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KINETICS AND MECHANISM OF THE ACID-CATALYZED HYDROLYSIS OF ARENEBORONIC ACIDS

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KINETICS AND MECHANISM OF
THE ACID-CATALYZED
HYDROLYSIS OF ARENEBORONIC ACIDS

BY

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Kevork V. Nahabedian

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INTRODUCTION

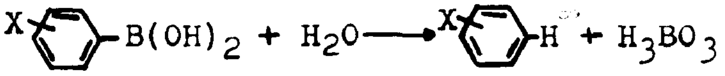
For a number of years work in these laboratories has been directed toward kinetic studies on the substitution reactions of areneboronic acids. In particular, the reactions involving displacement of the boronic acid group by halogen[24] and by hydrogen peroxide[23] have been given the most attention

$$\text{Ar-B(OH)}_2 + \text{X}_2 + \text{H}_2\text{O} \longrightarrow \text{ArX} + \text{HBr} + \text{H}_3\text{BO}_3 \qquad 1$$

$$\text{Ar-B(OH)}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{ArOH} + \text{H}_3\text{BO}_3 \qquad 2$$

(reactions 1 and 2). The results obtained demonstrate that, at least for the halodeboronation reaction, substitution of the boronic acid group results from an electrophilic attack by the displacing species on the aromatic carbon atom to which the boronic acid function is bonded. The bromodeboronation of meta- and para-substituted benzeneboronic acids[25] has therefore offered some insight into the effect of substituents in the ring on the reactivity of aromatic compounds toward an electrophile.

Ainley and Challenger[1] have reported that the hydrolysis of benzeneboronic acid is catalyzed by concentrated sodium hydroxide, by zinc and cadmium bromides, and by concentrated hydrochloric acid. The uncatalyzed reaction in water alone requires a temperature of 150°C. The hydrolysis can be represented by the equation



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The acid-catalyzed reaction is especially of interest because it appears to require an electrophilic substitution by a protonating[3] species. Assuming, then, that the mechanism can be elucidated, a study of the effect of ring substituents on reactivity would offer additional insight into the applicability to aromatic electrophilic substitution reactions of Hammett-type linear free energy relations[4]. In addition, since the reaction can be studied in concentrated mineral acid solutions, a knowledge of its mechanism might allow the determination of the kinetic behavior of acid catalysts in these strongly acidic media. It was for these reasons that this research was undertaken.

The kinetics of the acid-catalyzed hydrolysis of nine areneboronic acids (X = p-CH_3O, p-CH_3, p-F, H, p-Br, m-F, m-Cl, m-CF_3 and m-NO_2) have been studied. Dependences of rate on the Hammett acidity function[14,31] (see below) have been determined in the media aqueous sulfuric, perchloric and phosphoric acids, and in the solvent mixture formic acid - ethylene glycol dimethyl ether (EGDE) - water. Energies and entropies of activation have been obtained for the reactions of three areneboronic acids (X = p-CH_3O, H, m-F) in aqueous sulfuric acid solutions. The solvent hydrogen isotope effect in aqueous sulfuric acid has been determined for four of the substrates (X = p-CH_3O, p-CH_3, p-F and m-F), and the effect of solvent hydrogen isotope composition on the rate has been determined for the hydrolysis of p-methoxybenzeneboronic acid in 6.31 molar aqueous sulfuric acid at 25°C.

RESULTS and DISCUSSION

I. Kinetic Order of the Reaction

Each of the areneboronic acids studied has an ultraviolet absorption spectrum sufficiently different from that of its hydrolysis product so that a spectrophotometric method of analysis proved convenient for following the rates. The method is described in detail in the experimental section.

Except for the one run mentioned below, all of the rate experiments reported here showed first-order kinetics, that is, the data fit the rate equation

$$k_{obs.}t = 2.303 \log C + \text{constant} \qquad (4)$$

where k is the pseudo first-order rate constant and C is the concentration of areneboronic acid at time t. Figure 1 shows a typical first-order rate plot for m-nitrobenzeneboronic acid.

II. Aqueous Sulfuric Acid

Rates in aqueous sulfuric acid have been measured with all nine areneboronic acids at 60°C. These acids vary sufficiently in reactivity so that the region of acidities 3-97% by weight H_2SO_4 could be covered. For three of these acids ($X = p\text{-}CH_3O$, H and m-F) rates at other temperatures have also been obtained. All of the pertinent data are listed in table 1.

A. Course of the reaction

In aqueous sulfuric acid solutions, especially in the more concentrated regions, sulfonation is a possible side reaction. Gold and Satchell[10] have measured the sulfonation rates of benzene and have reported that, in 77.5% H_2SO_4 at 25°C., the first-order rate constant is 2.6×10^{-7} second^{-1}. If the sulfonation rate of benzene is 100 times greater at

Figure 1

Rate plot for run II_s-9

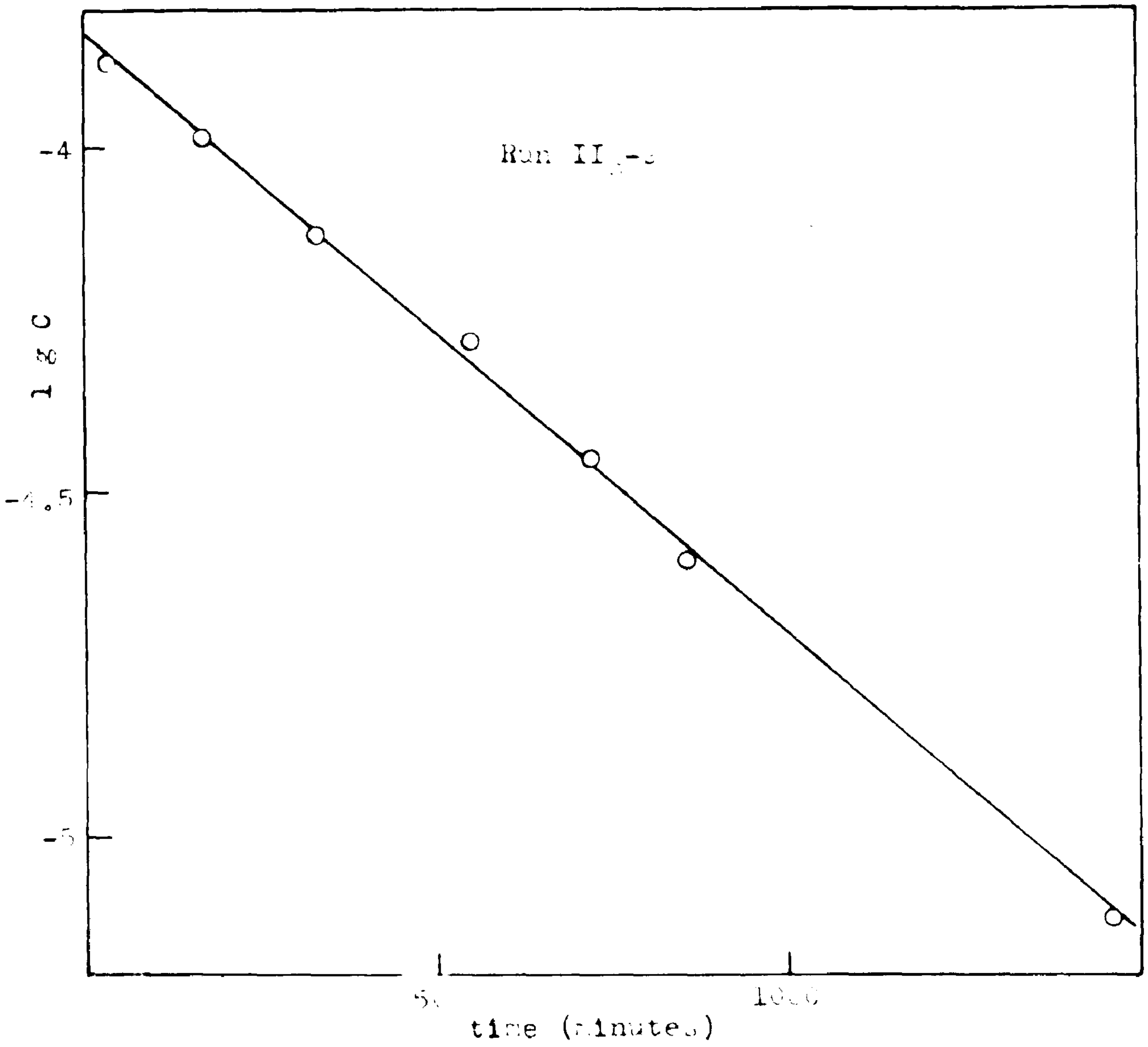


Table 1

Pseudo first-order rate constants, $k_{obs.}$, for aqueous sulfuric acid

run#	Temp., °C.	% H_2SO_4	$-H_o$	log $k_{obs.}$ + 7
		X = H (I)		
I_s-21	60	71.1	5.65	3.842
22		70.9	5.64	3.864
23		60.0	4.14	2.558
24		60.0	4.14	2.558
25		67.4	5.15	2.399
26		67.5	5.16	3.407
27		74.4	6.11	4.434
28		74.6	6.13	4.427
29		62.6	4.46	2.849
30		62.6	4.46	2.843
31		54.7	3.59	2.076
32		54.4	3.57	2.046
33		49.8	3.15	1.657
34		50.3	3.19	1.674
35		44.8	2.72	1.383
36		44.8	2.72	1.355
39		46.6	2.87	1.466
40		45.3	2.76	1.303
41		42.9	2.56	1.123
42		41.0	2.40	0.967
43	25	74.8	6.34	3.067
44		72.4	6.00	2.674
45		70.3	5.70	2.316
46	40	75.0	6.28	3.632
47		72.6	5.96	3.310
48		70.8	5.72	3.014
		X = m-NO_2 (II)		
II_s- 3	60	92.1	8.30	2.783
4		91.6	8.26	2.772
5		89.3	8.04	2.601
6		89.4	8.05	2.601
7		97.0	8.66	3.138
8		96.7	8.83	3.162
9		88.5	7.97	2.515
10		88.5	7.97	2.508
11		83.0	7.37	1.887
12		82.7	7.33	1.874
13		78.8	6.74	1.458

Table 1 (cont.)

run#	Temp., °C.	% H_2SO_4	$-H_o$	log $k_{obs.}$ + 7
X = m-NO_2 (II) (cont.)				
II_s-14	60	78.5	6.69	1.423
15		73.7	6.00	0.839
16		73.6	5.99	0.883
X = p-Br (III)				
III_s- 1	60	74.5	6.12	3.789
2		69.4	5.43	3.085
3		65.2	4.83	2.538
5		77.0	6.47	4.111
6		61.2	4.27	2.122
7		53.4	3.47	1.375
8		47.7	2.96	0.953
X = m-F (IV)				
IV_s- 1	60	83.8	7.48	4.196
2		78.5	6.70	3.423
3		74.1	6.06	2.739
4		68.5	5.30	2.007
5		62.2	4.41	1.403
6		55.2	3.64	0.821
19		69.4	5.43	2.152
20		70.3	5.55	2.193
7	25	83.3	7.64	2.817
8		80.9	7.29	2.318
9		79.0	7.00	1.960
10	40	84.2	7.67	3.520
11		82.4	7.42	3.180
12		80.4	7.11	2.884
13	69.4	64.9	4.76	2.068
14		61.0	4.23	1.720
15		56.9	3.80	1.399
16	79.4	65.4	4.78	2.499
17		61.3	4.24	2.136
18		57.4	3.83	1.821
X = m-CF_3 (V)				
V_s- 6	60	55.4	3.66	0.499

Table 1 (cont.)

run#	Temp., °C.	% H_2SO_4	$-H_o$	log $k_{obs.}$+7
		X = p-F (VI)		
VI_s- 1	60	64.7	4.76	3.455
2		60.1	4.14	2.938
3		54.9	3.62	2.492
4		49.5	3.12	2.039
		X = p-CH_3 (VII)		
VII_s- 1	60	55.5	3.67	3.641
2		49.6	3.13	3.100
3		40.7	2.38	2.363
4		28.6	1.53	1.455
		X = p-CH_3O (VIII)		
VIII_s- 1	60	29.6	1.60	3.748
2		20.3	1.00	3.061
3		10.1	0.37	2.362
4		5.14	-0.11	1.879
5		3.11	-0.37	1.603
8	40	30.1	1.62	2.891
9		24.7	1.28	2.476
10		20.1	0.95	2.131
HGK_s- 1*	25	16.1	0.67	1.073
2		29.4	1.56	2.095
3		40.6	2.37	3.075
4		50.4	3.21	3.969
5		54.6	3.63	4.403

* work done by H. G. Kuivila

run#	Temp., °C.	% H_2SO_4	$-H_o$	log $k_{obs.}$+7
		X = m-Cl (IX)		
IX_s- 1	60	59.3	4.05	1.094
2		62.9	4.51	1.411
3		66.3	4.99	1.686
4		69.9	5.50	2.075
5		74.5	6.11	2.748
6		79.9	6.91	3.523

60°C., then, since the boronic acid group is deactivating ($\sigma_m = 0.006$, $\sigma_p = 0.454$)[19], the value 3×10^{-5} second^{-1} can be considered a maximum for the sulfonation rate constant of either benzene or benzeneboronic acid. The hydrolysis rate constant of benzeneboronic acid in 74.5% H_2SO_4 at 60°C. is 2.7×10^{-3} second^{-1}, hence the hydrolysis should be at least 100 times faster than the sulfonation of either benzene or benzeneboronic acid in this medium. Indeed, the spectrum of a kinetic sample taken after twenty half-lives showed that the extent of sulfonation was less than 1%.

Sulfonation was found to interfere with the kinetics of hydrolysis in only one experiment reported here: with m-fluorobenzeneboronic acid in 83.9% H_2SO_4 at 60°C., the absorbances of kinetic samples taken after a half-life began to level off and then, after two half-lives, began to increase. Because every position available for sulfonation in this boronic acid is ortho- or para- to the boronic acid group ($\sigma_p = 0.454$)[19], or meta- to the fluorine atom ($\sigma_m = 0.337$)[19], sulfonation of fluorobenzene must be the side reaction. Hence the initial slope of a log C versus time plot was assumed to be a measure of the hydrolysis rate of m-fluorobenzeneboronic acid under the conditions of the experiment.

That the hydrolysis of the areneboronic acids in aqueous sulfuric acid media is quantitative is illustrated in figure 2, which shows the spectra of nitrobenzene and m-nitrobenzeneboronic acid. The circles represent the spectrum of a kinetic sample taken after essentially infinite time from a rate experiment in 97% H_2SO_4; the curve represents the spectrum expected.

Figure 2

Spectra of m-nitrobenzeneboronic acid
and nitrobenzene

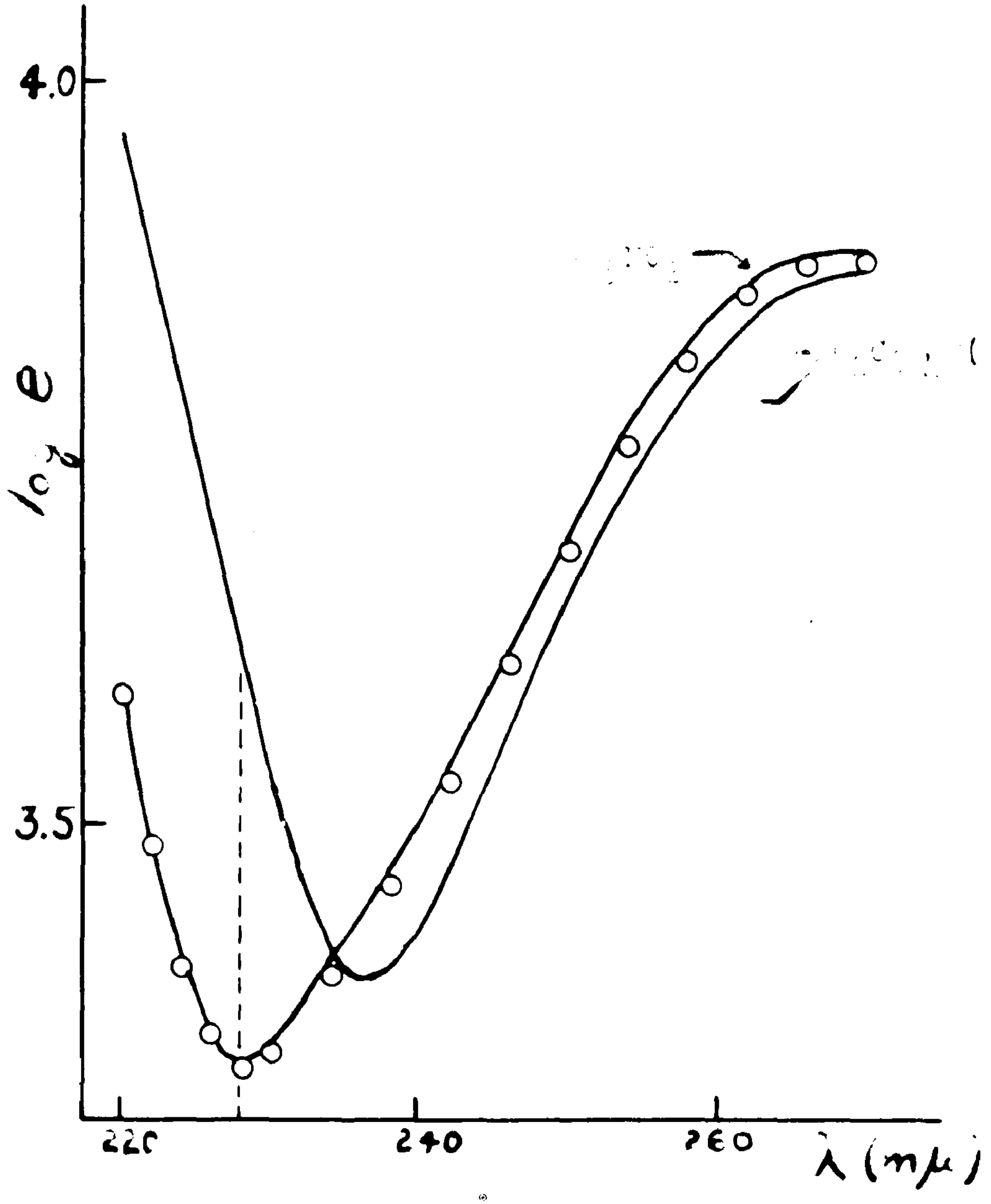


Table 1 lists only one rate constant for m-(trifluoromethyl)-benzeneboronic acid determined in 55.4% H_2SO_4. Experiments at higher acidities showed erratic kinetics. Evolution of hydrogen fluoride was detected, and flasks containing the kinetic solutions became etched. The erratic kinetics were therefore attributed to hydrolysis of the trifluoromethyl group in the substrate. With the one experiment reported, first-order kinetics were observed through 30% reaction, and the observed rate constant was assumed to be a measure of the hydrolysis rate of the boronic acid function in the substrate.

B. Dependence of rate on acidity

The Hammett indicator acidity function[14,31] is a quantitative measure of acidity derived from acid-base equilibria of the type

$$B + H^+ \rightleftharpoons BH^+ \qquad 5$$

where B is an uncharged Bronsted base and BH^+ is its conjugate acid. The function is defined by the equation

$$H_o = pK_{BH^+} - \log \frac{C_B}{C_{BH^+}} \qquad (6)$$

where C_B and C_{BH^+} are the spectrophotometrically determined concentrations of B and BH^+, and K_{BH^+} is the thermodynamic ionization constant of the acid BH^+ referred to infinite dilution in water. Since pK_{BH^+} is defined by

$$pK_{BH^+} = -\log K_{BH^+} = -\log \frac{C_B f_B}{C_{BH^+} f_{BH^+}} - \log a_{H^+} \qquad (7)$$

(f = molar activity coefficient), the definition of H_o reduces to

$$H_o = -\log a_{H^+} \frac{f_B}{f_{BH^+}} \qquad (8)$$

In general the value of H_o is independent of the dissolved base and depends only on the composition of the acidic solution. Hence the function H_o is assumed to measure the ability of an acidic medium to protonate a dissolved neutral base.

The following discussion illustrates the importance of the acidity function in kinetic and mechanistic studies of acid-catalyzed reactions. If a given acid-catalyzed reaction, in which a single reactant is converted into products, has a transition state composed of a reactant molecule and a proton, i. e.

$$S + H^+ \overset{K^*}{\rightleftharpoons} [S \overset{+}{—} H]^* \xrightarrow{k_1} \text{products} \qquad 9$$

transition state

the observed rate constant can be expressed by the equations

$$-\frac{dC_S}{dt} = k_1 K^* \, a_S a_{H^+} = k_{obs.} \, C_S$$

$$\log k_{obs.} = \log k_1 K^* + \log a_{H^+} + \log \frac{f_S}{f^*} \qquad (10)$$

Substitution of equation (8) into equation (10) yields

$$\log k_{obs.} = \log k_1 K^* - H_o + \log \frac{f_S f_{BH^+}}{f^* f_B} \qquad (11)$$

Since S and $[S \overset{+}{—} H]^*$ are similar in charge to B and BH^+, respectively, the activity coefficient ratio in equation (11) can be expected to remain constant with changing acidity. If this condition obtains, plots of log $k_{obs.}$ against $-H_o$ should be linear with unit slope.

In figures 3, 4, 5, 6 and 7 the logarithms of the pseudo first-order rate constants, $k_{obs.}$, for runs in aqueous sulfuric acid are plotted against the acidity function. The values of H_o, shown in table 1, are for the indicated temperatures and are taken from the data of Gelbshtein, Sheglova and Temkin[8]. Subject to the qualifications described and discussed below, these plots establish the correlation of rate by the acidity function.

To simplify further discussion, values for the log $k_{obs.}$ versus $-H_o$ slopes are shown in table 2. These slopes are generally non-unit in value. At 60°C. and for media weaker in acidity than about 70% H_2SO_4 the values of the slopes appear to be decreasing with decreasing reactivity of the substrate S.

Other characteristics of the correlation for this reaction are perhaps unique among those studied thus far. For example, for a given substrate a change in slope occurs on passing from media weaker to media stronger than about 70% H_2SO_4 ($-H_o = 5.5$). This change in slope on passing from the weaker to the stronger acid region is emphasized by the dependence of slope on temperature. In the lower acid region the slope appears to be independent of temperature, while in the higher acid region the slope appears to decrease with increasing temperature (for example see X = m-F).

The data in table 1 allow the determination of the Arrhenius activation energies and entropies for X = p-CH_3O, H and m-F. The values of ΔE^*, ΔH^* and ΔS^* obtained by plotting the logarithms of $k_{obs.}$ against the reciprocal of temp-

Figure 3

Log $k_{obs.}$ versus $-H_o$ for X = p-CH_3O and p-CH_3

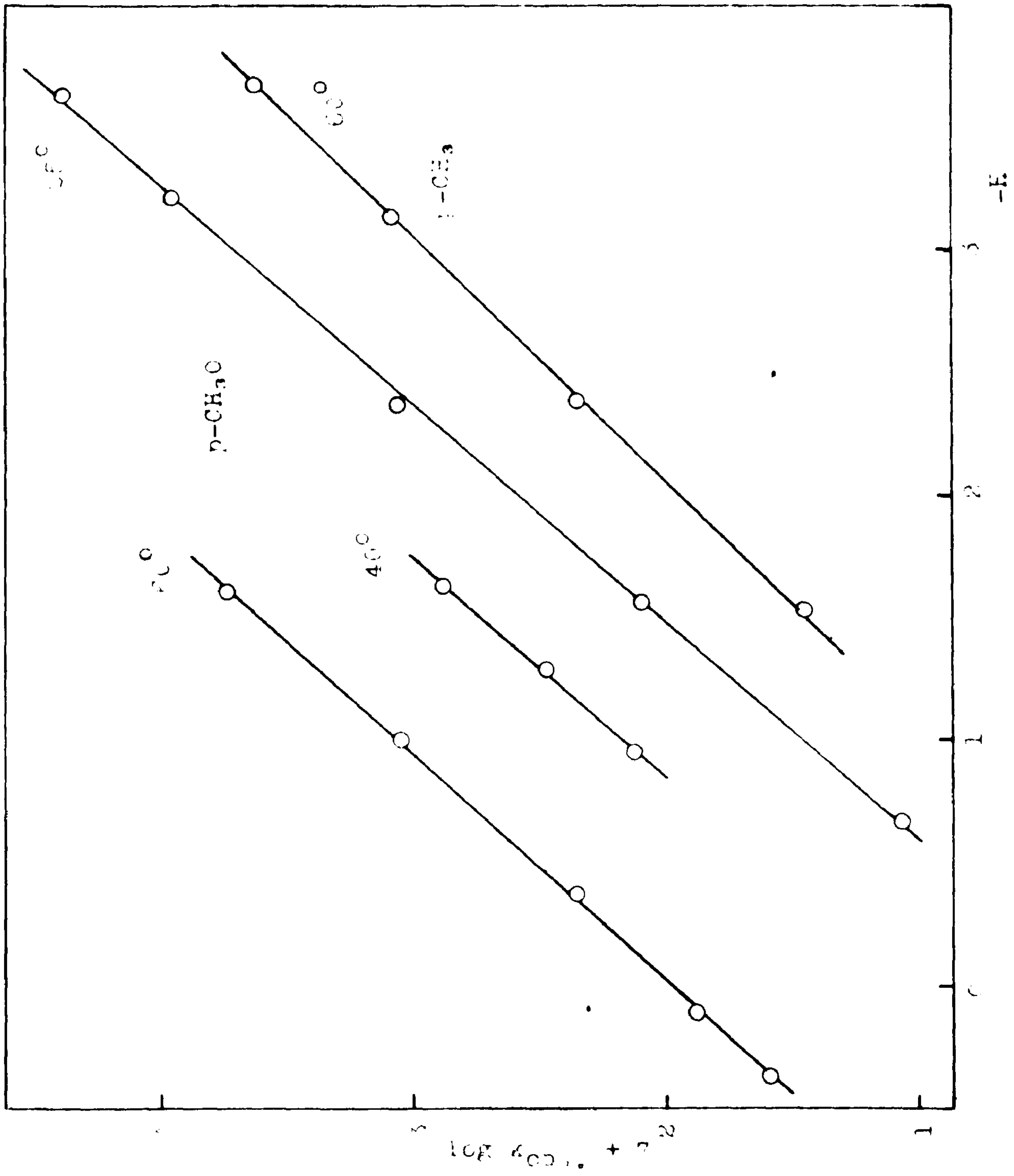


Figure 4

Log $k_{obs.}$ versus $-H_o$ for benzeneboronic acid

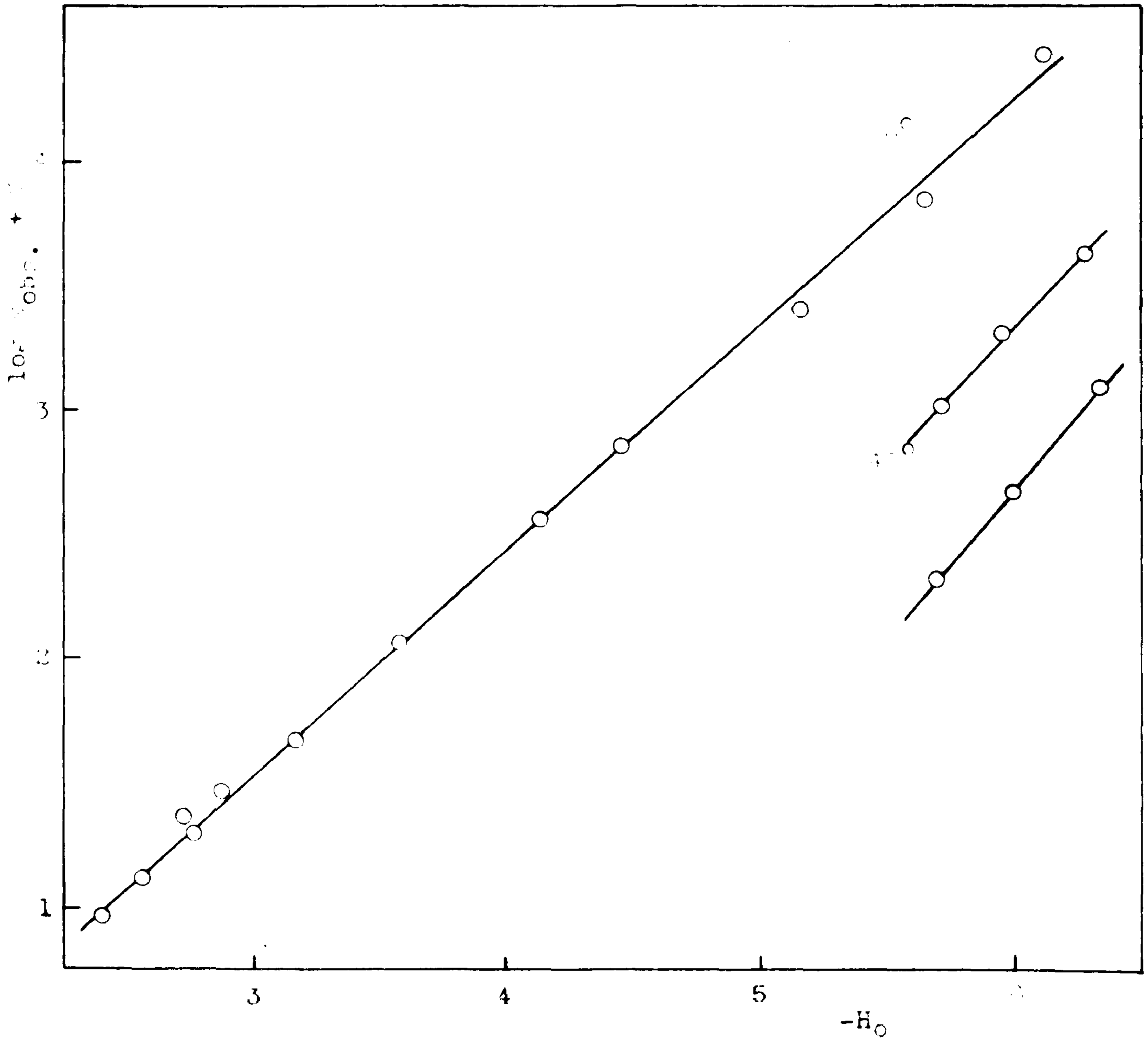


Figure 5

Log $k_{obs.}$ versus $-H_o$ for X = p-F and p-Br

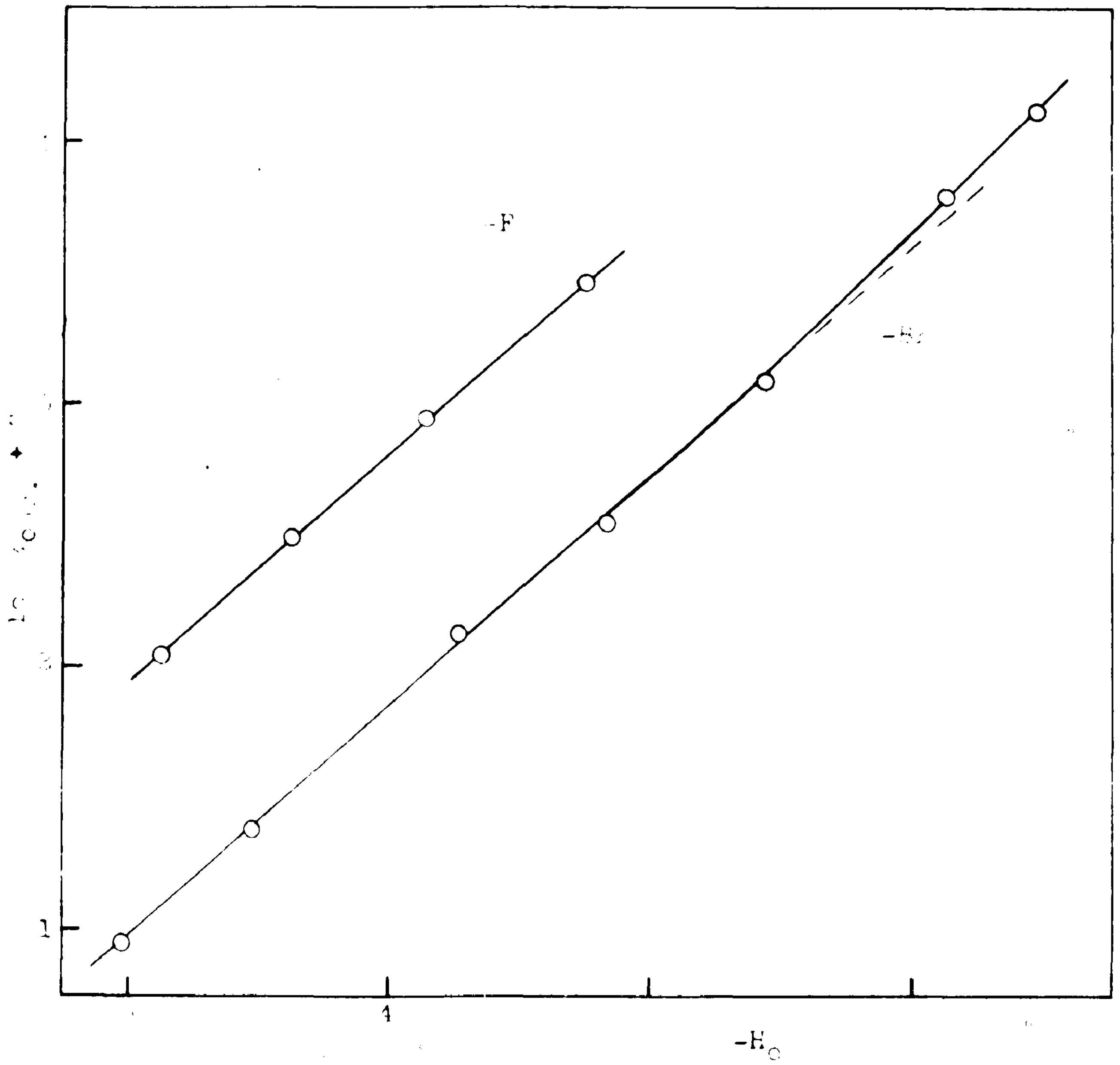


Figure 6

Log $k_{obs.}$ versus $-H_o$ for m-fluorobenzeneboronic acid

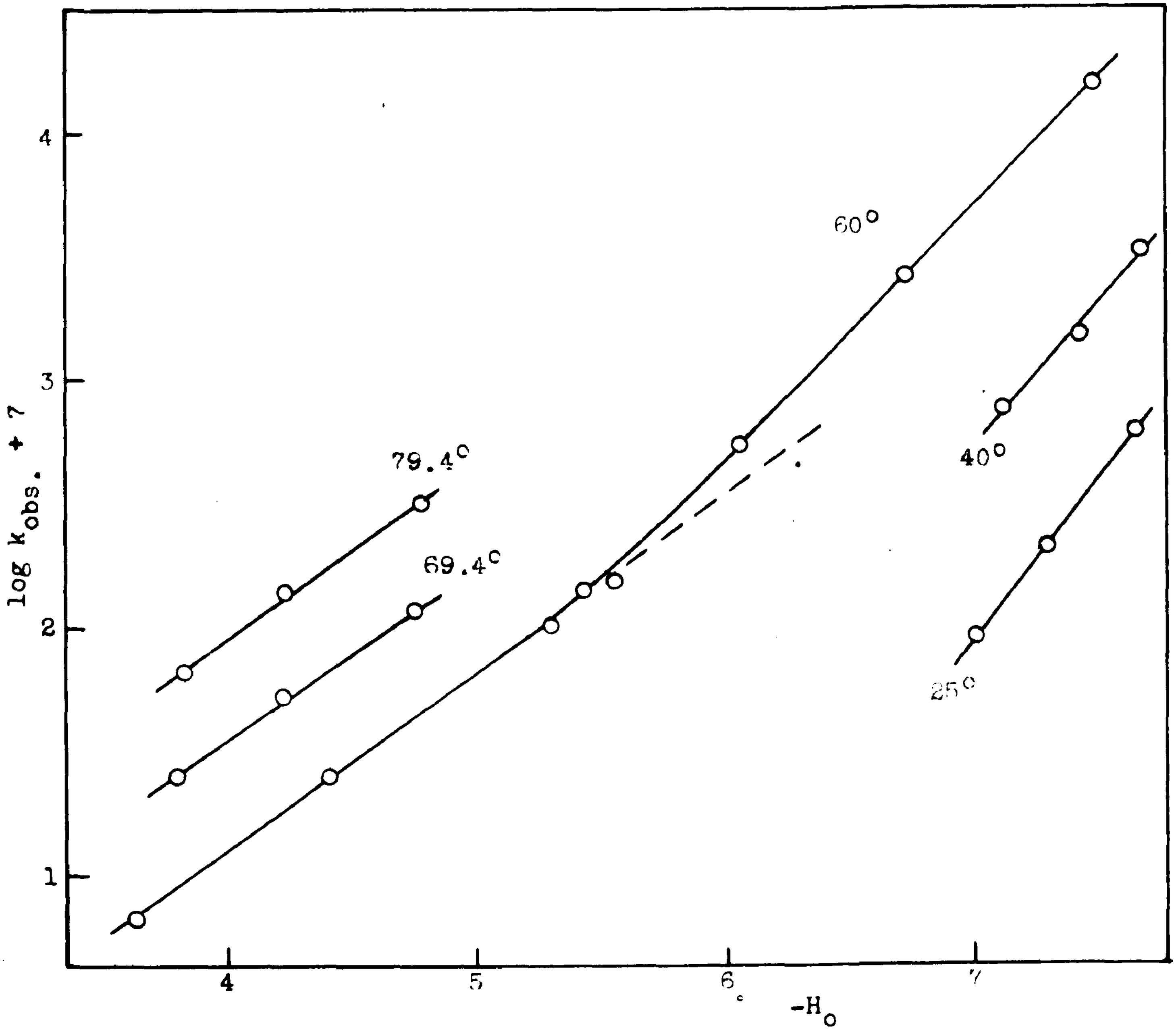


Figure 7

Log $k_{obs.}$ versus $-H_o$ for X = m-Cl and m-NO_2

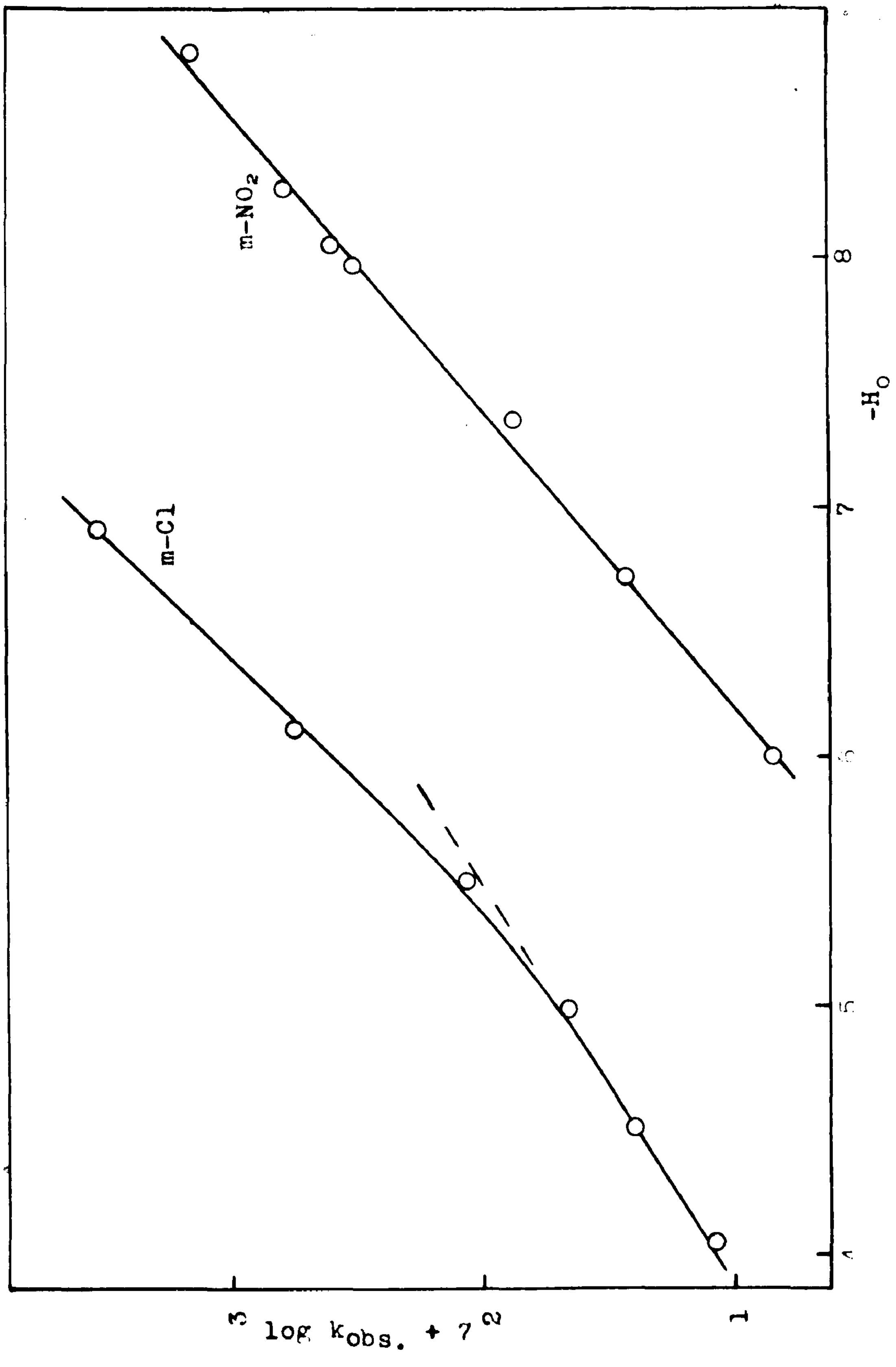


Table 2

Values of log $k_{obs.}$ versus $-H_o$ slopes for aqueous sulfuric acid

X	Temp., °C.	Acid region % H_2SO_4	log $k_{obs.}$ vs. $-H_o$ slope
p-CH_3O	60	3-30	1.10
	40	20-30	1.15
	25	16-55	1.15
p-CH_3	60	29-56	1.03
p-F	60	50-65	0.86
H	60	41-75	0.90
	40	71-71	1.10
	25	70-74	1.16
p-Br	60	48-70	0.87
		70-84	1.0
m-F	60	55-70	0.72
		70-84	1.0
	40	80-84	1.14
	25	79-83	1.35
	69.4	57-65	0.69
	79.4	57-65	0.71
m-Cl	60	59-70	0.65
		70-80	1.0
m-NO_2	60	75-97	0.84

erature are listed in table 3. Values of log $k_{obs.}$ were read from plots of log $k_{obs.}$ versus percent H_2SO_4.

There are two outstanding features evident in these activation data. In the weaker acid region (below 70% H_2SO_4) the activation energies are remarkably independent of substrate. Differences in reactivity appear to result from differences in the activation entropies. In this regard the data are similar to results obtained from a study of the protodedeuteration of alkylbenzenes in sulfuric acid - trifluoroacetic acid media[28]. The second feature arises from a comparison of the activation energies and entropies in the weaker and in the stronger (above 70% H_2SO_4) acid media. It is evident that the activation energy drops remarkably, even for a given substrate, on passing from the weaker to the stronger acid region, while the activation entropy continues to decrease. This change in activation energy, combined with the change in the value of log $k_{obs.}$ versus $-H_o$ slopes, clearly indicates that two kinetically distinguishable regions exist in aqueous sulfuric acid media for the hydrolysis of areneboronic acids.

Gold and Satchell have studied the kinetics of the protodedeuteration of several deuteroaromatic compounds in aqueous sulfuric acid solutions at 25°C., and have found that the rates are correlated by the acidity function. Of particular interest are their results with the substrates d-benzene[9], p-d-toluene[11] and p-d-anisole[12]. In order to compare the relative rates of deboronation and dedeuteration, the data for dedeuteration have been plotted against $-H_o$ values from the

Table 3

Activation energies and entropies for aqueous sulfuric acid (T 60°C.)

X	% H_2SO_4	$\Delta E^* \frac{\text{kcal.}}{\text{mole}}$	$\Delta H^* \frac{\text{kcal.}}{\text{mole}}$	ΔS^* e.u.
p-CH_3O	20	21.8	21.1	-13.7
	25	21.4	20.7	-13.0
	30	21.3	20.6	-11.7
	average:	21.5	20.8	-12.7
m-F	58	22.8	22.1	-19.7
	64	22.7	22.0	-17.6
	average:	22.8	22.1	-18.7
	81	18.4	17.7	-20.3
	83	17.1	16.4	-22.9
	average:	17.8	17.1	-21.6
H	72	18.3	17.6	-19.8
	74	18.1	17.4	-18.7
	average:	18.2	17.5	-19.3

same source as those in table 2. In contrast to the non-equal slopes which Gold and Satchell obtained from plots in which older values[14] of $-H_o$ were used, the slopes obtained with the newer values of $-H_o$ are essentially equal and are shown in table 4. The data for dedeuteration summarized in table 4 cover the acid region 28-83% H_2SO_4 continuously. A comparison of these slopes with those in table 2 illustrates the difference in the nature of the correlation of rate by the acidity function for the two reactions. While the log $k_{obs.}$ versus $-H_o$ slopes for dedeuteration appear to be independent of substrate reactivity, below 65% H_2SO_4 the slopes for deboronation decrease with decreasing substrate reactivity. In addition the slopes for dedeuteration are greater than those for deboronation. The rate of deboronation relative to dedeuteration, k_{dB}/k_{dD}, should therefore decrease with increasing acidity. Values of k_{dB}/k_{dD} are shown in table 5.

Table 4

Values of log $k_{obs.}$ versus $-H_o$ slopes for protodedeuteration

Substrate	Acid region ($-H_o$)	log $k_{obs.}$ vs. $-H_o$ slope
d-benzene	5.2-7.6	1.26
p-d-toluene	3.5-6.1	1.27
p-d-anisole	1.5-3.4	1.28

Table 5

Comparison of protodedeuteration and protodeboronation rates

Ar in the substrate Ar-Y	$-H_o$	k_{dB}/k_{dD}
C_6H_5	6.40	15.1
	5.60	17.8
$p\text{-}CH_3OC_6H_4$	3.40	20.0
	1.60	36.3

C. Mechanistic significance of the rate correlation

Following Zucker and Hammett[40], the assumption has generally been made that correlation of rate by the acidity function requires a mechanism in which an acid-base equilibrium involving the substrate is followed by a unimolecular rate-determining step in which the conjugate acid of the substrate proceeds to products. This mechanism, designated A-1, is illustrated by equations 12 and 13. The Bronsted rate equation

$$S + H^+ \rightleftharpoons SH^+ \text{ (equilibrium)} \qquad 12$$

(A-1)

$$SH^+ \xrightarrow{k_2} \text{products} + H^+ \text{ (rate-determining)} \qquad 13$$

for this mechanism is equation (14) in which K_{SH^+} is the ther-

$$k_{obs.} = \frac{k_2}{K_{SH^+}} a_{H^+} \frac{f_S}{f^{\neq}} = -\frac{1}{C_S}\frac{dC_S}{dt}$$

$$\log k_{obs.} = \log \frac{k_2}{K_{SH^+}} + \log a_{H^+} + \log \frac{f_S}{f^{\neq}} \qquad (14)$$

modynamic ionization constant of the acid SH^+. Substituting equation (8) into equation (14) yields equation (15) which is similar to (11) above.

$$\log k_{obs.} = \log \frac{k_2}{K_{SH^+}} - H_o + \log \frac{f_S f_{BH^+}}{f^* f_B} \qquad (15)$$

Recently[26] attention has been directed toward the possibility that, in aqueous mineral acid solutions, reactions resulting from a rate-determining protonation of substrate might also show rate dependence on the acidity function. Mechanisms involving rate-determining protonation are designated A-S_E2 and can be represented generally by the equations

$$S + H^+ \xrightarrow{k_1} SH^+ \quad \text{(rate-determining)} \qquad 16$$

$$SH^+ + Y \xrightarrow{k_2} \text{products} + H^+ \quad \text{(fast)} \qquad (A\text{-}S_E2) \qquad 17$$

The kinetic expression obtained by applying the Bronsted rate equation to this mechanism depends on how one chooses to represent the solvated proton in aqueous solution. If the solvated proton is assumed to be hydronium ion, one obtains

$$k_{obs.} = -\frac{1}{C_S}\ \frac{dC_S}{dt} = k_1 a_{H_3O^+} \frac{f_S}{f^*}$$

$$k_{obs.} = k_1 C_{H_3O^+} \frac{f_S f_{H_3O^+}}{f^*} \qquad (18)$$

On the other hand, if one chooses to associate no structural significance to the nature of proton solvation in aqueous media, the Bronsted rate expression becomes

$$k_{obs.} = k_1 a_{H^+} \frac{f_S}{f^*} \qquad (19)$$

Equation (19) is similar to equations (14) and (10) above, and shows that, provided the activity coefficient ratio f_S/f^* changes similarly to the ratio f_B/f_{BH^+} with changing acidity, a reaction proceeding by the A-S_E2 mechanism will show rates which parallel the acidity function. However, if instead the activity coefficient ratio shown in equation (18) remains constant with changing acidity, the rates will be correlated by the molar concentration of hydronium ion. Whether the rate of a given A-S_E2 reaction is correlated by the acidity function or by the concentration of hydronium ion therefore depends on whether the behavior of f^* with changing acidity parallels that of f_{BH^+} or of $f_S f_{H_3O^+}$, respectively. In this regard it should be noted that Deno and Perizzolo[5] have suggested that the behavior of the activity coefficient of a cation with changing acidity depends more on the disposition of the charge in the ion than on the composition of the ion.

It is apparent from the above discussion that until the kinetic requirements of A-S_E2 reactions in aqueous mineral acid solutions are determined, correlation of rate by the acidity function alone cannot serve as a means for distinguishing between A-1 and A-S_E2 mechanisms.

Experimental techniques which allow such a distinction are available, however. These other techniques take advantage of an inherent difference in the two mechanisms. In the A-1 mechanism the protonation of the substrate occurs in an equilibrium which precedes the rate-determining step, while in the A-S_E2 mechanism the protonation of the substrate is the rate-determining step. An A-1 mechanism should therefore show (1) specific hydrogen ion catalysis[26,40], (2) rates faster in deuterium oxide as solvent than in protium oxide[33,38], and (3) a dependence of rate on the composition of D_2O-H_2O mixtures which is predictable by the Gross-Butler theory[30,34]. A reaction proceeding by the A-S_E2 mechanism, however, should show (1) general acid catalysis under appropriate conditions[26], (2) rates in deuterium oxide as solvent either smaller than or equal to rates in protium oxide[27,38], and (3) a dependence of rate on the composition of D_2O-H_2O solvent mixtures which is perhaps linear[21] but in any event is not predicted by the Gross-Butler theory.

Each of these three criteria have been investigated. The results are described and discussed below.

D. The solvent hydrogen isotope effect

Rates of hydrolysis of four areneboronic acids (X = p-CH_3O, p-CH_3, p-F and m-F) have been measured in solutions of deuterium sulfate in deuterium oxide at a temperature of 60°C. Values of the solvent hydrogen isotope effect, k_H/k_D, for a given percent by weight acid, are shown in table 6.

In section C were listed three experimental criteria which would allow one to distinguish between the A-1 and A-S_E2 mechanisms. According to the second criterion, the k_H/k_D ratio for an A-1 reaction would have a value less than unity. The values of k_H/k_D shown in table 6 strongly suggest, therefore, that the hydrolysis of areneboronic acids does not occur by the A-1 mechanism.

An interesting feature is illustrated by the values of k_H/k_D for X = m-F. Above 68% acid the value of this ratio appears to be increasing and then, above 72% acid, leveling off. This is exactly the region of acidity in which the break in the correlation of rate by the acidity function and the change in the value for the activation energy occur. Therefore the solvent hydrogen isotope effect for X = m-F further substantiates the existence of two kinetically distinguishable acid regions for the hydrolysis of areneboronic acids in aqueous sulfuric acid.

Table 6

Solvent hydrogen isotope effect

X	% Acid	k_H/k_D
p-CH_3O	22.4	2.02
	32.5	1.93
p-CH_3[a]	40	1.60
	45	1.64
	50	1.69
	55	1.74
p-F	60.6	2.16
	65.4	2.27
m-F[b]	64	2.40
	68	2.48
	72	2.68
	76	2.99
	80	2.99

a. k's interpolated from log k versus H_o plots

b. k's interpolated from log k versus percent acid plots

E. The effect of solvent hydrogen isotope composition

A theory for the effect of composition of H_2O-D_2O solvent mixtures on reaction rates and equilibria has been developed by Gross and Butler, and has recently been evaluated by Purlee[34]. The theory relates acid-base equilibrium constants and rates of certain reactions to the activities of protons and deuterons in the H_2O-D_2O solvent mixtures.

For reactions in which an acid-base equilibrium involving the substrate precedes the rate-determing step and in which the rate-determing step does not show an appreciable solvent isotope effect (i.e. A-1 and some A-2 reactions), the theory shows that the effect of solvent hydrogen isotope composition is described by equation (20) (page 28). Since $(a_{H_2O})_n = (1-n)^2$, $(a_{D_2O})_n = n^2$ and $L = 11.0$[34], equation (20) reduces to equation (21).

The effect of solvent hydrogen isotope composition has been determined for p-methoxybenzeneboronic acid in 6.31 molar sulfuric acid at a temperature of 25°C. The observed rate constants, k_n, are tabulated in table 7, and are plotted against n in figure 8. The broken line describes values of k_n calculated according to equation (21).

That equation (21) does not apply to the hydrolysis reaction is clearly demonstrated by figure 8. Instead the data fit the equations

$$k_n = k_H(1-n) + k_Dn \qquad (22)$$

$$k_n = k_H(a_{H_2O})_n^{\frac{1}{2}} + k_D(a_{D_2O})_n^{\frac{1}{2}} \qquad (23)$$

The Gross-Butler equation

$$\frac{k_n}{k_H} = \frac{1}{Q'(n)} \left[(a_{H_2O})^{\frac{1}{2}}_{n} + \frac{k_D(a_{D_2O})^{\frac{1}{2}}_{n}}{k_H(L)^{\frac{1}{2}}} \right] \tag{20}$$

where

a = activity

n = atom fraction of deuterium in the solvent = $\frac{D}{H + D}$

k_H = observed rate constant when n = 0

k_D = observed rate constant when n = 1

Q'(n) is a function of the activities of the various isotopic solvent species. Its definition and values at various temperatures are given by Purlee[34]

$$L = \frac{(a_{H_3O^+})^2 \, (a_{D_2O})^3}{(a_{D_3O^+})^2 \, (a_{H_2O})^3}$$

$$k_n = \frac{1}{Q'(n)} \left[k_H + n \left(\frac{k_D}{3.316} - k_H \right) \right] \tag{21}$$

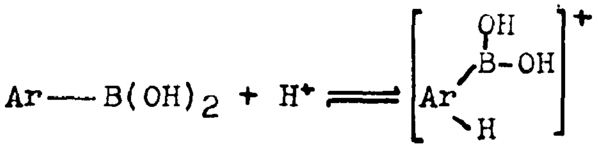
Table 7

The effect of solvent hydrogen isotope composition

run	n	$k_n \times 10^4$ sec.$^{-1}$
VIII$_{HD}$-1	0	3.45
5	1.00	0.940
6	.799	1.45
7	.598	2.02
8	.799	1.54
9	.598	1.96
10	.498	2.20
11	.221	3.02
12	.443	2.42

This lack of correlation by the Gross-Butler equation satisfies the second criterion for the A-S$_E$2 mechanism listed in section C above, and further substantiates the non-applicability of the A-1 mechanism.

There is a third possible mechanism, of the A-2 type, which can be disposed of at this time. This mechanism has two steps: the first a rapidly established acid-base equilibrium in which the conjugate acid of the substrate is formed, the second a rate-determining proton abstraction from the conjugate acid intermediate; it can be represented by the equations



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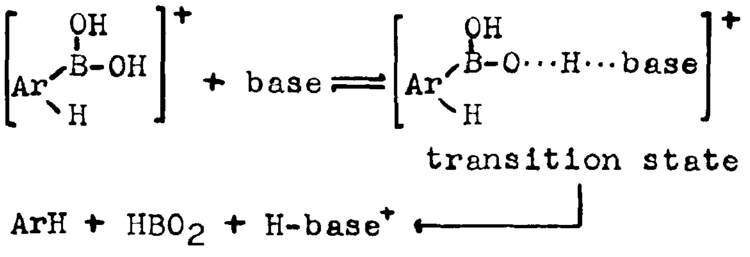

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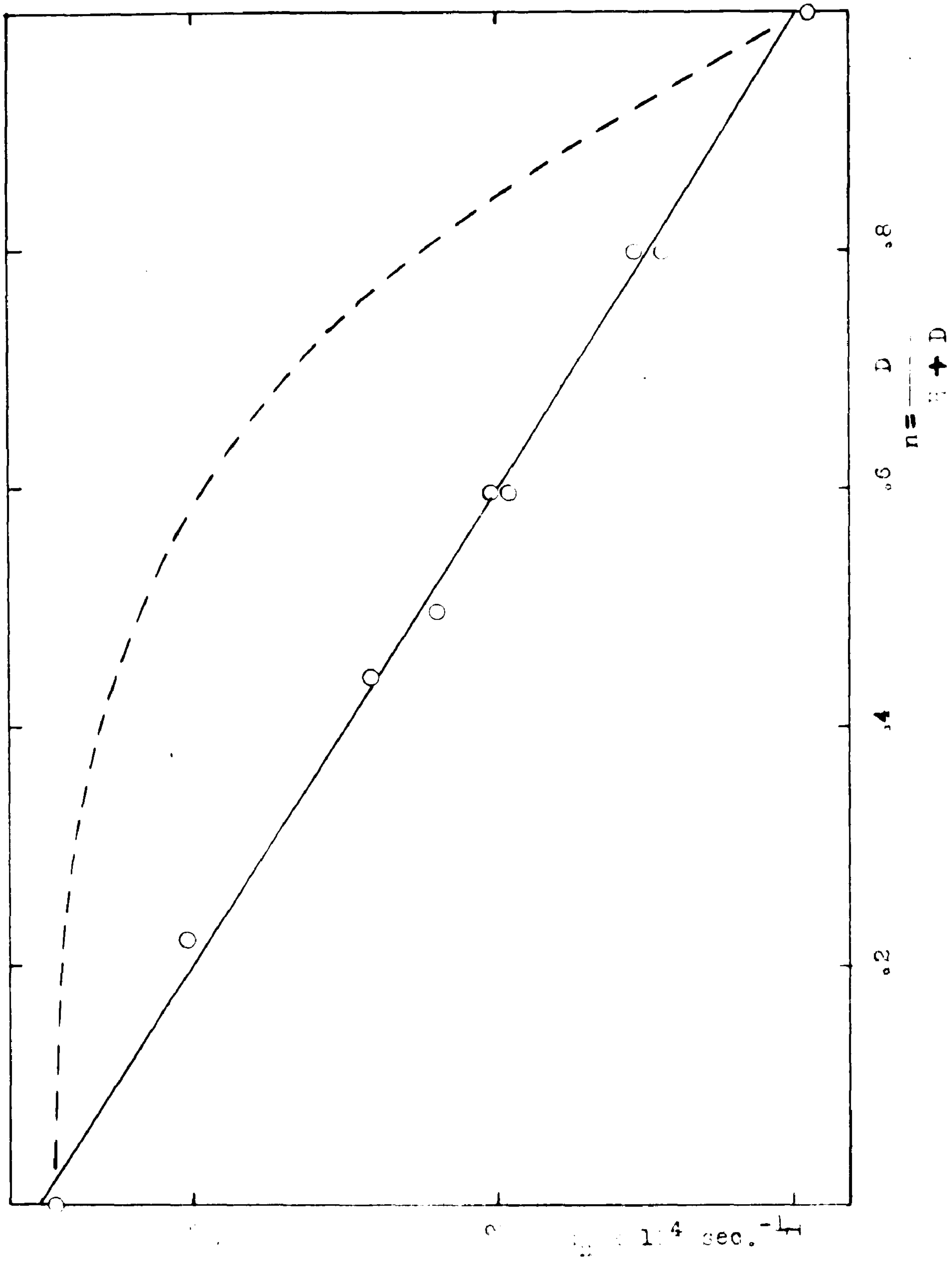
Figure 8

The effect of solvent hydrogen isotope composition



The boronic acid function has two hydrogens which probably equilibrate rapidly with the solvent. Since a transfer of one of these protons occurs in the transition state, this mechanism does not require correlation of the solvent hydrogen isotope composition effect by the Gross-Butler equation. Purlee[34] has shown that a mechanism of this type has k_n values at least as large as those predicted by equation (20). Figure 8 shows, however, that the values of k_n are substantially lower than those predicted by equation (20).

Another experimental fact also rules out an A-2 type mechanism. According to the Hammett-Zucker hypothesis an A-2 reaction occurring in aqueous mineral acid should show correlation of rate by the concentration of hydronium ion. Figure 2 shows that for X = p-CH_3O the rate of hydrolysis in a diagnostic region of acidities (3 – 30% H_2SO_4) is correlated by the acidity function and therefore not by the concentration of hydronium ion.

The linear dependence of k_n on n deserves further comment. To the author's knowledge such a linearity has previously been observed for only one reaction, and that is the acid-catalyzed mutarotation of glucose[13]. Two mechanisms might account for this linear relationship. These are a concerted A-2 type mechanism and, of course, the A-S_E2 mechanism. The concerted A-2 mechanism can be represented by the equation

$$\begin{array}{l} H^+ + SH + \text{base} \rightleftharpoons [H\cdots S\cdots H\cdots \text{base}]^+ \\ \qquad\qquad\qquad\qquad\qquad \text{transition state} \\ \qquad SH + H\text{-base}^+ \longleftarrow\!\!\!\!\longrightarrow\!\!\!\rfloor \end{array} \qquad 26$$

In this equation SH is a substrate containing a hydrogen atom which rapidly equilibrates with the solvent. This is a termolecular mechanism in which transfers of a hydrogen ion from the medium to the substrate and from the substrate to the medium occur simultaneously in the rate-determining step.

Long and Watson[27] have recently concluded that the magnitude of the solvent hydrogen isotope effect, k_H/k_D, for the transfer of a proton from the medium to the substrate depends on the strength of the acid species involved in the transfer, the weaker acid species showing the greater isotope effect. Indeed, their study of the hydrogen isotope effect on the acid-catalyzed enolization of methylacetylacetone shows that, for the neutralization of methylacetylacetone enolate ion by hydronium ion (or solvated proton), the solvent hydrogen isotope effect is small ($k_H/k_D = 1.1$).

In keeping with the results of Long and Watson, Purlee[34] has interpreted the results for the mutarotation of glucose in terms of the concerted A-2 type mechanism by assuming that the solvent isotope effect for hydrogen ion transfer from hydronium ion to glucose is negligibly small, and that the experimental value of k_H/k_D arises from the effect of the equilibrated hydrogen atom in the glucose molecule; that is, the isotope effect results from the transfer of hydrogen from glucose to the medium. Purlee has shown that these assumptions are adequate for explaining the linear dependence of k_n on n. Of course, the alternative assumption that the value of k_H/k_D arises from the medium-to-glucose hydrogen ion transfer, although at first glance inconsistent with the findings of Long and Watson, might also account for the effect of solvent hydrogen isotope composition. This latter assumption would assume that an A-S_E2 type reaction would show linear dependence of k_n on n also.

A discussion as to whether the A-S_E2 mechanism or the concerted A-2 mechanism is a better description for the course of the protodeboronation reaction is deferred until later.

III. Formic Acid Solutions

In the preceding section we saw that the results obtained from a study of the solvent hydrogen isotope composition effect on the rate of areneboronic acid hydrolysis indicated that the reaction occurred by either an A-S_E2 or a concerted A-2 mechanism. Therefore, under appropriate conditions, the hydrolysis reaction should show general acid catalysis. Since a demonstration of this property would make the two mechanisms suggested by the isotope work that much more compelling, a study of the catalysis in media having competing acidic (or basic) species was undertaken.

The hydrolysis of p-methoxybenzeneboronic acid has been studied at 25°C. in the medium 94.8% formic acid - 4% ethylene glycol dimethyl ether (EGDE) - 1.2% water. The EGDE was used as a cosolvent so that solutions of the boronic acid in the formic acid medium could be prepared rapidly. Values of the acidity function for solutions of sodium formate or sulfuric acid in this medium were determined colorimetrically by using o-nitroaniline as the indicator base. The effect of sodium formate and sulfuric acid on the rate of reaction has also been determined. These data are all listed in table 8, and figure 9 shows a plot of the observed pseudo first-order rate constants against the acidity function.

The data in table 8 qualitatively demonstrate that the hydrolysis reaction in this medium is general acid-catalyzed. This fact is borne out by the following observations. In a series of sodium formate solutions in which the acidity of the medium changes by a factor of ten (runs $VIII_f$-24, 25 and 26) the rate is essentially constant ($k_{obs.} = 1.8 \times 10^{-5}$ $second^{-1}$). This fact requires a reaction involving catalysis by molecular formic acid, a species whose concentration is essentially unaffected by a change in the acidity of the medium. When the acidity of the medium increases to values of $-H_0$ above 0.2 an increase in rate is observed. This increase in rate with increasing acidity can qualitatively be accounted for by incursion of reactions involving the more acidic lyonium ions; formic acidium, ($HCOOH_2^+$), and hydronium, (H_3O^+).

A rigorous quantitative treatment of these data cannot be made. However, there are sufficient data describing formic acid media reported in the literature so that a semi-quantitative treatment, which will account for the general shape of the curve in figure 9, can be given.

Figure 9

$k_{obs.}$ versus $-H_o$: formic acid solutions

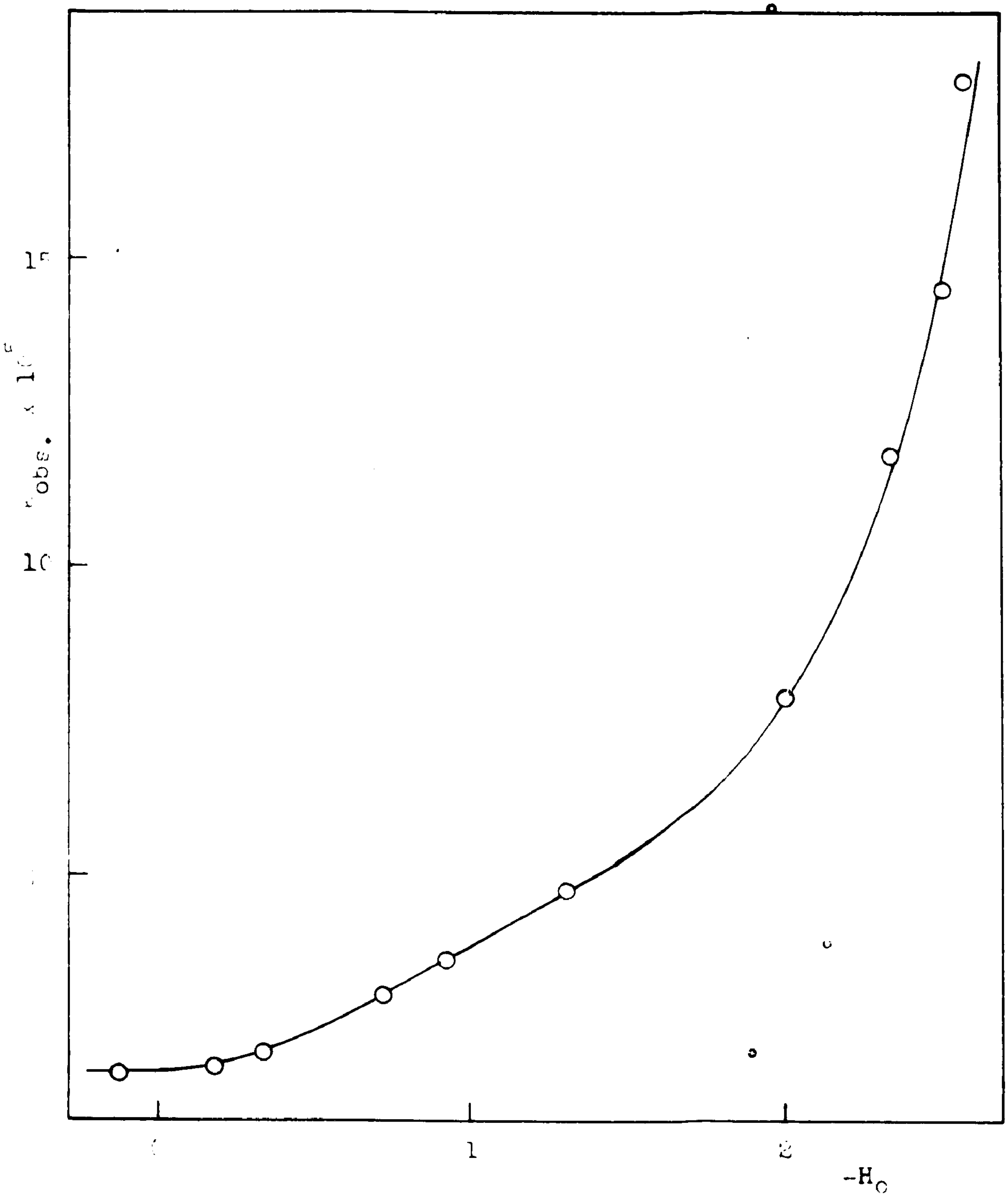


Table 8

Rate constants in the medium 94.8% formic acid - 4% EGDE - 1.2% water

run#	$NaCHO_2$ molar	H_2SO_4 molar	$-H_o$	k x 10^5 sec.$^{-1}$ observed	calculated
$VIII_f$-17			1.31	4.90	4.76
18				4.67	
19				4.58	
20		0.0482	2.58	17.9	17.8
21		0.0413	2.51	14.5	15.9
22		0.0258	2.34	11.8	12.4
23		0.01032	2.00	7.87	8.34
24	0.1963		-0.84	1.86	
25	0.0982		-0.14	1.78	
26	0.0491		0.17	1.89	
27	0.0295		0.33	2.12	2.43
28	0.00982		0.72	3.06	3.10
29	0.00491		0.92	3.61	3.58

Sulfuric acid behaves as a strong monoprotic acid[15] in formic acid solutions; hence there are four possible acidic species in the solutions under discussion. These are molecular formic acid, bisulfate ion, hydronium ion and formic acidium ion (represented here by H^+). In the solutions containing sulfuric acid the concentration of bisulfate ion is low enough so that its role as a catalyst, compared to that of molecular formic acid, is small and can be neglected. Then the rate equation for these solutions, neglecting activity coefficients, is

$$k_{obs.} = -\frac{1}{C_S}\frac{dC_S}{dt} = \sum k_{HA_i} C_{HA_i}$$

$$k_{obs.} = k_o + k_{H_3O^+} C_{H_3O^+} + k_{H^+} C_{H^+} \qquad (27)$$

In all of these solutions the concentration of water is 0.891 molar, therefore the concentration of hydronium ion can be expressed as

$$C_{H_3O^+} = \frac{0.891\ C_{H^+}}{K_{H_3O^+} + C_{H^+}} \qquad (28)$$

where $K_{H_3O^+}$ is the molar concentration dissociation constant for hydronium ion. Substituting into equation (27) yields

$$k_{obs.} = k_o + 0.891\ k_{H_3O^+} \frac{C_{H^+}}{K_{H_3O^+} + C_{H^+}} + k_{H^+} C_{H^+} \qquad (29)$$

The constants in equation (29) can be evaluated provided a means is found for determining C_{H^+} in the solutions studied.

Hammett and Deyrup[15] have measured acidity functions for solutions of sodium formate and sulfuric acid in anhydrous formic acid. This study shows that, in these solutions, there is a linear relationship between pH (-log C_{H^+}) and H_o, specifically

$$pH = H_o + 4.85 \qquad (30)$$

It appears reasonable to assume that sodium formate and sulfuric acid behave as a strong base and acid, respectively, in the solvent 96% formic acid - 4% EGDE, just as in anhydrous formic acid. This means that an equation of the type (30) obtains in the binary solvent also. To a crude first approximation, let us assume that equation (30) adequately describes the relationship between pH and H_o in the binary solvent. Then C_{H^+} is given by the equation

$$C_{H^+} = \text{antilog}(-H_o - 4.85) \qquad (31)$$

With equation (31) we can now evaluate the constants $k_{H_3O^+}$, $K_{H_3O^+}$ and k_{H^+} by using the rate and H_o data for three of the solutions in table 8 ($VIII_f$-23, 24 and the average of $VIII_f$-17, 18 and 19). Taking $k_o = 1.80 \times 10^{-5}$ second^{-1}, the values for the other constants become

$$k_{H_3O^+} = 4.2 \times 10^{-5} \text{ second}^{-1}$$

$$K_{H_3O^+} = 1.7 \times 10^{-4} \text{ mole liter}^{-1}$$

$$k_{H^+} = 2.3 \times 10^{-2} \text{ second}^{-1}$$

Using these constants in equation (29) we can now calculate a value of $k_{obs.}$ for each of the solutions in table 8. These calculated values are shown in the last column of the table.

While $K_{H_3O^+}$ is fairly insensitive to the value chosen for the constant in equation (31), the ratio $k_{H^+}/k_{H_3O^+}$ is extremely sensitive. Since equation (31) represents a very crude approximation, the values of the constants derived from it are regarded only as reflections on their relative orders of magnitude. Nevertheless, because the curve in figure 9 is so well approximated through the use of these values, the above treatment is regarded as a semiquantitative demonstration that the hydrolysis in these solutions is general acid-catalyzed.

IV. Aqueous Perchloric and Phosphoric Acids

The rates of hydrolysis of two substituted benzeneboronic acids (X = p-CH_3O and p-CH_3) in aqueous perchloric acid solutions and three benzeneboronic acids (X = p-CH_3O, p-CH_3 and H) in aqueous phosphoric acid solutions have been determined, and the values of the pseudo first-order rate constants, $k_{obs.}$, are listed in tables 9 and 10. The values of H_0 for the aqueous phosphoric acid solutions are for the indicated temperatures and are taken from the data of Gelbshtein, Sheglova and Temkin[7]. Those for the perchloric acid solutions are for 25°C. and are taken from the data of Hammett and co-workers[14,16].

The rates in aqueous perchloric acid are correlated by the acidity function. In aqueous phosphoric acid, however, the rates are not correlated by the acidity function, the activity of molecular acid or water[6], or by a combination of these parameters. These facts are illustrated in figures 10 and 11 in which the values of log $k_{obs.}$ for the hydrolysis of p-methoxybenzeneboronic acid in these two media and in aqueous sulfuric acid are plotted against the acidity function.

Table 9

Pseudo first-order rate constants, $k_{obs.}$, in aqueous perchloric acid

X	Temp., °C.	% $HClO_4$	$-H_0$	log $k_{obs.}$ + 7
p-CH_3O*	25°*	30.0	1.37	1.815
		40.7	2.23	2.667
		44.0	2.58	2.967
		50.5	3.48	3.672
		56.2	4.40	4.445
	60°	33.85	1.63	3.884
		30.95	1.43	3.708
		25.50	1.10	3.347
		18.57	0.72	2.915
p-CH_3	25°	64.7	5.86	3.371
		60.5	5.19	2.582
		56.3	4.42	1.827

* work done by H. G. Kuivila

Figure 10 allows a qualitative comparison of the data derived from the studies in aqueous perchloric and sulfuric acids. The line drawn through the two sets of data has unit slope. As the acidity increases, values of log $k_{obs.}$ for the two acids deviate from this line in opposite directions. These deviations are almost certainly due in part to specific effects of the different anions in the two acids[25]. The greater increase of log $k_{obs.}$ with increasing acidity in the sulfuric acid solutions might also be partly due to catalysis by bisulfate ion. The values of the activation energy and entropy in 30% $HClO_4$, derived from the data obtained at the temperatures 25°C. and 60°C., are $\Delta E^* = 23.6$ kcal./mole and $\Delta S^* = -5.2$ e.u. (T = 60°C.). The corresponding values for 30% H_2SO_4 (table 3) are 21.3 kcal./mole and - 11.7 e.u., respectively. In view of the specific effects by the two acids on the rates, these differences are perhaps to be expected.

Both figures 10 and 11 show that at a given value of H_o, the rate in aqueous phosphoric acid is much greater than those in the other two acids. Since the reaction has already been shown to be general acid-catalyzed, and since in addition to hydronium ion there is also a large concentration of molecular H_3PO_4 ($pK_a = 2$) in the aqueous solutions of this acid, the greater rate at a given value of H_o is to be expected. The system is sufficiently complicated so that no quantitative treatment has been attempted.

In solutions having a high concentration of phosphoric acid a kinetic complication was observed which was not investigated further. For example, in 82.7% H_3PO_4 at a temperature

Table 10

Pseudo first-order rate constants, $k_{obs.}$, for aqueous phosphoric acid

run#	T	% H_3PO_4	$-H_o$	log $k_{obs.}$ + 7
X = H				
I_{ph}-5	60°	74.3	2.38	3.587
6		65.7	1.69	2.702
7		52.9	1.01	1.733
9	25°	82.7	see figure 11	
X = p-CH_3				
VII_{ph}-1	60°	72.4	2.22	4.641
2		66.6	1.76	4.044
3		56.3	1.16	2.998
4		42.7	0.61	1.945
5	25°	71.3	2.40	3.273
6		68.3	2.11	2.887
7		63.9	1.75	2.379
8		60.7	1.55	2.054
9		56.3	1.32	1.574
10		73.5	2.63	3.657
11		76.7	2.92	4.133
X = p-CH_3O				
$VIII_{ph}$-1	60°	39.9	0.50	3.289
2		57.5	1.22	4.663
3		49.2	0.82	3.962
4		27.1	0.00	2.489
5		10.6	-0.73	1.532
HGK_{ph}-1*	25°	36.0	0.40	1.613
2		45.5	0.82	2.316
3		53.6	1.18	3.048
4		60.9	1.56	3.877
5		61.2	1.58	3.959
6		67.9	2.06	4.757

* Work done by H. G. Kuivila

Figure 10

Log $k_{obs.}$ versus $-H_o$ for p-methoxybenzeneboronic acid: T = 25°C.

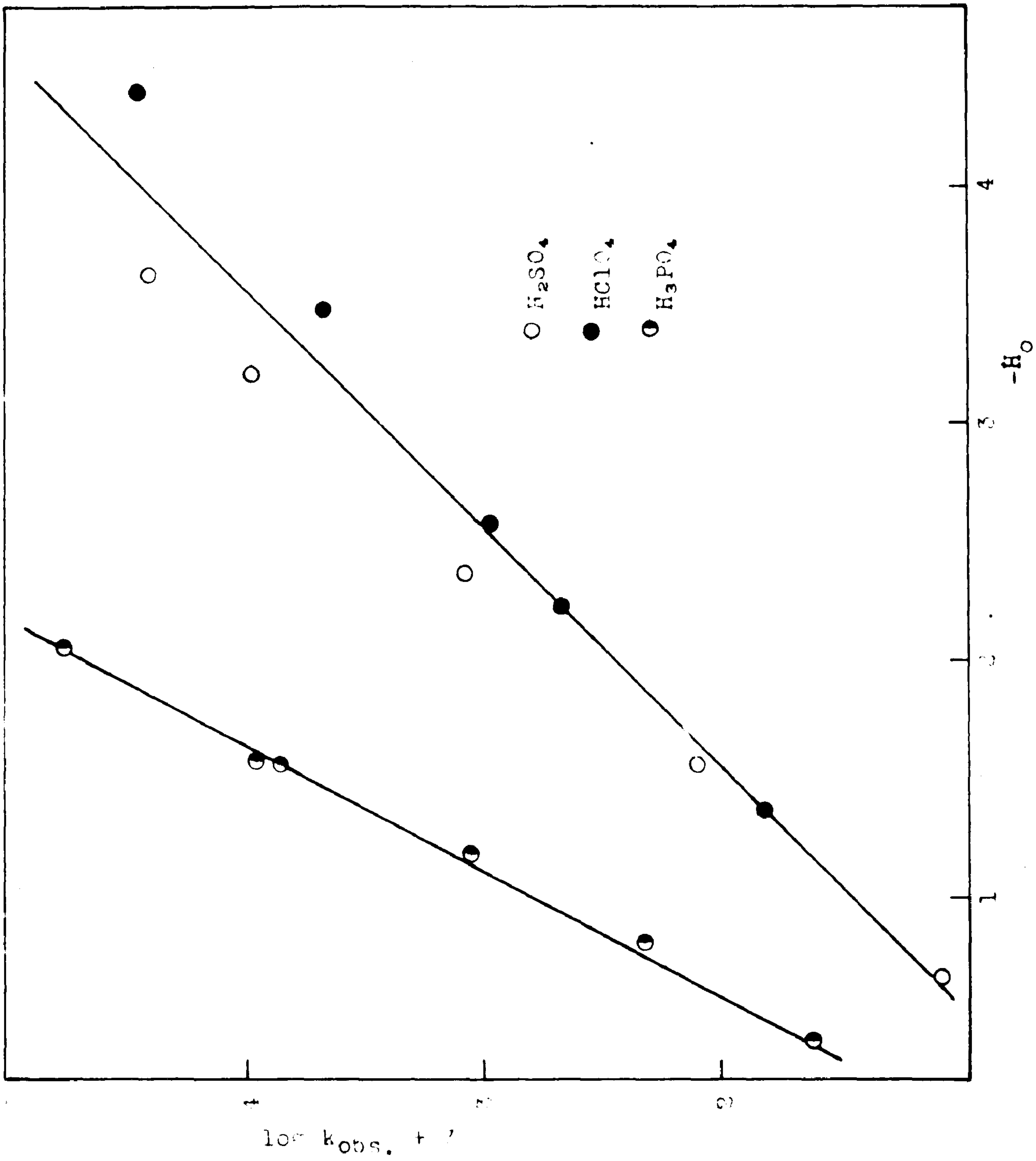


Figure 11

Log $k_{obs.}$ versus $-H_o$ for p-methoxybenzene-boronic acid: T = 60°C.

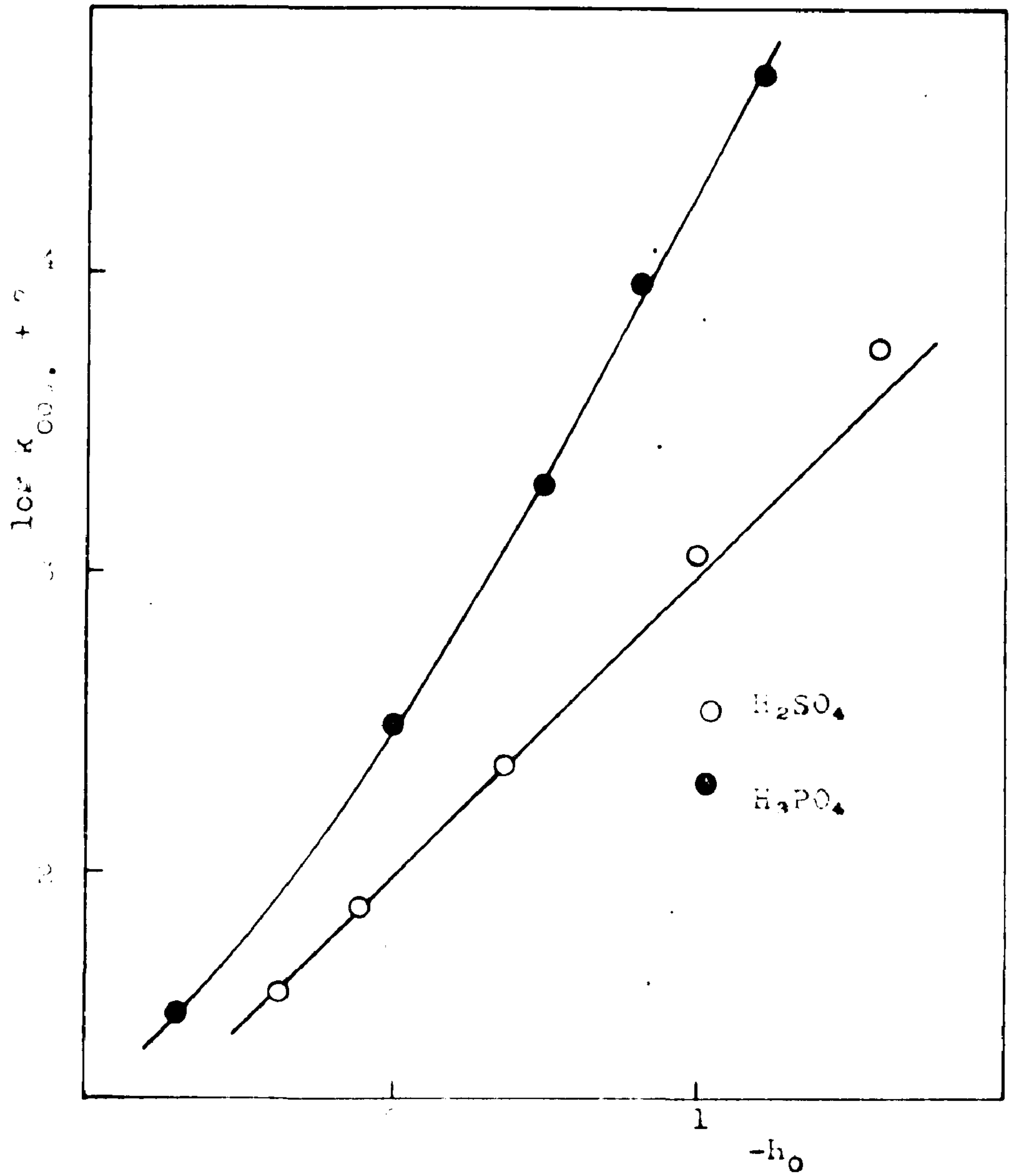


Figure 12

Rate plot for run I_{ph}-9

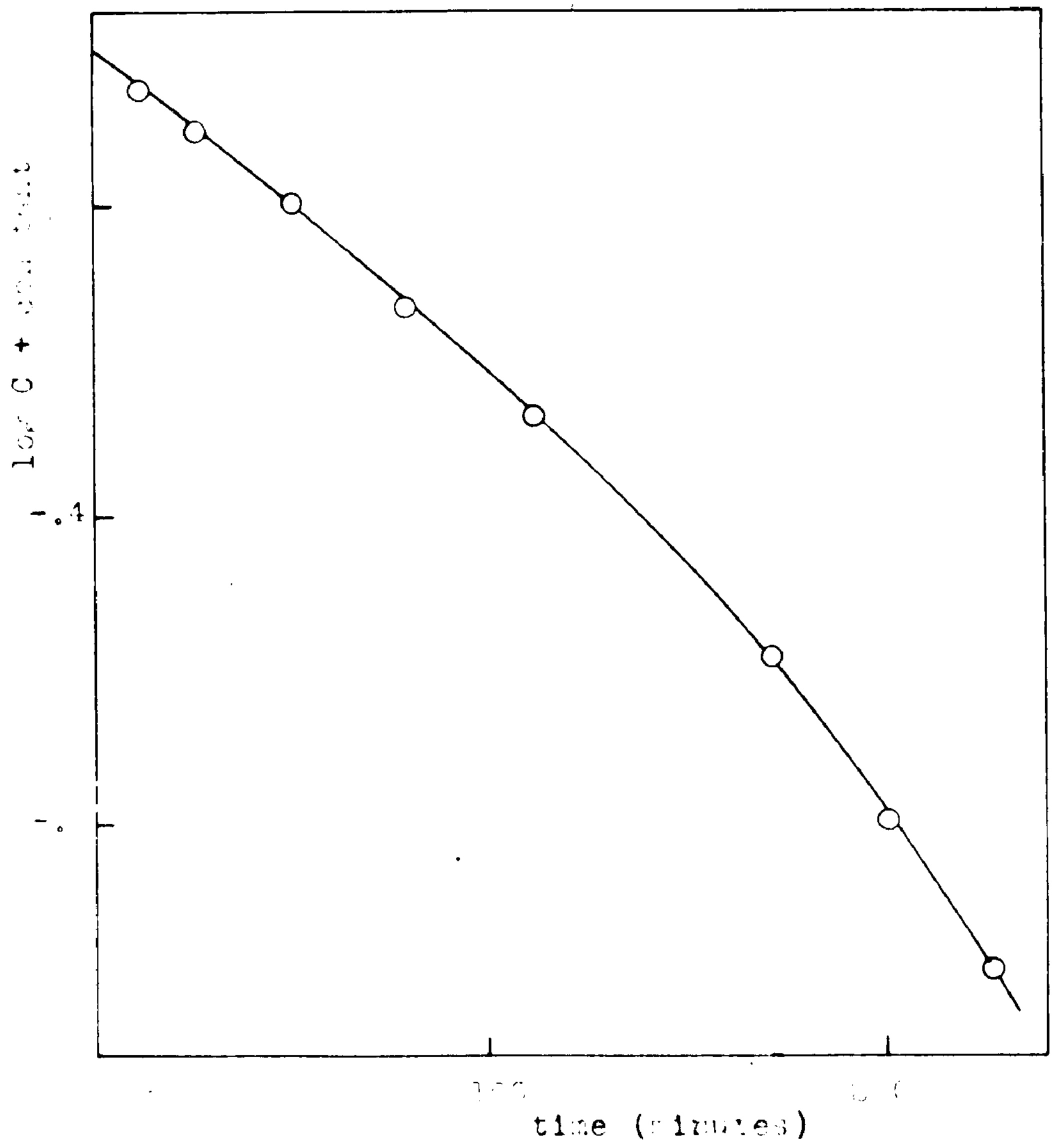
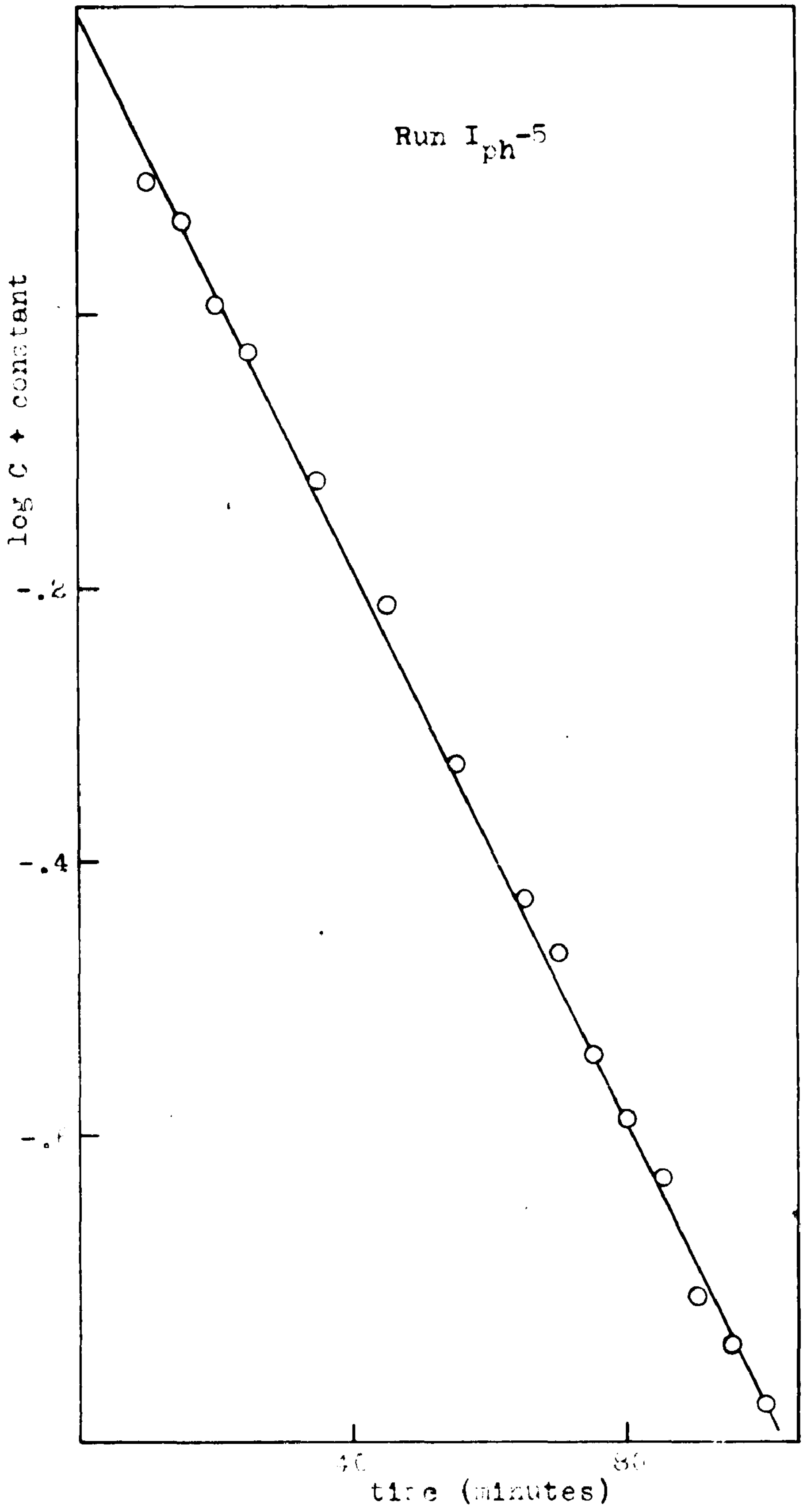


Figure 13

Rate plot for run I_{ph}-5



of 25°C., the pseudo first-order rate constant for the hydrolysis of benzeneboronic acid increased with time. This is illustrated by the rate plot for run I_{ph}-9 shown in figure 12. That this complication was not encountered in solutions weaker in acidity than 80% H_3PO_4 is illustrated by figure 13 which shows a first-order rate plot for run I_{ph}-5.

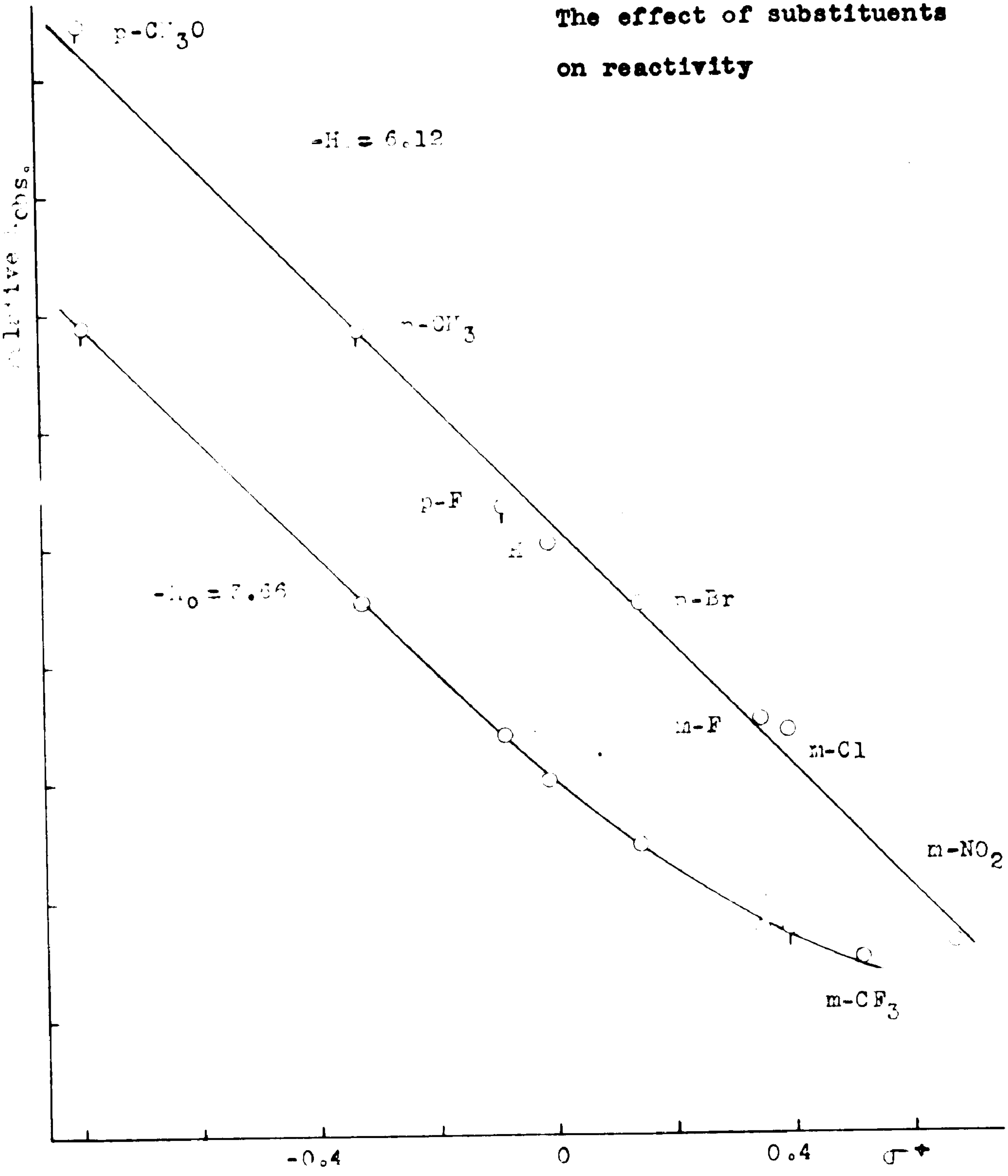
V. The Effect of Substituents on Reactivity

The data obtained in sulfuric acid solutions at a temperature of 60°C. (table 1) allow a determination of the areneboronic acid reactivities relative to that of benzeneboronic acid. Values of log $(k_X/k_{X=H})$ have been determined for two different solutions. The first of these, 55.5% H_2SO_4 $(-H_o = 3.66)$, is below the region of acidities in which a change in the nature of the acidity correlation occurs $(-H_o = 5\text{-}5.5)$, and the other solution, 74.5% H_2SO_4 $(-H_o = 6.12)$, is above the region. Both sets of values are listed in table 11 and, in figure 14, are plotted against the σ^+ substituent constants of Brown and Okamoto[4].

Two remarkable facts are illustrated by the plots in figure 14. The upper plot shows that the σ^+ constants give a fairly accurate measure of the substituent effects on reactivity. The lower plot, however, shows that while the constants correlate the effects on reactivity of the ring-activating substituents (X = p-CH_3O, p-CH_3 and p-F), they do not correlate the effects of the ring-deactivating substituents. The correlation represented by the upper plot might appear fortuitous inasmuch as the relative reactivities for

Figure 14

The effect of substituents on reactivity



X = p-CH_3O, p-CH_3 and p-F were obtained from extrapolations of log $k_{obs.}$ versus H_o plots through the region $-H_o$ = 5-5.5. This is the region in which the log $k_{obs.}$ versus H_o plots for X = p-Br, m-F and m-Cl show curvature. However, the degree of this curvature decreases in the order m-Cl, m-F, p-Br, and it seems likely that with a more reactive substrate (i.e. p-CH_3O or p-CH_3) such curvature would disappear. This point is raised at this time because the assumption that neither of the plots in figure 14 is fortuitous leads to a mechanistic picture which is consistent with the nature of the acidity function correlations. This picture is developed in the following section.

Table 11

The effect of substituents on reactivity

X	σ^+	log $(k_X/k_{X=H})$ $-H_o$ = 3.66	log $(k_X/k_{X=H})$ $-H_o$ = 6.12
p-CH_3O	-.778	3.88*	4.44*
p-CH_3	-.311	1.51	1.82*
p-F	-.073	0.39	0.32*
H	0	0	0
p-Br	.150	-0.57	-0.53
m-F	.352	-1.27	-1.50
m-Cl	.399	-1.28*	-1.60
m-CF_3	.520	-1.52	
m-NO_2	.674		-3.39

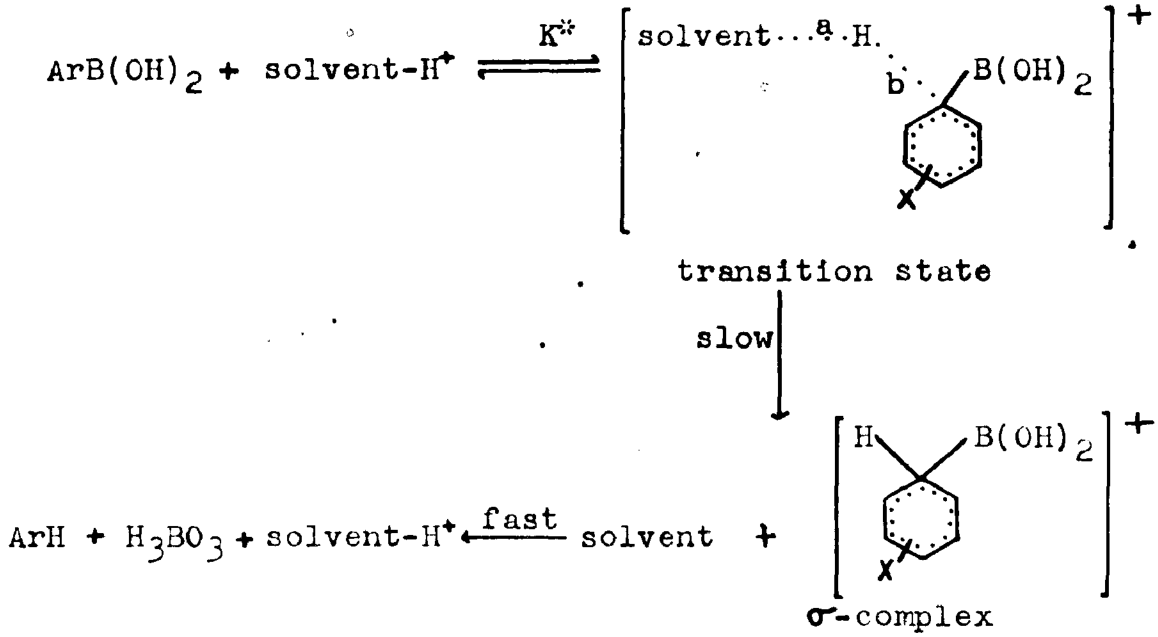
* Obtained by extrapolation of log $k_{obs.}$ versus H_o plots.

VI. The Mechanism of the Reaction

The protonolysis of p-methoxybenzeneboronic acid is general acid-catalyzed and, in aqueous sulfuric acid, the reaction shows a linear dependence of rate on the hydrogen isotope composition of the solvent. It was shown above that two different mechanisms are consistent with both of these facts. These are the A-S_E2 and the concerted A-2 (termolecular) mechanisms.

Electrophilic aromatic substitution reactions have been shown to proceed through a σ-complex. Schubert and Myhre[36] have recently reviewed the evidence and have also shown that the protodecarbonylation of sterically hindered aromatic aldehydes in concentrated solutions of sulfuric acid proceeds through the σ-complex with either the rate of its formation or its decomposition into products being rate-determining, depending on the composition of the acid medium.

The protonolysis of areneboronic acids is just another example of electrophilic aromatic substitution in which the electrophile is a protonating species. If the requirement that the reaction proceeds through a σ-complex intermediate is invoked, then the concerted A-2 mechanism can be eliminated as a possible mechanism. The A-S_E2 mechanism is therefore adopted as the correct one for the protonolysis of areneboronic acids. The mechanism for catalysis by hydronium ion is shown in the following scheme which includes a possible structure for the transition state.



Since this scheme requires a proton transfer from a solvated proton in the rate-determining step, the fact that a substantial solvent hydrogen isotope effect is observed might appear inconsistent with the insignificant effect found by Long and Watson for the protonation of an enolate ion by solvated proton[27]. However the lack of an isotope effect in the latter reaction can be explained by invoking the Hammond postulate[17]. Because the neutralization of an enolate ion by solvated proton requires a collapse of oppositely charged species, one might assume that the transition state closely resembles the reactants in structure, and therefore that the solvent to proton bond in the transition state is essentially intact. In this regard it is interesting to note that for the protonation of 2,4,6-triisopropylbenzaldehyde in 80% H_2SO_4 to form the σ-complex, Schubert and Myhre have reported a value of $k_H/k_D = 2.0$.

By using the structural representation for the transition state in the above mechanistic scheme an attempt will be made to explain the following experimental facts.

1.) The rates in aqueous sulfuric and perchloric acid solutions for the more reactive substrates are correlated by the acidity function.

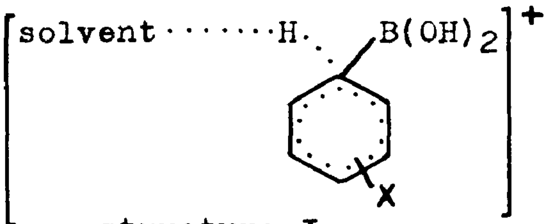
2.) Plots of log $k_{obs.}$ versus $-H_0$ for the less reactive substrates in sulfuric acid solutions below 70% H_2SO_4 show diminishing slopes with decreasing substrate reactivity.

3.) Below 70% H_2SO_4 the activation energy is essentially independent of substrate reactivity, with the decrease in activation entropy accounting for the decrease in substrate reactivity.

4.) For the less reactive substrates there are two kinetically distinguishable acid regions; these are the region below 66% H_2SO_4 and the region above 70% H_2SO_4.

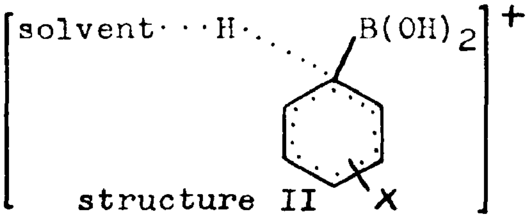
5.) In 74.5% H_2SO_4 the σ^+ constants give an accurate measure of the substituent effects. In 55.4% H_2SO_4 the less reactive substrates have reactivities greater than those predicted by the σ^+ constants.

In the transition state two changes are occurring which result in the formation of the σ-complex; the solvent to proton bond (bond a) is breaking while the proton to ring-carbon bond (bond b) is forming. It is reasonable to assume that the degree of bond breaking at a is directly dependent on the degree of bond formation at b. If in the transition state bond b is essentially completely formed, the transition state will resemble the system: solvent + σ-complex (structure I). This is a situation that might be expected to obtain



structure I

if X is a sufficiently activating (electron releasing) group. Then, since the σ-complex represents one of the possible conjugate acid species of the reactant molecule, for a sufficiently activating substituent, X, a correlation of rate by the acidity function may be expected. On the other hand, if in the transition state bond formation at b has not developed to a significant extent, that is, the bond at a is essentially intact, the transition state will resemble the system: solvent-H^+ + boronic acid (structure II). This latter situation is to be expected if the substituent, X, is a sufficiently



structure II

deactivating (electron withdrawing) group, and, to the extent to which it prevails, a greater dependence of rate on the acid concentration[20,22] rather than on the acidity function is to be expected. One way in which this latter situation would reveal itself would be in the exhibition of abnormally low log $k_{obs.}$ versus $-H_o$ slopes. The slopes of the log $k_{obs.}$ versus $-H_0$ plots below 70% H_2SO_4 suggest that the former situation (structure I) prevails in the case of the more reactive substrates (i.e. X = p-CH_3O and p-CH_3), while for the less reactive substrates (i.e. X = m-F and m-Cl) a prevalence to a certain degree of the latter situation (structure II) appears to be making itself evident.

This picture is consistent with the difference in the activation entropies of the substrates having X = p-CH_3O and m-F. With X = p-CH_3O the activation entropy is expected to be higher because in the formation of the transition state solvent molecules are being "melted away" due to the greater degree of bond breaking at <u>a</u> which leads to greater dispersal of the positive charge into the ring. The fact that the activation energies for both substrates appear to have the same value suggests that the change in potential energy accompanying the formation of the transition state is remarkably independent of the extent of bond formation at <u>b</u>. This would mean that a greater degree of solvation at <u>a</u> in the transition state can make up the increase in energy resulting from a lower degree of bond formation at <u>b</u>.

The existence of two kinetically distinguishable acid regions for the substrates X = m-Cl, m-F and probably p-Br will now be discussed by considering possible structural changes in the transition states which can account for the kinetic complication. Since there are two reactants which combine to form the transition state, either of these might be responsible for the structural change.

The kinetic complication occurs in the region 66-70%

H_2SO_4. As the acidity increases the medium becomes a stronger dehydrating system. One possible explanation, then, is the conversion of the areneboronic acid to a boronic anhydride species, with the latter predominating as the reactant entering the transition state as the acidity is increased. If this is the actual cause for the kinetic complication, then two conclusions can be made. The reaction continues to show first-order kinetics with increasing acidity both through the acid region in which the complication occurs and in the region of higher acidities. This fact requires any intervening anhydride species to be monomeric. Secondly, since now we would have two different species for one of the reactants, the correlation of substituent effects in 74.5% H_2SO_4 by the σ^+ constants would indeed be fortuitous. However this was shown to be unlikely in section V.

The other alternative is that a dramatic change in the nature of the solvated proton occurs in the region 66-70% H_2SO_4. As will be shown this alternative gives a more plausible account for the kinetic complication in this region.

In recent years[2,37,39] there has been an increasing amount of evidence supporting the fact that, in aqueous solutions, protons are hydrated by four water molecules, provided that these are available for hydration. In this regard it is interesting to note that 64.5% H_2SO_4 has the stoichiometric composition $H_2SO_4 \cdot 3H_2O$ and 73.1% H_2SO_4 the composition $H_2SO_4 \cdot 2H_2O$. This means that in solutions having intermediate compositions the greatest number of protons may have the structure $H(H_2O)_3^+$ and $H(H_2O)_2^+$, with the latter becoming more predominant as 73.1% H_2SO_4 is approached. This structural change in the nature of the solvated proton should be accompanied by a change in the acidity of the proton, that is, $H(H_2O)_2^+$ should be a stronger acid than $H(H_2O)_3^+$.

A greater solvated proton acidity would be expected to cause a greater extent of bond breaking at a and bond formation at b. Also, since the reactivity of one of the reactants is enhanced, the activation energy should be smaller. Indeed, the activation energy for X = m-F decreases by 5 kcal. mole^{-1} on passing from below to above the acid region 66-70% H_2SO_4 (table 3). This decrease in activation energy is accompanied by an increase in the solvent hydrogen isotope effect (k_H/k_D changes from 2.4 to 3.0), thus indicating a greater degree of bond breaking at a in the higher acidities.

These arguments can be extended to include an explanation for the correlation by the σ^+ constants of the substituent effects in 74.5% H_2SO_4. Because of the enhanced solvated proton acidity in this solution, the transition states for the less reactive substrates will resemble the corresponding σ-complexes to a greater extent than in lower acid solutions (i.e. 55.4% H_2SO_4). This means that the structure of the transition state will become less dependent on the nature of the substituent, and hence a greater probability for correlation of substituent effects by the σ^+ constants will result. The experimental facts suggest that, in 74.5% H_2SO_4, the structural nature of the transition state has become essentially independent of the substituent.

EXPERIMENTAL PART

I. Materials

The preparations of all but one (X = m-CF_3) of the areneboronic acids used in this study have been referred to previously[23,25]. m-(Trifluoromethyl)-benzeneboronic acid was prepared by the method of Bean and Johnson[3].

m-(Trifluoromethyl)-benzeneboronic acid: - A one liter three necked r.b. flask equipped with a stopcock on the bottom, a stirrer, a condenser and a dropping funnel was charged with 6.0 g. of magnesium, 100 ml. of diethyl ether and 5 ml. of m-bromobenzotrifluoride (Matheson, Coleman and Bell). After refluxing had started m-bromobenzotrifluoride was added dropwise until a total of 50 g. (0.22 mole) had been added to the system, and the system was stirred for an additional thirty minutes. The flask containing the Grignard reagent was then attached to a one liter three necked r.b. flask equipped with a stirrer, cooled in an acetone - dry ice bath, and containing a solution of 25 g. (0.24 mole) of methyl borate in 100 ml. of diethyl ether. The Grignard reagent was added dropwise during one hour, the bath was then removed, and stirring was continued for an additional ten minutes during which 50 ml. of diethyl ether was added to the system to unclog the stirrer. The resulting ether solution was hydrolyzed with 100 ml. of 2.5N hydrochloric acid. The aqueous layer was separated and extracted twice with diethyl ether. The combined ether solutions were extracted with a total of 100 ml. of 5N aqueous sodium hydroxide, then with 40 ml. of water. The combined aqueous extracts surprisingly had a volume of about 250 ml.

Acidification with 6N hydrochloric acid caused the separation of an organic liquid. The aqueous layer was extracted with ether, the combined organic layers were dried with anhydrous magnesium sulfate, and the ether was finally removed by heating on a steam bath. The resulting gummy residue weighed 28.5 g. and had a strong phenolic odor.

The crude product melted when added to hot water. Acetone was added until the oil dissolved, and the resulting solution was treated with norite. An oil separated on cooling. The mixture was heated on a steam bath to remove acetone, then the oil was separated. The aqueous solution was extracted with diethyl ether. The combined organic layers were again dried with anhydrous magnesium sulfate and evaporated to dryness. The residue, a gummy solid, weighed 21 g.

This residue was recrystallized twice from benzene after treatment with norite. The resulting crystals were then dissolved in hot water and the solution was treated with norite. An oil separated from solution but crystallized when cooled to room temperature.

Yield of m-(trifluoromethyl)-benzeneboronic acid:
12.5 g. (30%)

Melting point: sinters when placed in a bath at
60°C. but then dries and finally
melts at 160-162°C.

The boronic acid was converted to the anhydride by heating in an oven at 110°C. for thirty minutes. Recrystallization of the anhydride from benzene yielded 9.5 g. of a crystalline solid (m.p.160-162°C.)

Analyses:

	calculated	found
% carbon	48.91	49.03
% hydrogen	2.35	2.59
neutralization equivalent	171.9	171.8

The deuterium oxide was obtained from the Stuart Oxygen Company, and, according to the supplier, contained 99.5% D_2O. All of the other materials used were either analytical reagent grade or the best grade available commercially.

II. Kinetic Procedures

A. Temperature control

Each of the experiments reported here was done at one of the following temperatures: 25.0, 40.0, 60.0, 69.4 and 79.4°C. Two constant temperature baths were used, each of which controlled the temperature to within ±0.02°C. The differential thermometers in the baths were calibrated against a thermometer standardized at the National Bureau of Standards.

B. Aqueous sulfuric acid

Two different procedures, methods A and B, were used for following the rate of reaction. Method A was used for all except the slowest of the runs with benzeneboronic acid at 60°C. Method B was used in all of the other experiments except for the fastest runs with p-methoxy-, m-fluoro- and p-bromobenzeneboronic acids at 60°C.

The kinetic solutions were prepared by diluting appropriate amounts of sulfuric acid and an aqueous stock solution of the areneboronic acid to the desired volume. For the runs with m-nitrobenzeneboronic acid concentrated sulfuric acid

(96%) was used as solvent for the boronic acid stock solutions. The initial concentration of the boronic acid in the kinetic solution depended on the absorptivity of the boronic acid at the wavelength used to follow the rate of reaction, and was usually in the range 10^{-3} to 10^{-4} molar.

Method A: - A 10 ml. aliquot of the kinetic solution was pipetted into each of several 100 ml. volumetric flasks. These flasks were placed in the bath for appropriate times. The reaction was quenched by simultaneously cooling in an ice bath and diluting to 100 ml. with distilled water.

Method B: - A 125 ml. glass-stoppered Erlenmeyer flask containing the kinetic solution was placed in the bath and, at appropriate times, aliquots were removed with a 10 ml. pipette. The reaction was quenched by adding the aliquots to 100 ml. volumetric flasks containing ice-cold water.

Since each of the boronic acids has an ultraviolet absorption spectrum different from that of its hydrolysis product, it was found that the rate of the reaction could be followed conveniently by measuring the absorbances of the diluted kinetic samples in a Beckman DU spectrophotometer. The absorptivities of each boronic acid and its hydrolysis product at the wavelength used for following the reaction are listed in table 12.

For all but one ($X = m\text{-}NO_2$) of the areneboronic acids, the absorptivity of the corresponding hydrolysis product, relative to that of the boronic acid, is negligibly small; therefore the absorbance of a kinetic sample is essentially a direct

Table 12

Pertinent spectral data for aqueous solutions

		Absorptivity $(\text{mole}^{-1})^{a}$	
X	(mμ)	$XC_6H_4B(OH)_2$	C_6H_5X
H	218	8450	55^{b}
$m\text{-}NO_2$	228	4254	2206
p-Br	232	13700	50
m-F	218	7300	25
p-F	218	7380	
$p\text{-}CH_3$	226	10800	30
$p\text{-}CH_3O$	236	28200^{c}	600^{c}
	238	$>12000^{d}$	70^{d}
m-Cl	228	3000	63

a. In 10-14% aq. H_2SO_4 unless otherwise stated.
b. In 75% aq. H_2SO_4.
c. In water.
d. In 1% aq. HCOOH.

measure of the boronic acid concentration C, in the sample. Consequently rate constants were obtained from slopes of log absorbance versus time plots ($k_{obs.}$ = 2.303 x slope).

For X = $m\text{-}NO_2$, the absorptivities of substrate and product are of the same order of magnitude. For this reason, values of $k_{obs.}$ were obtained from slopes of log C versus time plots, where

$$C = \frac{\text{absorbance} - e_2 C_o}{e_1 - e_2}$$

e_1 = absorptivity of the substrate

e_2 = absorptivity of the product

C_o = initial concentration of the substrate

The amount of acid in a given kinetic solution was determined as follows. A weighed sample of the kinetic solution was diluted to an appropriate volume with water. Aliquots of the resulting solution were then titrated with standardized 0.1N sodium hydroxide.

C. Deuterosulfuric acid solutions

Solutions of deuterium sulfate in deuterium oxide were prepared by the method of Schubert and Burkett[35]. This method involves the evaporation of sulfur trioxide into deuterium oxide in a closed system under reduced pressure. Sulfur trioxide was introduced into the system before the addition of deuterium oxide by evaporating fuming sulfuric acid (20 wt.% SO_3). Despite the precautions taken to keep traces of moisture out of the system, the sulfur trioxide condensed as a silky white crystalline solid.

The kinetic procedure used for the rate measurements in these solutions was the same as with aqueous sulfuric acid (method B) except for minor changes. The total volume of each kinetic solution was only 10 ml., therefore kinetic samples were taken with a 1 ml. pipette and diluted to 10 ml. for the spectral measurements.

D. Solutions varying in solvent hydrogen isotope composition

A prepared solution of deuterium sulfate in deuterium oxide was found to have the composition 43.85% D_2SO_4. The density of this solution was found to be 1.442 and, therefore, the molar concentration of acid was 6.316M.

An aqueous solution of sulfuric acid having the composition 45.73% H_2SO_4 was then prepared. Since the specific gravity of this solution is 1.354 (interpolated)[18], the molar concentration of acid was 6.313M. Experimentally it was found that the combination of 5 ml. of this solution with 5 ml. of the deuteroacid solution resulted in a volume contraction amounting to 0.032% of the expected combined volume. This contraction was regarded as negligibly small.

The kinetic procedure was the same as described in section C above with only one change. Instead of using deuterium oxide, the solvent for the boronic acid stock solutions was either the protoacid or the deuteroacid having the concentration 6.31M. In this regard a minor difficulty was encountered; the boronic acid dissolved very slowly in these two solvents. This difficulty was overcome by pipetting samples of the stock solutions with sufficient care so that no solid boronic acid entered the kinetic solutions. The absorbance readings for these runs were therefore necessarily lower than originally desired.

E. 94.8% Formic acid - 4% EGDE - 1.2% water

A single batch of formic acid (Matheson, Coleman and Bell, 98-100%) was used as the main solvent constituent throughout this work. Karl Fischer titration[29] showed that this solvent contained 1.37% by weight water.

By dissolving a known weight of either sodium formate or sulfuric acid (97.0%) in the formic acid solvent, a stock solution of known concentration was prepared immediately prior to a series of runs. A stock solution of the boronic acid in freshly distilled EGDE (b.p. 85°C.) was also prepared. Appropriate amounts of the formic acid stock solution and solvent were added to a 50 ml. volumetric flask, 2 ml. of the boronic acid stock solution was added, and the volume was raised to 50 ml. with the formic acid solvent. The kinetic solution was then transferred to a 125 ml. glass-stoppered Erlenmeyer flask and the flask was placed in the constant temperature bath. At appropriate times aliquots were removed with a 1 ml. pipette and diluted to 100 ml. with water.

F. Aqueous perchloric and phosphoric acids

The procedures used in these solutions were identical to those described in section B above.

III. Acidity Functions in the Formic Acid Solutions

Only one indicator base, o-nitroaniline (recrystallized from ethyl alcohol, m.p. 72-3°C.) was used in this work. The required amount of a solution of this indicator in diethyl ether was pipetted into a 10 ml. volumetric flask. The flask was then heated on a steam bath to remove the diethyl ether. The solution whose acidity function was desired was added to the flask. The resulting solution was transferred to a colorimeter tube, the tube was placed in a Bausch and Lomb Spectronic Colorimeter, and the percent transmission at the wavelength 380mμ was recorded. The percent transmission of solutions having a value of H_o less than 0.36 decreased with time, the rate of decrease increasing with increasing acidity of the solution. For these solutions timed readings of percent transmission were extrapolated to zero time, and the zero-time percent transmission was used to calculate a value for the acidity function. The value -0.29[31] was used for the pK_a of o-nitroaniline.

It is interesting to note at this time that Hammett and Deyrup[15], and Plattner, Heilbronner and Weber[32] reported no difficulty when o-nitroaniline was used as an indicator in anhydrous formic acid solutions. In the present work both o-nitroaniline and p-nitroanile were found to be unstable in 98.6% aqueous formic acid. It appears, therefore, that the cause of the complication was the presence of water in the solvent.

In formic acid solution the absorptivities at the wavelength 380mμ of o-nitroaniline and its conjugate acid were found to be 3007 $mole^{-1}$ and 56 $mole^{-1}$, respectively. To check the absorptivity of the conjugate acid a solution of the indicator in 75% aqueous sulfuric acid was prepared and the absorptivity of the indicator in this solution was found to be 48 $mole^{-1}$.

Values of the acidity function for solutions of sodium formate and of sulfuric acid in 94.8% formic acid - 4% EGDE - 1.2% water are listed in tables 13 and 14, respectively. The value for 0.1963M sodium formate was obtained by extrapolation of an H_o versus log concentration plot.

Table 13

Acidity functions for solutions of sodium formate

[$NaCHO_2$] molar	[Indicator] molar	% T	$-H_o$
0	.000466	71.4	1.31
0		72.5	1.34
.00508		51.5	0.82
.00508		53.1	0.94
.01016		40.1	0.72
.02032		26.5	0.47
.03048	.0000931	74.0	0.36
.0508		72.4	0.31
.1016		61.1	-0.21
.1963		*	-0.81

* extrapolated, see page 64

Table 14

Acidity functions for solutions of sulfuric acid

[H_2SO_4] molar	[Indicator] molar	% T	$-H_o$
0	.000931	49.5	1.29
.00502		69.4	1.68
.01004		78.9	2.01
.01004		77.9	1.97
.02008	.00466	37.1	2.20
.03012		43.8	2.43
.0502		46.9	2.58
.1496		51.8	3.06

TABLES OF DATA

Benzeneboronic acid

Run I_s-21

71.1% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
13	2.20	.342
18	1.875	.273
23	1.592	.202
30	1.105	.043
40	.751	-.124
50	.460	-.337
60	.318	-.498
66	.243	-.614

$k_{obs.}$: 6.95×10^{-4} sec.$^{-1}$

Run I_s-22

70.9% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
6	1.396	.145
10	1.149	.060
15	.915	-.039
22	.684	-.165
30	.480	-.319
40	.294	-.532
55	.163	-.788

$k_{obs.}$: 7.31×10^{-4} sec.$^{-1}$

Run I_s-23

60.0% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
10	1.620	.210
110	1.312	.118
205	1.078	.033
375	.739	-.131
520	.537	-.270
885	.245	-.611

$k_{obs.}$: 3.61×10^{-5} sec.$^{-1}$

Benzeneboronic acid

Run I_s-24

$60.0\%\ H_2SO_4$; 60°

time (minutes)	absorbance	log absorbance
10	1.554	.191
120	1.256	.099
240	.958	-.019
393	.688	-.162
470	.598	-.223
720	.339	-.470
945	.214	-.670
1205	.114	-.943

$k_{obs.}$: 3.61×10^{-5} sec.$^{-1}$

Run I_s-25

$67.4\%\ H_2SO_4$; 60°

5	1.713	.234
20	1.402	.147
40	1.051	.022
60	.761	-.119
90	.498	-.303
130	.265	-.577
180	.123	-.910

$k_{obs.}$: 2.51×10^{-4} sec.$^{-1}$

Run I_s-26

$67.5\%\ H_2SO_4$; 60°

5	1.671	.223
15	1.482	.171
30	1.199	.079
45	.955	-.020
70	.677	-.169
105	.396	-.402
144	.215	-.668
175	.129	-.889

$k_{obs.}$: 2.55×10^{-4} sec.$^{-1}$

Benzeneboronic acid

Run I_s-27

74.4% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
4	2.09	.320
7	1.397	.145
9	1.105	.043
12	.683	-.166
15	.381	-.419
18	.205	-.688
21	.132	-.879

$k_{obs.}$: 2.72×10^{-3} sec.$^{-1}$

Run I_s-28

74.6% H_2SO_4; 60°

5	1.751	.243
7	1.345	.129
10	.840	-.076
13	.530	-.276
15	.380	-.420
17	.246	-.609
19	.195	-.710
21	.136	-.867

$k_{obs.}$: 2.67×10^{-3} sec.$^{-1}$

Run I_s-29

62.6% H_2SO_4; 60°

10	1.748	.243
70	1.397	.145
130	1.068	.029
180	.878	-.057
315	.482	-.317
480	.241	-.618
530	.193	-.714
570	.145	-.839

$k_{obs.}$: 7.06×10^{-5} sec.$^{-1}$

Benzeneboronic acid

Run I_s-30

62.6% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
10	1.738	.240
60	1.446	.160
120	1.132	.054
180	.858	-.067
270	.598	-.223
355	.430	-.367
495	.226	-.646
560	.164	-.785

$k_{obs.}$: 6.97 x 10^{-5} sec.$^{-1}$

Run I_s-31

54.7% H_2SO_4; 60°

0	1.583	.200
300	1.321	.121
1090	.760	-.119
1419	.617	-.210
2039	.392	-.407
2638	.237	-.625

$k_{obs.}$: 1.19 x 10^{-5} sec.$^{-1}$

Run I_s-32

54.4% H_2SO_4; 60°

0	1.613	.208
734	1.005	.002
1024	.838	-.077
1368	.641	-.193
2193	.390	-.409
2506	.305	-.516
3127	.193	-.714
3730	.135	-.870

$k_{obs.}$: 1.11 x 10^{-5} sec.$^{-1}$

Benzeneboronic acid

Run I_s-33

49.8% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
0	1.671	.223
1034	1.269	.104
2499	.858	-.067
3716	.602	-.220
6680	.272	-.565
7211	.238	-.623
7940	.190	-.721

$k_{obs.}$: 4.54×10^{-6} sec.$^{-1}$

Run I_s-34

50.3% H_2SO_4; 60°

0	1.675	.224
1033	1.269	.104
2496	.852	-.070
3715	.595	-.226
6681	.260	-.585
7208	.223	-.652
7936	.170	-.770

$k_{obs.}$: 4.72×10^{-6} sec.$^{-1}$

Run I_s-35

44.8% H_2SO_4; 60°

0	1.213	.084
1722	.967	-.015
2878	.816	-.088
5683	.537	-.270
6379	.472	-.326
7179	.430	-.367

$k_{obs.}$: 2.42×10^{-6} sec.$^{-1}$

Benzeneboronic acid

Run I_s-36

$44.8\%\ H_2SO_4;\ 60^\circ$

time (minutes)	absorbance	log absorbance
0	1.213	.084
1720	.968	-.014
2878	.835	-.078
5683	.565	-.248
6379	.520	-.284
7180	.457	-.340

$k_{obs.}$: 2.27×10^{-6} sec.$^{-1}$

Run I_s-39

$46.6\%\ H_2SO_4;\ 60^\circ$

time (minutes)	absorbance	log absorbance
0	1.806	.257
1410	1.445	.160
2188	1.254	.098
2948	1.109	.045
6648	.593	-.227
8702	.401	-.397
9226	.346	-.461
11000	.269	-.570

$k_{obs.}$: 2.92×10^{-6} sec.$^{-1}$

Run I_s-40

$45.3\%\ H_2SO_4;\ 60^\circ$

time (minutes)	absorbance	log absorbance
0	1.803	.256
1410	1.550	.190
2188	1.428	.155
2948	1.311	.118
6648	.831	-.080
9226	.595	-.226
10752	.510	-.292

$k_{obs.}$: 2.01×10^{-6} sec.$^{-1}$

Benzeneboronic acid

Run I_s-41

42.9% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
0	1.795	.254
1410	1.629	.212
6648	1.063	.027
9226	.866	-.063
10980	.764	-.117
16690	.477	-.322

$k_{obs.}$: 1.33×10^{-6} sec.$^{-1}$

Run I_s-42

41.0% H_2SO_4; 60°

0	1.810	.258
1410	1.662	.221
6648	1.238	.093
9226	1.075	.032
10980	.981	-.008
16690	.681	-.167

$k_{obs.}$: 9.27×10^{-7} sec.$^{-1}$

Run I_s-43

74.8% H_2SO_4; 25°

39	.792	-.101
106	.507	-.295
176	.314	-.503
243	.185	-.733
315	.093	-1.032

$k_{obs.}$: 1.17×10^{-4} sec.$^{-1}$

Benzeneboronic acid

Run I_s-44

72.4% H_2SO_4; 25°

time (minutes)	absorbance	log absorbance
43	.937	-.028
246	.562	-.250
319	.461	-.336
489	.283	-.548
597	.186	-.731

$k_{obs.}$: 4.72×10^{-5} sec.$^{-1}$

Run I_s-45

70.3% H_2SO_4; 25°

45	1.031	.013
323	.747	-.127
595	.520	-.284
704	.465	-.332
820	.395	-.403
945	.330	-.482

$k_{obs.}$: 2.07×10^{-5} sec.$^{-1}$

Run I_s-46

75.0% H_2SO_4; 40°

5	1.646	.216
10.5	1.455	.163
15	1.296	.113
24	1.044	.019
30.25	.880	-.056
38.25	.711	-.148

$k_{obs.}$: 4.29×10^{-4} sec.$^{-1}$

Benzeneboronic acid

Run I_s-47

$72.6\%\ H_2SO_4$; 40°

time (minutes)	absorbance	log absorbance
12	1.434	.157
29	1.169	.068
50	.906	-.043
72	.706	-.151
96	.512	-.291
123	.354	-.451

$k_{obs.}$: 2.04×10^{-4} sec.$^{-1}$

Run I_s-48

$70.8\%\ H_2SO_4$; 40°

8	1.646	.216
33	1.426	.154
68	1.139	.057
138	.743	-.129
163	.631	-.200

$k_{obs.}$: 1.03×10^{-4} sec.$^{-1}$

m-Nitrobenzeneboronic acid

Run II_s-3

C_o: 1.021 x 10^{-4}M; 92.1% H_2SO_4; 60°

time (minutes)	absorbance	log C
15	.429	-3.988
53	.400	-4.055
95	.384	-4.070
145	.358	-4.174
250	.315	-4.344
341	.284	-4.527
584	.274	-4.883

$k_{obs.}$: 6.07 x 10^{-5} sec.$^{-1}$

Run II_s-4

C_o: 1.021 x 10^{-4}M; 91.6% H_2SO_4; 60°

18	.413	-4.024
55	.385	-4.094
97	.370	-4.137
148	.350	-4.201
252	.301	-4.417
343	.287	-4.506
586	.273	-4.900

$k_{obs.}$: 5.92 x 10^{-5} sec.$^{-1}$

Run II_s-5

C_o: 1.021 x 10^{-4}M; 89.3% H_2SO_4; 60°

20	.424	-3.999
58	.396	-4.065
150	.364	-4.155
255	.341	-4.234
345	.315	-4.344
589	.296	-4.608
1069	.257	-5.094

$k_{obs.}$: 3.99 x 10^{-5} sec.$^{-1}$

m-Nitrobenzeneboronic acid

Run II_s-6

C_o: 1.021 x 10^{-4}M; 89.4% H_2SO_4; 60°

time (minutes)	absorbance	log C
22	.422	-4.004
60	.398	-4.060
152	.362	-4.161
257	.339	-4.241
347	.314	-4.349
591	.289	-4.582
1071	.254	-5.094

$k_{obs.}$: 3.99 x 10^{-5} sec.$^{-1}$

Run II_s-7

C_o: 1.376 x 10^{-4}M; 97.0% H_2SO_4; 60°

27	.551	-3.907
47	.514	-3.976
69	.476	-4.063
116	.422	-4.226
166	.384	-4.395
217	.352	-4.617
263	.336	-4.793
327	.325	-4.976

$k_{obs.}$: 1.37 x 10^{-4} sec.$^{-1}$

Run II_s-8

C_o: 1.376 x 10^{-4}M; 96.7% H_2SO_4; 60°

29	.543	-3.920
49	.509	-3.984
71	.474	-4.068
119	.417	-4.245
168	.382	-4.400
222	.349	-4.645
265	.333	-4.836
329	.322	-5.043

$k_{obs.}$: 1.45 x 10^{-4} sec.$^{-1}$

m-Nitrobenzeneboronic acid

Run II_s-9

C_o: 1.376 x 10^{-4}M; 88.5% H_2SO_4; 60°

time (minutes)	absorbance	log C
32	.570	-3.873
169	.509	-3.986
330	.452	-4.128
549	.407	-4.285
721	.374	-4.453
857	.354	-4.599
1463	.319	-5.122

$k_{obs.}$: 3.27 x 10^{-5} sec.$^{-1}$

Run II_s-10

C_o: 1.376 x 10^{-4}M; 88.5% H_2SO_4; 60°

34	.574	-3.867
171	.506	-3.993
332	.459	-4.108
551	.406	-4.294
723	.374	-4.453
860	.359	-4.558
1466	.323	-5.019

$k_{obs.}$: 3.22 x 10^{-5} sec.$^{-1}$

Run II_s-11

C_o: 1.258 x 10^{-4}M; 83.0% H_2SO_4; 60°

21	.535	-3.886
198	.516	-3.920
485	.481	-3.986
1015	.439	-4.088
1211	.425	-4.128
1415	.413	-4.165
1664	.399	-4.212

$k_{obs.}$: 7.71 x 10^{-6} sec.$^{-1}$

m-Nitrobenzeneboronic acid

Run II_s-12

C_o: 1.258 x 10^{-4}M; 82.7% H_2SO_4; 60°

time (minutes)	absorbance	log C
23	.534	-3.888
200	.511	-3.929
487	.489	-3.972
1017	.439	-4.089
1213	.426	-4.125
1417	.416	-4.155
1666	.401	-4.205

$k_{obs.}$: 7.48 x 10^{-6} sec.$^{-1}$

Run II_s-13

C_o: 1.258 x 10^{-4}M; 78.8% H_2SO_4; 60°

25	.537	-3.883
489	.513	-3.925
1035	.492	-3.966
1215	.485	-3.980
1671	.469	-4.015
1897	.462	-4.031
2742	.439	-4.089

$k_{obs.}$: 2.87 x 10^{-6} sec.$^{-1}$

Run II_s-14

C_o: 1.258 x 10^{-4}M; 78.5% H_2SO_4; 60°

27	.529	-3.897
491	.511	-3.929
1037	.495	-3.960
1217	.489	-3.972
1673	.470	-4.012
1899	.469	-4.015
2744	.444	-4.075
4165	.407	-4.184

$k_{obs.}$: 2.65 x 10^{-6} sec.$^{-1}$

m-Nitrobenzeneboronic acid

Run II_s-15

C_o: 1.258 x 10^{-4}M; 73.7% H_2SO_4; 60°

time (minutes)	absorbance	log C
30	.532	-3.892
500	.529	-3.897
1225	.522	-3.909
1905	.514	-3.923
2690	.506	-3.938
5630	.483	-3.984
7360	.474	-4.004

$k_{obs.}$: 6.90 x 10^{-7} sec.$^{-1}$

Run II_s-16

C_o: 1.258 x 10^{-4}M; 73.6% H_2SO_4; 60°

30	.535	-3.886
500	.527	-3.900
1225	.521	-3.911
1905	.514	-3.923
2690	.502	-3.946
5630	.474	-4.004
7360	.458	-4.040

$k_{obs.}$: 7.64 x 10^{-7} sec.$^{-1}$

p-Bromobenzeneboronic acid

Run III_s-1

74.5% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
5	.630	-.201
10	.533	-.273
17	.414	-.383
26	.300	-.523
40	.167	-.773
55	.100	-1.000

$k_{obs.}$: 6.15 x 10^{-4} sec.$^{-1}$

Run III_s-2

69.4% H_2SO_4; 60°

13	.703	-.153
36	.591	-.228
67	.459	-.338
115	.343	-.465
180	.207	-.684

$k_{obs.}$: 1.22 x 10^{-4} sec.$^{-1}$

Run III_s-3

65.2% H_2SO_4; 60°

19	.710	-.149
182	.501	-.300
368	.338	-.471
468	.290	-.538
670	.175	-.757

$k_{obs.}$: 3.45 x 10^{-5} sec.$^{-1}$

p-Bromobenzeneboronic acid

Run III_s-5

77.0% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
4	.727	-.139
5	.661	-.180
6	.611	-.214
8	.533	-.273
10	.464	-.334
12	.392	-.407
14	.322	-.492
16	.284	-.547
20	.209	-.680

$k_{obs.}$: 1.29×10^{-3} sec.$^{-1}$

Run III_s-6

61.2% H_2SO_4; 60°

15	.879	-.056
155	.801	-.096
485	.621	-.207
1155	.394	-.405
1365	.317	-.499
1530	.288	-.541
1725	.226	-.646
2530	.111	-.955

$k_{obs.}$: 1.32×10^{-5} sec.$^{-1}$

p-Bromobenzeneboronic acid

Run III_s-7

53.4% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
20	.868	-.062
770	.775	-.111
1610	.675	-.171
2280	.631	-.200
2960	.554	-.257
3660	.516	-.287

$k_{obs.}$: 2.37×10^{-6} sec.$^{-1}$

Run III_s-8

47.7% H_2SO_4; 60°

25	.890	-.051
775	.854	-.069
2280	.786	-.105
3720	.722	-.142
5200	.675	-.171

$k_{obs.}$: 8.97×10^{-7} sec.$^{-1}$

m-Fluorobenzeneboronic acid

Run IV_s-1

83.8% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
3	.681	-.167
6	.522	-.282
9	.390	-.409
12	.309	-.510
15	.275	-.561
18	.238	-.623
21	.242	-.616
24	.259	-.587

From the initial slope; $k_{obs.}$: 1.57×10^{-3} sec.$^{-1}$

Run IV_s-2

78.5% H_2SO_4; 60°

11	1.106	.044
25	.938	-.028
40	.700	-.155
64	.481	-.318
90	.330	-.482
127	.184	-.735
150	.124	-.907

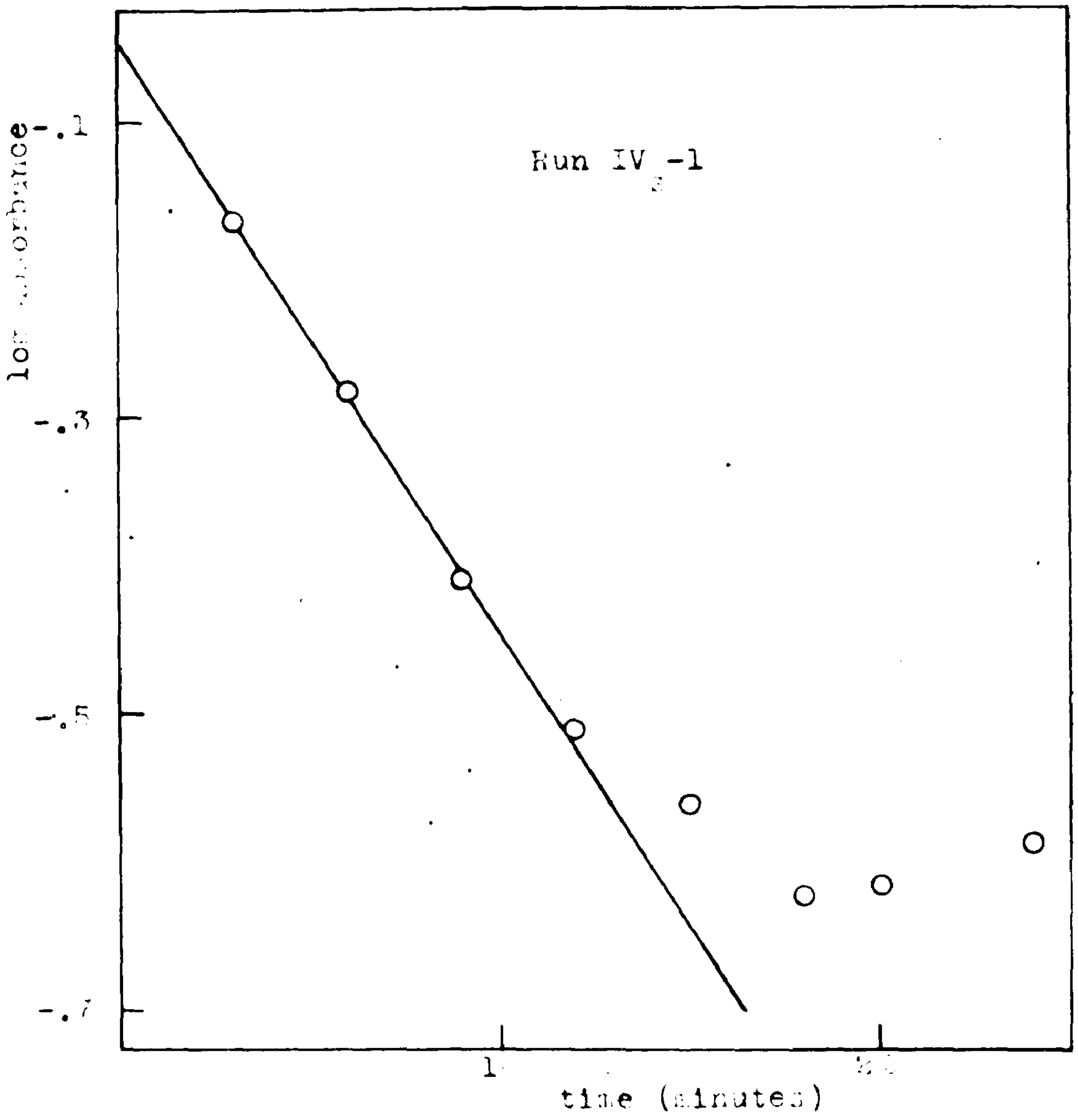
$k_{obs.}$: 2.65×10^{-4} sec.$^{-1}$

Run IV_s-3

74.1% H_2SO_4; 60°

14	1.262	.101
66	1.068	.029
130	.822	-.085
189	.721	-.142
239	.602	-.220
299	.492	-.308
413	.347	-.460
535	.222	-.654

$k_{obs.}$: 5.48×10^{-5} sec.$^{-1}$


Run IV_3-1
log absorbance
-.1
-.3
-.5
-.7
1
2
time (minutes)

m-Fluorobenzeneboronic acid

Run IV_s-4

$68.5\%\ H_2SO_4$; 60°

time (minutes)	absorbance	log absorbance
16	1.243	.094
132	1.189	.075
240	1.103	.043
415	.981	-.008
538	.924	-.034
723	.810	-.092

$k_{obs.}$: 1.02×10^{-5} sec.$^{-1}$

Run IV_s-5

$62.2\%\ H_2SO_4$; 60°

0	1.692	.228
1120	1.467	.167
2570	1.174	.070
5175	.795	-.100
10890	.323	-.491
12570	.255	-.594

$k_{obs.}$: 2.53×10^{-6} sec.$^{-1}$

Run IV_s-6

$55.2\%\ H_2SO_4$; 60°

0	1.639	.215
1120	1.591	.212
5175	1.380	.140
10890	1.089	.037
12570	1.025	.011
15660	.891	-.050
19750	.755	-.122

$k_{obs.}$: 6.62×10^{-7} sec.$^{-1}$

m-Fluorobenzeneboronic acid

Run IV_s-19

$69.4\%\ H_2SO_4$; 60°

time (minutes)	absorbance	log absorbance
9	1.115	.047
120	1.030	.013
250	.930	-.032
441	.744	-.128
617	.679	-.168
1407	.345	-.462

$k_{obs.}$: 1.42×10^{-5} sec.$^{-1}$

Run IV_s-20

$70.3\%\ H_2SO_4$; 60°

time (minutes)	absorbance	log absorbance
11	1.059	.025
121	.976	-.011
252	.812	-.090
443	.660	-.181
619	.564	-.249
1409	.212	-.674

$k_{obs.}$: 1.56×10^{-5} sec.$^{-1}$

Run IV_s-7

$83.3\%\ H_2SO_4$; 25°

time (minutes)	absorbance	log absorbance
25	.751	-.124
168	.438	-.359
305	.253	-.597
479	.136	-.867

$k_{obs.}$: 6.56×10^{-5} sec.$^{-1}$

m-Fluorobenzeneboronic acid

Run IV$_s$-8

80.9% H_2SO_4; 25°

time (minutes)	absorbance	log absorbance
27	.901	-.045
310	.642	-.193
584	.455	-.342
655	.420	-.377
715	.381	-.419

$k_{obs.}$: 2.08×10^{-5} sec.$^{-1}$

Run IV$_s$-9

79.0% H_2SO_4; 25°

31	.961	-.017
588	.712	-.148
710	.660	-.181
830	.620	-.208
950	.581	-.236

$k_{obs.}$: 9.12×10^{-6} sec.$^{-1}$

Run IV$_s$-10

84.2% H_2SO_4; 40°

10	.918	-.037
23	.698	-.156
37	.537	-.270
47	.441	-.356
68	.300	-.523
91	.221	-.656

$k_{obs.}$: 3.31×10^{-4} sec.$^{-1}$

m-Fluorobenzeneboronic acid

Run IV_s-11

82.4% H_2SO_4; 40°

time (minutes)	absorbance	log absorbance
14	.992	-.004
43	.752	-.124
73	.561	-.251
118	.377	-.424
153	.266	-.575
195	.201	-.697

$k_{obs.}$: 1.51×10^{-4} sec.$^{-1}$

Run IV_s-12

80.4% H_2SO_4; 40°

18	1.091	.038
77	.824	-.084
123	.672	-.173
199	.480	-.319
306	.286	-.544
369	.213	-.672

$k_{obs.}$: 7.66×10^{-5} sec.$^{-1}$

Run IV_s-13

64.9% H_2SO_4; 69.4°

17	1.144	.058
180	1.025	.011
371	.941	-.026
540	.800	-.097
690	.710	-.149
1065	.549	-.260

$k_{obs.}$: 1.17×10^{-5} sec.$^{-1}$

m-Fluorobenzeneboronic acid

Run IV_s-14

61.0% H_2SO_4; 69.4°

time (minutes)	absorbance	log absorbance
21	1.127	.052
375	1.011	.005
693	.913	-.040
1069	.850	-.071
1315	.781	-.107
2455	.551	-.259

$k_{obs.}$: 5.25×10^{-6} sec.$^{-1}$

Run IV_s-15

56.9% H_2SO_4; 69.4°

26	1.167	.067
380	1.098	.041
698	1.046	.020
1072	.999	.000
1319	.959	-.018
2460	.807	-.093

$k_{obs.}$: 2.51×10^{-6} sec.$^{-1}$

Run IV_s-16

65.4% H_2SO_4; 79.4°

4	1.195	.077
138	.979	-.009
263	.765	-.116
372	.628	-.202
500	.483	-.316
613	.384	-.416

$k_{obs.}$: 3.16×10^{-5} sec.$^{-1}$

m-Fluorobenzeneboronic acid

Run IV_s-17

61.3% H_2SO_4; 79.4°

time (minutes)	absorbance	log absorbance
17	1.235	.092
200	1.060	.025
376	.917	-.038
510	.836	-.078
616	.757	-.121
728	.685	-.164

$k_{obs.}$: 1.37×10^{-5} sec.$^{-1}$

Run IV_s-18

57.4% H_2SO_4; 79.4°

time (minutes)	absorbance	log absorbance
20	1.238	.093
268	1.115	.047
504	1.017	.007
730	.939	-.027
1354	.730	-.137

$k_{obs.}$: 6.62×10^{-6} sec.$^{-1}$

m-(Trifluoromethyl)-benzeneboronic acid

Run V_s-6

55.4% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
0	1.639	.215
1120	1.591	.202
5175	1.380	.140
10890	1.089	.037
12570	1.025	.011
15660	.891	-.050
19750	.755	-.122

$k_{obs.}$: 3.16×10^{-7} sec.$^{-1}$

p-Fluorobenzeneboronic acid

Run VI$_s$-1

$64.7\%\ H_2SO_4$; 60°

time (minutes)	absorbance	log absorbance
5	.769	-.114
11	.749	-.126
21	.635	-.197
30	.526	-.279
42	.422	-.375
62	.309	-.510
81	.214	-.670
107	.089	-1.051

$k_{obs.}$: 2.85×10^{-4} sec.$^{-1}$

Run VI$_s$-2

$60.1\%\ H_2SO_4$; 60°

14	.781	-.107
32	.691	-.161
57	.608	-.216
79	.561	-.251
109	.457	-.340
135	.420	-.377
181	.328	-.484

$k_{obs.}$: 8.67×10^{-5} sec.$^{-1}$

Run VI$_s$-3

$54.9\%\ H_2SO_4$; 60°

18	.791	-.102
71	.708	-.150
137	.624	-.205
192	.600	-.222
254	.539	-.268
327	.442	-.355
412	.407	-.390
556	.283	-.548

$k_{obs.}$: 3.11×10^{-5} sec.$^{-1}$

p-Fluorobenzeneboronic acid

Run VI_a-4

49.5% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
24	.789	-.103
184	.684	-.165
366	.611	-.214
560	.579	-.237
780	.501	-.300
1360	.313	-.505
1625	.279	-.554

$k_{obs.}$: 1.09×10^{-5} sec.$^{-1}$

p-Tolylboronic acid

Run VII_s-1

55.5% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
15	.764	-.117
22	.661	-.180
30	.514	-.289
41	.402	-.396
50	.314	-.503
59	.225	-.648
68	.169	-.772
79	.142	-.848

$k_{obs.}$: 4.38×10^{-4} sec.$^{-1}$

Run VII_s-2

49.6% H_2SO_4; 60°

18	.900	-.046
43	.740	-.131
55	.667	-.176
71	.615	-.211
90	.538	-.269
111	.440	-.357
130	.397	-.401
151	.321	-.494

$k_{obs.}$: 1.26×10^{-4} sec.$^{-1}$

Run VII_s-3

40.7% H_2SO_4; 60°

25	.996	-.002
75	.918	-.037
138	.838	-.077
201	.792	-.101
294	.709	-.149
375	.622	-.206
509	.525	-.280
686	.431	-.366

$k_{obs.}$: 2.31×10^{-5} sec.$^{-1}$

p-Tolylboronic acid

Run VII_a-4

28.6% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
34	.997	-.001
134	.956	-.020
299	.933	-.030
513	.922	-.035
690	.898	-.047
1320	.781	-.107
1580	.768	-.115

$k_{obs.}$: 2.85×10^{-6} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run VIII$_s$-1

29.6% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
4	1.353	.131
6	1.274	.105
9	1.164	.066
11	1.091	.038
15	.931	-.031
18	.843	-.074
22	.735	-.134
27	.630	-.201

$k_{obs.}$: 5.60×10^{-4} sec.$^{-1}$

Run VIII$_s$-2

20.3% H_2SO_4; 60°

15	.899	-.046
22	.871	-.060
35	.770	-.114
47	.727	-.139
57	.695	-.158
67	.628	-.202
86	.553	-.257
104	.481	-.318

$k_{obs.}$: 1.15×10^{-4} sec.$^{-1}$

Run VIII$_s$-3

10.1% H_2SO_4; 60°

18	.938	-.028
49	.908	-.042
84	.863	-.064
120	.826	-.083
197	.741	-.130
300	.640	-.194
430	.531	-.275
542	.454	-.343

$k_{obs.}$: 2.30×10^{-5} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run VIII$_s$-4

5.14% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
20	.905	-.043
80	.880	-.056
182	.831	-.080
313	.796	-.099
432	.743	-.129
544	.709	-.149
1234	.522	-.282
1328	.500	-.301

$k_{obs.}$: 7.57×10^{-6} sec.$^{-1}$

Run VIII$_s$-5

3.11% H_2SO_4; 60°

19	.969	-.014
180	.932	-.031
495	.852	-.070
1196	.739	-.131
1806	.620	-.208
2608	.529	-.277
4350	.334	-.476
5405	.267	-.574

$k_{obs.}$: 4.01×10^{-6} sec.$^{-1}$

Run VIII$_s$-8

30.1% H_2SO_4; 40°

16	1.506	.178
66	1.202	.080
128	.901	-.045
250	.521	-.283
306	.396	-.402
415	.232	-.635

$k_{obs.}$: 7.78×10^{-5} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run VIII$_s$-9

24.7% H_2SO_4; 40°

time (minutes)	absorbance	log absorbance
20	1.549	.190
70	1.410	.149
254	1.012	.005
377	.819	-.087
531	.615	-.211

$k_{obs.}$: 2.99×10^{-5} sec.$^{-1}$

Run VIII$_s$-10

20.1% H_2SO_4; 40°

22	1.584	.200
262	1.311	.118
535	1.040	.017

$k_{obs.}$: 1.35×10^{-5} sec.$^{-1}$

m-Chlorobenzeneboronic acid

Run IX_s-1

59.3% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
11	.905	-.043
2094	.791	-.101
4050	.670	-.174
5542	.610	-.214
6390	.564	-.249
7290	.531	-.275

$k_{obs.}$: 1.24×10^{-6} $sec.^{-1}$

Run IX_s-2

62.9% H_2SO_4; 60°

13	.916	-.038
732	.824	-.084
2100	.675	-.171
2770	.607	-.217
3305	.551	-.259
4518	.462	-.335
7115	.335	-.475

$k_{obs.}$: 2.58×10^{-6} $sec.^{-1}$

Run IX_s-3

66.3% H_2SO_4; 60°

15	.906	-.043
737	.761	-.119
1312	.660	-.181
2101	.489	-.311
2775	.396	-.402
3306	.351	-.455

$k_{obs.}$: 4.85×10^{-6} $sec.^{-1}$

m-Chlorobenzeneboronic acid

Run IX_s-4

69.9% H_2SO_4; 60°

time (minutes)	absorbance	log absorbance
17	.911	-.041
172	.819	-.087
491	.675	-.171
737	.551	-.259
1312	.377	-.424
2101	.190	-.721

$k_{obs.}$: 1.19×10^{-5} sec.$^{-1}$

Run IX_s-5

74.5% H_2SO_4; 60°

14	.357	-.447
46	.311	-.507
94	.271	-.567
162	.226	-.646
209	.182	-.740
269	.152	-.818
386	.103	-.987

$k_{obs.}$: 5.60×10^{-5} sec.$^{-1}$

Run IX_s-6

79.9% H_2SO_4; 60°

5	.345	-.462
10	.331	-.480
21	.268	-.572
30	.213	-.672
40	.182	-.740
51	.148	-.830
63	.107	-.971

$k_{obs.}$: 3.33×10^{-4} sec.$^{-1}$

p-Tolylboronic acid

Run VII_{pe}-1

64.7% $HClO_4$; 25°

time (minutes)	absorbance	log absorbance
5	.861	-.065
16	.741	-.130
26	.641	-.193
35	.568	-.246
45	.491	-.310
55	.417	-.380
66	.358	-.447
75	.323	-.491

$k_{obs.}$: 2.35×10^{-4} sec.$^{-1}$

Run VII_{pe}-2

60.5% $HClO_4$; 25°

time (minutes)	absorbance	log absorbance
7	1.202	.080
39	1.105	.043
64	1.045	.019
98	.955	-.020
143	.872	-.060
171	.820	-.086
203	.758	-.120
230	.718	-.144

$k_{obs.}$: 3.82×10^{-5} sec.$^{-1}$

Run VII_{pe}-3

56.3% $HClO_4$; 25°

time (minutes)	absorbance	log absorbance
14	1.196	.078
64	1.169	.068
154	1.145	.059
213	1.111	.046
265	1.078	.033
413	1.022	.009
520	.978	-.008

$k_{obs.}$: 6.71×10^{-6} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run VIII$_{pe}$-1

33.9% $HClO_4$; 60°

time (minutes)	absorbance	log absorbance
10	.720	-.143
19	.500	-.301
30	.285	-.545
51	.109	-.963

$k_{obs.}$: 7.66×10^{-4} sec.$^{-1}$

Run VIII$_{pe}$-2

31.0% $HClO_4$; 60°

time (minutes)	absorbance	log absorbance
13	.698	-.156
33	.380	-.420
53	.195	-.710
71	.117	-.932

$k_{obs.}$: 5.11×10^{-4} sec.$^{-1}$

Run VIII$_{pe}$-3

25.5% $HClO_4$; 60°

time (minutes)	absorbance	log absorbance
10	.775	-.111
19	.701	-.154
30	.570	-.244
40	.533	-.273
60	.399	-.399
80	.295	-.530
100	.240	-.620

$k_{obs.}$: 2.22×10^{-4} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_{pe}$-4

18.6% $HClO_4$; 60°

time (minutes)	absorbance	log absorbance
12	.780	-.108
21	.744	-.128
32	.714	-.146
42	.671	-.173
62	.602	-.220
82	.562	-.250
102	.500	-.301
119	.461	-.336

$k_{obs.}$: 8.22×10^{-5} sec.$^{-1}$

Benzeneboronic acid

Run I_{ph}-5

74.3% H_3PO_4; 60°

time (minutes)	absorbance	log absorbance
10	1.256	.099
15	1.178	.071
20	1.022	.009
25	.943	-.026
35	.757	-.121
45	.614	-.212
55	.471	-.327
65	.375	-.426
70	.341	-.467
75	.288	-.541
80	.259	-.587
85	.234	-.631
90	.192	-.717
95	.177	-.752
100	.160	-.796

$k_{obs.}$: 3.86×10^{-4} sec.$^{-1}$

Run I_{ph}-6

65.7% H_3PO_4; 60°

25	1.644	.216
60	1.509	.179
85	1.387	.142
142	1.170	.068
214	.962	-.017
295	.753	-.123
350	.622	-.206
550	.339	-.470
715	.195	-.710

$k_{obs.}$: 5.04×10^{-5} sec.$^{-1}$

Benzeneboronic acid

Run I_{ph}-7

52.9% H_3PO_4; 60°

time (minutes)	absorbance	log absorbance
30	1.539	.187
145	1.494	.174
420	1.389	.143
720	1.254	.098
1425	1.017	.007
1750	.914	-.039
2795	.622	-.206

$k_{obs.}$: 5.41×10^{-6} sec.$^{-1}$

Run I_{ph}-9

82.7% H_3PO_4; 25°

11	1.421	.153
26	1.258	.100
50	1.008	.003
79	.740	-.131
111	.534	-.273
171	.260	-.585
200	.159	-.799
226	.102	-.991

p-Tolylboronic acid

Run VII$_{ph}$-1

72.4% H_3PO_4; 60°

time (minutes)	absorbance	log absorbance
2	.530	-.276
5	.252	-.599
8	.110	-.959
11	.026	-1.569

$k_{obs.}$: 4.38×10^{-3} sec.$^{-1}$

Run VII$_{ph}$-2

66.6% H_3PO_4; 60°

10	.790	-.102
18	.480	-.319
25	.325	-.488
34	.177	-.752
41	.098	-1.011
50	.045	-1.347

$k_{obs.}$: 1.11×10^{-3} sec.$^{-1}$

Run VII$_{ph}$-3

56.3% H_3PO_4; 60°

15	1.005	.002
41	.842	-.075
83	.671	-.173
128	.520	-.284
145	.461	-.336
181	.388	-.411
237	.270	-.569
328	.144	-.842

$k_{obs.}$: 9.95×10^{-5} sec.$^{-1}$

p-Tolylboronic acid

Run VII_{ph}-4

$42.7\%\ H_3PO_4$; 60°

time (minutes)	absorbance	log absorbance
20	1.030	.013
700	.730	-.137
1045	.612	-.213
1495	.470	-.327
2155	.330	-.482

$k_{obs.}$: 8.81×10^{-6} sec.$^{-1}$

Run VII_{ph}-5

$71.3\%\ H_3PO_4$; 25°

time (minutes)	absorbance	log absorbance
7	1.074	.031
12	1.007	.003
20	.933	-.030
30	.825	-.084
40	.734	-.134
50	.660	-.181
62	.582	-.235
71	.517	-.287

$k_{obs.}$: 1.88×10^{-4} sec.$^{-1}$

Run VII_{ph}-6

$68.3\%\ H_3PO_4$; 25°

time (minutes)	absorbance	log absorbance
9	1.110	.045
28	1.028	.012
49	.911	-.041
69	.837	-.077
98	.743	-.129
130	.627	-.203
161	.549	-.260
184	.494	-.306

$k_{obs.}$: 7.71×10^{-5} sec.$^{-1}$

p-Tolylboronic acid

Run VII_{ph}-7

63.9% H_3PO_4; 25°

time (minutes)	absorbance	log absorbance
10	1.138	.056
68	1.046	.020
133	.955	-.020
195	.868	-.062
250	.813	-.090
319	.743	-.129
372	.668	-.175
430	.636	-.197

$k_{obs.}$: 2.39×10^{-5} sec.$^{-1}$

Run VII_{ph}-8

60.7% H_3PO_4; 25°

8	1.164	.066
225	.988	-.005
415	.878	-.057
610	.772	-.112
840	.650	-.187
1460	.430	-.367

$k_{obs.}$: 1.13×10^{-5} sec.$^{-1}$

Run VII_{ph}-9

56.3% H_3PO_4; 25°

15	1.177	.071
425	1.056	.024
1005	.937	-.028
1430	.855	-.068
1865	.766	-.116
2485	.674	-.171

$k_{obs.}$: 3.75×10^{-6} sec.$^{-1}$

p-Tolylboronic acid

Run VII_{ph}-10

73.5% H_3PO_4; 25°

time (minutes)	absorbance	log absorbance
9	.792	-.101
17	.628	-.202
25	.518	-.286
38.5	.360	-.444
47	.265	-.577
55	.216	-.666
65	.158	-.801

$k_{obs.}$: 4.54×10^{-4} sec.$^{-1}$

Run VII_{ph}-11

76.7% H_3PO_4; 25°

5	.516	-.287
9	.394	-.405
13	.292	-.535
18	.176	-.755
22	.125	-.903

$k_{obs.}$: 1.36×10^{-3} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_{ph}$-1

39.9% H_3PO_4; 60°

time (minutes)	absorbance	log absorbance
11	1.293	.112
18	1.227	.089
23	1.156	.063
28	1.105	.044
38	.939	-.027
58	.780	-.108
98	.468	-.330

$k_{obs.}$: 1.95×10^{-4} sec.$^{-1}$

Run $VIII_{ph}$-2

57.5% H_3PO_4; 60°

time (minutes)	absorbance	log absorbance
2	.584	-.234
3	.494	-.306
4	.325	-.488
5	.296	-.529
7	.137	-.863
10	.081	-1.092

$k_{obs.}$: 4.60×10^{-3} sec.$^{-1}$

Run $VIII_{ph}$-3

49.2% H_3PO_4; 60°

time (minutes)	absorbance	log absorbance
4	.984	-.007
8	.789	-.103
12	.631	-.200
16	.527	-.278
20	.411	-.386
24	.330	-.482
28	.283	-.548
32	.211	-.676

$k_{obs.}$: 9.16×10^{-4} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_{ph}$-4

27.1% H_3PO_4; 60°

time (minutes)	absorbance	log absorbance
17	1.089	.037
80	.942	-.026
148	.862	-.065
212	.749	-.126
325	.613	-.213
450	.493	-.307
684	.306	-.514

$k_{obs.}$: 3.08×10^{-5} sec.$^{-1}$

Run $VIII_{ph}$-5

10.6% H_3PO_4; 60°

time (minutes)	absorbance	log absorbance
20	1.157	.063
705	1.011	.005
1050	.923	-.035
1495	.845	-.073
2155	.751	-.124

$k_{obs.}$: 3.40×10^{-6} sec.$^{-1}$

m-Fluorobenzeneboronic acid

Run IV_D-1

72.9% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
6	1.085	.036
124	.988	-.005
199	.936	-.029
349	.835	-.078
490	.820	-.086
660	.650	-.187

$k_{obs.}$: 1.30×10^{-5} sec.$^{-1}$

Run IV_D-2

66.9% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
8	1.206	.081
200	1.176	.071
910	1.050	.021
1535	.941	-.026
2285	.803	-.095
3025	.729	-.137

$k_{obs.}$: 2.81×10^{-6} sec.$^{-1}$

Run IV_D-3

76.4% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
15	1.386	.142
74	1.182	.073
136	1.028	.012
197	.840	-.076
255	.728	-.138
312	.639	-.195

$k_{obs.}$: 4.42×10^{-5} sec.$^{-1}$

m-Fluorobenzeneboronic acid

Run IV_D-4

69.0% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
20	1.419	.152
315	1.304	.115
757	1.142	.058
1455	.920	-.036

$k_{obs.}$: 5.06×10^{-6} sec.$^{-1}$

Run IV_D-5

80.4% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
8	1.369	.136
29	1.111	.046
48	.920	-.036
67	.770	-.114
91	.636	-.197
110	.570	-.244

$k_{obs.}$: 1.63×10^{-4} sec.$^{-1}$

Run IV_D-8

64.5% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
30	1.238	.093
1640	1.052	.022
2890	.885	-.053
4395	.771	-.113

$k_{obs.}$: 1.91×10^{-6} sec.$^{-1}$

Run IV_D-9

63.1% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
35	1.204	.081
1640	1.105	.043
3120	.994	-.003
4400	.902	-.045

$k_{obs.}$: 1.14×10^{-6} sec.$^{-1}$

p-Fluorobenzeneboronic acid

Run VI_D-1

65.4% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
10	1.213	.084
33	1.050	.021
48	.875	-.058
80	.655	-.184
108	.507	-.295
145	.358	-.446

$k_{obs.}$: 1.55×10^{-4} sec.$^{-1}$

Run VI_D-2

60.6% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
13	1.213	.084
44	1.114	.047
84	1.000	.000
147	.858	-.067
206	.730	-.137
259	.629	-.201

$k_{obs.}$: 4.39×10^{-5} sec.$^{-1}$

p-Tolylboronic acid

Run VII$_D$-2

39.8% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
740	1.203	.080
900	1.060	.025
1040	.962	-.017
1230	.858	-.067
1460	.695	-.158

$k_{obs.}$: 1.22×10^{-5} sec.$^{-1}$

Run VII$_D$-3

43.5% D_2SO_4; 60°

140	1.022	.009
240	.923	-.035
369	.797	-.099
478	.690	-.161
1188	.272	-.565

$k_{obs.}$: 2.10×10^{-5} sec.$^{-1}$

Run VII$_D$-4

36.4% D_2SO_4; 60°

480	.966	-.016
1140	.781	-.107
1580	.641	-.193
2000	.540	-.268
2590	.423	-.374

$k_{obs.}$: 6.67×10^{-6} sec.$^{-1}$

p-Tolylboronic acid

Run VII_D-5

55.3% D_2SO_4; 60°

time (minutes)	absorbance	log absorbance
20	1.202	.080
40	.900	-.046
60	.678	-.169
80	.490	-.310
103	.349	-.457
121	.274	-.562

$k_{obs.}$: 2.46×10^{-4} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_D$-1

$32.5\%\ D_2SO_4$; 60°

time (minutes)	absorbance	log absorbance
12	1.204	.081
27	.748	-.126
56	.303	-.519
88	.096	-1.018

$k_{obs.}$: $4.65 \times 10^{-4}\ sec.^{-1}$

Run $VIII_D$-2

$22.4\%\ D_2SO_4$; 60°

time (minutes)	absorbance	log absorbance
15	1.533	.185
83	.967	-.015
211	.420	-.377
324	.205	-.688

$k_{obs.}$: $8.30 \times 10^{-5}\ sec.^{-1}$

p-Methoxybenzeneboronic acid

Run VIII$_{HD}$-1

6.31M sulfuric acid; n: 0; 25°

time (minutes)	absorbance	log absorbance
4	.276	-.559
13.75	.201	-.697
24.25	.177	-.752
35.25	.130	-.886
46	.115	-.939
58.25	.080	-1.095

k_n: 3.45×10^{-4} sec.$^{-1}$

Run VIII$_{HD}$-5

6.31M sulfuric acid; n: 1; 25°

6.25	.370	-.433
20.25	.339	-.470
39.75	.299	-.524
57.75	.280	-.553
80.25	.243	-.614
96	.218	-.662
113.5	.209	-.680
125.75	.188	-.726

k_n: 9.40×10^{-5} sec.$^{-1}$

Run VIII$_{HD}$-6

6.31M sulfuric acid; n: .799; 25°

9.25	.330	-.482
23.25	.311	-.507
33.5	.285	-.545
52.5	.225	-.648
73.25	.205	-.688
92.5	.170	-.770
106.25	.138	-.860
122.75	.138	-.860

k_n: 1.45×10^{-4} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_{HD}$-7

6.31M sulfuric acid; n: .598; 25°

time (minutes)	absorbance	log absorbance
12.5	.321	-.494
26.25	.265	-.577
36.5	.250	-.602
49.25	.208	-.682
69.5	.154	-.813
86.75	.149	-.827
99.5	.115	-.939
110	.099	-1.005

k_n: 2.02 x 10^{-4} sec.$^{-1}$

Run $VIII_{HD}$-8

6.31M sulfuric acid; n: .799; 25°

4.75	.425	-.372
14.5	.368	-.434
25.75	.334	-.476
36	.315	-.502
45.5	.275	-.561
54.5	.255	-.594
63.25	.248	-.606
71.75	.216	-.666

k_n: 1.54 x 10^{-4} sec.$^{-1}$

Run $VIII_{HD}$-9

6.31M sulfuric acid; n: .598; 25°

7.5	.375	-.426
17.5	.336	-.474
29	.282	-.550
39	.251	-.600
48	.235	-.629
57.5	.196	-.708
65.75	.181	-.742
78.75	.166	-.780

k_n: 1.96 x 10^{-4} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_{HD}$-10

6.31M sulfuric acid; n: .498; 25°

time (minutes)	absorbance	log absorbance
10.5	.345	-.462
21.25	.298	-.526
32	.267	-.573
42.25	.227	-.646
51	.200	-.699
60.25	.186	-.731
68.75	.154	-.814
83.25	.130	-.886

k_n: 2.20×10^{-4} sec.$^{-1}$

Run $VIII_{HD}$-11

6.31M sulfuric acid; n: .221; 25°

5.5	.670	-.174
13	.590	-.229
21	.499	-.302
28.75	.442	-.355
36.75	.377	-.424
46.5	.313	-.504
58	.265	-.577
69.5	.212	-.674

k_n: 3.02×10^{-4} sec.$^{-1}$

Run $VIII_{HD}$-12

6.31M sulfuric acid; n: .443; 25°

8.75	.677	-.169
16	.618	-.209
25.25	.535	-.272
33.75	.470	-.328
43.25	.429	-.368
55	.349	-.457
73	.261	-.583
89.25	.206	-.686

k_n: 2.42×10^{-4} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run VIII_f-17

25^{o}

time (minutes)	absorbance	log absorbance
27	.711	-.148
82	.596	-.225
150	.480	-.319
191	.424	-.373
248	.372	-.430
298	.325	-.488

$k_{obs.}$: 4.90×10^{-5} sec.$^{-1}$

Run VIII_f-18

25^{o}

29	.694	-.159
84	.584	-.234
152	.471	-.327
193	.410	-.387
250	.363	-.440
300	.315	-.502

$k_{obs.}$: 4.67×10^{-5} sec.$^{-1}$

Run VIII_f-19

25^{o}

30	.711	-.148
46	.672	-.173
65	.613	-.213
90	.582	-.235
121	.540	-.268
174	.460	-.337
230	.375	-.426
308	.332	-.479
405	.246	-.609
507	.187	-.728
612	.154	-.813

$k_{obs.}$: 4.58×10^{-5} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_f$-20

4.86×10^{-2}M sulfuric acid; 25°

time (minutes)	absorbance	log absorbance
8	.722	-.142
11.25	.701	-.154
14	.661	-.180
18	.640	-.194
23	.611	-.214
33.5	.542	-.266
46.5	.480	-.319
58.75	.412	-.385
93.5	.295	-.531

$k_{obs.}$: 1.79×10^{-4} sec.$^{-1}$

Run $VIII_f$-21

4.13×10^{-2}M sulfuric acid; 25°

23	.568	-.246
43	.492	-.308
53	.441	-.356
64	.411	-.386
87	.335	-.475
103	.277	-.558
121	.256	-.592
141	.205	-.688

$k_{obs.}$: 1.45×10^{-4} sec.$^{-1}$

Run $VIII_f$-22

2.58×10^{-2}M sulfuric acid; 25°

24	.593	-.227
45	.516	-.287
65	.437	-.360
88	.361	-.443
105	.334	-.476
143	.253	-.597
177	.190	-.721
220	.154	-.813

$k_{obs.}$: 1.18×10^{-4} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_r$-23

1.032×10^{-2}M sulfuric acid; 25°

time (minutes)	absorbance	log absorbance
26	.631	-.200
67	.490	-.310
106	.422	-.375
144	.357	-.447
179	.296	-.529
222	.246	-.609
252	.207	-.684
278	.189	-.724

$k_{obs.}$: 7.87×10^{-5} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_f$-24

1.963×10^{-1}M sodium formate; 25°

time (minutes)	absorbance	log absorbance
29	.401	-.397
90	.353	-.452
148	.348	-.458
218	.307	-.513
295	.273	-.564
390	.267	-.574
550	.226	-.646
680	.188	-.726

$k_{obs.}$: 1.86×10^{-5} sec.$^{-1}$

Run $VIII_f$-25

9.82×10^{-2}M sodium formate; 25°

30	.700	-.155
91	.640	-.194
149	.599	-.223
219	.560	-.252
296	.513	-.290
392	.460	-.337
551	.415	-.382
681	.359	-.445

$k_{obs.}$: 1.78×10^{-5} sec.$^{-1}$

Run $VIII_f$-26

4.91×10^{-2}M sodium formate; 25°

31	.706	-.151
92	.632	-.199
150	.590	-.229
220	.550	-.260
297	.500	-.301
552	.395	-.403
651	.346	-.462

$k_{obs.}$: 1.89×10^{-5} sec.$^{-1}$

p-Methoxybenzeneboronic acid

Run $VIII_f$-27

2.95×10^{-2}M sodium formate; 25°

time (minutes)	absorbance	log absorbance
32	.668	-.175
94	.600	-.222
151	.552	-.258
221	.510	-.292
298	.449	-.348
554	.332	-.479
653	.305	-.516

$k_{obs.}$: 2.12×10^{-5} sec.$^{-1}$

Run $VIII_f$-28

9.82×10^{-3}M sodium formate; 25°

20	.749	-.126
93	.630	-.201
161	.569	-.245
211	.509	-.293
256	.465	-.333
301	.451	-.346
361	.407	-.390
406	.365	-.438

$k_{obs.}$: 3.06×10^{-5} sec.$^{-1}$

Run $VIII_f$-29

4.91×10^{-3}M sodium formate; 25°

21	.717	-.145
94	.598	-.223
162	.510	-.292
212	.447	-.350
257	.424	-.373
302	.382	-.418
362	.333	-.478
407	.313	-.505

$k_{obs.}$: 3.61×10^{-5} sec.$^{-1}$

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