the solution was shaken vigorously as the acid chloride was added. The reaction mixture was neutralized with acetic acid, and treated with an excess of copper acetate. The dark green copper salt proved to be a normal copper salt of iodoacethydroxamic acid,

0.6372 g. gave 35.6 cc. N_2 at 28° and 731 mm.
Calc. for $C_4H_6O_4N_2I_2Cu$: N, 6.05. Found: N, 5.98.

The dried copper salt was suspended in absolute alcohol and decomposed by means of hydrogen sulfide. The filtrate was evaporated rapidly by means of a current of cold air, and the crystals of the hydroxamic acid were purified by recrystallization from ethyl acetate at a temperature not exceeding 60°.

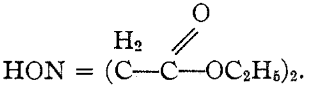
The hydroxamic acid was a white crystalline powder, which melted at 107.5° (corr). It was readily soluble in water, in ethyl and in methyl alcohol, slightly soluble in chloroform and in benzene, but insoluble in petroleum ether. Ethyl acetate was the best solvent for it. It gave a cherry red color reaction with ferric chloride.

0.2982 g. gave 19.6 cc. N_2 at 29° and 739 mm.
Calc. for $C_2H_4O_2NI$: N, 6.97. Found: N, 7.02.

Summary.

The preparation and properties of the hydroxylammonium salts of monochloro-, dichloro- and trichloroacetic acid were described. When heated carefully, these hydroxylammonium salts gave small quantities of the corresponding hydroxamic acids.

The methods of preparation and properties of monochloro-, monobromo-, and monoiodoacethydroxamic acids were described. The action of ethyl monobromoacetate and of monoiodoacetate upon hydroxylamine gave, among other substances, a new compound of the formula $C_8H_{15}NO_5$, which is probably a β,β-disubstituted hydroxylamine of the formula,



$$HON = (\overset{H_2}{C}-\overset{\overset{O}{/\!\!/}}{C}-OC_2H_5)_2.$$

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE CATALYTIC INFLUENCE OF ACIDS IN LACTONE FORMATION. PART I. VALEROLACTONE.

BY HUGH STOTT TAYLOR AND HAROLD WILBERFORCE CLOSE.

Received December 28, 1916.

The accelerating influence of acids on the velocity of a great many chemical reactions has long been known, and the approximate proportionality between this catalyzing power of acids and their hydrogen ion concentration was recognized upon the formulation of the electrolytic dissociation theory. Ostwald, however, pointed out that the proportionality was not exact, and while he attributed the deviations to some secondary influence, no effort was made for some time to locate the cause of the observed deviations. With the suggestion, made some years ago, that the undissociated molecule of the acid might also be catalytically active the subject received a new impetus and considerable work has since been done in a more careful study of acid catalysis.[1]

The results of these researches indicate that the facts of acid catalysis and of neutral salt action in aqueous solutions are capable of interpretations on a dualistic theory of acid catalysis whereby a specific activity is attributed to both hydrogen ion and undissociated molecule. In particular, this theory offers a formulation of the observed facts in regard to catalysis by strong acids in which, as the concentration of the acid is increased, the catalytic power increases faster than the hydrogen-ion concentration, and also of the fact that neutral salts of strong acids enhance the accelerating influence of the corresponding acid. If the catalytic activity of the undissociated molecule be represented by K_m and that of the hydrogen ion by K_H the reaction constant R may be expressed in the form of an equation:

$$R = n_m K_m + n_H K_H$$

where n_m and n_H are the concentrations of the undissociated acid and of the hydrogen ion, respectively. Knowing the ionization data it is then possible to calculate K_m and K_H by determining R either for two or more concentrations of catalyzing acid, or for one strength of acid in the presence of varying amounts of neutral salt.

As regards the actual mechanism of the catalytic action of acids several suggestions have been put forward by various investigators, but very little quantitative work has been done, and, for the most part, the theories advanced have lacked experimental foundation.[2] The theory to which a considerable body of opinion has gravitated is that of the formation of intermediate addition compounds. The cases of acid catalysis most extensively studied are the hydrolysis of cane sugar and of esters and the tautomerism of acetone. The fact that these reactions are influenced in such a strikingly similar manner by acids suggests that the key to the situation lies in the similarity of structure. These compounds resemble one another structurally in the possession of a carbonyl group and consequently, it is reasonable to attribute to this carbonyl group a fundamental importance. Stieglitz suggested a possible mechanism for the hydrolysis of an ester which involves the assumption of the quadrivalence of oxygen. Thus:

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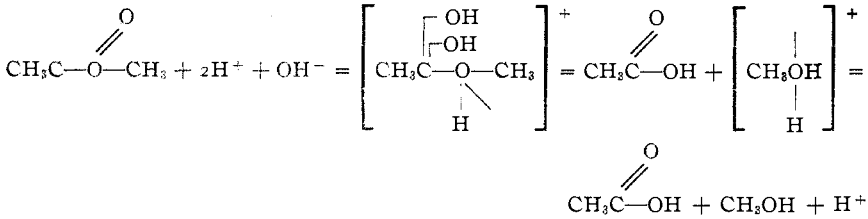
[1] For literature references see Taylor, THIS JOURNAL, **37**, 551 (1915).

[2] Kendall and Booge, *Ibid.*, **38**, 1713 (1916).

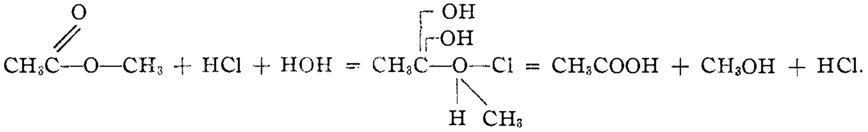


$$CH_3\overset{O}{\overset{/\!/}{C}}—O—CH_3 + 2H^+ + OH^- = \left[CH_3\overset{OH}{\overset{OH}{C}}—\underset{H}{O}—CH_3\right]^+ = CH_3\overset{O}{\overset{/\!/}{C}}—OH + \left[\underset{H}{CH_3OH}\right]^+ = CH_3\overset{O}{\overset{/\!/}{C}}—OH + CH_3OH + H^+$$

The application of the mass law to this reaction led to the expression

$$dx/dt = K_s \times C_{ester} \times C_{H^+} \times C_{H_2O},$$

which, as a first approximation, fits the experimental facts. Since the establishment of the fact that the reaction velocity increases faster than the hydrogen-ion concentration it has become evident that this interpretation of the mechanism is not wholly adequate. The theory of the activity of the undissociated acid molecule endeavors to explain this abnormal acceleration. A similar formulation of the mechanism of hydrolysis by means of the undissociated molecule would be



$$CH_3\overset{O}{\overset{/\!/}{C}}—O—CH_3 + HCl + HOH = CH_3\overset{OH}{\overset{OH}{C}}—\underset{H\ \ CH_3}{O}—Cl = CH_3COOH + CH_3OH + HCl.$$

In such case, according to the law of mass action there would follow

$$dx/dt = K_s' \times C_{ester} \times C_{HCl} \times C_{HOH}.$$

It will be seen that a combination of this equation with that previously developed for the hydrolysis with the hydrogen ion would give a combined reaction velocity equation corresponding to the formula adopted to interpret acid catalysis on the assumption of dual activity of hydrogen ion and undissociated acid molecule.

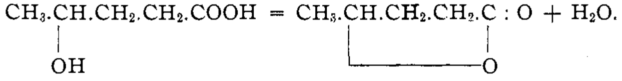
Kendall and Booge have proved the existence of intermediate compounds of the type R.COOR'.HX, which they consider to be the products of the initial stage of hydrolysis of the ester. The question of the existence of the more complex compounds of the type RCOOR'.HX.H involving the further addition of water preliminary to the final hydrolytic splitting off of the resulting compounds is a matter for further investigation.

Some few reactions, notably the hydrolysis of cane sugar and of esters and the keto-enol tautomerism of acetone, have been extensively studied in the light of the theory of the undissociated molecule, but the number and variety of the reactions which have thus far been thoroughly investigated have been limited. It has seemed highly advisable to extend the study to new reactions in the hope that in this way new light might be thrown on some of the following points with regard to the respective activities of the catalytic agencies. It is of interest to learn whether the concentration of the acid affects the activity of the undissociated molecule, in other words whether the value of K_m varies with variation in the normality of the acid. The question of the value of the catalytic ratio when obtained from experiments using different dilutions of acid alone and from those with one concentration of acid in presence of varying amounts of neutral salt is also a problem for additional investigation. Dawson and Reiman,[1] from their studies of keto-enol tautomerism of acetone, decided that the value was the same in the two cases for monochloroacetic acid and its salts. On the other hand, the investigations of Taylor and those of Ramstedt[2] on the hydrolysis of esters show that when K_m/K_H is calculated from experiments using acid and salt, a somewhat higher value for the ratio is obtained than when it is determined from acid alone. The dependence of the catalytic ratio for a given acid on the nature of the reaction is also a matter under consideration. Dawson and Powis write:

> "The important question as to whether the ratio for the given acid is independent of the nature of the reaction which is catalytically accelerated has not been answered in any satisfactory manner, although the data obtained by Taylor in experiments on the hydrolysis of different esters indicate that the ratio is independent of the nature of the ester."

The results obtained for keto-enol tautomerism of acetone showed, however, definite differences from those obtained in ester hydrolysis. Further, as was pointed out by Taylor, the action of neutral salts in the hydrolysis of cane sugar is considerably greater than in the catalysis of esters, which would point to a specific influence of the reaction studied.

The authors decided to test out these points by a study of the accelerating influence of acids upon the formation of lactones, considering in the present communication the conversion of hydroxyvaleric acid to valerolactone, which reaction may be expressed by the equation



$$CH_3.\underset{\displaystyle OH}{\underset{|}{CH}}.CH_2.CH_2.COOH = CH_3.CH.CH_2.CH_2.C:O + H_2O.$$

An investigation was carried out using as catalysts hydrochloric and monochloroacetic acids in varying concentrations both with and without their respective neutral salts.

The catalytic conversion of hydroxyvaleric acid to lactone was studied by Henry,[3] who found that it was accelerated by acids, the catalytic influence increasing with increase in the concentration of hydrogen ions. An examination of his results seems to indicate that the catalytic activity is exactly proportional to the hydrogen-ion concentration. Thus, his results using normal hydrochloric acid are a little less than ten times

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[1] *J. Chem. Soc.*, **107**, 1426 (1915).

[2] *Medd. K. Vetenskapsakad. Nobelinst.*, **3**, No. 7 (1915).

[3] *Z. physik. Chem.*, **10**, 96 (1892).

as great as those obtained with 0.1 N acid, as would be expected if the hydrogen-ion concentration were the sole determining factor. It has been found, however, with the employment of a more exact technique subsequently to be described, that the reaction velocity is not strictly proportional to the hydrogen-ion concentration, but that its behavior is similar in many respects to that found in ester catalysis and other such catalytic reactions. The reaction has been shown to lend itself readily to study and furthermore has an advantage over ester hydrolysis in that it proceeds much more rapidly. Consequently, the catalyzing acid used may be made dilute, in which case the laws of dilute solutions are more strictly obeyed.

The conversion of hydroxyacids to the corresponding γ and δ lactones is a monomolecular reaction, and hence the simple equation

$$k = 1/t \log a/(a - x)$$

may be used for calculating k, the velocity constant. The transformation of the acid to the lactone, however, is not complete, since the reaction is reversible and an equilibrium is established. The reverse reaction, the hydrolysis of the lactone, is, strictly speaking, a bimolecular reaction; but, when it is carried out in dilute aqueous solution the active mass of the water remains practically unchanged and the hydrolysis may therefore also be considered as monomolecular.

In reactions of this type the actual velocity observed represents the algebraic sum of the velocities in the two directions, and in general the simple formula cited above cannot be used. An expression must be employed which takes into account the reverse reaction. Such an equation is the following:

$$dx/dt = k_1(a - x) - k_2x,$$

where k_1 and k_2 are the velocity constants for the forward and the reverse reactions, respectively. On integration this expression becomes

$$\log \frac{a}{a - (1 + k_3)x} = t(k_1 + k_2)$$

where k_3 is substituted for the ratio k_2/k_1. When, however, the equilibrium point is not reached until most of the original hydroxyacid has been converted to lactone, it is obvious that the velocity in the forward direction must greatly exceed that in the reverse direction, especially in the early stages of the reaction. In other words, when the equilibrium point lies near the lactone side, k_3 is very small and the above expression can, without appreciable error, be written in the form,

$$\log a/(a - x) = t(k_1 + k_2).$$

Since k_1 and k_2 are constant, this equation reduces itself to the simple monomolecular equation cited above. Experiment showed, in agreement with the previous observations of Henry, that, in the case of the conversion of hydroxyvaleric acid to valerolactone, equilibrium is established when approximately 92% of the acid is changed to lactone. Consequently the monomolecular formula was found to give constant values for k and the use of the more complex formula embodying the reverse reaction did not cause any modification of the conclusions reached by use of the simpler form.

Since the hydroxyacids themselves yield hydrogen ions in water solution, autocatalysis is possible in such solutions. But, hydroxyvaleric acid is comparable in strength with acetic acid and hence its autocatalytic influence is small even when at its maximum, and, in the presence of strong acids its degree of dissociation is so repressed as to reduce its autocatalytic effect to a minimal amount.

Experimental.

Preparation of Valerolactone.—Hydroxyvaleric acid is less stable than its lactone. Consequently, a quantity of the lactone was prepared and was subsequently converted to the hydroxyacid in small quantities as required for each experiment. The lactone was prepared as follows: One hundred grams of cane sugar were heated on a water bath for twenty hours in contact with half a liter of 1:4 hydrochloric acid. The charry mass was then filtered and after the addition of a solution of 35 g. of caustic soda to the filtrate it was evaporated to 100 cc. and the sodium chloride which had separated out was filtered out. The crude levulinic acid so obtained was next extracted with ether and fractionally distilled, the quantity passing over between 140° and 170° under a pressure of 15–30 mm. being collected. Thirty cc. portions of this product were then reduced in alkaline solution by use of a 5% sodium amalgam. The reduction was carried out in a vessel surrounded by ice and the mixture was constantly stirred. Four hundred grams of amalgam were added in lots of 20 g. every few hours, small quantities of 2:1 hydrochloric acid being also added from time to time as required to prevent the mixture from becoming thick and viscous. The mercury was removed when reduction was completed and 75 cc. of concentrated hydrochloric acid were added. After boiling under a reflux for ten minutes the mixture was cooled and extracted with ether. The ether extract was dried over freshly ignited potassium carbonate, the ether distilled off and the residue repeatedly distilled until a constant boiling point testified to the purity of the product. The valerolactone thus obtained was a colorless, sweet-smelling liquid, boiling at 207°.

Preparation of Hydroxyvaleric Acid.—Henry prepared hydroxyvaleric acid from the lactone by forming the silver salt and then precipitating the silver with hydrochloric acid. In order to increase the yield of hydroxyacid from a given quantity of lactone it was decided to convert the lactone to its soluble barium salt by adding a slight excess of strong baryta to a solution of 1 g. of lactone in 10 cc. of water, and then to precipitate the barium by adding a calculated quantity of sulfuric acid of approximately equal strength (about 0.25 *N*), thus liberating the free hydroxyvaleric acid.

Determination of the Reaction Velocity.—To the solution of hydroxyvaleric acid obtained as described above, the catalyzing acid was then added without filtering off the barium sulfate, and the mixture was made up to 200 cc. This reaction mixture was then placed in a thermostat which was regulated to 25° ± 0.01° and the course of the reaction was followed by removing at regular intervals 20 cc. portions and titrating the free acid present with baryta. At the beginning of the experiment the 20 cc. of solution contained, in addition to the catalyzing acid, an amount of hydroxyvaleric acid equivalent to approximately 12 cc. of the baryta solution ($N/13$) but as the reaction proceeded this hydroxyvaleric acid was converted to lactone and the titer fell away. From the figures so obtained the velocity constant, k, was calculated by use of the ordinary monomolecular formula.

This method gave constant values for k, but it was found difficult to reproduce them as accurately as was desired. The error was due to imperfect neutralization with sulfuric acid, which, in order to keep the volume of the reaction mixture within workable limits, was necessarily so concentrated that a slight excess of one or other of the reagents had a considerable influence on the hydrogen-ion concentration and therefore on the rate of the reaction. For the purpose, however, of comparing the effect of neutral salt in varying concentrations in the presence of catalyzing acid of constant strength the method proved perfectly satisfactory; for it was only necessary to make the very reasonable assumption that, over the small range of variation due to imperfect neutralization, the reaction velocity is proportional to the concentration of the acid present. If this assumption be made, the results for a given series can be calculated to a constant end point, the value of which would be found by taking the mean of the several end points experimentally determined. On the other hand, the method could not be used in comparing a series of acids of varying strengths, because in such cases an error in neutralization of one drop of the sulfuric acid would cause an error in the results obtained with 0.01 *N* catalyzing acid ten times as great as when the catalyzing acid was 0.1 *N*. Consequently a new method of preparing the hydroxyvaleric acid was sought, which should not involve the use of a strong acid. After considerable experimentation it was found feasible to prepare the lead salt of hydroxyvaleric acid by rotating a definite quantity of lactone in water solution with a slight excess of lead hydroxide. A known fraction of the clear solution of the lead salt so produced was then pipetted off and the lead precipitated with hydrogen sulfide. After filtration, the solution was shaken while maintained under reduced pressure. The pressure was then brought back to normal by bubbling air through. This process was repeated until the hydrogen sulfide was removed as far as practicable. The resulting solution of free hydroxyvaleric acid was then used to determine reaction velocities in the manner previously outlined.

This method, when first employed, led to values for k which were considerably higher than those obtained in corresponding experiments by the baryta-sulfuric acid method. A comparison of the end points obtained experimentally with those arrived at by calculation revealed the presence of traces of some acid. The observed discrepancies in the end point were small, so that it was evident that the foreign acid must be a strong acid to produce the abnormally high reaction constants observed. Since the lead hydroxide used had been prepared from lead nitrate the presence of small but sufficient traces of nitric acid in the lead hydroxide was suspected. This suspicion was confirmed by means of a blank test. Consequently, lead acetate was substituted for the nitrate in the preparation of the lead hydroxide. The end points obtained with this preparation again revealed the presence of small quantities of a foreign acid, which, however, could only be sulfuretted hydrogen or acetic acid. As these are both very weak acids and were present in such small amounts their influence on the velocity of reaction, like that of the hydroxyacid itself, was negligible, especially if the catalyzing acid were hydrochloric acid. The lead-hydroxide method was adopted in all the later determinations, for experiment showed it to give much more accurate and reproducible results.

Experimental Results.—In the following tables are given the data obtained from experiments on the conversion of hydroxyvaleric acid to valerolactone, including a series with and without their respective neutral salts as well as a series of acid concentrations alone. In the former, for hydrochloric acid, the baryta-sulfuric acid method of preparing the hydroxyacid was used. The lead-hydroxide method was used for the results with monochloroacetic acid and its salts as well as in the experiments using hydrochloric acid alone. Considerations of space forbid the tabulation of the data in detail. For purposes of illustration, however, typical examples of both methods are given with the experiments carried out in duplicate. In Table I is illustrated the fact that the end points, as obtained by the baryta-sulfuric acid method, are dissimilar, but by calculation to the mean end point of several examples, duplicate constants are obtained which agree to the requisite degree of accuracy. A comparison of Table I with Table II brings out the fact of the greater accuracy of the lead hydroxide method in its independence of the presence of small quantities of foreign acid.

TABLE I.—BARYTA-SULFURIC ACID METHOD.

Catalyst: 0.05 N HCl + 0.25 N KCl.

Mins.	Titer.	$k \cdot 10^4$.	Mins.	Titer.	$k \cdot 10^4$.
0	31.38	...	0	31.80	...
43.5	27.71	35.45	26.5	29.25	37.22
76	25.65	35.95	56	27.10	36.35
106	24.17	36.24	86	25.36	36.31
137	23.09	35.64	120	23.80	36.67
173	22.03	35.98	153	22.70	36.59
202	21.42	35.82	180	22.00	36.56
230	20.90	36.26	210	21.42	36.22
...	19.10	...	...	19.24	...
	Mean k,	35.90		Mean k,	36.56

Mean corrected to end point, 19.10 : 36.30

TABLE II.—LEAD HYDROXIDE METHOD.

Catalyst: 0.05 N HCl.

Mins.	Titer.	$k \cdot 10^4$.	Mins.	Titer.	$k \cdot 10^4$.
0	19.04	...	0	18.55	...
48	17.60	17.17	46	17.11	17.13
76	16.90	16.96	125	15.18	17.07
124	15.80	17.25	174	14.22	17.24
204	14.41	17.28	221	13.49	17.18
238	13.94	17.28	262	12.97	17.07
289	13.37	17.15	307	12.45	17.16
...	10.71	...	...	9.87	...
	Mean,	17.18		Mean,	17.14

Tables III, IV and V give a complete summary of the results obtained.

TABLE III.—BARYTA-SULFURIC ACID METHOD.

	Reaction constant.				
Catalyst.	I.	II.	III.	IV.	Mean.
0.05 N HCl	33.27	33.82	32.84	32.97	33.23
0.05 N HCl + 0.25 N KCl	35.88	36.28	36.07	...	36.08
0.05 N HCl + 0.5 N KCl	37.90	37.73	37.99	...	37.87
0.05 N HCl + N KCl	42.48	43.18	43.14	...	42.93
0.025 N HCl	16.53	...	...	...	16.53
0.025 N HCl + 0.5 N KCl	18.84	...	...	...	18.84
0.01 N HCl	6.59	6.56	...	...	6.58
0.01 N HCl + 0.5 N KCl	7.51	...	...	...	7.51

TABLE IV.—LEAD HYDROXIDE METHOD.

	Reaction constant.				
Catalyst.	I.	II.	III.	IV.	Mean.
0.1 N HCl	68.1	67.4	67.1	68.1	67.7
0.05 N HCl	34.58	34.04	34.38	34.21	34.30
0.025 N HCl	17.18	17.11	17.14	(16.90)	17.14
0.01 N HCl	6.82	6.83	6.82	6.84	6.83

TABLE V.—LEAD HYDROXIDE METHOD.

Catalyst.	Reaction constant. I.	II.	Mean.
0.1 *N* $CH_2ClCOOH$	8.37	8.29	8.33
0.1 *N* $CH_2ClCOOH$ + 0.005 *N* Na Salt	7.26	7.26	7.26
0.1 *N* $CH_2ClCOOH$ + 0.01 *N* Na Salt	6.07	5.97	6.02
0.1 *N* $CH_2ClCOOH$ + 0.02 *N* Na Salt	4.45	..	4.45

Evaluation of the Experimental Results.

The experimental material may be discussed in two parts: (*a*) the results with hydrochloric acid, and (*b*) those with monochloroacetic acid. This may be prefaced, however, by an observation on the results obtained by the two methods of experiment. It will be observed that the values obtained by the lead hydroxide method are consistently higher than those obtained by the baryta-sulfuric acid method, and by about 3%. This represents a considerably greater difference than can be accounted for by an error in the neutralization of the baryta with sulfuric acid. That this is true is confirmed by the agreement repeatedly found between the observed and calculated end points in the baryta-sulfuric acid experiments, in which the variation from the calculated figure was never 1%. In explanation of the discrepancy all it is possible as yet to offer is the suggestion that possibly the barium sulfate, which was not filtered off but remained as a fine suspension in the reaction mixture, decreased the concentration of active catalyzing acid by adsorption in accordance with its well-known capacity for adsorbing electrolytes. Such a view cannot as yet be supported by actual experimental observations but it is proposed to give this point separate study. An examination of the preceding table, No. III, will reveal however that, whatever the cause, the effect is consistent and does not affect the reproducibility of the results. The calculations which follow will show also that its influence upon them is negligible.

Of the results with hydrochloric acid as catalyst consideration may first be given to those with acid and varying amounts of potassium chloride. It is evident that potassium chloride affects the reaction in a manner similar to that observed in ester catalysis, accelerating the reaction to a considerable extent. The magnitude of the effect has been determined by the assumption of activity of the undissociated molecule. The concentrations of hydrogen ion and undissociated acid molecule were calculated for each reaction mixture. For mixtures of acid and salt, use was made of the conductivity data of Kohlrausch and Holborn. For the hydrogen-ion concentrations in the two dilute acid solutions two figures have been used, those calculated from Kohlrausch and Holborn and those of Bray and Hunt.[1] At a concentration of 0.05 *N* these two sets of data are in accord. The influence of small modifications in the value for the degree of dissociation will be evident from observation

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[1] THIS JOURNAL, **33**, 781 (1911).

of the succeeding table. Col. 1 of the table records the catalyzing solution, Col. 2 the hydrogen-ion concentration, Col. 3 the origin of those data, Col. 4 the mean velocity constant, and Col. 5 the calculated constant assuming the activities of the hydrogen ion and undissociated hydrogen chloride to be in the ratio of 600 to 1660. These two figures were obtained by solving a number of equations in accordance with the procedure outlined in the introduction, using pairs of velocity data and ionic concentrations, choosing from the results obtained for the respective activities the best means and calculating with their aid the velocity constants recorded in the last column.

TABLE VI.—$K_m = 1660$; $K_H = 600$.

Catalyzing liquid.	C_H.	Ionization data.	*k* observed.	*k* calculated.
0.05 *N* HCl	0.047	B & H K & H	33.23	33.18
0.05 *N* HCl + 0.25 *N* KCl	0.044	K & H	36.08	36.36
0.05 *N* HCl + 0.5 *N* KCl	0.04265	K & H	37.87	37.79
0.05 *N* HCl + *N* KCl	0.0392	K & H	42.93	(41.44)
0.025 *N* HCl	0.024	K & H	16.53	(16.06)
0.025 *N* HCl	0.0238	B & H	16.53	(16.27)
0.025 *N* HCl + 0.5 *N* KCl	0.0214	K & H	18.84	18.81
0.01 *N* HCl	0.00989	K & H	6.58	(6.09)
0.01 *N* HCl	0.00971	B & H	6.58	(6.31)
0.01 *N* HCl + 0.5 *N* KCl	0.00858	K & H	7.51	7.51

It will be seen that, with one exception, the reaction constants for the various acid-salt mixtures are splendidly reproduced with the values employed for K_m and K_H; hence, it may be assumed that for such mixtures the ratio K_m/K_H is 1660/600 or 2.77. This figure is actually identical with the mean value obtained by Taylor for such solutions in ester catalysis.

The deviations between found and calculated results in the preceding table are most pronounced in the cases of catalysis by acid alone. The uncertainty in the dissociation data may account in part for this. Calculations, however, of the catalytic ratio from acid strengths alone give values differing widely from that deduced above. This is evident from Table VII, which gives the results of such calculations from the experimental results using both methods and also both series of dissociation data.

TABLE VII.

Strengths of acid used in calculation.	Experimental method.	K_m/K_H B & H.	K_m/K_H K & H.
0.05 and 0.025	Baryta-Sulfuric	1.43	1.28
0.05 and 0.01	Baryta-Sulfuric	1.29	1.21
0.025 and 0.01	Baryta-Sulfuric	1.24	1.16
0.1 and 0.05	Lead Hydroxide	(0.33)	(0.48)
0.05 and 0.025	Lead Hydroxide	1.05	1.03
0.05 and 0.01	Lead Hydroxide	1.18	1.11
0.025 and 0.01	Lead Hydroxide	1.27	1.16

This table gives conclusive evidence in support of the observations made previously in the case of ester catalysis both by Taylor and Ramstedt that the figures for the catalytic ratio are different according as they are derived from a series of acids or from a series of acid-salt mixtures. The figures used for the ionization data largely determine the value of the ratio obtained. It is possible therefore that, with strong acids at least, the divergencies might be due to the use of the mass law in determining the ionic concentrations. The deviations would then disappear in the case of a weak acid and mixtures with the salts. This has, for example, been found to be the case for monochloroacetic acid by Dawson and Reiman. The corresponding investigation for the present reaction with this acid promised therefore an interesting study.

The results with monochloroacetic acid when submitted to processes of calculation similar to those outlined above at once revealed a complex situation, the difficulties of which have so far eluded explanation. No concordant figures could be obtained from any pairs of results for the catalytic ratio. Further investigation showed at once that this could not be expected from the experimental results. For, when a table was compiled expressing the ratio of reaction velocity to hydrogen-ion concentration for a series of determinations it was readily seen that there was no proportionality between the two factors, nor was there any regular deviation from strict proportionality such as is found in the cases hitherto examined in which the theory of the undissociated molecule has found application. The situation may be more readily understood by a glance at Table VIII, which records the reaction velocity constants, the ionization data and the ratio between the hydrogen-ion concentration and reaction constant for the present series of measurements and for the corresponding measurements of Dawson and Reiman with their reaction in solutions of the same composition of catalyst.

TABLE VIII.—CATALYZING ACID : 0.1 *N* MONOCHLOROACETIC ACID.

Strength of added Na salt.	C_H.	k_{obs}. T and C.	k/C_H. T and C.	k_{obs}. D and R.	k/C_H. D and R.
0	0.122	8.33	683	7.80	639
0.005	0.1035	7.26	701	6.95	672
0.01	0.0884	6.02	681	6.18	699
0.02	0.0667	4.45	667	5.12	767

With the actual numerical figures for the several quantities the comparison is meaningless, since the two reactions studied are quite different. On the other hand, the different tendencies shown by the quantity k/C_H in the two cases are fundamental. With the reaction of Dawson and Reiman the value increases continuously, which is readily explained on the theory of the activity of the undissociated molecule, since depression of the hydrogen-ion concentration increases the number of the undissociated molecules, which therefore play a greater part in the course of the reaction. A similar tendency is observed in the present reaction with the first concentration of neutral salt. Further addition of salt, however, does not show this effect and the reaction velocity actually begins to decrease at a rate greater than the rate of decrease of the hydrogen-ion concentration. This result was so extraordinary that repeated investigations have been carried out to locate some possible abnormality in the working conditions.

Firstly, the acid itself was suspected, since it is capable of hydrolytic rearrangement with water to yield hydroxyacetic and hydrochloric acid. Freshly prepared solutions of the carefully redistilled acid were used in obtaining the results communicated in this paper so that the abnormalities which would obviously be caused by the presence of small amounts of hydrochloric acid were excluded. The acid itself was of high purity and a weighed quantity of the acid gave the theoretical titer.

Secondly, the solutions of the sodium salt were suspected. These were therefore prepared from the fresh solutions of the acid by neutralization with caustic soda prepared in two ways. The results communicated represent values obtained with two different samples of the sodium salt. The first was made from the purest caustic soda obtainable containing a minimum amount of carbonate. The second was prepared from caustic soda solution made from metallic sodium, carbon dioxide being rigorously excluded in the operation. The concordance of the two determinations with the different samples tends to show that imperfect neutralization of the soda is not the cause of the abnormal results.

So far it has been impossible for the authors to find any explanation which will cover all the published facts. The modifying influence which the hydroxyacid might cause owing to its own dissociation being marked in the presence of the weakly ionized solutions of the chloroacetic acid has been considered. The general effect of his influence would, however, have been in the opposite direction from that observed. In other words, the effect of ionization of the hydroxyacid and its possible interaction with the constituents of the catalyzing liquid would be to raise the ratio k/C_H whereas the value after attaining a maximum then falls away relatively rapidly.

The existence of the abnormality is unfortunate from another point of view. In what has preceded it has been demonstrated that different results are obtained for the catalytic ratio K_m/K_H according as one utilizes a series of varying concentrations of hydrochloric acid or a series with constant acid concentration and varying concentrations of added neutral salt. By the use of monochloroacetic acid, where difficulties due to the application of the mass law to the ionization data are absent, Dawson and Reiman obtained concordance between the two sets of values. Similar deductions in the present case have been rendered impossible by the existence of the abnormality recorded. As a consequence, definite decision upon the suggested explanation of the varying values must be deferred until the results yielded by the weak acid in the conversion of hydroxyacid to lactone have been explained. A promising line of investigation is being followed with other lactones, and it is hoped, that in a succeeding communication, progress may be reported.

Summary.

The conversion of hydroxyacids to lactones, a reaction which is catalytically assisted by acids, has been re-examined with a view to ascertaining whether effects similar to those obtained with acid catalysis in ester hydrolysis are to be found.

It has been shown (*a*) that the catalytic influence of hydrochloric is not strictly proportional to the hydrogen-ion concentration as determined from conductivity measurements,

(*b*) that neutral salts having a common anion increase the catalytic activity of the hydrochloric acid,

(*c*) that the effect may be expressed in terms of a catalytic activity of hydrogen ion and undissociated molecule,

(*d*) that the catalytic ratio of these two effects is different, however, if calculated from a series of acid concentrations or from a series of constant acid and varying neutral salt concentrations,

(*e*) that the catalytic ratio in the case of hydrochloric acid is of the same magnitude as that observed in ester catalysis.

Certain abnormalities have been observed with monochloroacetic acid as catalyst which lack as yet any satisfactory explanation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

HALOGENATION. XV. DIRECT IODINATION OF HYDROCARBONS BY MEANS OF IODINE AND NITRIC ACID.

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Iodine by itself cannot be directly introduced into aromatic hydrocarbons for reasons quite well known, but a separate oxidizing agent is needed to make clear the place for the occupation of iodine. Although some oxidizing agents, such as iodic acid, ferric chloride, potassium persulfate and sulfur iodide have been used for this purpose, the results obtained are of no practical utility, the yields of iodo compounds being quite insignificant. It has been found, as will be presently described, that iodine directly enters the ring in the presence of nitric acid with the production of iodo derivatives in very good yields. The nitric acid does not play the part of a catalyst but actually takes part in the reaction, being reduced to