Electrophilic Displacement Reactions. X. General Acid Catalysis in the Protodeboronation of Areneboronic Acids[1-3]

BY HENRY G. KUIVILA AND K. V. NAHABEDIAN[4]

The kinetics of the protodeboronation of p-methoxybenzeneboronic acid in aqueous sulfuric, phosphoric and perchloric acids, and in formic acid have been studied. The rate constants in the first three acids are correlated by the acidity function H_0, but they are considerably greater at given values of H_0 in phosphoric acid than in the other two. In formic acid containing 1.3% water and 4.0% ethylene glycol dimethyl ether the rate constants are not correlated by H_0. The presence of added sodium formate in amounts which change the acidity by a factor of ten does not change the rate constant, indicating reaction with molecular formic acid. The rate of protodeboronation of the more reactive 2,6-dimethoxybenzeneboronic acid up to 2.5 M in aqueous perchloric acid is correlated by H_0, and not by stoichiometric acid concentration. In solutions containing phosphoric acid and dihydrogen phosphate the rate constants depend upon both pH and molecular phosphoric acid concentration as would be expected of a reaction subject to general acid catalysis. These results are consistent with either an A-SE2 or A-2 mechanism, but not with an A-1 mechanism.

The aromatic boronic acids undergo a number of reactions in which the boronic acid (dihydroxyboron) group is replaced. Some of these, such as the brominolysis[5] and iodinolysis,[6] have been shown to have the characteristics of typical electrophilic aromatic displacements. The reaction of areneboronic acids with hydrogen peroxide, on the other hand, clearly proceeds by a different mechanism.[1,7]

Among the other reactions which have not been studied in detail the simple hydrolysis or protodeboronation (eq. 1) is a particularly interesting one. In the case of benzeneboronic acid, it

$$C_6H_5B(OH)_2 + H_2O \longrightarrow C_6H_6 + B(OH)_3 \quad (1)$$

has been shown by Ainley and Challenger[8] to proceed in water at 150°, and to be catalyzed by concentrated sodium hydroxide, by salts such as zinc bromide and cadmium bromide, and by concentrated hydrochloric acid. The acid-catalyzed reaction seemed to be a promising one to study in detail for two reasons in particular. First, if the mechanism could be elucidated in sufficient detail, it might be possible to gain a better understanding of the kinetic characteristics of acid catalysis in strongly acid media. Secondly, since it seemed very likely that it would be a reaction involving electrophilic attack by a proton donor, another test of the applicability of linear free energy relations to this type of reaction could be made.[5b,5d,9] Using p-methoxybenzeneboronic acid as substrate, the dependence of the rate constant on acidity in aqueous sulfuric, perchloric and phosphoric acids

(1) Preceding paper in this series: H. G. Kuivila and A. G. Armour, J. Am. Chem. Soc., 79, 5659 (1957).

(2) Based in major part on the doctoral dissertation of K. V. Nahabedian, June, 1959.

(3) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-312. Reproduction in whole or in part is permitted for any purpose of the United States Government. During the early stages of this work support was also provided by the Office of Naval Research.

(4) Present address: Department of Chemistry, Brown University, Providence 12, R. I.

(5) (a) H. G. Kuivila and E. K. Easterbrook, J. Am. Chem. Soc., 73, 123 (1951); (b) H. G. Kuivila and A. R. Hendrickson, ibid., 74, 5068 (1952); (c) H. G. Kuivila and E. J. Soboczenski, ibid., 76, 2675 (1954); (d) H. G. Kuivila and L. E. Benjamin, ibid., 77, 3834 (1955).

(6) H. G. Kuivila and R. M. Williams, ibid., 76, 2679 (1954).

(7) H. G. Kuivila, ibid., 76, 870 (1954).

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

(9) H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958).

and in formic acid has been studied; with the more reactive 2,6-dimethoxybenzeneboronic acid, kinetic studies could be extended into dilute solutions of perchloric acid and phosphoric acid–dihydrogen phosphate buffers. The results which are presented in this paper provide evidence for general acid catalysis. Solvent isotope effects and an extensive study of the effect of substituents in the benzene ring on the rate will be considered in the two succeeding papers.

Experimental

Reagents. p-Methoxybenzeneboronic Acid.—The preparation and properties of this compound have been described previously.[5b]

2,6-Dimethoxybenzeneboronic Acid.—Following the procedure of Gilman, et al.,[10] 55.3 g. (0.40 mole) of m-dimethoxybenzene was metalated with n-butyllithium. The resulting suspension of 2,6-dimethoxyphenyllithium in diethyl ether was added to a solution of 52 g. (0.50 mole) of methyl borate in 100 ml. of ether, which was cooled to −60°, over about an hour. The reaction mixture was stirred for another half-hour and allowed to warm to 0°, and hydrolyzed with 400 ml. of water. The water-insoluble lithium salt was filtered off and suspended in 200 ml. of water. Acidification of this suspension with acetic acid yielded 35 g. (31%) of the boronic acid. Recrystallization from benzene gave colorless crystals, m.p. 100–115°. Further recrystallization did not change the melting point. 2,6-Dimethoxybenzeneboronic acid slowly develops the odor of m-dimethoxybenzene on standing at room temperature. For this reason freshly recrystallized material was used in the rate experiments.

Anal. Calcd. for $C_8H_{11}O_4B$: C, 52.79; H, 6.09; neut. equiv., 182.0. Found: C, 52.83; H, 6.21; neut. equiv., 183.5, 180.3 (potentiometric titration in presence of mannitol).

Formic acid (Matheson, Coleman and Bell, 98–100%) was used. It was found to contain 1.37% water by Karl Fischer titration.[11] The ethylene glycol dimethyl ether was freshly distilled (b.p. 85°) from lithium aluminum hydride before use. All other materials were of the best grade available commercially.

Kinetic Methods.—For the rate experiments in aqueous media, kinetic solutions were prepared by diluting appropriate amounts of aqueous acid and aqueous boronic acid stock solutions to a desired volume. The initial concentration of boronic acid was usually in the range 0.001–0.0001 M. The kinetic solutions were placed in a thermostated bath whose temperature varied no more than 0.01°. At appropriate intervals aliquots were removed and the reaction quenched by dilution with water and cooling, simultaneously. In some cases with 2,6-dimethoxybenzeneboronic acid sufficient sodium acetate to neutralize the strong acid was used in the dilution so as to ensure complete quenching.

(10) H. Gilman, H. B. William, T. H. Cook, F. J. Webb and R. N. Meals, ibid., 62, 667 (1940).

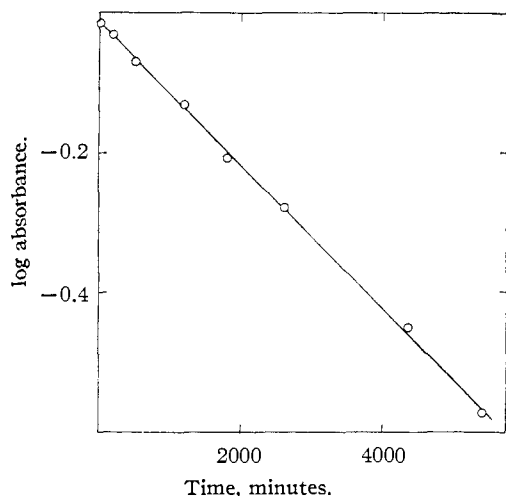(11) J. Mitchell, Jr., and W. Hawkins, ibid., 66, 1797 (1944).

Fig. 1.—Rate plot for the hydrolysis of p-methoxybenzene-boronic acid in 3.11% H_2SO_4 at 60°.

The concentration of unreacted boronic acid was determined spectrophotometrically using a Beckman DU spectrophotometer. At 236 mμ the absorptivity of p-methoxybenzeneboronic acid is 2.82 $\times$ 10⁵ whereas that for anisole is 70. Thus the absorbance of a given sample at this wave length is a direct measure of its boronic acid concentration. Plots of log absorbance vs. time were linear as required for a first-order rate law. A typical plot is shown in Fig. 1. Except in the case of the slowest reactions, data were taken over a period of 2 to 4 half-lives; in no cases were deviations, beyond those expected from experimental errors, noted.

In the case of 2,6-dimethoxybenzeneboronic acid the absorptivity at 245 mμ is 1850, whereas that for m-dimethoxybenzene is 180. In this case the concentration of unreacted substrate, C, is given by $C = $ (absorbance $- 180 C_0$)/1670, where C_0 is the initial concentration of substrate. Plots of log C vs. time were linear and slope $\times 2.303 = k$.

Acidity Functions.—Values of the acidity function, H_0, for the formic acid–water–ethylene glycol dimethyl ether solutions were measured using o-nitroaniline (m.p. 72–73°) as indicator. A complication similar to that reported by Bascombe and Bell[12] for aqueous formic acid solutions was encountered in the present work; the absorbances of the more strongly acidic solutions decreased with time. To correct for this, timed absorbance readings were extrapolated to zero time. The values of H_0 thus obtained are necessarily rather crude, but they serve the purposes of this work. All but two of the values listed in Table III were read from plots of H_0 vs. log concentration. The value for the solvent was experimental, and that involving 0.1963 M sodium formate was obtained by a linear extrapolation over 0.6 unit.

Results

Aqueous Sulfuric Acid.—The rates of protodeboronation of p-methoxybenzeneboronic acid were determined at three temperatures and covered the range 3–55% sulfuric acid. Values of the rate constants and other pertinent data are presented in Table I.

Plots of log k vs. H_0[13] which are shown in Fig. 2 demonstrate that the rate constants are correlated by the acidity function. The slopes at 60°, 40° and 25° are 1.10, 1.15 and 1.15, respectively.

Gold and Satchell[14a] have measured the proto-

(12) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

(13) Values of H_0 are for the temperatures indicated and are interpolated from the data of A. I. Gelbshtein, G. G. Sheglova and A. I. Temkin, *Zhur. Neorg. Khim.*, 1, 506 (1956).

(14) (a) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3911 (1956). (b) These investigators used the H_0 data of L. P. Hammett and M. A. Paul, *J. Am. Chem. Soc.*, 56, 828 (1934), which gave a slope of 1.18.
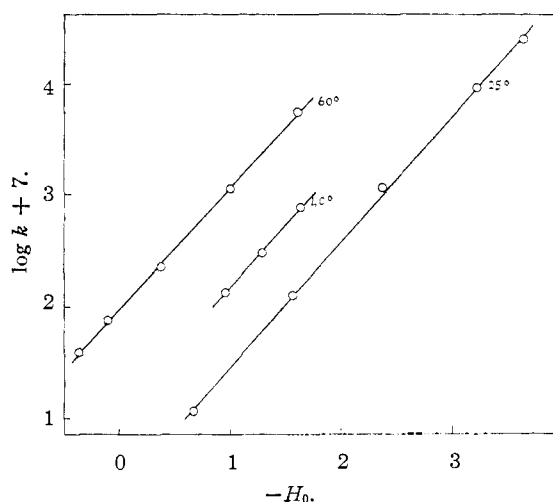
Fig. 2.—log k vs. $-H_0$ for p-methoxybenzeneboronic acid; aqueous sulfuric acid solution.

dedeuteration rates of p-deuterioanisole at 25° in aqueous sulfuric acid. A comparison of their data with ours shows that the rate of protodeboronation is substantially larger. Specifically, in 30% sulfuric acid it is faster by a factor of thirty-six, and in 52% acid, by a factor of twenty. This decrease in relative rate with increasing acidity is due to the greater slope (1.28) of the log k vs. H_0 plot for protodedeuteration.[14b]

TABLE I

RATE CONSTANTS FOR THE PROTODEBORONATION OF p-METHOXYBENZENEBORONIC ACID IN AQUEOUS SULFURIC ACID

Temp., °C.	% H_2SO_4	$-H_0$	$k \times 10^6$, sec.$^{-1}$
60.0	29.6	1.60	560
	20.3	1.00	115
	10.1	0.37	23.0
	5.14	-0.11	7.57
	3.11	-0.37	4.11
40.0	30.1	1.62	77.8
	24.7	1.28	29.9
	20.1	0.95	13.5
25.0	54.6	3.63	2530
	50.4	3.21	931
	40.6	2.37	119
	29.4	1.56	12.4
	16.1	0.67	1.18

Aqueous Perchloric and Phosphoric Acids.—The dependence of rate of protodeboronation of p-methoxybenzeneboronic acid on acidity in aqueous perchloric and phosphoric acids has also been examined. The results are compiled in Table II, and are compared graphically with those obtained in sulfuric acid in Figs. 3 and 4. In these plots the lines through the sets of data for sulfuric and perchloric acids are drawn with unit slope, and serve to illustrate the fact that, as the acidity decreases in these media, the dependence of log k on the acidity approaches ideality. That is to say, data for both acids fall on the same line with unit slope. The deviations are perhaps due in part to specific salt effects of the different anions in the
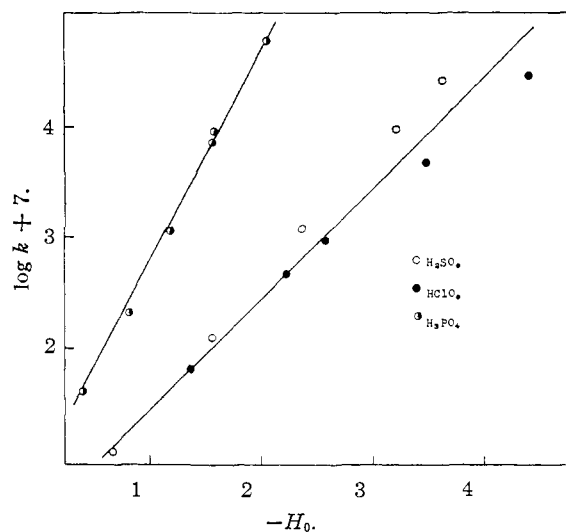
Fig. 3.—log k vs. $-H_0$ for p-methoxybenzeneboronic acid, 25°.

two acids[15]; or it may be that the greater increase in rate with increasing acidity in sulfuric acid is due to catalysis by bisulfate ion in addition to the solvated proton.

The data in phosphoric acid show that, at a given acidity, the rate is much greater than that in either of the other two acids. At high acid concentrations the log k vs. H_0 plot is linear with a slope of 1.85, and at lower acidities the slope diminishes rapidly and appears to approach the unit slope line asymptotically. This kind of behavior would be expected qualitatively for general acid catalysis involving the solvated proton and molecular phosphoric acid.

TABLE II

RATE CONSTANTS FOR THE PROTODEBORONATION OF p-METHOXYBENZENEBORONIC ACID IN AQUEOUS PERCHLORIC AND PHOSPHORIC ACIDS

Temp., °C.	Acid, %	$-H_0$	$k \times 10^5$, sec.$^{-1}$	Temp., °C.	Acid, %	$-H_0$	$k \times 10^5$, sec.$^{-1}$
	Perchloric acid				Phosphoric acid		
25.0	56.2	4.40	2790	25.0	67.9	2.06	5720
	50.5	3.48	470		61.2	1.58	910
	44.0	2.58	92.7		60.9	1.56	753
	40.7	2.23	46.5		53.6	1.18	101
	30.3	1.37	6.53		45.5	0.82	20.7
60.0	33.85	1.63[a]	76.6		36.0	0.40	4.10
	30.95	1.43[a]	51.1	60.0	57.5	1.22	4640
	25.50	1.10[a]	22.2		49.2	0.82	910
	18.57	0.72[a]	8.22		39.9	.50	195
					27.1	.00	30.8
					10.6	− .73	3.40

[a] at 25°; data at 60° not available.

Phosphate Buffers.—In order to examine the general acid catalysis phenomenon more quantitatively, it was necessary to work in dilute aqueous solutions. This could be done with p-methoxybenzeneboronic acid as substrate at higher temperatures or by using a more reactive substrate. The latter course was chosen. From the known rate of protodeboronation of o-methoxybenzeneboronic acid[16] it was estimated that 2,6-dimethoxybenzeneboronic acid would be sufficiently reactive.

(15) F. A. Long and M. A. Paul, Chem. Revs., 57, 935 (1957).
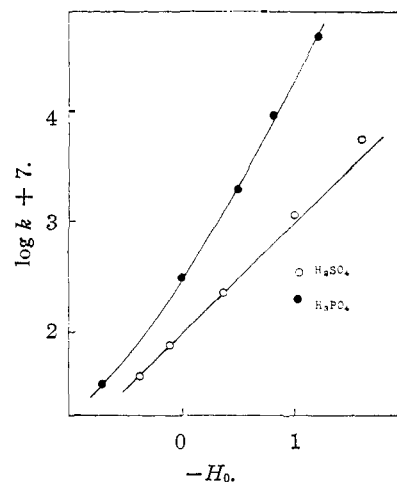(16) Measured by J. H. Polevy in these laboratories.

Fig. 4.—log k vs. $-H_0$ for p-methoxybenzeneboronic acid, 60°.

The kinetics in dilute solutions of perchloric acid at 60° were studied in order to establish the dependence of rate upon hydronium ion concentration. These were then extended into the diagnostic region at higher acid concentrations in which hydronium ion concentration and $-H_0$ increase at different rates. The results are gathered in Table III. Measured first-order rate constants are shown in the second column. These figures divided by the acid concentration are listed as second-order rate constants k_2 in the third column. The average value of k_2 at ionic strength 0.50 is 2.38×10^{-3} l. mole^{-1} sec.$^{-1}$. The expected linear dependence of rate on the concentration of hydronium ion in dilute solutions is thus established. For the five-fold increase in ionic strength from 0.10 to 0.50 the rate constant increases by only about 10% as might be expected for a reaction involving little change in polarity between ground and transition states.

TABLE III

RATE CONSTANTS FOR THE PRODEBORONATION OF 2,6-DIMETHOXYBENZENEBORONIC ACID IN PERCHLORIC ACID SOLUTIONS

Temp., °C.	$k \times 10^5$, sec.$^{-1}$	$k_2 \times 10^3$, l./mole sec.	$-\log C_{H^+}$[a]	pH[b]	$-H_0$[c]	Ionic strength[d]
60.0	21.4	2.19	1.011			0.10
	22.1	2.26	1.011			.20
	22.7	2.30	1.011			.30
	23.5	2.41	1.011	1.00		.50
	12.1	2.47	1.311	1.33		.50
	4.85	2.47	1.709	1.70		.50
	2.27	2.32	2.011	2.03		.50
	1.53	2.23	2.166	2.13		.57
25.0	39.5		−0.389		0.99	
	24.0		− .292		.76	
	14.7		− .167		.51	
	7.75		− .009		.20	

[a] Corrected for volume expansion to 60°. [b] Measured. [c] Reference. [d] $C_{HClO_4} + C_{NaClO_4}$.

At concentrations of hydronium ion greater than 1 M the rate constant is no longer a linear function of the acid concentration as shown by the data in the last four rows of the table: an increase in acid

concentration by a factor of 2.4 leads to an increase in rate constant by a factor of 5.1. The rate constants are correlated by the acidity function according to the equation

$$\log k = -0.90 H_0 - 4.29 \pm 0.01$$

The behavior of the rate constants in phosphoric acid–dihydrogen phosphate buffers was next examined. Results are collected in Table IV.

TABLE IV

RATE CONSTANTS FOR THE PROTODEBORONATION OF 2,6-DIMETHOXYBENZENEBORONIC ACID AT 60.0° IN PHOSPHATE BUFFERS, IONIC STRENGTH 0.50, STOICHIOMETRIC PHOSPHORIC ACID CONCENTRATION 0.1021 M IN EACH CASE

$C_{NaH_2PO_4}$	pH	$k \times 10^5$, sec.$^{-1}$	Actual $C_{H_3PO_4}{}^a$	$k_{H_3PO_4} \times 10^4$,[b] l. mole^{-1} sec.$^{-1}$
0.100	2.09	3.16	0.094	1.30
.200	2.32	2.24	.097	1.13
.200	2.32	2.14	.097	1.03
.400	2.69	1.82	.100	1.33
.500	2.73	1.90	.100	1.46
.500	2.78	1.81	.100	1.41

^{a} $C_{H_3PO_4}$ = 0.1021 − antilog ($-pH$). ^{b} $k_{H_3PO_4}$ = k − 2.38 × 10^{-3} antilog ($-pH$) / $C_{H_3PO_4}$.

These were obtained by maintaining a constant stoichiometric concentration of phosphoric acid (0.1021 M) and varying the concentration of dihydrogen phosphate. Rate constants did not change linearly with the resulting changes in hydrogen ion concentration, and were always larger than would be expected on the basis of k_2 obtained in dilute perchloric acid. This difference between k and k_2, when divided by the actual concentration of phosphoric acid, gave the values shown in the last column of the table as $k_{H_3PO_4}$, whose mean value is 1.28 × 10^{-4} l. mole^{-1}sec.$^{-1}$. At the highest pH this term accounts for 77% of the overall rate constant, and at the lowest pH, 31%. Similar experiments were carried out using formate buffers. The results are not presented here because they were somewhat inconclusive in that the rate constants were only 5 to 10% higher in the presence of the buffers than in their absence.

Formic Acid.—The search for general acid catalysis by formic acid was extended to the use of this reagent as the solvent. Due to the very slow rate of solution of the substrate p-methoxybenzeneboronic acid in this solvent, it was necessary to make stock solutions of the boronic acid in an inert solvent so that kinetic solutions could be made up rapidly. The reaction mixtures contained 4% by volume of ethylene glycol dimethyl ether and 96% by volume of formic acid containing 1.37% water. The results, presented in Table V, qualitatively demonstrate that the reaction is subject to general acid catalysis in this solvent.

This is borne out by the following observations. In a series of solutions containing added sodium formate (0.05–0.20 M) in which the acidity of the medium changes by a factor of ten, the rate constant is essentially invariant (1.8 × 10^{-5} sec.$^{-1}$). This fact suggests a reaction involving catalysis by molecular formic acid, a species whose concentration is essentially unaffected by changes in acidity in these experiments. When the acidity increases

TABLE V

RATE CONSTANTS FOR THE PROTODEBORONATION OF p-METHOXYBENZENEBORONIC ACID AT 25.0° IN FORMIC ACID (94.7%)–ETHYLENE GLYCOL DIMETHYL ETHER (4%)–WATER (1.3%)

HCOONa, mole/l.	H$_2$SO$_4$, mole/l.	$-H_0$	$k \times 10^5$, sec.$^{-1}$
0.1963		−0.84	1.86
.0982		− .14	1.78
.0491		.17	1.89
.0295		.33	2.12
.00982		.72	3.06
.00491		.92	3.61
		1.31	4.91
		1.31	4.67
		1.31	4.58
	0.01032	2.00	7.87
	.0258	2.34	11.8
	.0413	2.51	14.5
	.0482	2.58	17.9

to values of $-H_0$ greater than 0.2, an increase in rate is observed. This increase can be accounted for qualitatively as being due to the incursion of reactions involving the more acidic hydronium and formic acidium ions.

Discussion

Following Zucker and Hammett,[17] the assumption has generally been made that correlation of rates by the acidity function requires a mechanism, usually designated A-1, in which a pre-equilibrium proton transfer to the substrate is followed by a unimolecular rate-determining step in which the conjugate acid of the substrate is converted to product. Recently,[15] however, attention has been directed toward the possibility that reactions involving rate-determining protonation of the substrate might also show rate dependence on the acidity function. This follows if no structural significance is attached to the solvation of the proton in which case the experimental rate coefficient is the given by eq. 3 from which

$$k_{ex} = k a_{H^+}(f_S/f^{\neq}) \qquad (3)$$

eq. 5 results after inserting the definition of H_0 and taking logarithms. Correlation of rate with H_0 results if the activity coefficient ratio does not

$$\log k_{ex} = \log k - H_0 + \log ((f_S f_{BH^+})/(f^{\neq} f_B)) \qquad (5)$$

change with medium. On the other hand, if the hydronium ion is explicitly considered to be the protonating species, eq. 6 results and correlation with hydronium ion concentration is to be expected if the activity coefficient ratio in this equation remains constant with changing medium. Since f_S/f_B remains constant[18] the factor which determines whether the rates of a given A-S$_E$2 reaction are correlated by H_0 or by hydronium concentra-

$$\log k_{ex} = \log k + \log C_{H_3O^+} + \log (f_S f_{H_3O^+}/f^{\neq}) \qquad (6)$$

(17) L. Zucker and L. P. Hammett. J. Am. Chem. Soc., 61, 2791 (1939).

(18) The activity coefficients for several aromatic compounds containing different functional groups are independent of acidity in aqueous sulfuric acid solutions up to 60% acid. The substrate, S, and the indicator, B, are both aromatic compounds, and hence the ratio f_S/f_B should remain constant with changing acidity; N. C. Deno and C. Perizzolo, J. Am. Chem. Soc., 79, 1345 (1957).

tion depends on whether the behavior of $f^{\pm}$ with changing acidity parallels that of f_{BH^+} or of $f_S \cdot f_{H_3O^+}$, respectively.

An alternative way of considering the problem is from the standpoint of the structure of the transition state. Assume a slow proton transfer from hydronium ion to substrate. At one extreme the proton transfer may be considered to have hardly begun in the transition state, which then resembles a complex of the reactants and would have a rate dependent on hydronium ion concentration. At another extreme the proton transfer might be essentially complete in the transition state. This is tantamount to a predissociation of hydronium ion to proton plus water, followed by addition to the substrate, a situation similar to the A-1 mechanism which would give variation of rate with acidity as measured by H_0. According to this approach the kind of dependence to be expected for an A-SE2 reaction will vary with the degree to which the proton has been transferred to substrate in the transition state. It follows from these comments that the fact that the rate constants in sulfuric and perchloric acids are correlated well by the acidity function cannot be used as a criterion for distinguishing between the A-1 and A-SE2 mechanisms.

The results obtained with 2,6-dimethoxybenzeneboronic acid in the presence of phosphate buffers and with p-methoxybenzeneboronic acid in concentrated solutions of phosphoric acid and in formic acid, on the other hand, seem to provide a clearcut distinction. Although the data obtained in formic acid, for example, might be the result of appropriate changes in activity coefficient ratios, the simplest interpretation of all of the data is that the reaction is subject to general acid catalysis. Consequently the A-1 mechanism can be eliminated from consideration. However, ambiguity regarding the mechanism still remains.[19] Four possibilities which meet the requirement that the transition state contain the substrate and the elements of a molecule of acid might be mentioned: (1) A reaction involving the rate-determining pro-

ton transfer from acid to substrate—the A-SE2 mechanism; (2) a pre-equilibrium proton transfer followed by rate-determining attack by the conjugate base of the acid—the A-2 mechanism; (3) the same species attacking in reverse order so that the proton transfer is again rate-determining; (4) pre-equilibrium formation of an intermediate such as I followed by an intramolecular slow proton transfer.

$$\begin{array}{c} \text{OH} \\ | \ominus \\ \text{Ar—B—OH} \qquad \text{(I)} \\ | \ \oplus \\ \text{O—PO}_3\text{H}_3 \end{array}$$
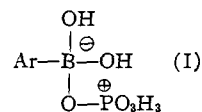
The comparison of the relative rates of protodeboronation and protodedeuteration mentioned earlier provides an opportunity to apply the "element effect" conceived by Bunnett, Garbisch and Pruitt as a mechanistic criterion in the case of nucleophilic aromatic substitution.[20] A direct comparison of rate constants cannot be made, however. Tritium is replaced from the 6-position of o-cresol one-half to one-third times as fast as deuterium.[21] This isotope effect on the departing group must be taken into account. This can be done by assuming that the departure of deuterium would be about one-sixth as fast as the departure of hydrogen. Assuming the A-SE2 type of mechanism preferred by Kresge,[22] the principle of microscopic reversibility leads to the conclusion that attack by proton is about six times as fast as exchange. Application of such a correction gives a faster rate for protodeboronation by factors of about three and five under the conditions mentioned. Thus no definite conclusion is provided by application of this criterion. One might have expected *a priori* that, if the mechanisms are similar, any difference in rates would favor protodedeuteration because the deuteron-bearing carbon should have a higher electron density than one bearing a boronic acid group.

(19) See for example, A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 204 ff.

(20) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Am. Chem. Soc.*, **79**, 385 (1957).

(21) V. Gold, R. Lambert and D. P. N. Satchell, *Chemistry & Industry*, 1312 (1959).

(22) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **81**, 5509 (1959).