2] = 3.3737$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.002 moles/l.

$[NaH_2PO_4]$ 0.002 moles/l.

"pH" = 7.57 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.294	0	7.46	4.82	0
8	0.574	1.44	6.02	3.38	0.0612
18	0.753	2.38	5.08	2.44	0.129
38	0.936	3.35	4.11	1.47	0.257
46	0.982	3.59	3.87	1.23	0.308
54	1.020	3.79	3.67	1.03	0.362
64	1.058	3.99	3.47	0.83	0.432

$k_{obs.} = 9.59$ l.mol^{-1}sec^{-1}

RUN #35A

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_0$ = 7.46 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_0$ = 4.82 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3995

$[C_6H_5B(OH)_2]$ = 3.3530

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.0048 moles/l.

$[NaH_2PO_4]$ 0.0012 moles/l.

"pH" = 8.14   μ = 0.02   λ = 227.5mμ

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.294	0	7.46	4.82	0
11	0.658	1.95	5.51	2.87	0.0938
18	0.804	2.73	4.73	2.09	0.165
27	0.894	3.21	4.25	1.61	0.232
34	0.941	3.46	4.00	1.36	0.279
45	1.013	3.85	3.61	0.97	0.381
53	1.049	4.04	3.42	0.78	0.452

$k_{obs.}$ = 12.2 l.mol^{-1}sec^{-1}

RUN 35B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.46 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.82 X 10^{-5} moles/l.

log $\mathcal{E}$

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3995

$[C_6H_5B(OH)_2]$ = 3.3530

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.0048 moles/l.

$[NaH_2PO_4]$ 0.0012 moles/l.

"pH" = 8.14 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]X10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.294	0	7.46	4.82	0
7	0.580	1.53	5.93	3.29	0.0663
15	0.752	2.45	5.01	2.37	0.136
23	0.858	3.02	4.44	1.80	0.203
30	0.940	3.46	4.00	1.36	0.279
50	1.052	4.06	3.40	0.76	0.461

$k_{obs.}$ = 13.3 $l.mol^{-1}sec^{-1}$

RUN #36

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.46 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.82 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3861

$[C_6H_5B(OH)_2]$ = 3.3621

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.0012 moles/l.

$[NaH_2PO_4]$ 0.0006 moles/l.

"pH" = 7.88 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.293	0	7.46	4.82	0
4	0.530	1.23	6.23	3.59	0.0499
9	0.660	1.91	5.55	2.91	0.0909
13	0.752	2.39	5.07	2.43	0.130
17	0.818	2.74	4.72	2.08	0.166
22	0.880	3.06	4.40	1.76	0.208
29	0.954	3.45	4.01	1.37	0.277
35	0.994	3.66	3.80	1.16	0.326
41	1.028	3.84	3.62	0.98	0.378

$k_{obs.}$ = 12.9 $l.mol^{-1}sec^{-1}$

RUN #37B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.056 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 7.010 X 10^{-5} moles/l.

$\underline{\log \varepsilon}$

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3593

$[C_6H_5B(OH)_2]$ = 3.3747

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.012 moles/l.

$[NaH_2PO_4]$ 0.006 moles/l.

"pH" = 7.88 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.304	0	7.01	6.06	0
9	0.525	1.18	5.83	4.88	0.0136
17	0.649	1.84	5.17	4.22	0.0246
26	0.742	2.34	4.67	3.72	0.0352
37	0.848	2.90	4.11	3.16	0.0505
46	0.928	3.33	3.68	2.73	0.0661
56	0.970	3.55	3.46	2.51	0.0758
64	1.029	3.87	3.14	2.19	0.0929
76	1.086	4.17	2.84	1.89	0.113

$k_{obs.}$ = 5.71 $l.mol^{-1}sec^{-1}$

RUN 38B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 6.055 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 7.010 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3593$

$[C_6H_5B(OH)_2] = 3.3747$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.006 moles/l.

$[NaH_2PO_4]$ 0.003 moles/l.

"pH" = 7.88　　u = 0.04　　λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.304	0	7.01	6.06	0
6	0.533	1.21	5.80	4.85	0.0141
14	0.719	2.20	4.81	3.86	0.0320
22	0.818	2.73	4.28	3.33	0.0454
31	0.924	3.30	3.71	2.76	0.0648
40	1.007	3.74	3.27	2.32	0.0854
49	1.077	4.11	2.90	1.95	0.109

$k_{obs.} = 8.74$ l.mol^{-1}sec^{-1}

RUN 39A

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.13 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.05 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3799

$[C_6H_5B(OH)_2]$ = 3.3574

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.012 moles/l.

$[NaH_2PO_4]$ 0.003 moles/l.

"pH" = 8.14 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.262	0	6.13	5.05	0
10	0.526	1.38	4.75	3.67	0.0278
30	0.759	2.59	3.54	2.46	0.0739
40	0.822	2.92	3.21	2.13	0.0940
51	0.888	3.26	2.87	1.79	0.120
62	0.932	3.49	2.64	1.56	0.144
70	0.972	3.70	2.43	1.35	0.171
78	0.992	3.81	2.32	1.24	0.188

$k_{obs.}$ = 8.52 $l.mol^{-1}sec^{-1}$

RUN 39B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.13 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.05 X 10^{-5} moles/l.

$\underline{\log \varepsilon}$

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3799

$[C_6H_5B(OH)_2]$ = 3.3574

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.012 moles/l.

$[NaH_2PO_4]$ 0.003 moles/l.

"pH" = 8.14 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.262	0	6.13	5.05	0
15	0.661	2.08	4.05	2.97	0.0505
27	0.723	2.40	3.73	2.65	0.0643
37	0.792	2.76	3.37	2.29	0.0836
48	0.868	3.16	2.97	1.89	0.112
59	0.919	3.43	2.70	1.62	0.138
67	0.954	3.61	2.52	1.44	0.159

$k_{obs.}$ = 8.37 $l.mol^{-1}sec^{-1}$

RUN 40

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.13 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.05 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3901

$[C_6H_5B(OH)_2]$ = 3.3686

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.0024 moles/l.

$[NaH_2PO_4]$ 0.0006 moles/l.

"pH" = 8.14 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.262	0	6.13	5.05	0
14	0.666	2.06	4.07	2.99	0.0498
21	0.816	2.85	3.28	2.20	0.0893
26	0.868	3.12	3.01	1.93	0.102
31	0.918	3.38	2.75	1.67	0.132
36	0.952	3.56	2.57	1.49	0.153
41	0.980	3.70	2.43	1.35	0.171
48	1.018	3.90	2.23	1.15	0.203
55	1.052	4.08	2.05	0.97	0.241

$k_{obs.}$ = 15.2 $l.mol^{-1}sec^{-1}$

RUN #41A

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 6.13 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 5.05 \times 10^{-5}$ moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3524$

$[C_6H_5B(OH)_2] = 3.3536$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.0012 moles/l.

$[NaH_2PO_4]$ 0.0048 moles/l.

"pH" = 6.99 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.252	0	6.13	5.05	0
9	0.428	0.910	5.22	4.14	0.0165
17	0.544	1.51	4.62	3.54	0.0315
25	0.611	1.86	4.27	3.19	0.0425
32	0.684	2.23	3.90	2.82	0.0566
40	0.746	2.55	3.58	2.50	0.0718
47	0.780	2.73	3.40	2.32	0.0818
60	0.840	3.04	3.09	2.01	0.103
73	0.886	3.28	2.85	1.77	0.123
89	0.934	3.53	2.60	1.52	0.149

$k_{obs.} = 6.26$ l.mol^{-1}sec^{-1}

RUN #41B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_0$ = 6.13 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_0$ = 5.05 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3524

$[C_6H_5B(OH)_2]$ = 3.3536

$[(C_6H_5)_2Hg]$ = 1.3774

Solvent = "[illegible]0%" EtOH

Buffer = $[Na_2HPO_4]$ 0.0012 moles/l.

$[NaH_2PO_4]$ 0.0048 moles/l.

"pH" = 6.99 μ = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.252	0	6.13	5.05	0
6	0.376	0.64	5.49	4.41	0.0110
14	0.497	1.27	4.86	3.78	0.0250
23	0.587	1.73	4.40	3.32	0.0378
29	0.651	2.06	4.07	2.99	0.0498
37	0.712	2.38	3.75	2.67	0.0634
44	0.765	2.65	3.48	2.40	0.0772
57	0.828	2.98	3.15	2.07	0.0982
70	0.868	3.19	2.94	1.86	0.115
86	0.926	3.49	2.64	1.56	0.144

$k_{obs.}$ = 6.19 $l.mol^{-1}sec^{-1}$

RUN 42

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.13 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.15 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3847

$[C_6H_5B(OH)_2]$ = 3.3704

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[Na_2HPO_4]$ 0.0025 moles/l.

$[NaH_2PO_4]$ 0.01 moles/l.

"pH" = 6.99 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.267	0	6.13	5.15	0
6	0.355	0.461	5.67	4.59	0.0076
15	0.438	0.896	5.23	4.15	0.0163
28	0.543	1.45	4.68	3.60	0.0298
40	0.612	1.81	4.32	3.24	0.0408
56	0.694	2.24	3.89	2.81	0.0571
74	0.774	2.66	3.47	2.39	0.0778
123	0.910	3.37	2.76	1.68	0.131
150	0.966	3.66	2.47	1.39	0.166

$k_{obs.}$ = 3.69 $l.mol^{-1}sec^{-1}$

RUN #44

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.13 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.05 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4832

$[C_6H_5B(OH)_2]$ = 3.3686

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = [HOAc] 0.01 moles/l.

[NaOAc] 0.01 moles/l.

"pH" = 5.37 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.304	0	6.13	5.05	0
8	0.343	0.211	5.92	4.84	0.00332
18	0.388	0.455	5.68	4.60	0.00751
34	0.446	0.769	5.36	4.28	0.0135
55	0.510	1.12	5.01	3.93	0.0213
76	0.563	1.40	4.73	3.65	0.0284
105	0.632	1.78	4.35	3.27	0.0398
125	0.667	1.97	4.16	3.08	0.0464
159	0.737	2.34	3.79	2.71	0.0615

$k_{obs.}$ = 1.38 l.mol^{-1}sec^{-1}

RUN #45

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.13 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.05 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4879

$[C_6H_5B(OH)_2]$ = 3.3971

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = [HOAc] 0.005 moles/l.

[NaOAc] 0.005 moles/l.

"pH" = 5.37 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.306	0	6.13	5.05	0
6	0.366	0.319	5.81	4.73	0.00513
15	0.438	0.709	5.42	4.34	0.0123
32	0.521	1.16	4.97	3.89	0.0222
53	0.618	1.68	4.45	3.37	0.0366
74	0.692	2.08	4.05	2.97	0.0505
103	0.779	2.56	3.57	2.49	0.0723
123	0.824	2.80	3.33	2.25	0.0861
157	0.874	3.07	3.06	1.98	0.105

$k_{obs.}$ = 2.46 $l.mol^{-1}sec^{-1}$

RUN #46

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.13 X 10^{-5} moles/1.

$[C_6H_5B(OH)_2]_o$ = 5.05 X 10^{-5} moles/1.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4879

$[C_6H_5B(OH)_2]$ = 3.3971

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = [HOAc] 0.0075 moles/1.

[NaOAc] 0.0075 moles/1.

"pH" = 5.36 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/1.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.314	0	6.13	5.05	0
11	0.383	0.378	5.75	4.67	0.0062
29	0.477	0.892	5.24	4.16	0.0161
58	0.582	1.47	4.66	3.58	0.0303
94	0.686	2.04	4.09	3.01	0.0490
136	0.742	2.34	3.79	2.71	0.0615
163	0.786	2.59	3.54	2.46	0.0739

$k_{obs.}$ = 1.86 $l.mol^{-1}sec^{-1}$

RUN #47

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.13 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.05 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4678

$[C_6H_5B(OH)_2]$ = 3.3813

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = [HOAc] 0.0025 moles/l.

[NaOAc] 0.0025 moles/l.

"pH" = 5.36 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.301	0	6.13	5.05	0
8	0.432	0.702	5.43	4.35	0.0122
17	0.520	1.18	4.95	3.87	0.0227
26	0.592	1.57	4.56	3.48	0.0332
39	0.670	1.94	4.19	3.11	0.0453
55	0.749	2.42	3.71	2.63	0.0652
70	0.794	2.66	3.47	2.39	0.0778
91	0.860	3.01	3.12	2.04	0.100
115	0.912	3.30	2.83	1.75	0.125

$k_{obs.}$ = 4.36 $l.mol^{-1}sec^{-1}$

RUN #49

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.255 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.480 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3856

$[C_6H_5B(OH)_2]$ = 3.3650

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[H_3PO_4]$ 0.001 moles/l.

$[NaH_2PO_4]$ 0.004 moles/l.

"pH" = 3.60 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.282	0	6.26	5.48	0
10	0.355	0.377	5.88	5.10	0.00495
28	0.439	0.817	5.44	4.66	0.00932
45	0.521	1.24	5.02	4.24	0.0159
67	0.583	1.57	4.69	3.91	0.0215
97	0.656	1.95	4.31	3.53	0.0293
124	0.723	2.30	5.96	3.18	0.0378
150	0.770	2.55	3.71	2.93	0.0451
185	0.804	2.73	3.53	2.75	0.0510

$k_{obs.}$ = 1.55 $l.mol^{-1}sec^{-1}$

RUN #51

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.255 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.480 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4146

$[C_6H_5B(OH)_2]$ = 3.3883

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[H_3PO_4]$ 0.0005 moles/l.

$[NaH_2PO_4]$ 0.002 moles/l.

"pH" = 3.60 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.296	0	6.26	5.48	0
9	0.432	0.723	5.53	4.76	0.00810
18	0.487	1.02	5.24	4.46	0.0126
29	0.571	1.46	4.80	4.02	0.0196
42	0.644	1.85	4.41	3.63	0.0271
53	0.712	2.21	4.05	3.27	0.0355
71	0.779	2.56	3.70	2.92	0.0454
85	0.830	2.84	3.42	2.64	0.0550
103	0.868	3.04	3.22	2.44	0.0630
128	0.934	3.39	2.87	2.09	0.0803

$k_{obs.}$ = 3.13 l.mol^{-1}sec^{-1}

RUN #52

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.255 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.480 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4278

$[C_6H_5B(OH)_2]$ = 3.3818

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[H_3PO_4]$ 0.005 moles/l.

$[NaH_2PO_4]$ 0.004 moles/l.

"pH" = 3.93 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.299	0	6.26	5.48	0
7	0.396	0.512	5.74	4.97	0.0055
16	0.453	0.816	5.44	4.66	0.0093
27	0.513	1.14	5.12	4.34	0.0143
40	0.602	1.61	4.65	3.87	0.0223
53	0.667	1.96	4.30	3.52	0.0295
69	0.718	2.23	4.03	3.25	0.0360
83	0.768	2.50	3.76	2.98	0.0435
126	0.874	3.06	3.20	2.42	0.639

$k_{obs.}$ = 2.68 $l.mol^{-1}sec^{-1}$

RUN #53

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.255 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.480 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3955

$[C_6H_5B(OH)_2]$ = 3.3458

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[H_3PO_4]$ 0.0015 moles/l.

$[NaH_2PO_4]$ 0.0090 moles/l.

"pH" = 3.76 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.277	0	6.26	5.48	0
56	0.461	0.956	5.30	4.52	0.0112
71	0.504	1.18	5.08	4.30	0.0149
92	0.540	1.37	4.89	4.11	0.0180
117	0.607	1.72	4.54	3.76	0.0244
147	0.659	1.99	4.27	3.49	0.0302
180	0.702	2.21	4.05	3.27	0.0355

$k_{obs.}$ = 1.01 l.mol^{-1}sec^{-1}

RUN #54

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 6.255 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.480 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3828

$[C_6H_5B(OH)_2]$ = 3.3458

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[H_3PO_4]$ 0.00125 moles/l.

$[NaH_2PO_4]$ 0.0075 moles/l.

"pH" = 3.76 u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.272	0	6.26	5.48	0
23	0.391	0.614	5.64	4.87	0.0067
39	0.451	0.926	5.33	4.55	0.0108
53	0.478	1.07	5.19	4.41	0.0133
68	0.557	1.48	4.78	4.00	0.0199
90	0.592	1.66	4.60	3.82	0.0232
114	0.612	1.76	4.50	3.72	0.0252
144	0.679	2.11	4.15	3.37	0.0330
178	0.707	2.26	4.00	3.22	0.0368

$k_{obs.}$ = 1.37 l.mol^{-1}sec^{-1}

RUN #61

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 5.90 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 3.58 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4013

$[C_6H_5B(OH)_2]$ = 3.2943

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = No Buffer

u = 0.04 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.219	0	5.90	3.58	0
10	0.528	1.60	4.30	1.98	0.120
19	0.640	2.18	3.72	1.40	0.209
29	0.723	2.61	3.29	0.97	0.314
41	0.791	2.96	2.94	0.62	0.459
53	0.820	3.11	2.79	0.47	0.557
64	0.844	3.23	2.67	0.35	0.666
76	0.870	3.37	2.53	0.21	0.864
88	0.880	3.42	2.48	0.16	1.07

$k_{obs.}$ = 18.4 l.mol^{-1}sec^{-1}

RUN #62

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 5.90 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 3.58 \times 10^{-5}$ moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.4185$

$[C_6H_5B(OH)_2] = 3.3438$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "40%" EtOH

Buffer = No Buffer

u = 0.16 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] \times 10^5$ moles/l.	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.233	0	5.90	3.58	0
8	0.509	1.45	4.45	2.13	0.103
17	0.626	2.07	3.83	1.51	0.188
27	0.708	2.50	3.40	1.08	0.281
40	0.791	2.93	2.97	0.65	0.443
51	0.820	3.09	2.81	0.49	0.542
62	0.844	3.22	2.68	0.36	0.655
74	0.870	3.35	2.55	0.23	0.720
86	0.880	3.40	2.50	0.18	0.926

$k_{obs.} = 17.9$ $l.mol^{-1}sec^{-1}$

RUN #64

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 5.90 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 7.16 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4282

$[C_6H_5B(OH)_2]$ = 2.8971

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[NaHCO_3]$ 0.03 moles/l.

$[Na_2CO_3]$ 0.03 moles/l.

"pH" = 10.53 u = 0.15 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg] X 10^5$ moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.215	0	7.16	5.90	0
6	0.290	0.373	6.79	5.52	0.0052
24	0.447	1.14	6.02	4.76	0.0176
49	0.631	2.05	5.11	3.85	0.0385
76	0.762	2.69	4.47	3.21	0.0594
106	0.874	3.24	3.92	2.66	0.0840
128	0.918	3.45	3.71	2.45	0.0958
145	0.960	3.66	3.50	2.24	0.109

$k_{obs.}$ = 2.36 $l.mol^{-1}sec^{-1}$

RUN #65

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 5.90 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 7.16 X 10^{-5} moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.4114

$[C_6H_5B(OH)_2]$ = 2.8353

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[NaHCO_3]$ 0.01 moles/l.

$[Na_2CO_3]$ 0.03 moles/l.

"pH" = 10.96 u = 0.15 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.201	0	7.16	5.90	0
11	0.262	0.296	6.86	5.60	0.0040
44	0.434	1.13	6.03	4.77	0.0174
81	0.556	1.72	5.44	4.18	0.0300
158	0.737	2.60	4.56	3.30	0.0560
209	0.844	3.12	4.04	2.78	0.0779
249	0.902	3.41	3.75	2.49	0.0934
299	0.959	3.68	3.48	2.22	0.111

$k_{obs.}$ = 1.13 l.mol^{-1}sec^{-1}

RUN #66

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 5.90 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 7.16 X 10^{-5} moles/l.

<u>log $\mathcal{E}$</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.3939

$[C_6H_5B(OH)_2]$ = 2.8125

$[(C_6H_5)_2Hg]$ = 4.3774

Solvent = "40%" EtOH

Buffer = $[NaHCO_3]$ 0.01 moles/l.

$[Na_2CO_3]$ 0.045 moles/l.

"pH" = 11.15 u = 0.15 λ = 227.5mu

t (min.)	Optical Density	$[(C_6H_5)_2Hg]$X10^5 moles/l.	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.193	0	7.16	5.90	0
42	0.337	0.696	6.46	5.20	0.0102
78	0.457	1.27	5.89	4.63	0.0201
155	0.591	1.92	5.24	3.98	0.0350
206	0.691	2.40	4.76	3.50	0.0491
247	0.744	2.65	4.51	3.25	0.0579
296	0.788	2.86	4.30	3.04	0.0662
348	0.864	3.23	3.93	2.67	0.0834

$k_{obs.}$ = 0.726 $l.mol^{-1}sec^{-1}$

RUN #70A

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 3.667 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 5.205 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.40183$

$[C_6H_5B(OH)_2] = 3.36994$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "50%" EtOH

λ = 227.5mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x}$
0	0.214	0	5.21	3.67	0
9	0.360	1.09	4.11	2.58	0.0501
18	0.463	1.63	3.57	2.04	0.0909
28	0.537	2.02	3.18	1.65	0.133
36	0.572	2.20	3.00	1.47	0.158
46	0.610	2.40	2.80	1.27	0.191
58	0.660	2.67	2.53	1.00	0.251
73	0.703	2.89	2.31	0.78	0.319
85	0.727	3.02	2.18	0.65	0.373

$k_{obs.} = 7.72$ l.mol^{-1}sec^{-1}

RUN #70B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 3.667 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 5.205 \times 10^{-5}$ moles/l.

$\log \varepsilon$

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.40183$

$[C_6H_5B(OH)_2] = 3.36994$

$[(C_6H_5)_2Hg] = 4.3774$

Solvent = "50%" EtOH

$\lambda = 227.5$mu

t (min.)	Optical Density	X	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.214	0	5.21	3.67	0
6	0.305	0.796	4.41	2.87	0.0342
25	0.520	1.93	3.27	1.74	0.122
35	0.575	2.22	2.98	1.45	0.161
43	0.610	2.40	2.80	1.27	0.191
56	0.662	2.68	2.52	0.99	0.254
71	0.694	2.85	2.35	0.82	0.305
82	0.737	3.07	2.13	0.60	0.398

$k_{obs.} = 8.22$ l.mol^{-1}sec^{-1}

RUN #71B

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 1.834 X 10^{-5} moles/l.

$[\underline{p}\text{-}CH_3C_6H_4B(OH)_2]_o$ = 2.305 X 10^{-5} moles/l.

<u>log ε</u>

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 2.45688

$[\underline{p}\text{-}CH_3C_6H_4B(OH)_2]$ = 3.4864

$[\underline{p}\text{-}CH_3C_6H_4HgC_6H_5]$ = 4.29551

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.075	0	2.31	1.83	0
3	0.100	0.154	2.15	1.68	0.0079
9	0.141	0.406	1.89	1.42	0.0249
15	0.172	0.598	1.70	1.23	0.0413
22	0.206	0.808	1.49	1.02	0.0653
30	0.223	0.912	1.39	0.92	0.0800
41	0.256	1.12	1.18	0.71	0.121
54	0.284	1.29	1.01	0.54	0.173
66	0.300	1.37	0.93	0.46	0.216

$k_{obs.}$ = 25.9 $l.mol^{-1}sec^{-1}$

RUN #72B

$[C_6H_5HgOH \cdot C_6H_5HgClO_4]_o = 1.834 \times 10^{-5}$ moles/l.

$[\underline{p}\text{-}CH_3OC_6H_4B(OH)_2]_o = 1.895 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[C_6H_5HgOH \cdot C_6H_5HgClO_4] = 2.1461$

$[\underline{p}\text{-}CH_3OC_6H_4B(OH)_2] = 3.62002$

$[\underline{p}\text{-}CH_3OC_6H_4HgC_6H_5] = 4.1294$

Solvent = "50%" EtOH

λ = 248mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.081	0	1.89	1.83	0
4	0.147	0.708	1.19	1.13	0.0087
7 1/2	0.168	0.937	0.958	0.897	0.0144
11 1/2	0.197	1.25	0.645	0.584	0.0289
16	0.200	1.29	0.605	0.544	0.0320
21 1/2	0.213	1.43	0.465	0.404	0.0469
29	0.222	1.53	0.365	0.304	0.0652
39 1/2	0.238	1.70	0.195	0.131	0.159

$k_{obs.} = 115.9 \; l.mol^{-1}sec^{-1}$

RUN #74

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o$ = 7.334 X 10^{-5} moles/l.

$[\underline{m}\text{-}NO_2C_6H_4B(OH)_2]_o$ = 5.625 X 10^{-5} moles/l.

log $\mathcal{E}$

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]$ = 3.37918

$[\underline{m}\text{-}NO_2C_6H_4B(OH)_2]$ = 3.6521

$[\underline{m}\text{-}NO_2C_6H_4HgC_6H_5]$ = 4.2730

Solvent = "50%" EtOH

λ = 228mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.428	0	7.33	5.63	0
32	0.479	0.430	6.90	5.20	0.0083
79	0.532	0.876	6.45	4.75	0.0183
150	0.577	1.26	6.07	4.37	0.0281
249	0.659	1.95	5.38	3.68	0.0503
363	0.710	2.38	4.95	3.25	0.0681
645	0.822	3.32	4.01	2.31	0.125
770	0.872	3.74	3.59	1.89	0.164
915	0.932	4.25	3.08	1.38	0.234

$k_{obs.}$ = 0.429 $l.mol^{-1}sec^{-1}$

RUN #75A

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH]_o = 3.667 \times 10^{-5}$ moles/l.

$[\underline{p}\text{-}FC_6H_4B(OH)_2]_o = 4.942 \times 10^{-5}$ moles/l.

log ε

$[C_6H_5HgClO_4 \cdot C_6H_5HgOH] = 3.3960$

$[\underline{p}\text{-}FC_6H_4B(OH)_2] = 3.2651$

$[\underline{p}\text{-}FC_6H_4HgC_6H_5] = 4.3390$

Solvent = "50%" EtOH

λ = 228mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.175	0	4.94	3.67	0
4	0.264	0.509	4.43	3.16	0.0177
10	0.341	0.949	3.99	2.72	0.0375
19	0.409	1.34	3.60	2.33	0.0594
28	0.463	1.65	3.29	2.02	0.0823
40	0.530	2.03	2.91	1.64	0.119
52	0.567	2.24	2.70	1.43	0.146
63	0.611	2.49	2.45	1.18	0.188
86	0.653	2.73	2.21	0.94	0.242

$k_{obs.} = 8.20$ l.mol^{-1}sec^{-1}

RUN #77A

$[C_6H_5HgOH]_o$ = 3.427 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.850 X 10^{-5} moles/l.

log ε

$[C_6H_5HgOH]$ = 3.5986

$[C_6H_5B(OH)_2]$ = 3.3556

$[C_6H_5HgC_6H_5]$ = 4.3774

Solvent = "50%" EtOH

λ = 227.5mu

t (min.)	Optical Density	X	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.246	0	4.85	3.43	0
9	0.437	1.09	3.76	2.34	0.0551
21	0.498	1.43	3.42	2.00	0.0822
31	0.563	1.80	3.05	1.63	0.121
43	0.591	1.96	2.89	1.47	0.143
60	0.642	2.25	2.60	1.18	0.193
78	0.667	2.39	2.46	1.04	0.223
108	0.720	2.69	2.16	0.74	0.314
143	0.750	2.86	1.99	0.57	0.392
207	0.783	3.05	1.80	0.38	0.525

$k_{obs.}$ = 8.30 $l.mol^{-1}sec^{-1}$

RUN #77B

$[C_6H_5HgOH]_o$ = 3.427 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.850 X 10^{-5} moles/l.

<u>log $\mathcal{E}$</u>

$[C_6H_5HgOH]$ = 3.5986

$[C_6H_5B(OH)_2]$ = 3.3556

$[C_6H_5HgC_6H_5]$ = 4.3774

Solvent = "50%" EtOH

λ = 227.5mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.246	0	4.85	3.43	0
6	0.357	0.630	4.22	2.80	0.0273
28	0.530	1.61	3.24	1.82	0.0997
40	0.588	1.94	2.91	1.49	0.140
57	0.634	2.20	2.65	1.23	0.183
75	0.671	2.41	2.44	1.02	0.228
105	0.722	2.70	2.15	0.73	0.318
140	0.758	2.91	1.94	0.52	0.421
204	0.791	3.10	1.75	0.33	0.574

$k_{obs.}$ = 8.10 $l.mol^{-1}sec^{-1}$

RUN #78B

$[C_6H_5HgOH]_o$ = 3.393 X 10^{-5} moles/l.

[$\underline{m}$-$FC_6H_4B(OH)_2]_o$ = 4.484 X 10^{-5} moles/l.

log ε

$[C_6H_5HgOH]$ = 3.58669

[$\underline{m}$-$FC_6H_4B(OH)_2$] = 3.2746

[$\underline{m}$-$FC_6H_4HgC_6H_5$] = 4.3278

Solvent = "50%" EtOH

λ = 226mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.213	0	4.48	3.39	0
9	0.264	0.327	4.19	3.07	0.0112
22	0.312	0.634	3.88	2.76	0.0241
43	0.351	0.884	3.63	2.51	0.0365
57	0.389	1.13	3.39	2.26	0.0519
94	0.450	1.52	3.00	1.87	0.0811
124	0.472	1.66	2.86	1.73	0.0942
173	0.533	2.05	2.47	1.34	0.141
203	0.560	2.23	2.29	1.16	0.171

$k_{obs.}$ = 2.63 $l.mol^{-1}sec^{-1}$

RUN #79A

$[C_6H_5HgOH]_o$ = 3.393 X 10^{-5} moles/l.

$[p\text{-}ClC_6H_4B(OH)_2]_o$ = 3.846 X 10^{-5} moles/l.

log ϵ

$[C_6H_5HgOH]$ = 2.4694

$[p\text{-}ClC_6H_4B(OH)_2]$ = 3.5596

$[p\text{-}ClC_6H_4HgC_6H_5]$ = 4.2525

Solvent = "50%" EtOH

λ = 238mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.149	0	3.85	3.39	0
45	0.252	0.730	3.12	2.66	0.0138
69	0.293	1.02	2.83	2.37	0.0226
105	0.333	1.31	2.54	2.08	0.0323
125	0.361	1.51	2.34	1.88	0.0406
154	0.390	1.72	2.12	1.67	0.0492
195	0.411	1.87	1.98	1.52	0.0604
239	0.447	2.12	1.73	1.27	0.0798

$k_{obs.}$ = 2.87 $l.mol^{-1}sec^{-1}$

RUN #79B

$[C_6H_5HgOH]_o$ = 3.393 X 10^{-5} moles/l.

$[p\text{-}ClC_6H_4B(OH)_2]_o$ = 3.846 X 10^{-5} moles/l.

log ε

$[C_6H_5HgOH]$ = 2.4694

$[p\text{-}ClC_6H_4B(OH)_2]$ = 3.5596

$[p\text{-}ClC_6H_4HgC_6H_5]$ = 4.2525

Solvent = "50%" EtOH

λ = 238mu

t (min.)	Optical Density	X	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.149	0	3.85	3.39	0
43	0.266	0.830	3.02	2.56	0.0162
67	0.296	1.05	2.80	2.34	0.0235
101	0.343	1.39	2.46	2.00	0.0355
122	0.369	1.57	2.28	1.82	0.0434
151	0.400	1.79	2.06	1.60	0.0553
192	0.432	2.02	1.83	1.37	0.0713

$k_{obs.}$ = 3.13 $l.mol^{-1}sec^{-1}$

RUN #81

$[C_6H_5HgOCOCH_3]_o = 3.018 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 4.978 \times 10^{-5}$ moles/l.

$[CH_3COOH] = 14.34 \times 10^{-4}$ moles/l.

<u>log ε</u>

$[C_6H_5HgOCOCH_3] = 3.4912$

$[C_6H_5B(OH)_2] = 3.3116$

$[C_6H_5HgC_6H_5] = 4.3770$

Solvent = "50%" EtOH

λ= 227.5mu

t (min.)	Optical Density	X	a-x	b-x	$\log \frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.193	0	4.98	3.02	0
8	0.248	0.278	4.70	2.74	0.0170
18	0.287	0.487	4.49	2.53	0.0217
39	0.343	0.786	4.19	2.23	0.0564
56	0.374	0.952	4.03	2.07	0.0724
77	0.414	1.17	3.81	1.85	0.0964
97	0.443	1.32	3.66	1.70	0.116

$k_{obs.} = 2.20$ $l.mol^{-1}sec^{-1}$

RUN #82

$[C_6H_5HgOCOCH_3]_o$ = 3.018 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.978 X 10^{-5} moles/l.

$[CH_3COOH]$ = 27.51 X 10^{-4} moles/l.

log $\mathcal{E}$

$[C_6H_5HgOCOCH_3]$ = 3.4912

$[C_6H_5B(OH)_2]$ = 3.3116

$[C_6H_5HgC_6H_5]$ = 4.3770

Solvent = "50%" EtOH

λ = 227.5mu

t (min.)	Optical Density	X	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.193	0	4.98	3.02	0
28	0.261	0.348	4.63	2.67	0.0217
64	0.320	0.663	4.32	2.36	0.0457
97	0.381	0.989	3.99	2.03	0.0762
114	0.412	1.16	3.82	1.86	0.0952
150	0.441	1.31	3.67	1.71	0.114
190	0.460	1.41	3.57	1.61	0.128
228	0.483	1.54	3.44	1.48	0.149
267	0.498	1.62	3.36	1.40	0.163

$k_{obs.}$ = 1.49 $l.mol^{-1}sec^{-1}$

RUN #84

$[p\text{-}CH_3C_6H_4HgOCOCH_3]_o$ = 2.99 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.98 X 10^{-5} moles/l.

$[CH_3COOH]$ = 2.39 X 10^{-4} moles/l.

<u>log ε</u>

$[p\text{-}CH_3C_6H_4HgOCOCH_3]$ = 3.5501

$[C_6H_5B(OH)_2]$ = 1.9080

$[p\text{-}CH_3C_6H_4HgC_6H_5]$ = 4.2915

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.106	0	4.98	2.99	0
11	0.235	0.813	4.17	2.18	0.0605
26	0.307	1.27	3.73	1.74	0.110
64	0.400	1.84	3.16	1.17	0.210
91	0.456	2.18	2.82	0.83	0.310

$k_{obs.}$ = 6.08 $l.mol^{-1}sec^{-1}$

RUN #85

[p-$CH_3C_6H_4HgOCOCH_3$]$_o$ = 3.044 X 10^{-5} moles/l.

[$C_6H_5B(OH)_2$]$_o$ = 5.060 X 10^{-5} moles/l.

[CH_3COOH] = 8.34 X 10^{-4} moles/l.

log ε

[p-$CH_3C_6H_4HgOCOCH_3$] = 3.5501

[$C_6H_5B(OH)_2$] = 1.9080

[p-$CH_3C_6H_4HgC_6H_5$] = 4.2915

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.113	0	5.06	3.04	0
13	0.184	0.456	4.60	2.59	0.0295
32	0.249	0.874	4.19	2.17	0.0646
58	0.316	1.31	3.75	1.73	0.115
91	0.375	1.68	3.38	1.36	0.175
122	0.413	1.93	3.13	1.11	0.230
150	0.444	2.13	2.93	0.91	0.287
188	0.458	2.22	2.84	0.82	0.319

$k_{obs.}$ = 3.56 $l.mol^{-1}sec^{-1}$

RUN #86

$[\underline{p}\text{-}CH_3C_6H_4HgOCOCH_3]_o$ = 2.99 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.98 X 10^{-5} moles/l.

$[CH_3COOH]$ = 9.56 X 10^{-4} moles/l.

<u>log $\mathcal{E}$</u>

$[\underline{p}\text{-}CH_3C_6H_4HgOCOCH_3]$ = 3.5501

$[C_6H_5B(OH)_2]$ = 1.9080

$[\underline{p}\text{-}CH_3C_6H_4HgC_6H_5]$ = 4.2915

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.106	0	4.98	2.99	0
9	0.196	0.575	4.35	2.41	0.0389
24	0.242	0.856	4.07	2.13	0.0637
61	0.334	1.42	3.51	1.57	0.132
89	0.398	1.81	3.12	1.18	0.205
132	0.422	1.96	2.97	1.03	0.243
168	0.444	2.09	2.84	0.90	0.282

$k_{obs.}$ = 3.34 l.mol^{-1}sec^{-1} .

RUN #88

$[\underline{p}\text{-}CH_3C_6H_4HgOCOCH_3]_o$ = 2.99 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 4.98 x 10^{-5} moles/l.

$[CH_3COOH]$ = 23.90 X 10^{-4} moles/l.

<u>log ε</u>

$[\underline{p}\text{-}CH_3C_6H_4HgOCOCH_3]$ = 3.5501

$[C_6H_5B(OH)_2]$ = 1.9080

$[\underline{p}\text{-}CH_3C_6H_4HgC_6H_5]$ = 4.2915

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.106	0	4.98	2.99	0
9	0.164	0.414	4.57	2.58	0.0267
43	0.232	0.841	4.14	2.15	0.0630
76	0.284	1.17	3.81	1.82	0.0993
115	0.328	1.44	3.54	1.55	0.137
150	0.369	1.70	3.28	1.29	0.184
169	0.387	1.81	3.17	1.18	0.208

$k_{obs.}$ = 2.20 $l.mol^{-1}sec^{-1}$

RUN #89

$[\underline{p}\text{-}CH_3C_6H_4HgOCOCH_3]_o$ = 3.044 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.060 X 10^{-5} moles/l.

$[CH_3COOH]$ = 25.02 X 10^{-4} moles/l.

log ε

$[\underline{p}\text{-}CH_3C_6H_4HgOCOCH_3]$ = 3.5501

$[C_6H_5B(OH)_2]$ = 1.9080

$[\underline{p}\text{-}CH_3C_6H_4HgC_6H_5]$ = 4.2915

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.113	0	5.06	3.04	0
32	0.178	0.418	4.64	2.63	0.0267
57	0.230	0.752	4.31	2.29	0.0534
93	0.291	1.14	3.92	1.90	0.0938
135	0.336	1.43	3.63	1.61	0.132
172	0.360	1.59	3.47	1.45	0.158
196	0.384	1.74	3.32	1.30	0.186

$k_{obs.}$ = 1.84 l.mol^{-1}sec^{-1}

RUN #91A

$[\underline{p}\text{-}CH_3C_6H_4HgOH]_o = 8.910 \times 10^{-5}$ moles/l.

$[\underline{m}\text{-}NO_2C_6H_4B(OH)_2]_o = 3.563 \times 10^{-5}$ moles/l.

<u>log ε</u>

$[\underline{p}\text{-}CH_3C_6H_4HgOH] = 3.4871$

$[\underline{m}\text{-}NO_2C_6H_4B(OH)_2] = 3.3877$

$[\underline{p}\text{-}CH_3C_6H_4HgC_6H_4\underline{m}\text{-}NO_2] = 4.2209$

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.361	0	8.91	3.56	0
20	0.388	0.243	8.67	3.32	0.0187
37	0.404	0.387	8.52	3.18	0.0307
89	0.440	0.710	8.20	2.85	0.0604
177	0.471	0.989	7.92	2.57	0.0901
337	0.528	1.50	7.41	2.06	0.158
590	0.622	2.35	6.56	1.21	0.336
703	0.641	2.52	6.39	1.04	0.390

$k_{obs.} = 0.406\ l.mol^{-1}sec^{-1}$

RUN #91B

$[\underline{p}\text{-}CH_3C_6H_4HgOH]_o$ = 8.910 X 10^{-5} moles/l.

$[\underline{m}\text{-}NO_2C_6H_4B(OH)_2]_o$ = 3.563 X 10^{-5} moles/l.

<u>log ε</u>

$[\underline{p}\text{-}CH_3C_6H_4HgOH]$ = 3.4871

$[\underline{m}\text{-}NO_2C_6H_4B(OH)_2]$ = 3.3877

$[\underline{p}\text{-}CH_3C_6H_4HgC_6H_4\underline{m}\text{-}NO_2]$ = 4.2209

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.361	0	8.91	3.56	0
18	0.408	0.423	8.49	3.14	0.0338
34	0.417	0.504	8.41	3.06	0.0410
84	0.457	0.863	8.05	2.70	0.0762
174	0.479	1.06	7.85	2.50	0.0989
335	0.538	1.59	7.32	1.97	0.172
589	0.619	2.32	6.59	1.24	0.333
700	0.658	2.67	6.24	0.89	0.448

$k_{obs.}$ = 0.378 $l.mol^{-1}sec^{-1}$

RUN #92

$[p\text{-}CH_3C_6H_4HgOCOCH_3]_o$ = 3.044 X 10^{-5} moles/l.

$[p\text{-}CH_3C_6H_4B(OH)_2]_o$ = 2.148 X 10^{-5} moles/l.

$[CH_3COOH]$ = 2.78 X 10^{-4} moles/l.

log ϵ

$[p\text{-}CH_3C_6H_4HgOCOCH_3]$ = 3.4610

$[p\text{-}CH_3C_6H_4B(OH)_2]$ = 3.5162

$[p\text{-}CH_3C_6H_4HgC_6H_4p\text{-}CH_3]$ = 4.3953

Solvent = "50%" EtOH

λ = 236mu

t (min.)	Optical Density	X	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.159	0	3.04	2.15	0
4	0.243	0.412	2.63	1.74	0.0293
8	0.287	0.648	2.40	1.50	0.0520
13	0.325	0.851	2.19	1.30	0.0767
18	0.369	1.09	1.95	1.06	0.113
24	0.392	1.21	1.83	0.94	0.138
30	0.423	1.38	1.66	0.77	0.182
37	0.443	1.48	1.56	0.67	0.216
46	0.472	1.64	1.40	0.51	0.287
56	0.487	1.72	1.32	0.43	0.336

$k_{obs.}$ = 25.9 $l.mol^{-1}sec^{-1}$

RUN #94

$[p\text{-}CH_3C_6H_4HgOCOCH_3]_o = 3.044 \times 10^{-5}$ moles/l.

$[p\text{-}CH_3C_6H_4B(OH)_2]_o = 2.148 \times 10^{-5}$ moles/l.

$[CH_3COOH] = 19.46 \times 10^{-4}$ moles/l.

Log E

$[p\text{-}CH_3C_6H_4HgOCOCH_3] = 3.4610$

$[p\text{-}CH_3C_6H_4B(OH)_2] = 3.5162$

$[p\text{-}CH_3C_6H_4HgC_6H_4p\text{-}CH_3] = 4.3953$

Solvent = "50%" EtOH

= 230mμ

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.159	0	3.04	2.15	0
11	0.239	0.434	2.61	1.71	0.0312
22	0.275	0.626	2.42	1.52	0.0496
35	0.322	0.878	2.17	1.27	0.0804
47	0.342	0.985	2.06	1.16	0.0967
57	0.379	1.18	1.86	0.97	0.131
90	0.420	1.40	1.64	0.75	0.188
111	0.437	1.49	1.55	0.66	0.219

$k_{obs.} = 9.97$ l.mol-1sec-1

RUN #96

$[\underline{m}\text{-}NO_2C_6H_4HgOH]_o$ = 3.008 X 10^{-5} moles/l.

$[\underline{p}\text{-}CH_3C_6H_4B(OH)_2]_o$ = 2.148 X 10^{-5} moles/l.

log $\mathcal{E}$

$[\underline{m}\text{-}NO_2C_6H_4HgOH]$ = 3.4055

$[\underline{p}\text{-}CH_3C_6H_4B(OH)_2]$ = 3.4162

$[\underline{m}\text{-}NO_2C_6H_4HgC_6H_4\underline{p}\text{-}CH_3]$ = 4.2209

Solvent = "50%" EtOH

λ= 236mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.147	0	3.01	2.15	0
8	0.172	0.356	2.65	1.79	0.0240
17	0.214	0.729	2.28	1.42	0.0495
29	0.256	1.10	1.91	1.05	0.114
39	0.271	1.24	1.77	0.91	0.143
49	0.278	1.30	1.71	0.85	0.157

$k_{obs.}$ = 20.1 $l.mol^{-1}sec^{-1}$

RUN #97

$[\underline{m}\text{-}NO_2C_6H_4HgOH]_o$ = 5.975 X 10^{-5} moles/l.

$[C_6H_5B(OH)_2]_o$ = 5.405 X 10^{-5} moles/l.

log ε

$[\underline{m}\text{-}NO_2C_6H_4HgOH]$ = 3.5956

$[C_6H_5B(OH)_2]$ = 3.2357

$[\underline{m}\text{-}NO_2C_6H_4HgC_6H_5]$ = 4.2730

Solvent = "50%" EtOH

λ = 228mu

t (min.)	Optical Density	X	a-x	b-x	$\log \frac{b}{a} \frac{(a-x)}{(b-x)}$
0	0.329	0	5.98	5.41	0
10	0.511	1.41	4.57	3.99	0.0154
21	0.602	2.11	3.87	3.29	0.0270
32	0.697	2.84	3.14	2.56	0.0452
45	0.744	3.20	2.78	2.20	0.0581
58	0.783	3.50	2.48	1.90	0.0722
74	0.814	3.74	2.24	1.66	0.0866
97	0.836	3.91	2.07	1.49	0.0992

$k_{obs.}$ = 8.89 $l.mol^{-1}sec^{-1}$

RUN #98

$[\underline{m}\text{-}NO_2C_6H_4HgOCOCH_3]_o = 2.758 \times 10^{-5}$ moles/l.

$[C_6H_5B(OH)_2]_o = 5.405 \times 10^{-5}$ moles/l.

$[CH_3COOH] = 2.840 \times 10^{-4}$ moles/l.

log ε

$[\underline{m}\text{-}NO_2C_6H_4HgOCOCH_3] = 3.667$

$[C_6H_5B(OH)_2] = 3.2606$

$[\underline{m}\text{-}NO_2C_6H_4HgC_6H_5] = 4.2730$

Solvent = "50%" EtOH

λ = 228mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.226	0	5.40	2.76	0
10	0.315	0.724	4.70	2.05	0.0674
21	0.366	1.14	4.26	1.62	0.128
33	0.399	1.41	3.99	1.35	0.178
72	0.497	2.21	3.19	0.55	0.471
98	0.524	2.43	2.97	0.33	0.662

$k_{obs.} = 8.23$ $l.mol^{-1}sec^{-1}$

RUN #100

$[\underline{m}\text{-}NO_2C_6H_4HgOH]_o$ = 5.975 X 10^{-5} moles/l.

$[\underline{m}\text{-}FC_6H_4B(OH)_2]_o$ = 13.20 X 10^{-5} moles/l.

log ε

$[\underline{m}\text{-}NO_2C_6H_4HgOH]$ = 3.5956

$[\underline{m}\text{-}FC_6H_4B(OH)_2]$ = 2.9377

$[\underline{m}\text{-}NO_2C_6H_4HgC_6H_4\underline{m}\text{-}F]$ = 4.2534

Solvent = "50%" EtOH

λ = 228mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.350	0	13.20	5.98	0
9	0.436	0.664	12.54	5.31	0.0262
18	0.489	1.07	12.13	4.91	0.0458
31	0.584	1.79	11.41	4.19	0.0882
43	0.633	2.17	11.03	3.81	0.115
55	0.671	2.46	10.74	3.52	0.138
74	0.750	3.06	10.14	2.92	0.194
94	0.792	3.38	9.82	2.60	0.230

$k_{obs.}$ = 1.48 l.mol^{-1}sec^{-1}

RUN #101

$[\underline{m}\text{-}NO_2C_6H_4HgOCOCH_3]_o$ = 2.75 X 10^{-5} moles/l.

$[\underline{m}\text{-}FC_6H_4B(OH)_2]_o$ = 13.20 X 10^{-5} moles/l.

$[CH_3COOH]$ = 2.840 X 10^{-4} moles/l.

<u>log ε</u>

$[\underline{m}\text{-}NO_2C_6H_4HgOCOCH_3]$ = 3.7010

$[\underline{m}\text{-}FC_6H_4B(OH)_2]$ = 2.8502

$[\underline{m}\text{-}NO_2C_6H_4HgC_6H_4\underline{m}\text{-}F]$ = 4.2534

Solvent = "50%" EtOH

λ = 228mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.242	0	13.20	2.75	0
21	0.260	0.230	12.97	2.53	0.0298
43	0.275	0.353	12.85	2.41	0.047
60	0.322	0.738	12.46	2.02	0.110
85	0.361	1.06	12.14	1.70	0.174
118	0.368	1.12	12.08	1.66	0.182
148	0.408	1.44	11.76	1.32	0.270
179	0.420	1.54	11.66	1.22	0.300
209	0.441	1.72	11.48	1.04	0.363
238	0.461	1.88	11.32	0.88	0.419

$k_{obs.}$ = 0.629 $l.mol^{-1}sec^{-1}$

RUN #102

$[\underline{m}\text{-}NO_2C_6H_4HgOCOCH_3]_o$ = 2.75 X 10^{-5} moles/l.

$[\underline{m}\text{-}FC_6H_4B(OH)_2]_o$ = 13.20 X 10^{-5} moles/l.

$[CH_3COOH]$ = 5.680 X 10^{-4} moles/l.

log ε

$[\underline{m}\text{-}NO_2C_6H_4HgOCOCH_3]$ = 3.7010

$[\underline{m}\text{-}FC_6H_4B(OH)_2]$ = 2.8502

$[\underline{m}\text{-}NO_2C_6H_4HgC_6H_4\underline{m}\text{-}F]$ = 4.2534

Solvent = "50%" EtOH

λ = 228mu

t (min.)	Optical Density	X	a-x	b-x	log $\frac{b}{a}\frac{(a-x)}{(b-x)}$
0	0.242	0	13.20	2.75	0
42	0.279	0.386	12.81	2.37	0.0528
63	0.314	0.673	12.53	2.09	0.0978
83	0.331	0.813	12.39	1.95	0.123
116	0.348	0.951	12.25	1.81	0.150
158	0.396	1.35	11.85	1.41	0.244
180	0.408	1.44	11.76	1.32	0.270

$k_{obs.}$ = 0.553 l.mol^{-1}sec^{-1}