3. The constants of hydrogen, propionate, acetate and formate ion catalysis have been determined. They are in the order

$$k_{\text{propionate}} < k_{\text{H}_3\text{O}^+} < k_{\text{acetate}} < k_{\text{formate}}$$

4. The hydration of propionic anhydride is retarded by butyric acid. It is further retarded by the butyrate ion.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

CATALYSIS IN THE HYDRATION OF ACETOPROPIONIC ANHYDRIDE[1]

BY MARTIN KILPATRICK, JR., AND MARY L. KILPATRICK

RECEIVED DECEMBER 3, 1929 PUBLISHED APRIL 7, 1930

In two previous papers[2] there have been presented the results of a study of the hydration of acetic and of propionic anhydride. The hydration is catalyzed by the hydrogen ion and the hydroxyl ion, and by bases other than the hydroxyl ion; the catalytic constants of the bases are not, however, in the order of their basic strength. Moreover, the propionate ion retards the hydration of acetic anhydride, and accelerates the hydration of propionic anhydride, while the butyrate ion retards both processes. It was suggested that, where retardation occurs, there is formation of the mixed anhydride, or some other intermediate compound, of the order of stability of the mixed anhydride, formed between the simple anhydride and the anion. In the present paper are given the results of the measurement of the rate of hydration of one of these mixed anhydrides, the acetopropionic, at 0°.

Experimental Part

The apparatus, experimental procedure and the method of calculation have already been described.[2]

The existence of mixed anhydrides has been the subject of much discussion, due, primarily, to their property of slowly decomposing during distillation into the simple anhydrides.[3] Because of the lack of a definite boiling point, many chemists regarded the mixed anhydrides as equimolecular mixtures of the corresponding simple anhydrides. With the preparation of certain of the higher mixed anhydrides, which are crystalline solids at ordinary temperatures, the doubt of the existence of this class of compounds disappeared. Verkade[4] succeeded in preparing the liquid aceto-

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[1] Paper presented at the Minneapolis Meeting of the American Chemical Society, September, 1929.

[2] (a) Kilpatrick, THIS JOURNAL, **50**, 2891 (1928); (b) Kilpatrick, *ibid.*, **52**, 1410 (1930).

[3] Behal, *Ann. chim. phys.*, [7] 19, 274 (1900).

[4] Verkade, *Rec. trav. chim.*, **35**, 299 (1915).

propionic anhydride in a state of purity such that it reacted with water in dilute aqueous solution according to the monomolecular law. If Verkade had had a mixture of acetic and propionic anhydrides, he would have obtained a constant only in the event that the two simple anhydrides took up water at the same rate, which is not true.

The acetopropionic anhydride used in the present investigation was prepared by two methods: from propionyl chloride and anhydrous sodium acetate, as described by Verkade,[4] and from acetyl chloride and propionic acid in the presence of pyridine, in ethereal solution.[5] The first three columns of Table I list the samples, their boiling points, and the pressures under which they distilled.[6]

TABLE I

THE SPONTANEOUS REACTION

Temperature, 0°. All solutions 0.0004 M in HCl

Sample	Boiling point, °C.	Pressure, mm.	k_0	Volume change, cc. per liter per 0.05 mole of anhydride
A	53-56	17-19	0.0222, 0.0223	0.14_5, 0.14
B	57.8-60.5	19	.0220	.14
C	52-55	17	.0225	.14
D	55-58.5	18	0.0221, 0.0225, 0.0227	0.14, 0.14, 0.14
E	57.4-59.4	22	.0223	$.12_5$
F	51-51.5	15.5	.0226	$.13_5$

Samples A, B, C, D and E were prepared according to Verkade; in the preparation of F the pyridine method was employed. All except F gave a negative test for chloride. A weighed portion of D, the anhydride used in all the subsequent experiments, was dissolved in water and titrated against standard sodium hydroxide solution. The molecular weight was calculated from the titer to be 115.8; the theoretical is 116.1, and the value found by Verkade, 115.6. The presence of 2% of acetic anhydride as impurity in Sample D would cause the difference of 0.3 between the theoretical and the calculated molecular weight; the determination of the molecular weight is, therefore, not a sensitive test of the purity of the mixed anhydride. The fourth column of Table I records the constant of the spontaneous (water) reaction. In the fifth column of the table is shown the decrease in volume accompanying hydration, calculated for a liter of solution initially containing 0.05 mole anhydride.

To test the possibility of the immediate and complete reaction of the simple anhydrides in aqueous solutions to form the mixed anhydride, the rate of hydration of an equimolecular mixture of acetic and propionic anhydrides was measured. The monomolecular "constant" decreased steadily

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[5] Knoll and Co., German patent 117,267, *Chem. Centr.*, I, 347 (1901); Wedekind, *Ber.*, **35**, 2070 (1901).

[6] The authors are indebted to Mr. Clifton Kerns for the preparation of a preliminary sample of acetopropionic anhydride.

with the progress of the reaction. Acetopropionic anhydride is therefore not a mixture.

It will be shown presently that the hydration of acetopropionic anhydride is accelerated by the acetate ion, and retarded by the propionate ion. Both of these ions are present after the start of the reaction, but at concentrations too slight to affect the rate of hydration to a detectable extent.

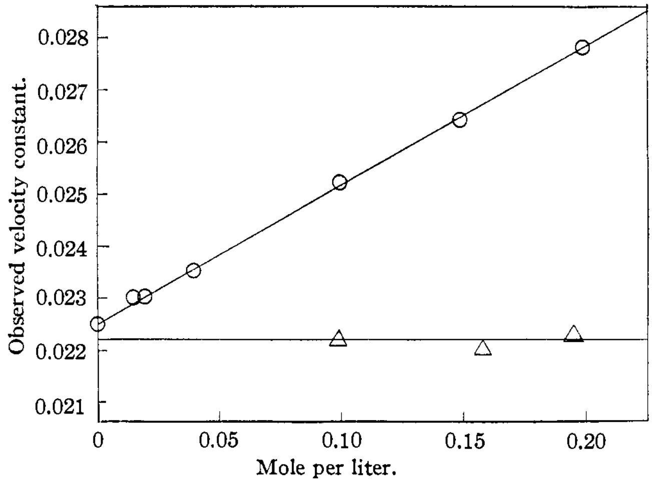

Fig. 1.—Effect of H_3O^+ on reaction rate. Effect of NaCl.

The lower line of Fig. 1 and the data given in Table II show the effect of sodium chloride upon the spontaneous reaction.

TABLE II

THE EFFECT OF SODIUM CHLORIDE

Temperature, 0°. All solutions 0.0004 *M* in HCl

NaCl, moles per liter	0.099	0.158	0.195
k_{observed}	.0222	.0220	.0223

In all the experiments the solutions were 0.0004 *M* in hydrochloric acid and 0.06 *M* in acetopropionic anhydride, the anhydride concentration being that used throughout the work. If an electrolyte effect exists in dilute solution, it is negligibly small, as in the case of propionic anhydride.

Table III gives the results of the experiments carried out to determine the effect of the hydrogen ion.

In the third column one has the difference between the observed velocity constant and k_0, which is taken as 0.0224 for solutions having equivalent salt concentrations not greater than 0.2. The proportionality between the increase in the velocity constant and the acid concentration is represented by the upper line of Fig. 1.

TABLE III

EFFECT OF HYDROGEN ION

HCl, moles per liter	$k_{obs.}$	$k_{obs.} - k_0$	$k_{H_3O^+}$
0.0004	0.0224	....	....
.0149	.0230	0.0006	0.040[a]
.0198	.0230	.0006	.030
.0398	.0235	.0011	.028
.0994	.0252	.0028	.028
.1490	.0264	.0040	.027
.1990	.0278	.0054	.027
		Average,	.028 a. d. 3%

[a] Omitted from average.

In Table IV are shown the results of the experiments in sodium acetate–acetic acid buffer solutions. Since it was expected that the medium effect of acetic acid upon k_0 would not differ in character from the medium effect in the hydration of acetic anhydride or propionic anhydride, an investigation of the effect was avoided by using an acid concentration of 0.974 *M* in all the experiments.

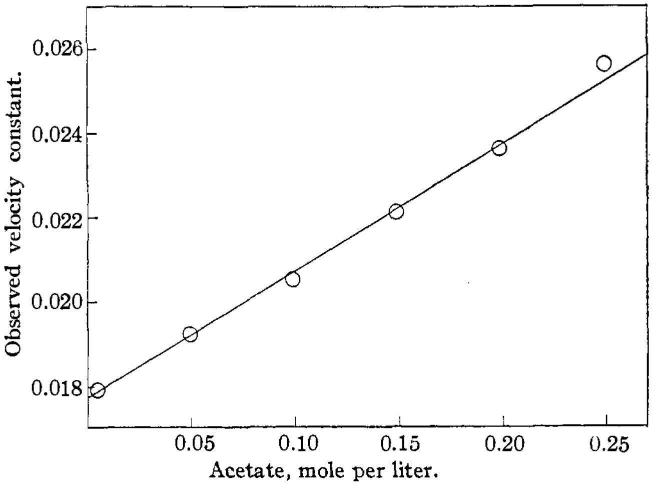

Fig. 2.—Effect of acetate.

In Fig. 2 the observed velocity constants are plotted against the corresponding acetate concentrations; the intercept of the line on the axis of velocity constants gives k_0', the constant of the spontaneous reaction in 0.97 *M* acetic acid; k_0' is 0.0177.

In the third column of Table IV is recorded the amount of the reaction due to the acetate ion, $k_{obs.} - k_0'$, and in the fourth, the constant of acetate ion catalysis.

Similar experiments were performed in sodium propionate–propionic acid buffer solutions in which the concentration of propionic acid was kept

TABLE IV

EFFECT OF ACETATE

All solutions 0.974 M in CH_3COOH. $k'_0 = 0.0177$

CH_3COO^-, moles per liter	$k_{obs.}$	$k_{obs.} - k'_0$	k_{AC^-}
0.005	0.0179	....	...
.0497	.0192	0.0015	0.030
.0994	.0205	.0028	.028
.1490	.0221	.0044	.029
.1990	.0236	.0059	.030
.2495	.0256	.0079	.032
		Average,	.030 a. d. 3%

0.987 M. The reaction being no longer strictly monomolecular, the velocity constants are recorded as approximate. The deviation from monomolecularity is less with aceto propionic anhydride (not exceeding 5% in any case) than with acetic anhydride, or with propionic anhydride in the presence of butyrate. In Fig. 3 the observed velocity constants are plotted against the propionate concentrations. The constant of the spontaneous reaction in 0.987 M propionic acid, k'_0, is 0.0171 as given by the intercept of the line upon the axis of velocity constants.

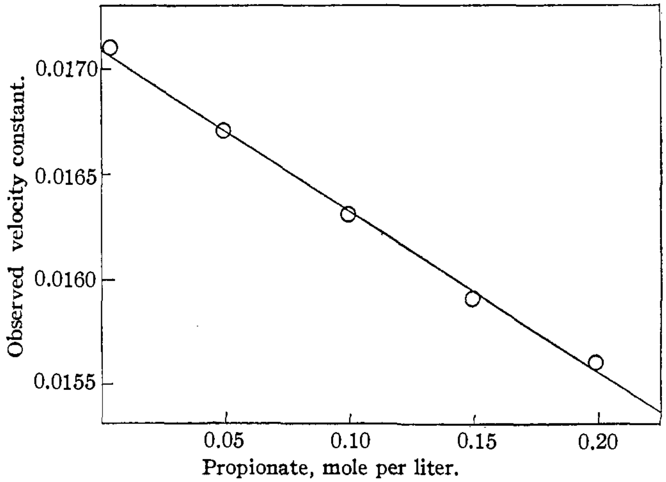

Fig. 3.—Effect of propionate.

TABLE V

EFFECT OF PROPIONATE

All solutions 0.987 M in C_2H_5COOH. $k'_0 = 0.0171$

$C_2H_5COO^-$, moles per liter	0.005	0.0497	0.0994	0.1490	0.1990
$k_{obs. (approx.)}$	.0171	.0167	.0163	.0159	.0156

With increasing propionate concentration the observed velocity constant decreases, and the rate of decrease is proportional to the propionate-ion concentration. In 0.99 *M* propionic acid solution the constant may be calculated from the equation

$$k = 0.0171 - 0.0077c$$

where c represents the concentration of propionate. It may be recalled that the propionate ion retards the hydration of acetic anhydride and accelerates the hydration of propionic anhydride.

The butyrate ion, like the propionate, retards the hydration of acetopropionic anhydride. In 0.995 *M* butyric acid solution the constant of the spontaneous reaction was found to be 0.0166, and in a buffer solution 0.997 *M* in butyric acid and 0.0498 *M* in sodium butyrate the observed velocity constant (approximate) was 0.0149. The effect of the butyrate ion is therefore (0.0149 − 0.0166)/(0.0497) or −0.025. Butyrate retards the hydration of all three anhydrides studied—acetic, propionic and acetopropionic.

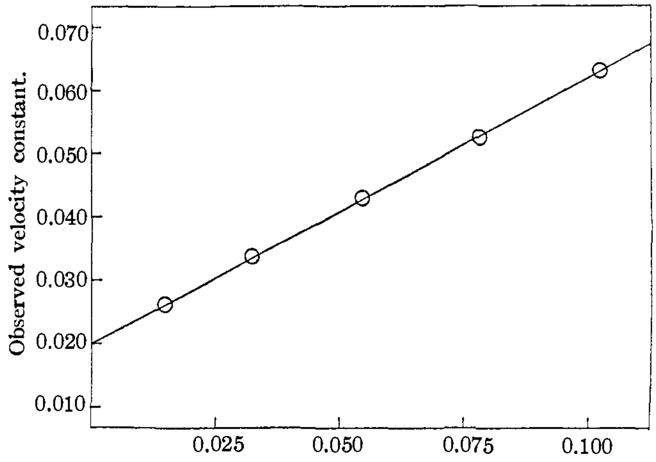

Fig. 4.—Effect of formate.

In Table VI and Fig. 4 are shown the results of the experiments in sodium formate–formic acid buffer solutions. The effect of the 1 *M* formic

TABLE VI

EFFECT OF FORMATE

HCOOH, moles per liter	HCOONa, moles per liter	H_3O^+, moles per liter	$HCOO^-$, moles per liter	$k_{obs.}$	$k_{obs.} - k'_0$	k_{F^-}
0.992	0	0.0148	0.0148	0.0260	0.0065	0.43[a]
.985	0.0249	.0075	.0324	$.0336_5$	$.0141_5$	.435
.987	.0497	.0048	.0545	.0431	.0236	.433
.989	.0746	.0035	.0781	.0525	.0330	.423
.990	.0994	.0030	.1024	.0631	.0436	.426

Average, 0.429 a. d. 1%

[a] Omitted from average.

acid upon the spontaneous reaction was again obtained by plotting $k_{\text{obs.}}$ against the formate concentration; the intercept of the line in Fig. 4 upon the axis of velocity constants, 0.0195, represents k_0 or the constant of the spontaneous reaction in 1 *M* formic acid.

The hydrogen- and formate-ion concentrations were calculated as previously described.[2b] The amount of the reaction due to the hydrogen ion, $(H_3O^+)k_{H_3O^+}$, varies from 0.0004 to 0.0001 in the experiments listed in the table. In view of the smallness of the correction for hydrogen-ion catalysis, and in view of the uncertainty of the intercept (there may exist a small salt effect upon the formate ion catalyzed reaction), no correction for catalysis by the hydrogen ion is made. The sixth column of the table gives the amount of the reaction due to the formate ion, $k_{\text{obs.}} - 0.0195$, and the last column, the constant of formate ion catalysis.

Discussion

The results of the work with the three anhydrides are collected in Table VII.

TABLE VII

SUMMARY OF RESULTS

Anhydride	k_0	$k_{H_2O} = k_0/55.6$	$k_{H_3O^+}$	$k_{CH_3COO^-}$	k_{HCOO^-}	$k_{C_2H_5COO^-}$	$k_{C_3H_7COO^-}$
Acetic	0.0269	0.000484	0.031	0.038_5	0.680	(−0.035)	(−0.049)
Propionic	.0166	.000299	.022	.034	.322	.015	(− .020)
Acetopropionic	.0224	.000403	.028	.030	.429	(− .008)	(− .025)

It will be noticed that the catalytic constants do not stand in the order of basic strength of catalyst, which would require that

$$k_{H_2O} < k_{\text{formate}} < k_{\text{acetate}} < k_{\text{propionate}} < k_{\text{butyrate}}$$

With acetic and with acetopropionic anhydride, the existing order is

$$k_{H_2O} < k_{\text{acetate}} < k_{\text{formate}}$$

while the propionate and the butyrate ion retard the hydration; with propionic anhydride the order is

$$k_{H_2O} < k_{\text{propionate}} < k_{\text{acetate}} < k_{\text{formate}}$$

the butyrate ion again retarding hydration.

An examination of Table VII reveals that with the three anhydrides studied the following statement holds. An anion which has the possibility of reacting with the anhydride to form a different anhydride, and a different anion, accelerates the reaction if the anhydride which might be formed hydrates more rapidly than does the original anhydride, and it retards the reaction when the intermediate anhydride hydrates more slowly than the original. The order in which the anions stand in regard to acceleration or retardation is also the expected order. Thus in the hydration of propionic anhydride

$$k_{\text{acetate}} < k_{\text{formate}}$$

corresponding to the greater reactivity of formic–propionic anhydride than of acetopropionic.

Brönsted's[7] general formula for the velocity of the reaction between A and B has been derived by Bjerrum[8] from the consideration of an equilibrium between the reactants and an intermediate collision complex of which a small fraction reacts in unit time. The concentration of the collision complex S is related to the concentrations of A and B through the equation

$$K = (\mathrm{S})f_{\mathrm{S}}/(\mathrm{A})(\mathrm{B})f_{\mathrm{A}}f_{\mathrm{B}}$$

Since the rate-determining process is the reaction of the complex (either spontaneously or with the solvent) to form the products

$$v = k(\mathrm{S})$$

where k is small, *i. e.*, only exceptionally do A and B collide with sufficient energy to react. Substituting for the concentration of S its value from the equation above, Bjerrum obtained

$$v = kK(\mathrm{A})(\mathrm{B})f_{\mathrm{A}}f_{\mathrm{B}}/f_{\mathrm{S}}$$

Provided the concentration of S is small, so that it is not necessary to distinguish between the concentration of free A or B and its total, measured concentration, and provided the solution is so dilute that the activity coefficient of the complex S may be set equal to the activity coefficient of an ion whose charge equals the algebraic sum of the charges of A and B, the formula is identical with Brönsted's.

The hydration of acetic anhydride may therefore be thought of as proceeding, in water alone, through the formation of the complex $\mathrm{A{\cdot}H_2O}$(A representing the anhydride) which then reacts, alone or with water molecules, to give two molecules of acetic acid. The presence of catalysts opens other paths. Thus in the solution of a strong acid

$$\mathrm{A + H_2O \rightleftharpoons A{\cdot}H_2O} \qquad (1)$$

$$\mathrm{A{\cdot}H_2O + H_2O \longrightarrow 2CH_3COOH + H_2O}$$

$$\mathrm{A + H_3O^+ \rightleftharpoons A{\cdot}H_3O^+} \qquad (2)$$

$$\mathrm{A{\cdot}H_3O^+ + H_2O \longrightarrow 2CH_3COOH + H_3O^+}$$

$$-\mathrm{dA}/\mathrm{d}t = k_0(\mathrm{A}) + k_{\mathrm{H_3O^+}}(\mathrm{A})(\mathrm{H_3O^+})$$

In a sodium formate–formic acid buffer solution the reaction also proceeds via the formation of $\mathrm{A{\cdot}HCOO^-}$; in a sodium acetate–acetic acid buffer solution, via the formation of $\mathrm{A{\cdot}CH_3COO^-}$.

Whenever the formation of a complex of the type $\mathrm{A{\cdot}HCOO^-}$ occurs, its reactivity appears to be of the order of magnitude of the reactivity of the mixed anhydride. Table VII shows that the hydration of acetic anhydride is greatly accelerated by the formate ion; this is in accord with the known instability of anhydrides of formic acid. The hydration of propionic anhydride is accelerated by the acetate ion and by the formate ion, the latter

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[7] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[8] Bjerrum, *ibid.*, **108**, 82 (1924).

effect being greater, which is to be expected from the greater instability of formic–propionic anhydride as compared with acetopropionic.

The rate-determining complex formed in the catalyzed reaction cannot, however, be the mixed anhydride itself. If the original anhydride and the catalyzing anion of the buffer reacted to form the mixed anhydride, we should have, for acetic anhydride, say, in a formate–formic acid buffer solution

$$\mathrm{A} + \mathrm{HCOO}^- \rightleftharpoons \mathrm{AF} + \mathrm{CH_3COO}^-$$
$$K = (\mathrm{AF})(\mathrm{CH_3COO}^-)f_{\mathrm{AF}}f_{\mathrm{CH_3COO}^-}/(\mathrm{A})(\mathrm{HCOO}^-)f_{\mathrm{A}}f_{\mathrm{HCOO}^-}$$

where A represents acetic anhydride, AF, formic–acetic anhydride. The expression for the velocity of reaction becomes

$$v = k(\mathrm{AF})$$
$$v = kK(\mathrm{A})(\mathrm{HCOO}^-)f_{\mathrm{A}}f_{\mathrm{HCOO}^-}/(\mathrm{CH_3COO}^-)f_{\mathrm{AF}}f_{\mathrm{CH_3COO}^-}$$

Since the concentration of the acetate ion changes during the reaction, the mechanism above is not in agreement with the observed monomolecularity of the reaction.

The experimental method employed does not permit wide variation in the initial concentration of anhydride. However, in the study of the hydration of propionic anhydride, in acetate–acetic acid buffer solution, the initial anhydride concentration was changed by 25% without detectable effect upon the velocity constant.

In sodium butyrate–butyric acid buffer solution the hydration of all three anhydrides is retarded; in sodium propionate–propionic acid buffer solution the hydration of acetic and of acetopropionic anhydride is retarded. In these cases there must be immediate chemical reaction to a considerable extent between the anhydride and a constituent of the buffer. Several possibilities present themselves. If the initial anhydride reacted with the anion of the buffer to form another anhydride, and another anion, the rate measured would be the rate of hydration of a mixture of anhydrides, which would not give a monomolecular velocity constant. With increasing concentration of the anion of the buffer the concentration of the intermediate, less reactive, anhydride would increase, making hydration slower. If the anhydride combined with the anion of the buffer to form an addition compound[9] which was itself non-reactive, the rate of hydration would follow the monomolecular law and would decrease with increasing concentration of the anion. The results of the formation of such a compound, in equilibrium with the anhydride, would not be distinguishable from a salt effect. In addition, both processes might go on simultaneously. With acetic anhydride and with acetopropionic anhydride in the presence of propionate or butyrate, and with propionic anhydride in the presence of butyrate, the deviation of the rate of hydration from monomolecularity indicates that there is intermediate anhydride formation.

[9] Franzen, *Ber.*, 41, 3641 (1908): Tsakalotos, *Bull. soc. chim.*, [4] 7, 461 (1910).

Summary

1. The salt effect of sodium chloride, in concentrations up to 0.2 *M*, upon the rate of hydration of acetopropionic anhydride is negligibly small at 0°.

2. The constants of hydrogen, acetate and formate-ion catalysis have been determined. They are in the order

$$k_{H_3O^+} < k_{CH_3COO^-} < k_{HCOO^-}$$

3. The hydration is retarded by the propionate ion and by the butyrate ion.

4. The results obtained with acetic, propionic and acetopropionic anhydrides have been collected. An examination of the catalytic constants suggests that, when the reaction is accelerated in a buffer solution, the collision complex formed between the anhydride and the anion of the buffer is of the order of stability of the mixed anhydride. In those buffer solutions in which the hydration is retarded there is reason to believe that a part of the initial anhydride has reacted with the anion of the buffer to form another anhydride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE AUTOCATALYTIC REDUCTION OF BROMATE BY HYDROGEN PEROXIDE IN ACID SOLUTION

BY WILLIAM C. BRAY AND PAUL R. DAVIS

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The autocatalytic reduction of bromate ion by hydrogen peroxide has been described briefly by Bray and Livingston.[1] At the acid concentration they used, over 0.7 *N*, some bromine is formed; its concentration, when hydrogen peroxide is present in excess, rises to a maximum and then gradually decreases to a constant value. We have found that the amount of bromine formed decreases rapidly as the concentration of acid is lowered, and that at moderate or low concentrations of acid (and bromide) the main reaction is

$$BrO_3^- + 3H_2O_2 = Br^- + 3O_2 + 3H_2O \tag{1}$$

The present investigation was undertaken to measure the rate of this autocatalytic reaction, and to test quantitatively the conclusion[1] that the autocatalysis is due to the reaction

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \tag{2}$$

followed by

$$Br_2 + H_2O_2 = O_2 + 2Br^- + 2H^+ \tag{3}$$

The progress of the reaction was followed by collecting the oxygen over water and measuring its volume. The temperature of the oxygen buret

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[1] Bray and Livingston, THIS JOURNAL, **45**, 1254 (1923).