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Electrophilic Displacement Reactions. VI. Catalysis by Strong Acids in the Reaction between Hydrogen Peroxide and Benzeneboronic Acid[1,2]

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The kinetics of the reaction between hydrogen peroxide and benzeneboronic acid has been investigated using aqueous solutions of sulfuric, perchloric and phosphoric acids as solvents. The rate in each case increases more rapidly than the stoichiometric concentration of acid. H_0 correlates the data for phosphoric acid; log $a_{HX} \times a_{H_2O}$ correlates the data for perchloric acid. No simple correlation of the data for sulfuric acid has been found.

An earlier investigation of the kinetics of the reaction between benzeneboronic acid and hydrogen peroxide which yields phenol and boric acid as products dealt with the characteristics of the reaction in the *p*H range 2 to 6.[3] Two ionic reactions were clearly distinguished in this range: each is first order in peroxide; one is first order and the other is second order in boronic acid; both have specific rate constants which increase linearly with the first power of hydroxide ion concentration. In addition the data indicated the appearance of a *p*H-independent reaction which is detectable between *p*H 3 and *p*H 1.5. This paper is a report on the kinetics of the reaction beginning at *p*H 3 and extending to about 9 molar solutions of sulfuric, perchloric and phosphoric acids.

Results and Discussion

Perchloric Acid.—The data for solutions of perchloric acid are assembled in Table I. It is apparent from the first four items in the table that a minimum extending over about one-half *p*H unit exists in the observed specific rate constant. Therefore the value 7.7×10^{-4} l. mole^{-1} sec.$^{-1}$ is taken as the value for an *uncatalyzed* reaction. The specific rate constant k_a for the acid-catalyzed reaction is then the difference between k_{obs} and 7.7×10^{-4}.

TABLE I

KINETIC DATA IN AQUEOUS PERCHLORIC ACID

$HClO_4$, moles/l.	H_0[b] or pH[a]	10^3 k_{obs}[c]	10^3 k_a[c,d]	$-\log$ k_a	log $a_{H_2O} \times a_{HClO_4}$[e]	$-\Delta$[f]
0.0025	2.62[a]	0.781	....	...	.....	..
.0050	2.32[a]	.771	....	...	.....	..
.0075	2.15[a]	.773	....	...	.....	..
.0100	2.00[a]	.793	....	...	.....	..
.200	0.70	1.56	0.79	3.102	−0.808	2.31
.750	0.02	3.94	3.17	2.499	−0.222	2.28
2.469	−0.88	16.0	15.2	1.818	+0.507	2.34
3.73	−1 44	31.9	31.2	1.507	0.958	2.47
4.12	−1.64	44.0	43.2	1.364	1.041	2.40
5.93	−2.58	137	136	0.866	1.707	2.57
8.15	−4.31	605	604	0.219	2.333	2.56

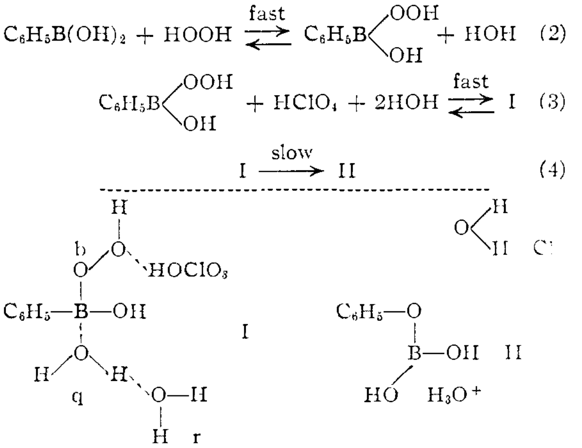
[a] Measured. [b] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934). [c] Units l. mole^{-1} sec.$^{-1}$. [d] $k_{obs} - 0.00077 = k_a$. [e] J. N. Pearce and A. F. Nelson, *ibid.*, **55**, 3075 (1933). [f] $\Delta = \log k_a - \log a_{H_2O} \times a_{HClO_4}$; mean value = −2.42.

Items in the table beyond the fourth reveal several significant facts. First, a forty-fold increase in acid concentration leads to a seven hundred fifty-fold increase in rate constant. Thus the latter is not a simple function of acid concentration. Furthermore it is not a simple function of H_0[4] which varies over five units while log k_a varies over less than three units. This is also shown in Fig. 1 which represents a summary of all of the data on acid dependence of the reaction over a range of more than ten powers of ten in acidity.

The last two columns of Table I demonstrate that k_a can be correlated with the product of the activities of perchloric acid and water, eq. 1

$$\log k_a = \text{const.} + \log a_{H_2O} \times a_{HClO_4} \qquad (1)$$

A log–log plot (Fig. 2) gives a line with a slope 0.95. This type of correlation in strongly acid media appears to be unique and resembles the termolecular mechanism for general acid and base catalysis originally suggested by Lowry[5] and more recently favored by Swain.[6] In the present case the transition state complex must be built up from one molecule each of boronic acid, perchloric acid, hydrogen peroxide and water. As one possible example reactions 2 and 3 could lead to structure I from which assembly II could be formed *via* the transition state complex (reaction 4). Two molecules of water are needed in I: that demanded by equation (1) and that formed in reaction (2). This can be seen by adding reactions (2) and (3).



$$C_6H_5B(OH)_2 + HOOH \overset{\text{fast}}{\rightleftharpoons} C_6H_5B(OOH)(OH) + HOH \qquad (2)$$

$$C_6H_5B(OOH)(OH) + HClO_4 + 2HOH \overset{\text{fast}}{\rightleftharpoons} \text{I} \qquad (3)$$

$$\text{I} \xrightarrow{\text{slow}} \text{II} \qquad (4)$$

A proton transfer from the perchloric acid molecule to a peroxidic oxygen facilitates ionic cleavage at

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[1] For preceding paper in this series see H. G. Kuivila and R. M. Williams, THIS JOURNAL, **76**, 2679 (1954).

[2] Substantial support of this work by the Office of Naval Research is gratefully acknowledged.

[3] H. G. Kuivila, THIS JOURNAL, **76**, 870 (1954).

(4) L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 267ff.

(5) T. M. Lowry and I. J. Faulkner, *J. Chem. Soc.*, **127**, 2883 (1925).

(6) (a) C. G. Swain and J. F. Brown, THIS JOURNAL, **74**, 2534 (1952), and preceding papers in that series; (b) *ibid.*, **74**, 2538 (1952).

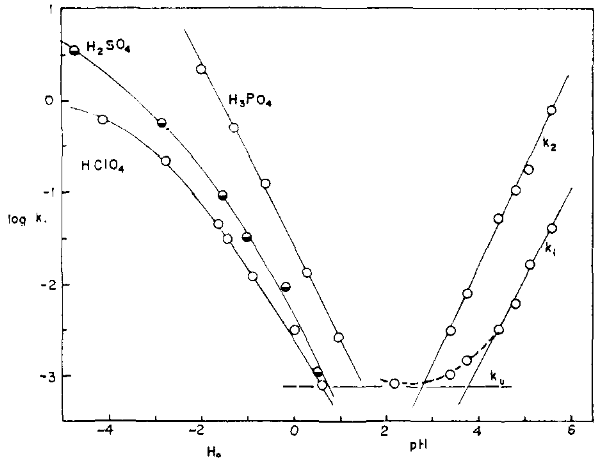


Fig. 1.—Dependence of velocity constants on acidity in water and strong acids. The points on the broken line are values of $k_{obs} = k_u + k_1$; all others are corrected for k_u.

b leaving an electron deficient oxygen to which the phenyl group migrates. Water molecule q is in a position to expedite the migration by supplying a pair of electrons to fill the sp^2 orbital vacated by the departing phenide group. Water molecule r is in a position to solvate the proton thus released. Details such as the extent of covalent bonding between q and boron or the degree of participation by phenide in promoting the cleavage of the peroxide link must be unspecified at this point.

Phosphoric Acid.—Kinetic runs were made in phosphoric acid solutions ranging in concentration from 7 to 65%. The data are presented in Table II.

TABLE II

KINETIC DATA IN AQUEOUS PHOSPHORIC ACID

H_3PO_4, moles/l.	H_0[a]	10^2 k_{obs}[b]	10^2 k_a[b]	$-\log$[c] k_a	Δ[d]	$\log \frac{a_{H_3PO_4}}{a_{H_2O}}$	Δ[e]
0.725	0.99	0.332	0.255	2.593	1.60	−0.20	2.39
2.267	0.28	1.40	1.32	1.879	1.60	+0.50	2.38
5.19	−0.61	12.1	12.0	0.921	1.53	1.43	2.35
6.87	−1.29	49.8	49.7	0.304	1.59	2.11	2.41
9.67	−1.98	214	214	−0.330	1.65	2.81	2.48

[a] E. Heilbronner and S. Weber, *Helv. Chim. Acta*, **32**, 1513 (1949). [b] Units, l. mole^{-1} sec.$^{-1}$. [c] K. L. Elmore, C. M. Mason and J. H. Christensen, THIS JOURNAL, **68**, 2528 (1946). [d] $-\Delta = H_0 + \log k_a$; mean $\Delta = 1.59$. [e] $\Delta = \log a_{H_3PO_4}/a_{H_2O} - \log k_a$; mean $\Delta = 2.40$.

Here again it is clear that the rate does not vary in a simple manner with the concentration of phosphoric acid since a thirteen-fold increase in its concentration produces an eight hundred forty-fold increase in specific rate constant. However, the rate constant is now correlated accurately by H_0 (columns 2, 5 and 6). This appears to be the first recorded example of a reaction whose rate constant is correlated by one function in solutions of one acid and by a distinctly different function in solutions of another acid.

Dependence on H_0 demands a transition state composed of a molecule of boronic acid, one of peroxide and a proton. This might be similar to that formed from I with water molecule r omitted and the perchloric acid molecule replaced by a proton. III. Thus the combination, HX + H_2O in aqueous perchloric acid plays the same role as H^+ in aqueous phosphoric acid. In the latter case we may write the following equations where BA is boronic acid, P is peroxide and III is the intermediate

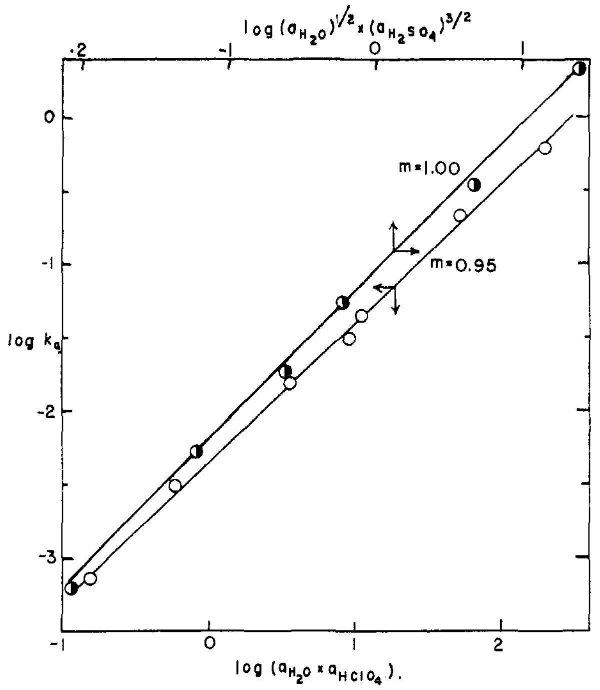
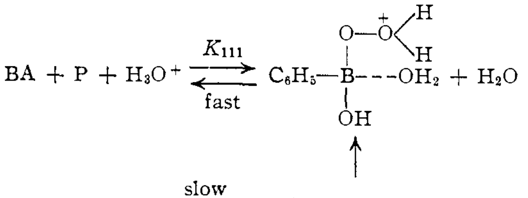


Fig. 2.—Correlation of rate constants in perchloric and sulfuric acids.



$$BA + P + H_3O^+ \underset{\text{fast}}{\overset{K_{111}}{\rightleftharpoons}} C_6H_5\text{—}\overset{\overset{\displaystyle O\text{—}\overset{+}{O}H_2}{|}}{\underset{\underset{\displaystyle OH}{|}}{B}}\text{---}OH_2 + H_2O \quad (5)$$

$$III \xrightarrow[k]{\text{slow}} \text{products III} \quad (6)$$

which is converted to products through a transition state X^+. Now, the rate expression is

$$\frac{dx}{dt} = k_{[111]} = kK_{111}\frac{[BA][P]\,a_{H_3O^+}}{a_{H_2O}} \times \frac{f_{BA}f_P}{f_{X^+}} \quad (7)$$

or

$$k_a = kK_{111}\frac{a_{H^+}f_{BA}f_P}{f_{X^+}} \quad (8)$$

By definition,[4] $h_0 = a_{H^+}f_B/f_{BH^+}$ where f_B and f_{BH^+} are the activity coefficients of a base and its conjugate acid. The proportionality between k_a and h_0 implies that $f_{BA}f_P/f_{X^+}$ is affected by the medium in the same way as f_B/f_{BH^+}, a reasonable implication for a transition state consisting of an activated complex of BA, P and a proton.

From columns 7 and 8 of Table II it is evident that the rate constants are also proportional to the ratio of the activity of phosphoric acid to the activity of water.[7] An intermediate like IV can accommodate this fact. The difference in mechanism between phosphoric and perchloric acids can be at-

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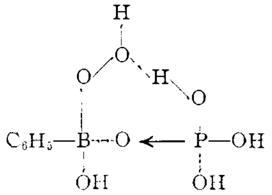
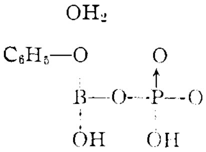
[7] H_0 must therefore be a linear function of the log of this ratio. This obtains also for hydrochloric and perchloric acids but not for sulfuric acid: H. G. Kuivila, *J. Phys. Chem.*, in press.

tributed to the fact that much un-ionized acid is present in the solutions of the former but not in solutions of the latter. The passage of IV through the transition state to V is an example of bifunctional catalysis.[6b] In the proton transfer to a peroxide oxygen the phosphoric acid is playing the role of electrophilic reagent while in the formation of the covalent boron–oxygen bond it is a nucleophilic reagent. Its ability to function in this dual role accounts for its exceptional catalytic ability.


IV


V

Thus we have two mechanisms which differ significantly but obey the same kinetic law. Of these, the second is more attractive for at least three reasons. First, there seems to be no reason why one acid should catalyze via assembly I and a second via assembly III. Secondly, the extreme effectiveness of phosphoric acid is easily understood in terms of IV. Finally, the fact that the two acids show different kinds of correlation with acidity becomes reasonable: it is based on a fundamental difference in the nature of solutions of these acids.

Sulfuric Acid.—Table III contains the data obtained in solutions ranging from 2 to 60% sulfuric acid.

TABLE III

KINETIC DATA IN AQUEOUS SULFURIC ACID

H_2SO_4, mole/l.	$-H_0$[a]	10^2 $k_{obs.}$[d]	10^2 k_a[d]	$-\log k_a$	$\log (a_{A_2O})^{1/2} (a_{H_2SO_4})^{3/2}$[b]	$-\Delta$[c]
0.193	−0.53	0.184	0.107	2.971	−2.08	0.89
0.386	−0.36	0.286	0.209	2.680	−1.79	.89
1.13	+0.20	0.989	0.912	2.040	−1.23	.81
2.26	0.88	3.17	3.09	1.510	−0.63	.88
3.64	1.53	9.19	9.11	1.040	−0.23	.81
6.38	2.85	59.1	59.0	0.229	+0.67	.90
8.99	4.30	360	360	−0.57	+1.41	.84

[a] See footnote *b* in Table I. [b] S. Shankman and A. R. Gordon, THIS JOURNAL, *61*, 2370 (1939). [c] $\Delta = \log k_a - \log[(a_{H_2O})^{1/2}.(a_{H_2SO_4})^{3/2}]$; mean $\Delta = -0.86$. [d] Units, l. mole^{-1} sec.$^{-1}$

It is clear that in the range of acidity covered H_0 does not correlate the data as it does with phosphoric acid. Nor is the product of activities of water and sulfuric acid a linear function of the rate constant as in the case of perchloric acid. Examination of combinations of various exponents (up to two) in the activities of water and acid showed that only the product $(a_{H_2O})^{1/2}(a_{H_2SO_4})^{3/2}$ as indicated in the table correlates the data over the entire range. The correlation is remarkably precise as shown by the fact that a log–log plot of rate constant and activity product has a slope, 1.00 (Fig. 2). However, the actual mechanistic significance of the fractional exponents is not apparent. In view of the effectiveness of phosphoric acid as a catalyst it seems probable that the stronger acid bisulfate plays a significant role in the sulfuric acid solutions. Since it is largely undissociated and is structurally analogous to phosphoric acid it could possibly replace the latter in structure IV.

More information concerning sulfuric acid solutions than is now available would be necessary before the kinetic data could be analyzed reliably.

Experimental

Reagents.—Reagent grade acids were used without further treatment.

Rate Measurements.—The procedure was the same as that previously described[3] with two exceptions. When the stronger acid solutions were used ice was added to the iodide quenching solution to prevent undue heating when the sample was added. The titrations also had to be done more slowly to avoid overtitration. Phosphoric acid diminished the effectiveness of molybdate as a catalyst for the iodide–peroxide reaction to such an extent that when the more concentrated solutions were used the peroxide was determined colorimetrically.[3]

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[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

The Acyloin Condensation. II. Free Radical Formation Accompanying the Decarbonylation of An Aliphatic Ester by Sodium

BY EARLE VAN HEYNINGEN

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A completely aliphatic ester underwent the acyloin condensation to give products expected from the decomposition or coupling of free radicals.

A recent intensive investigation of the acyloin condensation of certain aralkyl esters has furnished further support for the formulation of the acyloin condensation as a free radical reaction.[1] The purpose of the present study was to determine whether similar evidence could be obtained using a purely aliphatic ester.

Aliphatic esters in the acyloin condensation generally give good yields of the expected acyloins. This is no doubt due to the high reactivity (instability as free radicals) of the initial sodium ketyls which immediately couple with each other. An aliphatic ester, which in the course of the acyloin condensation could give a resonance stabilized free radical, might form products that would be more indicative of the free radical nature of the reaction. Such an ester is ethyl 2,2,3,4-tetramethyl-3-pentenoate (V). In view of the earlier work with aralkyl esters, it would be expected to form the free radical

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[1] E. Van Heyningen, THIS JOURNAL, **74**, 4861 (1952).