[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Electrophilic Displacement Reactions. VII. Catalysis by Chelating Agents in the Reaction between Hydrogen Peroxide and Benzeneboronic Acid[1,2,3]

BY HENRY G. KUIVILA AND ROBERT A. WILES

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Nineteen chelating agents have been tested for catalytic activity on the reaction between benzeneboronic acid and hydrogen peroxide. Free oxalic and malonic acids have no effect. Malonate and/or acid malonate retard the reaction. Of five vicinal diols and two 1,3-diols only one, pinacol, has a catalytic effect. Among ten hydroxy acids the order of catalytic activity is: benzilic > 1-hydroxycyclohexanecarboxylic > α-hydroxyisobutyric > salicylic > tartaric > mandelic > lactic > glycolic > hydracrylic. A detailed study with α-hydroxyisobutyric acid indicates that it functions as a catalyst in a *p*H-independent reaction. It also ties up boronic acid in an unreactive complex anion; the behavior of citric acid is similar.

Benzeneboronic acid reacts with hydrogen peroxide to yield phenol and boric acid. Among the interesting characteristics of this reaction[4] and of the reactions of areneboronic acids with bromine[5] and iodine[6] is the fact that they are catalyzed by certain chelating agents. The present paper describes a survey of the effects of nineteen chelating agents on the peroxide–benzeneboronic acid reaction and a detailed examination of the nature of the catalysis by α-hydroxyisobutyric acid.

General Survey

The preceding study[3] on the kinetics of the reaction was carried out in solutions at ionic strength 0.2. In order to provide more latitude in varying concentrations of ionic species the present work was carried out at ionic strength 0.5. It was therefore necessary to prepare new *p*H *vs.* log *k* curves for the reactions first and second order in boronic acid. The results are summarized in equations 1 and 2. Values of k_1 indicate a positive salt

$$\log k_1 = -6.87 + pH\ (\mu = 0.5) \qquad (1)$$

$$\log k_2 = -5.80 + pH\ (\mu = 0.5) \qquad (2)$$

effect; the data for k_2 and k_3 (*p*H-independent reaction) are essentially the same as those at μ 0.20. The chief source of error was the *p*H measurement which at best gave values precise to 0.03 unit, corresponding to ±7% in the value of the specific rate constants.

Dicarboxylic Acids.—Malonic and oxalic acids were chosen as the simplest dicarboxylic acids which might have some effect due to their chelating abilities. The data obtained with these acids are presented in Table I. It is evident that the free acids have no significant effect on the rate of the reaction. In solutions containing 55% malonate and 45% acid malonate (*p*H 3.2) a pronounced decrease in rate occurs as the concentration of buffer is increased. In half-molar malonate the rate is decreased by 35%. The simplest interpretation is that the malonate or acid malonate and boronic acid react to form a complex which reacts very slowly if at all with hydrogen peroxide.

TABLE I

SUMMARY OF THE EFFECTS OF MALONIC AND OXALIC ACIDS

Acid	Concn., moles/l.	No. of runs	*p*H range	$C_6H_5B(OH)_2$, moles/l.[a]	10^3k, l. mole^{-1} sec.$^{-1}$
None			1.45	1.00	0.87
			2.00	1.00	0.83
			3.21	2.00	1.00
Malonic	0.05	4	1.95–2.04	1.00–5.00[b]	0.92[c]
	.10	1	3.24	2.00	.98
	.30	1	3.19	2.00	.82
	.50	1	3.21	2.00	.65
Oxalic	.05	4	1.42–1.56	1.00–5.00[b]	.86[c]

[a] Initial concn. [b] Range. [c] Mean value.

Diols.—The specific rate constants in the presence of five vicinal diols and two 1,3-diols are summarized in Table II. Of these diols catechol, pinacol and *cis*-indane-1,2-diol have previously been shown to form water-stable esters with benzeneboronic acid.[7] It was observed in this work that 2,2-

TABLE II

SUMMARY OF CATALYTIC EFFECTS OF DIOLS

(Diols, 0.05 *M*; acetate buffers, *p*H 4.72.)

Diol	10^2-$[C_6H_5B(OH)_2]$[a]	10^3kobsd., l. mole^{-1} sec.$^{-1}$	10^3k_1, l. mole^{-1} sec.$^{-1}$	10^3k_2, l. mole^{-2} sec.$^{-2}$
None	0.40	8.39		
	1.00	8.98		
	3.00	9.96		
	5.00	10.94	8.00	98
Ethylene glycol	1.00	8.7		
	3.00	11.0		
	5.00	13.1	7.6	110
Pinacol	0.400	10.6		
	.700	11.3		
	1.00	11.4	10.2	130
Catechol	1.00	9.2		
	3.00	11.1		
	5.00	13.3	8.1	104
cis-Cyclohexane-1,2-diol[b]	1.00	8.5		
	3.00	10.8		
	5.00	12.8	7.4	118
cis-Indane-1,2-diol	0.04	9.0		
	.07	7.9		
	.10	8.4		
Propane-1,3-diol	1.00	8.9		
	3.00	10.9		
	5.00	12.8	8.0	98
2,2-Dimethylpropane-1,3-diol[c]	0.40	8.6		
	.70	9.1		
	1.00	9.2	8.3	100

[a] Initial concn., moles/l. [b] 0.001 *M*. [c] 0.01 *M*.

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(1) For the preceding paper in this series see H. G. Kuivila, THIS JOURNAL, **77**, 4014 (1955).

(2) From the M.S. Thesis of R. A. Wiles, August, 1954.

(3) Supported in part by the Office of Naval Research.

(4) H. G. Kuivila, THIS JOURNAL, **76**, 870 (1954).

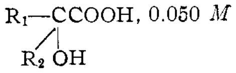
(5) H. G. Kuivila and E. J. Soboczenski, *ibid.*, **76**, 2675 (1954).

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

(7) H. G. Kuivila, A. H. Keough and E. J. Soboczenski, *J. Org. Chem.*, **19**, 780 (1954).

TABLE III

SUMMARY OF EFFECTS OF HYDROXY ACIDS



$\mathrm{R_1{-}\underset{R_2\quad OH}{C}COOH}$, 0.050 M

R_1	R_2		No. of runs	pH range	$[C_6H_5B(OH)_2]^a$	$10^3k_{obsd.}$, l. mole^{-1} sec.$^{-1}$ mean	$10^2k_c{}^g$ l. mole^{-1} sec.$^{-1}$ mean
CH_2COOH	CH_2COOH		4	1.96–2.07	1.00–5.00	84	167
		b	1	1.86	1.00	150	149
		c	1	1.71	1.00	263	131
H	H		4	2.42–2.53	1.00–5.00	2.07	2.5
H	CH_3		4	2.38–2.45	1.00–5.00	8.7	15.8
CH_3	CH_3		4	2.31–2.45	1.00–5.00	38.0	74.4
		b	1	2.23	2.00	72.3	71.5
		c	1	2.40	2.00	160	80.0
$(CH_2)_5$			4	2.26–2.46	1.00–5.00	61	120
C_6H_5	H		1	2.22	1.00	18.3	35
			1	2.07	3.00	18.3	35
			1	2.21	4.00	19.7	38
			1	2.10	5.00	19.9	38
		d	1	(2.63)	1.00	25.8	51.4^h
		d	1	(2.58)	3.00	27.3	54.4^h
		d	1	(2.62)	4.00	30.0	59.8^h
C_6H_5	C_6H_5	*d, e*	1	(2.73)	0.400	135	1350^h
		d, e	1	(2.73)	.700	161	1610^h
		d, e	1	(2.73)	1.00	156	1560^h
CHOHCOOH	H		1	2.08	1.00	23.4	46^f
			1	2.03	3.00	27.7	57^f
			1	1.96	4.00	31.4	61^f
			1	2.01	5.00	32.4	63^f
Salicylic acid		*i*	3	2.50–2.60	1.00–5.00	3.80	59
3-Hydroxypropanoic acid			4	2.71–2.88	1.00–5.00	0.95	0.2

[a] $10^2 \times$ initial concn., moles/l. [b] Hydroxy acid, 0.10 M. [c] Hydroxy acid, 0.20 M. [d] Solvent, 50% methanol by volume. [e] Hydroxy acid, 0.10 M. [f] k_{1c} = 40 l. mole^{-1} sec.$^{-1}$; k_{2c} = 460 l. mole^{-2} sec.$^{-2}$. [g] $k_c = (k_{obsd} - 8.0 \times 10^{-4})/[\text{cat.}]$. [h] $k_{uncatalyzed} = (1.40 \pm 0.02) \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ in the pH range 2.44–2.76 (measured by Mr. Albert G. Armour). [i] Hydroxy acid, 0.0050 M.

dimethylpropane-1,3-diol reacts in a similar manner. Because of the relatively low solubility of the esters, it was necessary to use low concentrations of diol or boronic acid or both to avoid precipitation. *cis*-Indane-1,2-diol had to be used in especially low concentration. Pinacol is the only one of the diols which shows unmistakable catalysis of both of the reactions. The effects of the others, with ethylene glycol and *cis*-cyclohexane-1,2-diol as possible exceptions, are negligible. It is thus apparent that formation of a chelate with the boronic acid is not of itself a guarantee of catalysis whether the boron is present in a five- or six-membered ring. The indanediol is a catalyst for the iodinolysis of p-methoxybenzeneboronic acid[5] but not for the present reactions. This may be due to the difference in mechanism in the two reactions.

Hydroxy Acids.—Eight α-hydroxy acids and two β-hydroxy acids were examined in unbuffered solutions and all but one proved to be catalysts. Results are summarized in Table III. Runs were usually carried out with four different concentrations of boronic acid. When the rate increased with boronic acid concentration data for individual runs are given; otherwise the mean value of the rate constant for the set of runs is given. The order of effectiveness of the free hydroxy acids in catalyzing the reaction first order in boronic acid is benzilic > citric > 1-hydroxycyclohexanecarboxylic > α-hydroxyisobutyric > salicylic > tartaric > mandelic > lactic > glycolic > hydracrylic. Thus, replacement of the α-hydrogens of glycolic acid by methyl, pentamethylene, phenyl, carboxymethyl or hydroxycarboxymethyl results in greater catalytic activity.

Mandelic acid was studied in water and in 50% aqueous methanol. This provided a link for examining benzilic acid which is insoluble in water and only slightly soluble in the aqueous methanol. Each acid catalyzes reactions first and second order in boronic acid, benzilic acid being far more effective in each case. The reactions proceed faster in the 50% methanol than in water. Tartaric acid is a slightly better catalyst than mandelic acid for both reactions.

The catalytic rate constant for citric acid decreases as its concentration increases. This implies that a significant fraction of the boronic acid forms a complex at the lowest citric acid concentration, 0.05 M. Then as this is increased to 0.10 M and further to 0.20 M, the concentration of the complex increases, but not linearly as would be necessary for constancy in k_c. An alternative explanation (*vide post*) is that an unreactive complex is formed decreasing the actual concentration of free boronic acid with increasing citric acid concentration. Consequently the rate constants are low because no correction for this has been made in their computation.

Citric and α-Hydroxyisobutyric Acids, Effect of *p*H

Citric Acid.—A number of runs, in addition to those reported in Table III, involving variation in *p*H were made with citric acid. The data thus obtained are presented in Table IV. A striking pattern is observed. At low *p*H catalysis of the reaction first order in boronic acid is very important. As the *p*H increases catalysis becomes less important. Above *p*H 5 the over-all reaction rate is lower than in the absence of citrate, *i.e.*, the citric acid is retarding the reaction. Thus at *p*H 6.0 with 0.01 M boronic acid the observed rate constant is 0.0490 l. mole^{-1} sec.$^{-1}$ whereas in the absence of citrate the rate constant at the same *p*H is 0.134 l. mole^{-1} sec.$^{-1}$. Citric acid does not catalyze the reaction second order in boronic acid at any *p*H in the range observed but it obviously retards this reaction decreasing its observed specific rate constant to less than 8.5% of its normal value at *p*H 6.0.

TABLE IV

EFFECT OF *p*H ON CITRIC ACID[a] CATALYSIS

*p*H	10^2 [$C_6H_5B(OH)_2$][b]	$k_{obsd.}$ l. mole^{-1} sec.$^{-1}$	10^3k_1 Obsd.	10^3k_1 Calcd.[c]	10^3k_2 Obsd.	10^3k_2 Calcd.[c]
3.22	1.00	27.5				
3.19	2.00	28.1				
3.12	3.00	28.2				
3.11	4.00	28.0				
3.02	5.00	29.6	28.3	0.96	..	2.2
4.61	1.00	12.8				
4.62	3.00	12.4				
4.66	4.00	12.5				
4.62	5.00	12.6	12.6	5.6	..	63
5.45	0.50	21.0				
5.45	1.00	20.3				
5.44	2.00	21.7				
5.42	3.00	24.5				
5.48	4.00	27.3				
5.45	5.00	30.6	16.2	38	188	436
5.92	1.00	49.0				
5.90	2.00	66.0				
6.00	3.00	72.0				
6.04	5.00	96.0	37	120	118	1410

[a] Total citrate 0.05 M in all runs. [b] Initial concn., moles/l. [c] At mean value of *p*H range.

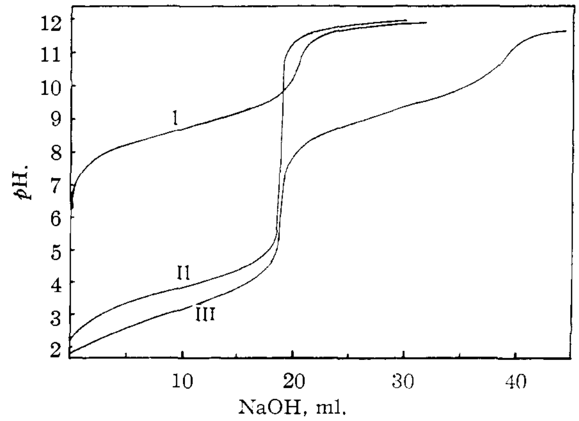
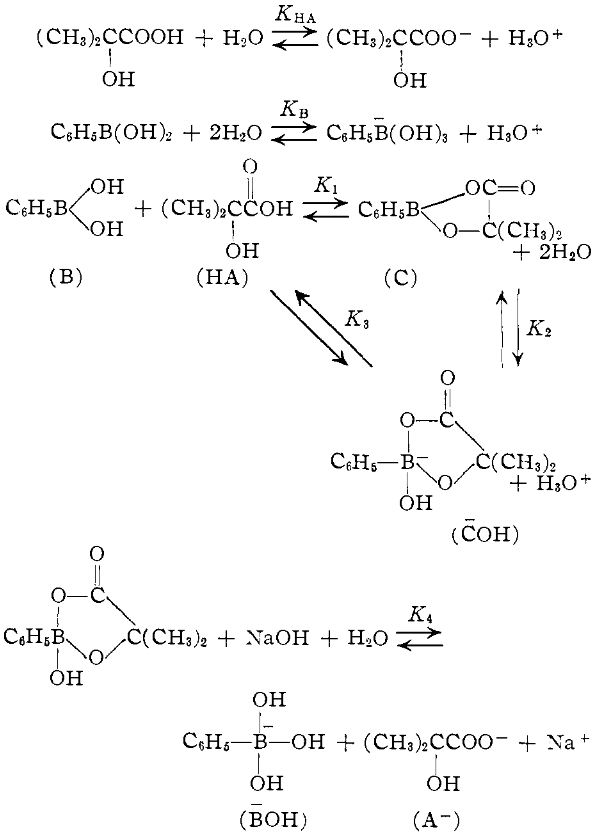


Fig. 1.—Titration curves of 50 ml. of solutions with 0.495 N NaOH; each solution 0.50 M in $NaNO_3$: I, 0.200 M $C_6H_5B(OH)_2$, μ 0.50 throughout; II, 0.187 M α-hydroxyisobutyric acid; μ 0.51 at start and 0.50 at end of titration; III, 0.187 M α-hydroxyisobutyric acid, 0.200 M $C_6H_5B(OH)_2$; μ 0.51 at start and 0,49 at end of titration.

Samples of citric acid alone and in the presence of equimolar benzeneboronic acid were titrated with sodium hydroxide. Two distinct *p*H *vs.* titer curves were obtained. Below 1.2 equivalents of base the boronic acid decreases the *p*H; above this point it increases the *p*H. Inflections in the presence of the boronic acid occur at 1.2, 3.0 and 4.0 equivalents of base. The last inflection indicates that the complex which is formed breaks down completely at high values of the *p*H. Because citric acid is tribasic it was decided to use the simpler α-hydroxyisobutyric acid for more detailed examination of the α-hydroxy acid catalysis.

α-Hydroxyisobutyric Acid. Complex Formation.—The catalytic behavior of α-hydroxyisobutyric acid is similar in all respects to that of citric acid as can be deduced from the data of Table V. Curves of *p*H *vs.* titer are depicted in Fig. 1, for benzeneboronic acid, α-hydroxyisobutyric acid and a combination of the two using sodium hydroxide as titrant. As manifested by these plots a species more acidic than either of those introduced is formed in the mixed solution. Furthermore, the second inflection in this curve indicates that the species breaks down to yield benzeneboronic acid and, presumably, α-hydroxyisobutyrate above *p*H 6.

These titration data can be treated in a manner similar to that applied by Vermaas[8] to solutions of boric acid and glycols. The following equilibria are assumed in any solution prepared from benzenebor-



$$(CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}COOH + H_2O \overset{K_{HA}}{\rightleftarrows} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}COO^- + H_3O^+$$

$$C_6H_5B(OH)_2 + 2H_2O \overset{K_B}{\rightleftarrows} C_6H_5\bar{B}(OH)_3 + H_3O^+$$

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(8) N. Vermaas, *Rec. trav. chim.*, **51**, 67 (1932).

TABLE V

DATA ON THE EVALUATION OF THE CATALYTIC CONSTANT FOR α-HYDROXYISOBUTYRIC ACID[a]

*p*H	100 B,[b] moles/l.	100 $k_{\text{obs.}}$	100 $k_{\text{cor.}}$	100 $k_{\text{uncat.}}$	100 Δk	100 HA,[c] moles/l.	100 B, moles/l.	$10^3 K_3$	k_c
2.45	1.00	3.66	4.36	0.08	4.28	4.65	0.84	14.5	0.92
2.40	2.00	3.92	4.43	.08	4.35	4.60	1.77	11.3	.95
2.32	4.00	3.70	3.93	.08	3.85	4.52	3.66	9.8	.85
2.31	5.00	3.42	4.21	.08	4.13	4.51	4.63	8.2	.92
2.23	2.00	7.23	8.74	.08	8.66	9.41[d]	1.65	13.2	.92
2.10	2.00	16.0	20.9	.08	20.8	19.37[e]	1.53	12.6	1.08
2.96	3.00	2.90	3.98	.09	3.89	3.69	2.19	11.0	1.05
2.84	4.00	3.16	4.16	.09	4.07	3.66	3.04	12.8	1.11
2.83	5.00	3.11	3.86	.09	3.77	3.65	4.02	9.6	1.03
3.57	1.00	1.93	3.21	.12	3.05	2.97	0.60	6.0	1.03
3.40	3.00	2.28	3.32	.11	3.21	2.96	2.06	6.2	1.08
3.33	4.00	2.40	3.32	.11	3.21	2.95	2.89	6.1	1.09
3.30	5.00	2.54	3.32	.11	3.21	2.95	3.82	5.2	1.09
4.10	1.00	1.20	1.97	.19	1.78	1.54	0.61	3.1	1.15
3.99	3.00	1.40	2.08	.20	1.87	1.64	2.02	3.0	1.15
3.91	4.00	1.51	2.31	.20	2.13	1.64	2.61	4.0	1.30
3.81	5.00	1.56	2.36	.19	2.18	1.64	3.31	4.5	1.34

[a] Total hydroxy acid 0.05 *M* except where noted. [b] Boronic acid. [c] α-Hydroxyisobutyric acid. [d] Total, 0.10 *M*. [e] Total, 0.20 *M*.

onic acid, α-hydroxyisobutyric acid and sodium hydroxide.

At any given point in the titration the following are known quantities: K_{HA} and K_{B} from previous titrations, K_w, initial concentrations of boronic acid and hydroxy acid, concentrations of sodium ions and hydronium ions. From these, nine equations in the following ten unknowns can be assembled[2]: K_1, K_2, K_3, K_4, B, BOH^-, HA, A^-, C, COH^-. Above *p*H 8 the concentrations of HA, C and H_3O^+ are small enough to be neglected when they are added to or subtracted from other terms. With these approximations it is possible to evaluate K_4. From the titration curve at 0.50 ionic strength K_{B} at 25° is 1.9×10^{-9}. From data at one-half *p*H unit intervals between *p*H 8.1 and 10.4 the value of K_4, $(5.0 \pm 0.2) \times 10^3$, is obtained.

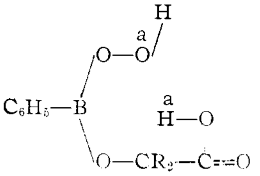
It can be shown that $K_3 = K_{\text{B}}K_{\text{HA}}/K_4K_w$.[2] Using K_{B}, 1.5×10^{-4}; K_w, 10^{-14} and the above value for K_4 we compute K_3, 6.0×10^{-3}. Alternatively K_3 can be estimated from data at low *p*H where BOH^- and HO^- are present in very low concentration and can be neglected. It is also assumed that the concentration of C is small. When this is done the values of K_3 drift downward from 6.5×10^{-3} at *p*H 2 to 4.9×10^{-3} at *p*H 4. This is seen to be good agreement when it is realized that an error of 0.03 unit in the *p*H measurement leads to ±7% in value of K_3. The value of K_{HA} is subject to the same error and is used in evaluating K_3. Above *p*H 4 small errors in stoichiometric concentrations of HA or NaOH loom very large in the values of K_3.

In principle it should be possible to evaluate K_1 and K_2 also, but their values are extremely sensitive to variation in K_4. The best that can be deduced from attempts at their estimation is that K_1 is very small and K_2 is very large.

Mechanism of α-Hydroxyisobutric Acid Catalysis.—Now that the equilibria portrayed above have been shown to be consistent with the titration data we may proceed to examine the kinetic results obtained with α-hydroxyisobutyric acid at different values of *p*H and initial boronic acid concentrations. It will be assumed that the catalytic reaction involves *free* boronic acid and *free* hydroxy acid or their kinetic equivalent, species C for example. The reaction rate is therefore *independent* of *p*H. Species COH^- then is simply the product of a side reaction which ties up boronic acid and hydroxy acid, thereby decreasing their effective concentrations. In order to treat the data properly the concentration of free boronic acid must be known and can be computed. Fortunately the fraction of free acid changed very little (less than 3%) in any of the runs because the initial concentration of peroxide was always about 3×10^{-3} *M*. This fraction was therefore calculated for the initial concentration of boronic acid and then used throughout the run in the calculation of a corrected specific rate constant, $k_{\text{cor.}}$. Using k_1 and k_2 from equations 1 and 2 and the corrected boronic acid concentration the rate constant for the uncatalyzed reaction, $k_{\text{uncat.}}$ was estimated and the difference, $k_{\text{cor.}} - k_{\text{uncat.}} = \Delta k$, measured the catalytic effect of the hydroxy acid. Dividing Δk by the concentration of free α-hydroxyisobutyric acid then gave the specific rate constants, k_c, for the catalyzed reaction.

Pertinent data in the *p*H range 2.45–4.10 are gathered in Table V. Values of K_3 were evaluated for each run. Lacking the internal consistency provided in a single titration, these vary somewhat more widely than those previously cited. Nevertheless these were used in estimating the concentrations of the various species. Values of k_c drift upward with *p*H but not enough to invalidate the assumptions outlined above. Beyond *p*H 4.1 attempted calculations were fruitless because of the great sensitivity of the quantities to be calculated to small errors in those measured.

In view of the above discussion the transition state complex for the α-hydroxyisobutyric acid-catalyzed reaction must be made up from a molecule each of boronic acid, peroxide and hydroxy acid. The chelating tendency of the catalyst must play an important role in making it effective. One possible intermediate is represented by structure I.



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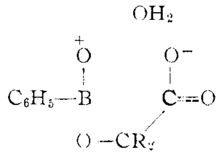
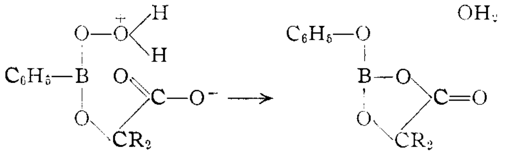


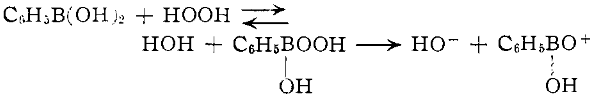
II

Transfer of H^a to O^a and cleavage of the peroxide bond to give II would occur in the slow step. An alternate path from the same intermediate could involve the processes I ⇄ III → IV with the last step rate determining. The conformational possibilities for I are such that the proton transfer and



III IV

boron--oxygen bond formation cannot occur simultaneously. This path is attractive in that the slow step involves the loss of opposite charges. This process should be favored by a decrease in polarity of the solvent and, being a rate process, the effect should overbalance the opposing effect on the equilibrium I ⇄ III. Changing from water to 50% methanol does in fact increase the rate of the mandelic acid-catalyzed reaction. This same solvent change has the opposite effect on the rate of the uncatalyzed reaction (compare the first three data in Table I and that in Table III, footnote *h*) for which the rate determining process V → VI appears to be reasonable.



$$C_6H_5B(OH)_2 + HOOH \rightleftharpoons HOH + \underset{\text{V}}{\underset{OH}{C_6H_5BOOH}} \longrightarrow HO^- + \underset{\text{VI}}{\underset{OH}{C_6H_5BO^+}}$$

Experimental

Materials.—Benzeneboronic acid was prepared from butyl borate and phenylmagnesium bromide by the method of Bean and Johnson.[9] The samples, used as the anhydride, had neutral equivalents of 103.9 ± 0.5.

1-Hydroxycyclohexanecarboxylic acid was graciously provided by Dr. R. E. Lyle.

The α-hydroxyisobutyric acid had m.p. 78.0-79.0°.

Anhydrous pinacol was prepared from the crude hydrate.[10]

3-Hydroxypropanoic acid was prepared by warming a solution of β-propiolactone on the steam-bath. The resulting solution was assayed by titration with sodium hydroxide and used as such.

All other reagents were C.P. or reagent grade where available and used without further purification, or were prepared by conventional methods and had melting points agreeing with those given in the literature.

Rate Measurements.—These were made as described previously[3] using the colorimetric method of Eisenberg[11] for determining the concentrations of unreacted peroxide. The optical density of the pertitanate was diminished in the presence of oxalic acid so that a separate calibration curve was prepared in this case. All kinetic runs were made at 24.93 ±0.02° at ionic strength 0.50.

Titrations.—All *p*H measurements were made with a Beckman Model H-2 meter and were usually reproducible to 0.03 *p*H unit. When ionic strengths were adjusted with sodium perchlorate difficulties were encountered in the titrations after some time probably because of the formation of potassium perchlorate at the calomel electrode. When sodium nitrate was used in adjusting ionic strengths the difficulty disappeared. Sodium perchlorate was used in all the kinetic runs.

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DURHAM, N. H.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Electrophilic Displacement Reactions. VIII.[1] Rates of Brominolysis of Substituted Benzeneboronic Acids. Correlation of Rates of Aromatic Electrophilic Displacement Reactions[2,3]

BY HENRY G. KUIVILA AND LAWRENCE E. BENJAMIN

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The rates of brominolysis of six *meta*- and *para*-substituted benzeneboronic acids in "20%" acetic acid have been measured. Correlation of the rates by the Hammett equation and with rates of other aromatic electrophilic displacement reactions are discussed.

In a previous investigation[1] the rates of brominolysis (equation 1) of ten *meta*- and *para*-substituted

$$ArB(OH)_2 + Br_2 \xrightarrow{H_2O} ArBr + B(OH)_3 + HBr \quad (1)$$

benzeneboronic acids were reported. We are using this reaction as a starting point in the study of quantitative relationships among the rates of aromatic electrophilic displacement reactions. To make our series more representative of various electronic effects seven additional members of the series have been investigated. The substituents included are *m*-Br, *p*-F, *m*-F, *p*-I, *m*-I and *p*-C_6H_5.

Results and Discussion

Kinetic Data.—The new data on the brominolysis of substituted benzeneboronic acids in "20%" acetic acid at 25° are summarized in Table I. In Fig. 1 these, along with the previous data, are represented in a typical plot for testing applicability of

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(1) For the previous publication in this series see H. G. Kuivila and R. A. Wiles, THIS JOURNAL, **77**, 4830 (1955).

(2) From the Bachelor's (1953) and Master's (1954) theses of L. E. Benjamin.

(3) Substantial support of this investigation by the Office of Naval Research is gratefully acknowledged.

(4) H. G. Kuivila and A. R. Hendrickson, THIS JOURNAL, **74**, 5068 (1952)