CCXXVI.—*The Catalytic Activity of Acids. Evaluation of the Activities of the Hydrogen Ion and the Undissociated Acid.*

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THE view that the activity of acids in accelerating chemical change is due to the hydrogen ion rests to a large extent on the approximate proportionality between the relative catalysing powers and the corresponding values of the electrical conductivities of the acids. The velocity-coefficients used by Ostwald in making this comparison were those relating to the rate of inversion of sucrose or the rate of hydrolysis of esters.

At the time that this comparison was first instituted it was, however, recognised that the proportionality is by no means an exact one, and Ostwald supposed that the observed deviations were due to the interference of secondary factors of relatively small importance. Largely no doubt by reason of its simplicity, the theory that the catalytic activity of acids is essentially due to the hydrogen ion was accorded a most favourable reception, and for many years no serious attempt appears to have been made to challenge its validity. It is at any rate noteworthy that the efforts which were made to explain the anomalous variation of the activity of the mineral acids with concentration, and the influence of neutral salt on the activity of these acids, were not such as to bring into question the assumed relation between the velocity of the catalysed chemical change and the hydrogen-ion concentration of the catalysing acid.

In recent years the question of acid catalysis has entered into a new phase, and as a result of the accumulation of new observations and of increased accuracy in the measurement of reaction-velocities, evidence has been obtained in support of the view that the catalysing power of an acid is not entirely due to the hydrogen ion, but that the undissociated acid also contributes to the observed effect.

Observations of Acree and Johnson (*Amer. Chem. J.*, 1907, **38**, 267) on the rate of intramolecular transformation of acetylchloroaminobenzene led these authors to suggest that the catalysing acid is active in the non-ionised condition. The researches carried out by Goldschmidt on the velocity of esterification in alcoholic solution (compare *Zeitsch. physikal. Chem.*, 1910, **70**, 627; *Zeitsch. Elektrochem.*, 1911, **17**, 684; Goldschmidt and Thuesen, *Zeitsch. physikal. Chem.*, 1912, **81**, 30) have led to the expression of a similar opinion, and recent work on the rate of decomposition of methyl and ethyl diazoacetate in alcoholic solution (Bredig, Millar, and Braune,

Zeitsch. Elektrochem., 1912, **18**, 535; Snethlage, *ibid.*, p. 539) affords evidence which is distinctly favourable to the theory.

So far as aqueous solutions are concerned, the only two reactions which have been made use of in the investigation of the catalytic activity of acids and of the extent to which this varies with the acid concentration, with the temperature and pressure, and on the addition of the corresponding neutral salts, are the inversion of sucrose and the hydrolysis of esters. The latter reaction has been employed by Taylor (*Meddel. K. Vetensk. Nobelinstitut*, **2**, Nos. 34, 35, 37), whose observations relating to the influence of neutral salt and of varying concentration of the acid on the velocity of hydrolysis, are interpreted in terms of the theory that the catalytic effect is composite in character, being partly due to the hydrogen ion and partly to the undissociated acid.

If k_H denotes the catalytic activity of the hydrogen ion and k_M that of the undissociated acid, then from two experiments at different concentrations of the catalysing acid, or from two experiments with and without neutral salts in which the acid concentration is fixed, it is possible to evaluate k_H and k_M , provided that the degree of ionisation of the acid is known. The available data suffice to show that the ratio k_M/k_H varies very considerably from one acid to another, and that it decreases with the strength of the acid. In the case of the mineral acids, the ratio is greater than unity, and various observations seem to show that the activity of undissociated hydrogen chloride is about twice as great as that of the hydrogen ion. As yet, however, the accuracy attained in the evaluation of the ratio is very limited, and results obtained by different observers are not very consistent. The important question as to whether the ratio for a given acid is independent of the nature of the reaction which is catalytically accelerated has also not been answered in any satisfactory manner, although the data obtained by Taylor (*loc. cit.*) in experiments on the hydrolysis of different esters indicate that the ratio is independent of the nature of the ester.

The authors have now succeeded in obtaining experimental data which not only lend considerable support to the theory of the catalytic activity of the undissociated acid, but for the first time afford a means of determining with a fair degree of accuracy the catalysing powers of acids in the non-ionised condition.

The catalytically accelerated reaction made use of in these experiments was the isomeric transformation of acetone from the keto- to the enol-form, a reaction which takes place in aqueous solution with conveniently measurable velocity at 25°, and can be readily followed in the presence of iodine, which reacts very quickly with the enolic form (Dawson and Leslie, T., 1909, **95**, 1860). Under

favourable conditions the speed of this reaction is practically constant, and in this respect the isomeric transformation of the ketone possesses a distinct advantage over the two reactions (sugar inversion and ester hydrolysis) which have been mainly used in the examination of the catalysing power of acids. This constancy in the rate of disappearance of the iodine is attained if the circumstances are such that the concentration of the acetone is not appreciably altered during the progress of the reaction, and if the catalytic activity of the hydriodic acid, which is formed as one of the final products of the reaction, is negligibly small in comparison with the activity of the acid under investigation. In actual practice it is an easy matter to avoid the former source of disturbance, but the autocatalytic effect is more difficult to deal with when weak acids are under examination. In such cases the speed of the reaction increases continuously in consequence of the autocatalytic effect (compare T., 1912, 101, 1503), and it is necessary to eliminate this in order to obtain the catalytic activity of the acid originally present in the solution. The method finally adopted to attain this end is very simple, and depends on the fact that the mean velocity of reaction during successive time intervals is a linear function of the mean concentration of the hydriodic acid which is liberated during the progress of the reaction. All that is necessary, therefore, in order to obtain the required initial velocity is to plot the observed reaction-velocities for successive time intervals as ordinates against the corresponding mean concentrations of hydriodic acid as abscissæ and extrapolate to zero concentration of hydriodic acid. An example may be given to illustrate the influence of the autocatalytic effect, and also the method by which it has been eliminated. In this experiment the catalyst employed was 0.02 molar $\alpha\beta$ -dibromopropionic acid, the concentration of the acetone 20 c.c. per litre (0.272 molar) and the original concentration of the iodine 0.00394 mol. per litre. From time to time 25 c.c. of the reaction mixture were removed to a flask containing sodium acetate in excess of the quantity of acid used as catalyst, and titrated with freshly standardised sodium thiosulphate solution of about 0.01 normality.

TABLE I.

No. of observation.	<i>t</i> (mins.).	Thiosulphate. c.c.	Iodine concentration (<i>c</i>). Mols. per litre.	Hydrogen iodide concentration. Mols. per litre.
1	0	21.40	0.003860	0.000080
2	100	18.74	0.003380	0.000560
3	270	14.02	0.002530	0.001410
4	430	9.29	0.001675	0.002265
5	530	6.22	0.001122	0.002818

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By suitably combining these data, the following results are obtained for the connexion between the rate at which the iodine disappears and the mean concentration of the hydriodic acid.

From combin-

ation of	1 and 2.	1 and 3.	2 and 3.	2 and 4	3 and 4.	3 and 5.	4 and 5.
Mean HI concen-							
tration	0.00032	0.00375	0.0098	0.02141	0.02184	0.02211	0.02254
$-\Delta c/\Delta t \times 10^6$...	4.80	4.93	5.00	5.17	5.34	5.42	5.53

From these numbers we obtain by extrapolation an initial velocity $= 4.69 \times 10^{-6}$ mols. per litre per min., and this represents the rate of change due to the catalytic action of 0.02 molar $\alpha\beta$ -dibromopropionic acid.

In general, the acceleration due to the hydriodic acid formed increases as the ionisation-coefficient of the catalysing acid diminishes, and in the case of a given acid it increases with increasing dilution. By reducing the concentration of the iodine and increasing the quantity of the solution removed for titration, it has been found possible to determine the activity of moderately weak acids in dilute solution without difficulty.

A point to which reference should be made is the fact that all the solutions contained a certain amount of potassium iodide, the iodine being added to the reaction-mixture in the form of an iodide solution, in which the molar ratio KI/I_2 was approximately equal to 2. That the presence of potassium iodide is without measurable influence on the initial velocity of the reaction is shown by a comparison of the results obtained in experiments with monochloroacetic acid in 0.05 molar solution, in which the concentration of the potassium iodide was varied considerably. The results in question are grouped in table II.

TABLE II.

Iodine concentration. Mols. per litre.	Potassium iodide concentration. Mols. per litre.	Initial velocity.
0.004	0.008	4.55×10^{-6}
0.004	0.08	4.65×10^{-6}
0.0125	0.025	4.60×10^{-6}

The divergence of the values from the mean is probably not greater than can be accounted for on the basis of experimental error.

The results communicated in this paper have reference to the five acids—hydrochloric, dichloroacetic, $\alpha\beta$ -dibromopropionic, monochloroacetic, and acetic—which form a series of gradually decreasing strength. In the tables which follow, the concentration of the catalysing acid (c) is indicated in the first column, the degree of

ionisation (α) in the second, the hydrogen ion concentration (C_{H^+}) in the third, the initial velocity (v)* of the isomeric change in the fourth, whilst the fifth gives the ratio of the reaction-velocity to the total acid concentration, and the sixth the ratio of the velocity to the hydrogen-ion concentration. In the case of hydrochloric acid, the degree of ionisation at concentrations between 0.01 and 0.2 mol. per litre has been taken from the table given by Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781), and that for the two more concentrated solutions from Ostwald's data, which have been reduced to the scale of Bray and Hunt's figures by comparing the two ionisation-concentration curves. For the other acids, the degree of ionisation is that calculated from the mass law by means of the ionisation-coefficients recorded in Kohlrausch and Holborn's tables.

TABLE III.

Hydrochloric Acid.

c .	α .	C_{H^+} .	v .	v/c .	v/C_{H^+} .
0.01	0.971	0.00971	4.48	448	461
0.02	0.959	0.01918	9.10	455	474
0.05	0.940	0.0470	22.9	458	487
0.1	0.921	0.0921	46.5	465	505
0.2	0.897	0.1794	95.3	476	531
0.5	0.858	0.429	243.0	486	566
1.0	0.792	0.792	515.0	515	650

Dichloroacetic Acid.

0.01	0.856	0.00856	4.10	410	479
0.02	0.769	0.0154	7.95	398	516
0.05	0.621	0.0311	18.1	362	582
0.1	0.503	0.0503	32.7	327	650
0.2	0.393	0.0786	59.6	298	758

 $\alpha\beta$ -Dibromopropionic Acid.

0.01	0.549	0.00549	2.75	275	500
0.02	0.435	0.00870	4.69	234.5	539
0.05	0.305	0.01525	8.98	179.5	589
0.1	0.2275	0.02275	14.65	146.5	644
0.2	0.167	0.0334	27.05	135	810

Monochloroacetic Acid.

0.05	0.161	0.00805	4.6	92	571
0.1	0.117	0.0117	7.6	76	650
0.2	0.0842	0.0168	11.9	59.5	708
0.5	0.0542	0.0271	23.8	47.6	878
1.0	0.0386	0.0386	40.1	40.1	1039

Acetic Acid.

0.1	0.01332	0.00133	0.72	7.2	540
0.2	0.00945	0.00189	1.20	6.0	635
0.5	0.00598	0.00299	2.07	4.14	690
1.0	0.00423	0.00423	3.35	3.35	790

* v = velocity in mols. per litre per min. $\times 10^6$.

From the values of the ratio v/C_H , in the last column of the tables it is evident that in no case is there an approximation to constancy, but that for all five acids the ratio increases as the concentration increases. The observed variation indicates very definitely that the catalysing power of an acid is very far from being determined solely by the hydrogen-ion concentration of its solutions, and that in this respect there is no difference between the behaviour of strong and weak acids. On inspection of the values of the ratio of the reaction-velocity to the total acid concentration (v/c) it will be noted that this also increases with increasing concentration of the acid in the case of hydrochloric, but that it decreases with increasing concentration for the four remaining acids which have been examined.

The existence of these relations suggested that the chemical change is catalysed, not only by the hydrogen ion, but also by the non-ionised acid, and that the observed effect is the sum of the two separate effects. If c is the concentration of the catalysing acid, α its degree of ionisation, k_H and k_M the activities of the ionised and non-ionised acid, and v_H and v_M the velocities due to these components respectively, then $v_H = k_H \alpha c$ and $v_M = k_M (1 - \alpha)c$. If, further, v is the measured velocity of the reaction, then

$$v = v_H + v_M = k_H \alpha c + k_M (1 - \alpha)c,$$

and if at a different concentration c' , at which the ionisation amounts to α' , the corresponding reaction-velocities are v' , v'_H , and v'_M , then

$$v' = v'_H + v'_M = k_H \alpha' c' + k_M (1 - \alpha')c'.$$

From such a pair of equations it is possible to determine k_H and k_M , and this has been done for each of the five acids.

Apart from the varying accuracy of the experimental determination of the reaction-velocity at the different concentrations, it is apparent, from a consideration of these equations, that the most favourable conditions for the evaluation of k_H and k_M are obtained by the combination of two experiments in which the ratio of the component reaction-velocities undergoes the largest possible variation. On this account the experiments made with the highest and lowest concentrations of the catalysing acid have been utilised for the calculation of k_H and k_M in each of the five series. The values thus obtained, which are placed at the head of each of the following series of data, have then been utilised in the calculation of the reaction-velocities at the intermediate concentrations, and these numbers are recorded in the fourth column, the corresponding observed values being given in the fifth. The second and third columns give numbers which represent the component velocities due to the hydrogen ion and the undissociated acid respectively.

TABLE IV.
Hydrochloric Acid.

$$k_H = 437. \quad k_M = 811.$$

Concentration.	v_H .	v_M .	v .	$v_{obs.}$
0.02	8.38	0.66	9.04	9.10
0.05	20.54	2.43	23.0	22.9
0.1	40.25	6.40	46.65	46.5
0.2	78.4	16.7	95.1	95.3
0.5	187.5	57.6	245	243

Dichloroacetic Acid.

$$k_H = 445. \quad k_M = 203.$$

0.02	6.85	0.94	7.79	7.95
0.05	13.84	3.85	17.7	18.1
0.1	22.38	10.09	32.5	32.7

$\alpha\beta$ -Dibromopropionic Acid.

$$k_H = 440. \quad k_M = 74.$$

0.02	3.83	0.84	4.67	4.69
0.05	6.71	2.57	9.3	9.0
0.1	10.01	5.72	15.7	14.65

Monochloroacetic Acid.

$$k_H = 448. \quad k_M = 23.7.$$

0.1	5.24	2.09	7.33	7.60
0.2	7.54	4.34	11.9	11.9
0.5	12.14	11.21	23.35	23.8

Acetic Acid.

$$k_H = 425. \quad k_M = 1.55.$$

0.2	0.803	0.307	1.11	1.20
0.5	1.27	0.77	2.04	2.07

In a second series of experiments with monochloroacetic acid, the concentration of the acetone was 50 c.c. per litre. If the constants obtained ($k_H=1055$ and $k_M=59.6$) are reduced to a concentration of 20 c.c. per litre, the values obtained are $k_H=422$ and $k_M=23.8$. The latter is identical with the k_M value in the tabulated series of experiments, and the k_H values are not very different. A comparison of the observed and calculated values of the reaction-velocity in the previous table shows that the two series of numbers are, on the whole, in good agreement, and it cannot be denied that substantial evidence is thereby obtained in support of the view that the catalytic activity is due to the composite influence of the ionised and non-ionised acid.

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The data for the five acids afford five independent values for the activity of the hydrogen ion, which are brought together in the following table.

TABLE V.

Nature of catalysing acid.	k_H .
Hydrochloric	437
Dichloroacetic	445
$\alpha\beta$ -Dibromopropionic	440
Monochloroacetic	448
Acetic.....	425
Mean.....	439, say 440

When the magnitude of the possible experimental error which is associated with the determination of the reaction velocities is taken into consideration, it must be admitted that the agreement between the individual values is remarkably good. If the mean value $k_H = 440$ is taken as representing the true activity of the hydrogen ion, it is possible to utilise all the available experimental data for the evaluation of the activities of the various acids in the non-ionised form. From each measurement of the reaction-velocity v , k_M will be obtained by means of the equation:

$$v = 440ca + k_M c(1 - \alpha).$$

The values thus deduced are collected in the following table, the particular experiment from which each number is obtained being indicated by reference to the concentration of the acid solution.

TABLE VI.

Nature of catalysing acid.	Calculated values of k_M .						
	Mols. acid per litre.						
	0.01	0.02	0.05	0.1	0.2	0.5	1.0
Hydrochloric	725	805	740	755	795	765	800
Dichloroacetic	230	255	233	212	206	—	—
$\alpha\beta$ -Dibromopropionic	74	76	65	60	74	—	—
Monochloroacetic.....	—	—	25.2	27.7	24.6	25.1	24.1
Acetic	—	—	—	1.36	1.87	1.50	1.49

The agreement between the k_M values obtained from the experiments at different acid concentrations is as good as that which could reasonably be anticipated when the nature of the experimental data and the probable error attaching to the reaction-velocity values is taken into account.

In consequence of the greater influence of the autocatalytic effect at the higher dilutions, it is probable that the degree of trustworthiness attaching to the several k_M values increases to some extent as the concentration increases. In deducing those values which have been adopted as the most probable values of

k_M , this circumstance has been taken into account as far as possible. The values referred to are recorded in the second column of the following table; in the third column is given the value k_M/k_H or the activity of undissociated acid in terms of that of the hydrogen ion.

TABLE VII.

Acid.	k_M .	k_M/k_H .	K .
Hydrochloric	780	1.77	—
Dichloroacetic	220	0.50	5.1×10^{-2}
$\alpha\beta$ -Dibromopropionic	67	0.152	0.67×10^{-2}
Monochloroacetic	24.5	0.055	0.155×10^{-2}
Acetic	1.50	0.0034	0.0018×10^{-2}

It will be seen from the above table that the catalysing power of the undissociated acid diminishes rapidly as the ionisation tendency decreases, a relation which has already been pointed out by Snethlage (*loc. cit.*). As yet, however, it has not been possible to find any quantitative relationship between the activity of the undissociated acid and the specific affinity-coefficient, the values of which are recorded in the fourth column of the table.

It is of some interest to compare the values of k_M/k_H in the above table with those which have been calculated from observations on other catalysed reactions in aqueous solution. From Palmaer's data (*Zeitsch. physikal. Chem.*, 1897, **22**, 492) for the velocity of inversion of sucrose by hydrochloric acid at different concentrations, Snethlage has obtained $k_M/k_H = 2$. According to Taylor's observations on ester hydrolysis under the influence of hydrochloric acid (*loc. cit.*), the value of k_M/k_H is of the order 2—3. Although these numbers can only be regarded as approximate, the order of magnitude of the activity ratio is in accord with the result obtained in our experiments.

From his experiments on the rate of hydrolysis of ethyl acetate with dichloroacetic acid as catalyst, Taylor has obtained $k_M/k_H = 0.16, 0.07$, and 0.02 from three pairs of velocity-measurements. In view of the wide divergence between the three values it might be argued that the experimental results in question are opposed to the existence of a velocity-coefficient characteristic of the undissociated acid. It is, however, much more probable that the divergence is due to experimental errors on the one hand and the unsuitability of the experiments as a combination on the other. If the arithmetic mean $k_M/k_H = 0.08$ is taken as an approximate measure of the relative activity of the undissociated acid, it is seen that this value is very much smaller than that obtained by us, for according to the previous table, the activity of the undissociated dichloroacetic acid is exactly one-half that of the hydrogen ion.

A third comparison which may be made has reference to acetic

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acid, for which, according to Snethlage's calculation from Arrhenius' experiments on the inversion of sucrose, $k_M/k_H = 0.006$. This is larger, but of the same order as the value obtained by us, $k_M/k_H = 0.0034$.

The question as to whether the ratio k_M/k_H is independent of the nature of the catalysed reaction has already been discussed by Snethlage and by Taylor (*loc. cit.*). According to Snethlage, the ratio is practically independent of the nature of the solvent as well as of the catalysed reaction, and is mainly determined by the magnitude of the ionisation-coefficient of the acid.* In our opinion the available experimental material is not nearly sufficient to permit of the expression of any definite opinion with regard to the connexion between k_M/k_H and the nature of the catalysed reaction. On the one hand, the values of k_M/k_H for hydrochloric and acetic acid are approximately the same, whether these are deduced from experiments on the rate of isomeric change of acetone or the velocity of sucrose hydrolysis. On the other hand, the values of k_M/k_H for dichloroacetic acid appear to differ widely according to whether the rate of isomeric change of acetone or the rate of hydrolysis of ethyl acetate is the catalysed reaction. The evidence in respect of these three reactions is therefore quite inconclusive, and for the present we are scarcely justified in assuming that the activity ratios recorded in the previous table are independent of the nature of the change which has been made use of in these experiments.

In conclusion a comparison may be made between the observed reaction-velocities and those calculated from the constants in the previous table (VII). The arrangement of the table is similar to that in table IV, except that a column is added giving the ratio of the velocity due to the non-ionised acid to that due to the hydrogen ions, that is, v_M/v_H , at each concentration.

TABLE VIII.
Hydrochloric Acid.

$k_H = 440$. $k_M = 780$.

Concentration. Mols./litre.	v_H .	v_M .	v_M/v_H .	v .	$v_{obs.}$
0.01	4.27	0.23	0.054	4.50	4.48
0.02	8.44	0.64	0.076	9.08	9.10
0.05	20.68	2.34	0.113	23.0	22.9
0.1	40.52	6.16	0.152	46.7	46.5
0.2	78.93	16.07	0.205	95.0	95.3
0.5	188.8	55.4	0.295	244	243
1.0	348.5	162.2	0.465	511	515

* We would point out that the ratio k_M/k_H for a given acid cannot be independent of the solvent if it is determined by the ionisation-coefficient, for the ionisation-coefficient of an acid varies with the solvent.

Dichloroacetic Acid.

$$k_H = 440. \quad k_M = 220.$$

0.01	3.77	0.32	0.085	4.09	4.10
0.02	6.77	1.02	0.151	7.79	7.95
0.05	13.68	4.17	0.305	17.85	18.1
0.1	22.13	10.93	0.495	33.1	32.7
0.2	34.58	26.70	0.775	61.3	59.6

 $\alpha\beta$ -Dibromopropionic Acid.

$$k_H = 440. \quad k_M = 67.$$

0.01	2.42	0.30	0.125	2.72	2.75
0.02	3.83	0.76	0.20	4.59	4.69
0.05	6.71	2.33	0.345	9.04	8.98
0.1	10.01	5.17	0.515	15.2	14.65
0.2	14.70	11.16	0.76	25.85	27.05

Monochloroacetic Acid.

$$k_H = 440. \quad k_M = 24.5.$$

0.05	3.54	1.03	0.29	4.55	4.6
0.1	5.15	2.16	0.42	7.3	7.6
0.2	7.39	4.49	0.61	11.9	11.9
0.5	11.88	11.59	0.975	23.5	23.8
1.0	16.98	23.54	1.39	40.5	40.1

Acetic Acid.

$$k_H = 440. \quad k_M = 1.50.$$

0.1	0.585	0.15	0.255	0.73	0.72
0.2	0.83	0.30	0.36	1.13	1.20
0.5	1.32	0.75	0.57	2.07	2.07
1.0	1.86	1.49	0.80	3.35	3.35

The degree of concordance between the calculated and observed velocities of reaction recorded in the fifth and sixth columns is convincingly in favour of the view that the catalytic action of an acid is of composite character, and that it is additively determined by the activities of the ionised and non-ionised acid.

It is of interest to compare the magnitude of the effects due to the hydrogen ion and the undissociated acid as measured by v_H and v_M . As was to be expected, the relative importance of the undissociated acid increases with increasing concentration, and one instance is afforded by the experiments in which the catalytic effect of the undissociated acid is appreciably greater than that of the hydrogen ion. This relationship is found in the case of monochloroacetic acid in *N*-solution, where $v_M/v_H = 1.39$. Assuming that the mass law is applicable to the ionisation of weak acids in more concentrated solutions, it is possible to calculate the concentration at

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which the observed catalytic effect is equally shared between the hydrogen ion and the non-ionised acid. This is the case when

$$k_M c(1 - \alpha) = k_H c\alpha$$

that is,

$$k_M/k_H = \alpha/(1 - \alpha).$$

The acid concentration at which the ratio $\alpha/(1 - \alpha)$ is equal to k_M/k_H may be deduced from the ionisation-coefficient of the acid, and in this way the following values are obtained:

TABLE IX.

Dichloroacetic acid	0.31 mol. per litre.
$\alpha\beta$ -Dibromopropionic acid	0.34 ,,
Monochloroacetic acid.....	0.52 ,,
Acetic acid	1.56 ,,

It is rather surprising to find that the concentrations for which the catalytic effects of the ionised and non-ionised acids are equal should be so close together, but this becomes intelligible if the rapid fall in the activity of the non-ionised acid with its tendency to ionise is taken into consideration.

Summary.

The catalytic activity of a series of acids has been investigated by experiments on the velocity of the keto-enol transformation of acetone. The variation of the catalysing power of the several acids with concentration can be very satisfactorily interpreted on the supposition that the observed effect is due to the sum of the catalytic activities of the ionised and non-ionised acids. The activity of the non-ionised acid has been determined in terms of that of the hydrogen ion, and it is found that this diminishes rapidly as the ionising tendency of the acid decreases.

The activity ratio k_M/k_H for hydrochloric and acetic acids has approximately the same value as the ratio obtained for these acids from observations on the hydrolysis of sucrose. It cannot yet be said, however, that this ratio is independent of the nature of the catalysed reaction.

The experiments afford instances of catalysis in which the effect of the undissociated acid is equal to, and even considerably greater than, that due to the hydrogen ion.

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