Summary

The cell Hg | Hg_2SO_4, xMH_2SO_4 | xMH_2SO_4, $Hg_2SO_4,3HgO \cdot SO_3$ | (Au) has been set up and its electromotive force measured. It is fairly reproducible, and constant in electromotive force for a short period soon after it is set up, but the e. m. f. decreases slowly over a period of several months.

The solubility of basic mercuric sulfate in some of the sulfuric acid electrolytes was measured.

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

CATALYSIS IN THE HYDRATION OF PROPIONIC ANHYDRIDE[1]

BY MARTIN KILPATRICK, JR.

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In a recent investigation of catalysis in the hydration of acetic anhydride[2] it was shown that while bases other than hydroxyl ion exert a catalytic effect, the magnitude of the effect is not in the order of increasing basic strength of the catalyst as it is in other cases.[3] Thus it was found that the formate ion accelerates the reaction to a marked degree, the acetate ion to a lesser extent, while in the presence of propionate ion the reaction is slower than in water alone. From the theory the reverse order was to be expected. The possibility of mixed anhydride formation was offered in explanation of the experimental results.

The question may be raised as to whether the hydration of acetic anhydride is an exception to the general theory, or a chemical process which may not be classed as a catalytic reaction at all. It remains, however, that a study of the facts is far more useful than debating the catalytic or non-catalytic nature of the reaction.[4]

The experimental results obtained in the case of acetic anhydride suggest that when the reaction is retarded there is partial formation of the mixed anhydride, or some other intermediate compound formed from the anhydride and the ion in question, which has the same order of stability as the mixed anhydride. It is therefore desirable to know the relationships which exist in the hydration of propionic and acetopropionic anhydrides. The present paper deals with the effect on the hydration of propionic

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

[2] Kilpatrick, THIS JOURNAL, **50**, 2891 (1928).

[3] Brönsted and Pedersen, *Z. physik. Chem.*, **113**, 389 (1924); Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927); Brönsted, *Trans. Faraday Soc.*, **24**, 630 (1928).

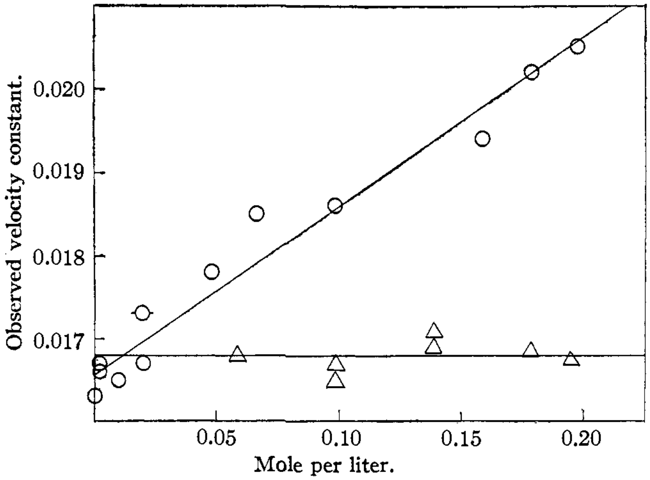
[4] In this connection see Hinshelwood, *ibid.*, **24**, 552 (1928).

anhydride of hydrogen, formate, acetate and propionate ions; it also includes a study of the "solute effect"[5] upon the reaction.

Experimental Part

The apparatus, the experimental procedure and the method of calculation were the same as those described in the previous paper. As before, all experiments were carried out at 0°.[2]

Propionic anhydride was obtained from three different sources. The first sample distilled at 164–165° under 769 mm.; it gave the same rate of hydration as the second, which under 16 mm. distilled at 62.5–63.3°. In fact both samples gave, within the experimental reproducibility of the measurements (2%), the same rate as the third sample, c. p. propionic anhydride.



○, HCl; △, NaCl; -⊙-, 0.02 HCl + 0.06 NaCl.

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

The velocity constant of the spontaneous reaction was measured in solutions 0.002 *M* in hydrochloric acid; here any catalytic effects of the hydrogen, hydroxyl and acetate ions are negligible. The velocity constant, k_0, was found to be 0.0166 min.$^{-1}$; the value given by Verkade[6] is 0.0161. The half time of the reaction is forty-three minutes as compared with twenty-six minutes in the case of acetic anhydride.

The effect upon k_0 of the addition of sodium chloride is shown by the data recorded in Table I, and again, graphically, by the lower line of Fig. 1. In all cases the solutions were 0.002 *M* in hydrochloric acid and 0.046 *M* in propionic anhydride.

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[5] This term has been proposed by Walker to designate the effect of non-electrolytes as well as of electrolytes (other than catalysts) upon the reaction. Walker, *Trans. Faraday Soc.*, **24**, 722 (1928).

[6] Verkade, *Rec. trav. chim.*, **35**, 79 (1915).

TABLE I

EFFECT OF SODIUM CHLORIDE

All solutions 0.002 M in HCl. Temperature, 0°

NaCl, moles per liter	0.0	0.059	0.099	0.139	0.179	0.195	0.743
k, observed	.0166	.0168	.0165	.0171	.0168$_5$	.0167$_5$	.0133
			.0167	.0169			

There is possibly an increase in rate in dilute solution with addition of sodium chloride; its magnitude, however, does not exceed the experimental error of the measurements.

Table II shows the effect of the hydrogen ion upon the rate of hydration. In the second column are recorded the observed velocity constants, in the third, the differences between $k_{\text{obs.}}$ and k_0, k_0 being taken as 0.0166 on the assumption that the salt effect upon the spontaneous reaction is negligible. The constant of hydrogen ion catalysis, $k_{H_3O^+}$, is obtained by dividing $k_{\text{obs.}} - k_0$ by the concentration of hydrochloric acid.

TABLE II

EFFECT OF HYDROGEN ION

HCl, moles per liter	k, observed	$k_{\text{obs.}} - k_0$	$k_{H_3O^+}$
0.0020	0.0166	....	...
.0100	.0165	....	...
.0200	.0167	....	...
.0485	.0178	0.0012	0.025
.0667	.0185	.0019	.028
.0990	.0186	.0020	.020
.1590	.0194	.0028	.018
.1790	.0202	.0036	.020
.1980	.0205	.0039	.020
.743	.0334	.0201	.027[a]
		Average,	.022 a. d. 15%

[a] Omitted from average; k_0 here 0.0133.

In taking the average value of $k_{H_3O^+}$, the last experiment in the table was omitted, for at a concentration of 0.7 M one cannot assume that the salt effects of hydrochloric acid and of sodium chloride are the same. In fact, there is some doubt of the justifiability of this assumption in dilute solution. In the case of acetylchloro-aminobenzene, Soper and Pryde[7] have shown that the effects may even be in opposite directions. It is also possible that a salt effect upon the hydrogen ion catalyzed reaction is coming into evidence at this high concentration.

The reaction is retarded by acetic acid and by propionic acid, as is shown in Table III and Fig. 2.

For acid concentrations up to 1 M, the effect of acetic acid upon k_0 may

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[7] Soper and Pryde, *J. Chem. Soc.*, 2761 (1927).

Table III

Effects of Acetic and Propionic Acids

Init. concn. of acetic acid, moles per liter	$k_{obs.}$		Init. concn. propionic acid, moles per liter	$k_{obs.}$	
0.194	0.0155				
.388	.0156		0.394	0.0150	
.582	.0148,	0.0151	.594	.0144	
.799	.0144		.795	.0136	0.0136
.970	.0139		.990	.0128	0.0127
1.940	.0118		1.970	.0101	

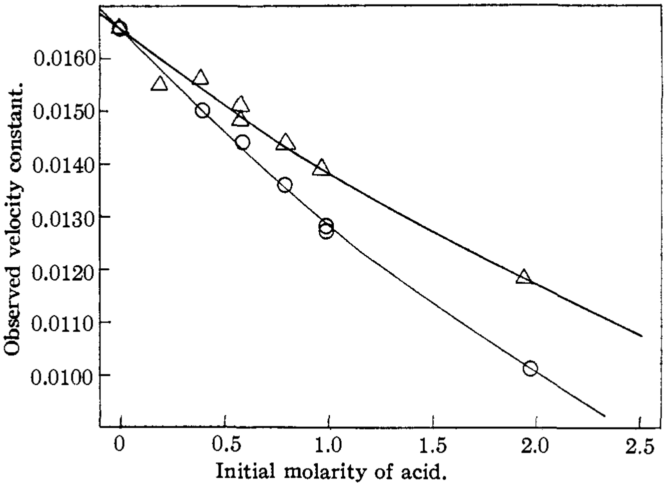
be expressed, with an accuracy greater than the experimental reproducibility, by the equation

$$k_{obs.} = 0.0166 - 0.0028\, m$$

and the effect of propionic acid by the equation

$$k_{obs.} = 0.0166 - 0.0039\, m$$

The effects are accordingly spoken of as "linear."



△, Acetic; ○, propionic.

Fig. 2.—Effect of acetic acid. Effect of propionic acid.

This term is in itself somewhat incomplete. The rate of the reaction between two non-electrolytes A and B is given, according to Brönsted, by the equation

$$v = k(\mathrm{A})(\mathrm{B})f_{\mathrm{A}}f_{\mathrm{B}}/f_{\mathrm{AB}} \tag{1}$$

where k, the velocity constant, is constant for a given reaction, temperature and medium. When the reaction is carried out in the presence of the non-electrolyte or the weak electrolyte C, a change in the rate, accompanying the change in medium, may be expected. This change in rate may result from change in the velocity constant k, or from changes in the activity coefficients f_A, f_B and f_{AB}. From the rather scanty evidence existing[8] it appears justifiable to assume that

$$\ln f_A = \beta_A m \qquad (2)$$

where β_A is a constant for the substance A dissolved in an aqueous solution of C, and m is the concentration of C present. If we for the moment assume that k remains unchanged in the presence of C and that change in rate arises only from changes in the activity coefficients

$$k_{\text{obs.}} = kf_Af_B/f_{AB} \qquad (3)$$

Substituting the values of the activity coefficients from Equation 2 in 3, we have

$$k_{\text{obs.}} = ke^{m(\beta_A + \beta_B - \beta_{AB})}$$

or

$$k_{\text{obs.}} = ke^{m\sigma},\text{ where } \sigma = \beta_A + \beta_B - \beta_{AB} \qquad (4)$$

When $e^{m\sigma}$ is expanded into a series, (4) becomes

$$k_{\text{obs.}} = k(1 + (\sigma m)/1! + (\sigma m)^2/2! + (\sigma m)^3/3! + \ldots.) \qquad (5)$$

The initial slope of the curve obtained by plotting $k_{\text{obs.}}$ against m determines σ. The same type of equation is applicable in the case of a reaction between a non-electrolyte and an ion in dilute electrolyte solution.[9]

In order to apply Equation 5 to the results given in Table III, it is necessary to calculate the velocity constants per liter of solution in terms of equal weights of water, water being a reactant, and to make a small correction for catalysis by hydrogen and acetate or propionate ions. In Table IIIA are recorded the observed values of the velocity constant per liter of solution per 1000 g. of water, and the values of this constant calculated by Equation 5.

Table IIIA

Medium Effects of Acetic and Propionic Acids

CH_3COOH, moles per liter	k/liter/ 1000 g. H_2O, obs.	k/liter/ 1000 g. H_2O, calcd.	C_2H_5COOH, moles per liter	k/liter/ 1000 g. H_2O, obs.	k/liter/ 1000 g. H_2O, calcd.
0.194	0.0156	0.0162			
.388	.0158	.0157	0.394	0.0154	0.0154
.582	.01525	.01535	.594	.0150	.0149
.799	.01485	.0149	.795	.0143	.01435
.970	.0144	.0146	.990	.01355	.01385
1.940	.0128	.0128	1.970	.01145	.0116
	$\sigma = -0.134$			$\sigma = -0.182$	

It should therefore be borne in mind that the statement that the effect of change in the nature of the medium upon the velocity constant is a linear effect does not mean that the relationship between the velocity constant and the concentration of added solute is exactly

$$k = k_0 + \sigma m$$

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[8] Randall and Failey, *Chemical Reviews*, **4**, 271 (1927). See also Scatchard, This Journal, **52**, 52 (1930).

[9] Brönsted, "Om Syre-og Basekatalyse," Festskrift, Københavns Universitet, **1926**, p. 51.

It means, rather, that for a given range of concentration the relationship above expresses the experimental results with sufficient accuracy. While k in Equation 1 remains constant, the magnitude of σ obviously determines the extent of the valid range.

Table IV gives the results of the experiments carried out in sodium propionate–propionic acid buffer solutions.

TABLE IV

EFFECT OF PROPIONATE

C_2H_5COONa, moles per liter	C_2H_5COOH, moles per liter	$k_{obs.}$	k_0'	$k_{obs.} - k_0'$	k_{P^-}
0.0497	0.940	0.0139	0.01305	0.00085	0.017
.0994	.885	.0151	.01325	.00185	.018
.1490	.835	.0155	.0134	.0021	.014
.1990	.785	.0162	.0136	.0026	.013
.1980	.394	.0170	.0147	.0023	.012
.247	.736	.0172	.01375	.00345	.014
				Average,	0.015 a. d., 13%

Here k_0' (Col. 4) is k_0 corrected for the effect of the propionic acid; the effect of the electrolyte upon the medium is assumed to be negligible, as was found in the case of sodium chloride. The constant of propionate ion catalysis (Col. 6) is obtained by dividing $k_{obs.} - k_0'$ by the propionate ion concentration, which may be taken equal to the concentration of the sodium salt.

In an entirely similar way Table V records the results of the experiments in sodium acetate–acetic acid buffer solutions.

TABLE V

EFFECT OF ACETATE

CH_3COONa, moles per liter	CH_3COOH, moles per liter	$k_{obs.}$	k_0'	$k_{obs.} - k_0'$	k_{AC^-}
0.0497	0.920	0.0157	0.01405	0.00165	0.035
.0994	.881	.0174	.01415	.00325	.033
.1490	.831	.0194	.01425	.00515	.0345
.1990	.771	.0210	.0144	.0066	.033
.1980	.933	.0212	.0140	.0072	.036
				Average,	0.034 a. d., 3%

The catalytic effect of the acetate ion is more than twice that of the propionate ion. Tables II, IV and V show the parallelism between the magnitude of the catalytic constant and the average deviation of its experimental values from the mean. It may be mentioned that, for the lowest concentration of catalyst employed, an error of 1% in $k_{obs.}$ causes an error of 15% in $k_{H_3O^+}$, an error of 17% in $k_{propionate}$, and an error of 10% in $k_{acetate}$.

The results of the experiments in sodium formate–formic acid buffer solutions are summarized in Table VI and are represented graphically in Fig. 3.

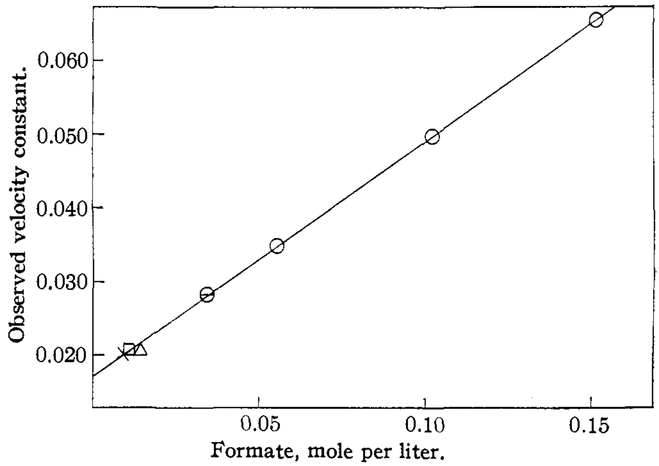
Table VI

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^-}
0.397	0	0.0093	0.0093	0.0202	0.0033	0.355[a]
.593	0	.0114	.0114	.0205	.0036	.315[a]
.937	0	.0145	.0145	.0206	.0037	.26[a]
.971	.0249	.0096	.0345	.0281	.0112	.325
.994	.0497	.0051	.0548	.0347	.0178	.325
.994	.0992	.0031	.1023	.0496	.0327	.319
.994	.1491	.0023	.1514	.0652	.0483	.319
						Average, 0.322, a. d. 1%

[a] Not included in average.

In calculating the hydrogen- and formate-ion concentrations, values of the dissociation constant of formic acid were obtained from the empirical equation given by Brönsted[10] for solutions less than 0.05 M in sodium formate, while for the more concentrated salt solutions preliminary values[11] determined in this Laboratory were used.



Formic acid: ×, 0.397; □, 0.593; △, 0.937; ⊖, 0.971; ⊙, 0.994 mole per liter.

Fig. 3.—Effect of formate.

For several reasons it is hardly feasible to determine the medium effect of formic acid upon the rate of hydration by carrying out a series of experiments in solutions of constant formate and varying formic acid concentration. In the first place, the concentration of formic acid must be kept high enough to prevent a shift in the buffer equilibrium. In the second

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[10] Brönsted and Volquartz, *Z. physik. Chem.*, **134**, 100 (1928).

[11] The dissociation constant was measured catalytically by the method employed by Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

place, the catalytic effect of the formate ion is so large compared to the effect sought that the latter would be concealed by a slight change in the formate-ion concentration. The intercept on the axis of velocity constants (Fig. 3) has therefore been taken to represent the velocity constant of the spontaneous reaction in a solution 1 M in formic acid. The intercept is 0.0169, a value which may be in error due to a salt effect upon the formate ion catalyzed reaction. The product $(H_3O^+)k_{H_3O^+}$ varies from 0.00021 to 0.00007 in the second group of experiments listed in Table VI, the experiments from which k_{formate} has been calculated. In view of the smallness of the correction, and the uncertainty of the intercept, the hydrogen-ion catalysis has been neglected. The sixth column of Table VI gives the difference between the observed velocity constant and k_0', which is k_0 corrected for the effect of the formic acid, or 0.0169.

A few experiments were carried out to determine the effect of the butyrate ion. In a solution 0.995 M in butyric acid, $k_{\text{obs.}}$ was found to be 0.0123; in a solution 0.0497 M in sodium butyrate and 0.995 M in butyric acid, $k_{\text{obs.}}$ was approximately 0.0113. The velocity constant obtained in the presence of butyrate is recorded as "approximate" because the reaction in the butyrate–butyric acid buffer solution was not exactly monomolecular. The effect of butyrate is $(0.0113 - 0.0123)/(0.050)$ or -0.020.

Again, the catalytic effects of the anions studied fail to follow the order of basic strength of the catalyst. With propionic, as with acetic anhydride, the formate ion is a remarkably good catalyst. No catalytic effect of molecular acid upon the reaction has been detected; if it exists, it is masked by the effect of the acid upon the medium. In the present investigation no new fact has come to light which invalidates the idea of mixed anhydride formation suggested in the previous paper. In a following paper there will be presented the results of a study of the hydration of acetopropionic anhydride.

The author wishes to express his gratitude to the Laboratory of Physical Chemistry of the Polytechnic Institute of Copenhagen for the gift of the dilatometer in which these measurements were made. He wishes also to thank the Department of Physiological Chemistry of the University of Pennsylvania for the use of its refrigerator room, which made possible work at 0° during the summer months.

Summary

1. The salt or electrolyte effect of sodium chloride upon k_0, the velocity constant of the spontaneous hydration of propionic anhydride, has been found to be negligibly small, in dilute solution, at 0°

2. The hydration of propionic anhydride is retarded by acetic acid and by propionic acid. The linear nature of these effects has been discussed.

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

$$k_{\text{propionate}} < k_{H_3O^+} < k_{\text{acetate}} < k_{\text{formate}}$$

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

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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).