CLXI.—*Acid and Salt Effects in Catalysed Reactions. Part XIII. Inert Salt Effects in the Catalytic Action of Acids.*

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It is probable that the velocity of all catalysed reactions will show some alteration when a catalytically inert salt is added to the solution in which the reaction occurs. The effects produced in the case of strong acid catalysts have been frequently examined and various attempts, which need not be recapitulated here, have been made to account for the observed velocity increments. The increased activity of weak acids which results from the addition of catalytically inert salts of the strong acids was established by Arrhenius (*Z. physikal. Chem.*, 1899, **31**, 197), who suggested that this effect was mainly due to an increase in the degree of ionisation of the weak acid. Later writers seem to have associated this with an increase in the dielectric capacity of the reaction medium. The theory of Arrhenius has received some criticism, and an alternative explanation, based in part on the dual theory, has been proposed (compare McBain and Coleman, J., 1914, **105**, 1517; McBain and Kam, J., 1919, **115**, 1332). Since the older arguments for and against the Arrhenius view were based on the classical form of the ionic theory, according to which the strongest acids, as well as salts, are far from completely ionised, they can no longer be considered to have much bearing on the problem as it stands at the present time, when such electrolytes must be regarded as completely ionised or very nearly so.

According to Brönsted (J., 1921, **119**, 574), the modern conception of the strong electrolytes does not invalidate the suggestion made by Arrhenius, and further evidence in support of the view that fully ionised salts increase the ionisation of weak electrolytes has been furnished by observations on the rate of decomposition of diazoacetic ester catalysed by $0{\cdot}05N$-acetic acid in the presence of small quantities of potassium nitrate (Brönsted and Teeter, *J. Physical Chem.*, 1924, **28**, 579). From *E.M.F.* measurements, Harned (*J. Amer. Chem. Soc.*, 1925, **47**, 930) concluded that the product of the activities of the hydrogen and hydroxyl ions for pure water diminishes at first on the addition of alkali-metal halides, passes through a minimum, and then increases. From this it follows that the ionisation constant of water passes through a maximum value as the concentration of the added salt increases.

The inert salt effects described in this paper have reference, for the most part, to changes in the velocity of the acetone–iodine reaction catalysed by acetic acid in presence of various quantities of the catalytically inert chlorides and nitrates of the alkali metals. Since the results obtained would appear to suggest the existence of some connexion with the conclusions which follow from the application of the concept of thermodynamic activity to the ionisation of weak electrolytes in salt solutions, it seems desirable to recapitulate the standpoint which has been provisionally adopted in the interpretation of our previous catalytic experiments with mixtures of weak acids and their corresponding salts. Such experiments have shown that catalytic activity must be ascribed to weak negative ions and to undissociated molecules, as well as to the hydrogen ion. The identification of the catalytically active constituents would appear to be the first step in the quantitative interpretation of the experimental observations. The further question whether the effects should be expressed in terms of the concentrations of the active entities or in terms of their respective activities has not been ignored, but for the sake of simplicity, and in consideration of the fact that there is no acceptable method for the derivation of individual ion activities, we have interpreted the catalytic data for the abovementioned mixtures on the assumption (1) that the salts are completely ionised, and (2) that the ionisation of the weak acids is determined by a mass-law constant which is not affected by the salt content of the various solutions. This procedure has been justified by the results and is not to be interpreted in any sense as a denial of the existence of inert salt effects. It is, indeed, probable that such effects are always present, but their importance varies greatly with the particular circumstances. If, for instance, we consider the solution $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H + 1{\cdot}0N\text{-}CH_3{\cdot}CO_2Na$, the concentration of the hydrogen ion is so greatly reduced by the corresponding salt that its catalytic effect in the acetone–iodine reaction can be ignored in comparison with that of the acetate ion and the undissociated acetic acid. If the inert salt effect due to the sodium acetate were such as to produce a change in the hydrogen-ion concentration equivalent to an increase of 200% (compare Soper and Pryde, J., 1927, 2761) in the ionisation constant, this would make no difference to the interpretation of our observations on the catalytic activity of this solution. If, indeed, the alteration were 2000%, the partial velocity due to the hydrogen ion would still be almost negligible.

If, on the other hand, sodium chloride is substituted for sodium acetate, giving a solution $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H + 1{\cdot}0N\text{-}NaCl$, there is now no common ion effect, and since the sodium and chlorine ions are catalytically inert, such solutions obviously afford suitable conditions for the study of the changes which are produced in the catalytic properties of the weak acid by the presence of the inert salt. These changes may be due to an alteration in the ionisation constant of the weak acid, or to variations in the magnitude of the coefficients which express the catalytic activity of the hydrogen ion, the acetate ion, and the undissociated acetic acid.

Although the literature relating to inert salt effects in reactions catalysed by the strong acids is very considerable, and some attention has also been given to the behaviour of weak acids, there appears to have been no systematic investigation of the dependence of these effects on the strength of the catalysing acid. In these circumstances, a comparative study has been made of the changes produced in the velocity of the acetone–iodine reaction by the addition of sodium chloride when the reaction is catalysed by hydrochloric, dichloroacetic, monochloroacetic, or acetic acid in 0·1N-solutions. The results obtained with an acetone concentration of 20 c.c. per litre and from 0·1 to 4·0 molar sodium chloride solutions are shown in Table I, the velocities shown for zero concentration of sodium chloride being those for salt-free solutions. Fig. 1 shows the curves which are obtained when the velocities for the salt solutions, expressed in terms of the corresponding velocity for the pure aqueous solutions, are plotted against the salt concentration.

TABLE I.

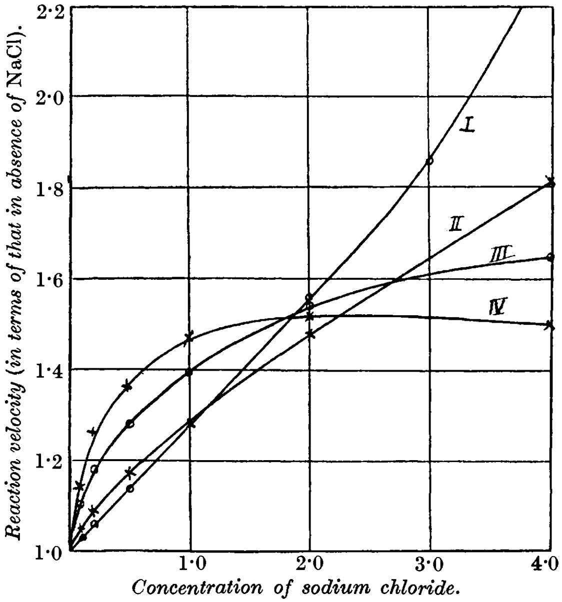
Reaction velocities (mols./litre/min.) × 10^6 at 25°.

	Concentration of NaCl.						
Catalyst.	0·0.	0·1.	0·2.	0·5.	1·0.	2·0.	4·0.
$0{\cdot}1N\text{-}CH_3{\cdot}CO_2H$	0·777	—	0·975	1·055	1·143	1·18	1·165
$0{\cdot}1N\text{-}CH_2Cl{\cdot}CO_2H$	7·28	8·06	8·56	9·30	10·1	11·2	12·0
$0{\cdot}1N\text{-}CHCl_2{\cdot}CO_2H$	32·9	34·6	35·8	38·5	42·2	48·6	61·0
$0{\cdot}1N\text{-}HCl$	46·5	—	49·3	53·0	59·5	72·5	111

It is apparent that there is a gradual change in the character of the inert salt effect as the strength of the catalysing acid changes. For hydrochloric acid, the relations are represented by a straight line up to nearly 3N-sodium chloride; at higher salt concentrations, the velocity increases more rapidly. For the three weaker acids, there is a very marked departure from linearity, and this deviation increases as the strength of the acid diminishes. At low salt concentrations, the influence of the inert salt on the reaction velocity is greatest for acetic and least for hydrochloric acid, but the order of the acids is reversed when the relative salt effects at the highest salt concentrations are compared.

With reference to the form of the hydrochloric acid curve, which is similar to that obtained when other acid-catalysed reactions are examined, we would point out that undissociated hydrogen chloride would seem to be the only constituent, other than the hydrogen ion, to which catalytic activity can be ascribed in these solutions.

FIG. 1.



Curves showing influence of inert salt on catalytic activity of hydrochloric (I), *dichloroacetic* (II), *chloroacetic* (III), *and acetic* (IV) *acids in* 0·1N-*solution.*

As a matter of history, it may be recalled that in accordance with the dual theory, values for the catalytic activity of the hydrogen chloride molecule have been derived for various reactions (sucrose inversion, ester hydrolysis, iodination of acetone, etc.), but since all such values were based on degrees of ionisation derived from conductivity and osmotic measurements, they are now devoid of significance. Measurements of the partial pressures of hydrochloric acid solutions (Dunn and Rideal, J., 1924, **125**, 676) and of the distribution of hydrogen chloride between water and benzene (Knight and Hinshelwood, J., 1927, 466) would, indeed, seem to have established the fact that the proportion of hydrogen chloride molecules in a dilute solution ($< 1N$) of hydrochloric acid is extremely small. For many purposes the ionisation of such solutions may be regarded as complete. On the other hand, it must be remembered that the catalytic activity of undissociated acid molecules increases rapidly with the strength of the acid, and there is evidence to support the view that undissociated hydrogen chloride is an extremely active catalyst. This activity has been noted repeatedly for reactions in non-aqueous media. The very high speed of the auto-catalysed reaction between acetone and iodine in solvents such as benzene, nitrobenzene and carbon tetrachloride (Dawson and Leslie, J., 1909, **95**, 1860) may also be cited in support of this view. In these circumstances, the possibility that the very small amount of non-ionised hydrogen chloride, which is present in aqueous solutions of the acid, may under certain conditions be partly responsible for the observed catalytic effect cannot be entirely ignored. Alternatively, it may be assumed that the observed increase in the catalytic activity of the hydrochloric acid on the addition of salt is entirely due to an inert salt effect in the sense that this increases the magnitude of the catalytic coefficient which is characteristic of the hydrogen ion. If k_x denote this coefficient for an inert salt solution of concentration x, v the corresponding reaction velocity, and c the concentration of the strong acid, then $k_x = v/c$. The value thus obtained for k_x has been adopted as a measure of the coefficient for the hydrogen ion in the corresponding salt solutions of the weak acids. In connexion with this procedure, it may be pointed out that it is not of primary importance to know whether the difference between k_x and the corresponding value k_0 for a salt-free solution is due to the stimulating action of the inert salt on the hydrogen ion or to a minute quantity of the highly active undissociated strong acid. It is possible that both effects are involved.

When the relative velocity curves in Fig. 1 are compared, one is forced to the conclusion that the inert salt effects shown by the weaker acids involve some factor which is practically ineffective in the case of the strong acid. As will be shown presently, there is reason to believe that this factor is represented by a change in the ionisation constant of the acid.

Before proceeding to describe the results obtained in connexion with this view, it should be mentioned that the study of the catalytic effects produced by acetic acid–acetate mixtures represented by the general formula $0{\cdot}1CH_3{\cdot}CO_2H + yCH_3{\cdot}CO_2Na$ in sodium chloride solutions, has shown that the relations are closely similar to those which are afforded by the same mixtures in pure aqueous solution. As the concentration of the sodium acetate increases, the velocity falls to a minimum and subsequently increases with y in a linear manner. From these results it has been possible to derive the values of the catalytic coefficients which characterise the acetate ion and the undissociated acetic acid in the inert salt solutions. For our present purpose, it is sufficient to note that the value of k_m for acetic acid is practically the same for sodium chloride solutions as for pure water, *viz.*, $k_m = 1{\cdot}5 \times 10^{-6}$.

In conformity with previous results the reaction velocity for the mixture $c\mathrm{CH_3{\cdot}CO_2H} + x\mathrm{NaCl}$ may be written

$$\begin{aligned} v &= k_x[\mathrm{H}^+] + k_a[\mathrm{A}^-] + k_m[\mathrm{HA}] \quad . \quad . \quad . \quad . \quad (1) \\ &= (k_x + k_a - k_m)[\mathrm{H}^+] + k_m c \end{aligned}$$

and since k_a and k_m are very small compared with k_x

$$v = k_x[\mathrm{H}^+] + k_m c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since v, k_x, k_m, and c are known, this equation may be utilised for the derivation of the concentration of the hydrogen ion resulting

TABLE II.

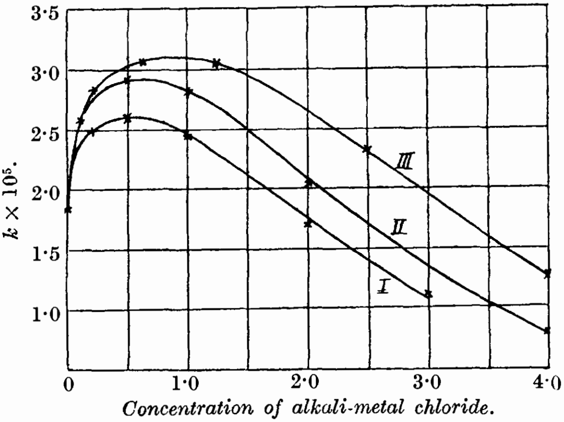
x.	$v\,.\,10^6$.	$k_x\,.\,10^4$.	$[\mathrm{H}^+]\,.\,10^3$.	$K\,.\,10^5$.
		Potassium chloride.		
0	0·777	4·65	1·35	1·82
0·2	0·919	4·88	1·58	2·50
0·5	0·990	5·23	1·61	2·59
1·0	1·052	5·82	1·56	2·43
2·0	1·056	6·99	1·30	1·69
3·0	1·040	8·30	1·07	1·15
		Sodium chloride.		
0·2	0·975	4·91	1·68	2·82
0·5	1·055	5·30	1·71	2·91
1·0	1·143	5·95	1·67	2·79
2·0	1·18	7·26	1·42	2·02
4·0	1·165	11·10	0·91	0·84
		Lithium chloride.		
0·125	0·924	4·83	1·60	2·57
0·625	1·115	5·50	1·75	3·06
1·25	1·26	6·36	1·74	3·04
2·5	1·39	8·07	1·54	2·36
4·0	1·39	11·0	1·13	1·27
		Potassium nitrate.		
0·05	0·867	4·69	1·53	2·33
0·1	0·895	4·73	1·58	2·48
0·5	0·985	5·04	1·66	2·74
1·0	1·007	5·43	1·58	2·48
2·0	0·955	6·20	1·30	1·69
		Sodium nitrate.		
0·1	0·923	4·74	1·63	2·66
0·5	1·025	5·11	1·71	2·93
1·0	1·06	5·57	1·635	2·67
2·0	1·07	6·48	1·42	2·02
4·0	1·03	8·30	1·035	1·07

from the ionisation of the acetic acid in the inert salt solution. The corresponding value of the ionisation constant is then given by

$$K = [H^+]^2/(c - [H^+]) = (v - k_m c)^2/k_x^2 c \quad . \quad . \quad (3)$$

Table II records the values obtained in this way from the data for 0·1N-acetic acid solutions. Col. 1 gives the concentration x of the inert salt, col. 2 the observed reaction velocity v, col. 3 the value of k_x derived from the corresponding experiments with 0·1N-hydrochloric acid as catalyst, col. 4 the calculated hydrogen-ion concentration, and col. 5 the corresponding ionisation constant. From the tabulated values of K it is apparent that the addition of gradually increasing quantities of inert salt is associated in the first instance with an increase in the ionisation constant of the acetic acid; the ionisation, however, reaches a maximum and shows a marked fall in the more concentrated salt solutions. For the strongest salt solutions, the value of K is, indeed, much smaller than for the salt-free acid solution.

FIG. 2.



Curves showing the variation of the ionisation constant of acetic acid in solutions of potassium (I), *sodium* (II), *and lithium* (III) *chlorides.*

The relations between the effects produced by potassium, sodium, and lithium chlorides are shown by Fig. 2, in which K is plotted against the molar salt concentration. These curves are clearly similar to those obtained by Harned (*loc. cit.*) for the influence of the three chlorides on the ionisation of water. In both cases, the maximum value for the ionisation constant is greatest for the lithium and least for the potassium chloride solutions, and it would appear that the effectiveness of the factor which is responsible for the fall in the ionisation constant is greatest for the potassium and least for the lithium salt. Harned's data are based on potentiometric measurements of the thermodynamic activity of the hydrogen ion in salt solutions, and the similarity between the two sets of results would seem to suggest some connexion between the thermodynamic activity and the catalytic activity of the hydrogen ion. We are not, however, prepared to draw any general conclusions from the similarity of the curves.

So far as our own results are concerned, they seem to afford substantial evidence for the view that the ionisation constants of the weak acids are appreciably affected by the addition of salts to the aqueous solutions of the acids. It does not appear possible to refer these variations entirely to changes in the dielectric capacity of the solvent medium. The nature of the variations would rather suggest that attention must be directed to the localised interactions between the molecules of the weak electrolyte and the ions of the salt. These molecules are of the polar type, and on the average the positive poles will be in closer proximity to the negative ions than to the positive ions. In the same way, the negative poles of the dissociable molecules will be nearer on the average to the positive ions than to the negative ions. The polar molecules will thus be subjected to forces which increase the tendency to ionisation. This effect may be expected to increase at first with the number of the ions which are present per unit of volume, but it seems probable that the influence of individual ions will ultimately be overshadowed by that due to the whole group of positive and negative ions which are within range of the poles of the ionisable molecule, and in the limit it would seem that the dielectric capacity of the surrounding medium will be the chief factor which determines the degree of ionisation of the weak electrolyte. This hypothesis would seem to afford a qualitative explanation of the ionisation curves in Fig. 2.

That the results obtained with acetic acid are not peculiar to this acid may be seen by reference to Table III in which are recorded the corresponding data derived from experiments with $0{\cdot}1N$-chloroacetic acid. Since the catalytic activity of the chloroacetate ion is negligibly small, the equation for the velocity of reaction may be written

$$v = (k_x - k_m) \,.\, [\mathrm{H}^+] + k_m c \quad . \quad . \quad . \quad . \quad (4)$$

Experiments with chloroacetic acid–sodium chloroacetate mixtures in sodium chloride solutions have shown that the value of k_m varies but slightly with the concentration of the inert salt, and $k_m = 22 \times 10^{-6}$ has been taken as the mean value of the catalytic coefficient for the chloroacetic acid molecule in the calculation of $[\mathrm{H}^+]$ and of the corresponding value of K.

TABLE III.

Ionisation of Chloroacetic Acid in Sodium Chloride Solutions.

x.	$v \cdot 10^6$.	$k_x \cdot 10^4$.	$[H^+] \cdot 10^2$.	$K \cdot 10^3$.
0	7·28	4·65	1·15	1·49
0·1	8·06	4·78	1·285	1·90
0·2	8·56	4·91	1·355	2·13
0·5	9·30	5·30	1·40	2·28
1·0	10·1	5·95	1·38	2·20
2·0	11·2	7·26	1·28	1·87
4·0	12·0	11·1	0·90	0·89

As in the case of acetic acid, the ionisation constant of chloroacetic acid first increases and then decreases as the concentration of the sodium chloride increases. The salt concentrations which correspond with the respective maximum values of the ionisation constants are approximately the same for the two acids. The ratios between the maximum values and the values for pure water are also approximately the same. The available material is, however, insufficient to permit of the conclusion that the effect is independent of the strength of the acid.

In conclusion, it may be pointed out that inert salt effects such as are described in this paper must play some part in all acid-catalysed reactions which take place in the presence of salts. In so far as the kinetic studies described in previous papers of this series are concerned, the inert salt effects are, however, not of any great significance, and the general conclusions which have been drawn from the experiments with mixtures of weak acids and their corresponding salts are not affected thereby.

Summary.

Measurements have been made of the velocity of the acetone-iodine reaction when catalysed by hydrochloric, dichloroacetic, monochloroacetic, and acetic acids in solutions of sodium chloride (0—4 molar).

The nature of the influence of the catalytically inert sodium chloride varies with the strength of the acid.

On the assumption that the increase in the reaction velocity produced by the addition of inert salts to a strong acid (hydrochloric acid) is due to a change in the catalytic activity of the hydrogen ion, it is shown that the ionisation constant of a weak acid is first increased by the added salt and then diminished at higher salt concentrations.

Similar variations in the influence of salts on the ionisation of water are indicated by *E.M.F.* measurements.

The general conclusions drawn from the study of the catalytic properties of mixtures of weak acids and the corresponding salts are not affected by the inert salt effects described in this paper.

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