261 *The Nature of the Catalytic Action of Hydrochloric Acid in the Intramolecular Change of* N-*Chloroacetanilide.*

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IT is well known that hydrochloric acid has a very pronounced and specific catalytic influence on the conversion of *N*-chloroacetanilide into the corresponding nuclear-substituted isomerides. Concordant results obtained by various observers show that the reaction is unimolecular with respect to the chloroamine, and that the reaction velocity for pure hydrochloric acid solutions is approximately proportional to the square of the concentration (c) of the acid. If k is the specific reaction velocity derived from the unimolecular formula $k = 1/t \,.\, \log a/(a - x)$, these observations show, however, quite definitely that k/c^2 has a minimum value when the concentration of the acid is about $0{\cdot}5M$.

Since at moderate concentrations the acid is almost completely ionised, it follows that the concentration of the hydrogen and chlorine ions is practically identical with the total concentration of the acid, and the approximate constancy of k/c^2 has suggested that the catalytic activity of the hydrochloric acid is to be attributed to the joint action of the ions or possibly to the action of un-ionised hydrogen chloride, the concentration of which would be proportional to the square of the total acid concentration if the classical mass action equation $[\mathrm{HCl}] = [\mathrm{H}^{\cdot}][\mathrm{Cl}\ ]/K = \text{const.} \times c^2$ were applicable.

In accordance with the views of Orton and Jones (*Brit. Ass. Rep.*, 1910, 85), the reaction appears to take place in stages represented by

$Ac{\cdot}NClPh+H^{\bullet}+Cl' \rightleftarrows Ac{\cdot}NHPh+Cl_2 \longrightarrow Ac{\cdot}NH{\cdot}C_6H_4Cl+H^{\bullet}+Cl'$
the first stage being relatively slow and for that reason determining the observed rate of transformation. Since the temperature coefficient of the reaction is much greater than would be expected for a termolecular change, Soper (*J. Physical Chem.*, 1927, **31**, 1192) favours the view that the first stage is bimolecular with un-ionised hydrogen chloride as the catalytic reactant.

To account for the inconstancy of k/c^2, Harned and Seltz (*J. Amer. Chem. Soc.*, 1922, **44**, 1475) have suggested that the catalytic effect of the acid is determined by the activities of the ions and not by their concentrations, and their experimental data show that $k/a_{H^{\bullet}}{\cdot}a_{Cl'}$ remains very constant for hydrochloric acid solutions over the range $c = 0{\cdot}1$—$1{\cdot}0$ mols. per litre. Soper and Pryde (J., 1927, 2761) consider that the concentration of the chloroamine should also be replaced by its activity, and in support of this view have put forward reaction-velocity data (corrected for two oppositely directed sources of disturbance) which show equally good constancy of $k/a_{H^{\bullet}}{\cdot}a_{Cl'}{\cdot}f_N$, where f_N is the activity coefficient of the chloroamine. The two sets of experimental data are not very divergent, and the fact that the two different assumptions agree so closely with experiment is largely due to the circumstance that the values of f_N for 0·1 to 1·0*N*-hydrochloric solutions show comparatively little change.

In reference to the above activity-rate hypotheses, it may be remarked that the equation of Soper and Pryde, in which all the concentration terms are replaced by activities, would seem to be the more acceptable form.

More recent experiments in this laboratory (compare Belton, J., 1930, 116) have been concerned with the catalytic effect of hydrochloric acid in the presence of variable quantities of sodium chloride. The data for the series $0{\cdot}05HCl + xNaCl$ have shown that the Harned–Seltz expression $k/a_{H^{\bullet}}{\cdot}a_{Cl'}$ decreases continuously from 0·063 for $x = 0{\cdot}1$ to 0·018 for $x = 4{\cdot}0$, whilst the Soper–Pryde constant $k/a_{H^{\bullet}}{\cdot}a_{Cl'}{\cdot}f_N$ falls continuously from 0·060 to 0·0037 for the same changes in the concentration of the sodium chloride. These figures indicate quite definitely that the observed velocities of reaction for this series of solutions are incompatible with the activity-rate hypothesis in either of these forms. The much greater fall in the value of $k/a_{H^{\bullet}}{\cdot}a_{Cl'}{\cdot}f_N$ shows that the more completely the concentrations of the reactants are replaced by their activities, the greater is the difference between the actual and calculated results. It is to be noted that $k/[H^{\bullet}][Cl']$ falls from 0·040 for $x = 0{\cdot}1$ to 0·032 for $x = 1{\cdot}0$ and then increases to 0·048 for $x = 4{\cdot}0$. From this it is clear that the measured velocities for the series $0{\cdot}05HCl + xNaCl$ cannot be adequately explained by the assumption that the specific reaction velocity is exactly proportional to the product of the concentrations of $H^{\cdot}$ and Cl'. On the other hand, it would seem possible to account for the facts if the catalytic effect is attributed to the hydrogen chloride molecule.

The connexion between the concentrations of the un-ionised acid and its ions is given by $K = [H^{\cdot}][Cl']/[HCl]$ in which the mass-action coefficient K varies with the ionic content of the solvent. Arrhenius was the first to show that the ionisation of a weak acid is increased by the addition of chemically inert salts, and the further investigation of this effect (Dawson and Lowson, J., 1929, 1217; Dawson, Hoskins, and Smith, *ibid.*, p. 1884; Dawson and Smith, *ibid.*, p. 2530) has given results which indicate that the dependence of the ionisation coefficient of a weak acid on the salt concentration may be expressed by the equation

$$K = K_0\,10^{a\sqrt{\mu} - b\mu}$$
$$\text{or } \log K/K_0 = a\sqrt{\mu} - b\mu \quad . \quad . \quad . \quad . \quad (1)$$

in which K is the ionisation coefficient in a solution of a uni-univalent electrolyte of equivalent concentration μ, and K_0 is the value of K in the absence of electrolyte. From this equation it follows that K has a maximum value when $\mu = a^2/4b^2$, and further that K has the same value for pairs of solutions of the same electrolyte when the equivalent concentrations are connected by the relation

$$\sqrt{\mu} + \sqrt{\mu'} = a/b \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is of considerable importance in connexion with the determination of the constants a and b from the experimental data.

Although equation (1) is based on experimental observations, it should be noted that it is of precisely the same type as that which follows from the relation $K_a = Kf_{H^{\cdot}}{\cdot}f_{A'}/f_{HA}$ expressing the connexion between the thermodynamic ionisation constant K_a and the corresponding mass-action coefficient K when the activity coefficients are evaluated in terms of the Debye–Hückel formula $\log f = -\alpha z^2\sqrt{\mu} + \beta\mu$. The value of the coefficient a in equation (1) is, however, very much smaller than the constant which would appear in the similar equation derived by this procedure.

Actual experiments have shown that equation (1) holds for weak acids differing widely in their K values, and there is no reason to suppose that it will not apply equally well to the strongest acids if appropriate consideration is given to the contribution which these acids make to the ionic strength of the solution. If such strong acids are ionised to an extent of the order of 99%, it is obvious that the variation of the degree of ionisation with the electrolyte content of the solution could not be investigated in precisely the same way as the corresponding variation for the weak acids, *i.e.*, by measurements of the reaction velocity of a hydrogen-ion-catalysed reaction, for the changes in hydrogen-ion concentration would of necessity be relatively very small. By the use of a reaction which is catalysed by the undissociated acid, but not by the corresponding ions, it would, however, be possible to study the influence of the ionic environment on the degree of ionisation of the strong acids in the same way as this is possible for weak acids by the use of suitably selected hydrogen-ion-catalysed reactions.

On the assumption that the catalytic effect of hydrochloric acid solutions on the chloroamine transformation is due to the undissociated hydrogen chloride, and that the influence of the ionic environment on the K value is given by equation (1), we may write

$$k = k'[\mathrm{HCl}] = k'[\mathrm{H}^{\cdot}][\mathrm{Cl}']/K$$

$$\text{or } \frac{k}{[\mathrm{H}^{\cdot}][\mathrm{Cl}']} \cdot \frac{K}{K_0} = \frac{k'}{K_0} = \text{const.} \quad . \quad . \quad . \quad . \quad (3)$$

The assumption that k' is constant may not be entirely justified, but from such evidence as is available, it would seem that the catalytic coefficients of neutral molecules are but slightly affected by very considerable changes in the salt content of the reaction medium (compare Dawson and Key, J., 1928, 1248).

According to equation (3), $[\mathrm{H}^{\cdot}][\mathrm{Cl}']/k$ is proportional to K/K_0, and in a preliminary examination of the experimental data in Tables I—III for hydrochloric acid solutions of gradually increasing ionic strength, it was found that the plot of log $[\mathrm{H}^{\cdot}][\mathrm{Cl}']/k$ against μ gives in all cases curves which conform very closely to the requirements of the relation expressed by equation (2). This concordance provided strong evidence for the general validity of equation (3).

In the expectation that the maintenance of a constant value of the product $[\mathrm{H}^{\cdot}][\mathrm{Cl}']$ would simplify the investigation of the effect of ionic environment, experiments were made with solutions containing a fixed amount of hydrochloric acid and variable amounts of a salt (sodium nitrate) which does not alter the value of the above ionic product. As will be seen, the anticipation was not entirely justified by the results, in that a distinction must be made between the environmental effects which are due to the two electrolytes concerned.

In the first attempts to interpret the data for the series $c\mathrm{HCl} + x\mathrm{NaNO_3}$ (c constant, x variable), it was assumed that the same values of a and of b could be used to express the environmental effects of the two electrolytes. With this assumption it was found that, when the observed values of $[\mathrm{H}^{\cdot}][\mathrm{Cl}']/k$ and the calculated values of K/K_0 were in close agreement at the higher values of μ, there were systematic deviations at lower μ values, and a subsequent examination of the data for pure hydrochloric acid solutions of varying concentration made it quite clear that there is a considerable difference between the environmental effects measured by b for the two electrolytes in question. When this difference is taken into account, equation (1) assumes the modified form

$$\log K/K_0 = a\sqrt{x + c} - bx - b'c \quad . \quad . \quad . \quad . \quad (4)$$

in which b refers to $Na^{\bullet} + NO_3'$ and b' to $H^{\bullet} + Cl'$. The modification does not, however, affect the relation expressed by equation (2) when c is constant.

The solutions of this type actually used were $0{\cdot}2HCl + xNaNO_3$, for which the reaction proceeds at a convenient rate at 25°. The results (Table I) show that $k/[H^{\bullet}][Cl']$ passes through a minimum when the concentration of the sodium nitrate is about $1{\cdot}0M$.

TABLE I.

Reaction velocity in the series $0{\cdot}2HCl + xNaNO_3$ ($\mu = x + 0{\cdot}2$).

x.	k . 10^3.	$k/[H^{\bullet}][Cl']$.	$\log K/K_0$.	K/K_0.	$kK/K_0[H^{\bullet}][Cl']$.
0	1·71	0·0427	0·166	1·46	0·0626
0·1	1·58	0·0395	0·201	1·59	0·0628
0·2	1·46	0·0365	0·226	1·685	0·0614
0·5	1·37	0·0342	0·274	1·88	0·0643
0·75	1·245	0·0311	0·297	1·98	0·0616
1·0	1·21	0·0303	0·310	2·04	0·0618
1·5	1·235	0·0309	0·316	2·07	0·0639
2·0	1·265	0·0316	0·307	2·03	0·0641
2·5	1·30	0·0325	0·286	1·93	0·0628
3·0	1·39	0·0347	0·257	1·805	0·0627
3·5	1·46	0·0365	0·223	1·67	0·0610
					Mean 0·0626

Table II gives the results for the series $0{\cdot}2HCl + xNaCl$, which resembles closely the sodium nitrate series, but differs from the latter in that the product $[H^{\bullet}][Cl']$ increases proportionately with the ionic strength. The value of μ for which $k/[H^{\bullet}][Cl']$ is a minimum is appreciably less than in the nitrate series.

Results for a series of pure hydrochloric acid solutions are shown in Table III. The measurements of Rivett (*Z. physikal. Chem.*, 1913, **82**, 201) and of Harned and Seltz (*loc. cit.*) for such solutions are in close agreement, and the reaction velocities in this table are those determined by the latter at 25° for the range 0·1005—1·022*N*-HCl (weight molar, 0·1—1·0). The ionic environment in this series is provided exclusively by hydrogen and chlorine ions, and the ionic strength corresponding with the minimum value of $k/[H^{\bullet}][Cl']$ is less than in either of the previous series.

The procedure followed in the preliminary evaluation of the coefficients a, b, and b' may be briefly described. In the case of a,

TABLE II.

Reaction velocity in the series $0{\cdot}2\text{HCl} + x\text{NaCl}$ ($\mu = x + 0{\cdot}2$).

x.	$k \,.\, 10^3$.	$k/[\text{H}^\bullet][\text{Cl}']$.	$\log K/K_0$.	K/K_0.	$kK/K_0[\text{H}^\bullet][\text{Cl}']$.
0	1·71	0·0427	0·166	1·46	0·0626
0·1	2·34	0·0390	0·196	1·57	0·0612
0·2	2·96	0·0370	0·217	1·65	0·0610
0·5	4·91	0·0351	0·252	1·785	0·0626
1·0	8·48	0·0353	0·265	1·84	0·0649
2·0	17·00	0·0388	0·217	1·65	0·0639
3·0	31·00	0·0484	0·122	1·325	0·0641
3·5	39·5	0·0534	0·0655	1·16	0·0620
					Mean 0·0628

previous observations relating to the influence of sodium chloride (and sodium nitrate) on the ionisation of weak acids (Dawson and Lowson, *loc. cit.*) have shown that the environmental coefficient represented by a is not far removed from $a = 0{\cdot}55$. By plotting $\log [\text{H}^\bullet][\text{Cl}']/k$ against μ, curves are obtained which conform very closely to the characteristic relation expressed by equation (2) and thus give the value of a/b from which b (b' in the case of HCl) follows at once. The values finally adopted are $a = 0{\cdot}56$, $b = 0{\cdot}42$ for ($\text{H}^\bullet + \text{Cl}'$), 0·265 for ($\text{Na}^\bullet + \text{Cl}'$), and 0·22 for ($\text{Na}^\bullet + \text{NO}'_3$). These have been used in the calculation of K/K_0 from equation (1) for the pure hydrochloric acid solutions, and from equation (4) for the mixed electrolyte solutions in Tables I and II. The significance of the first five columns of figures requires no further explanation. The last column gives the values of the product of $k/[\text{H}^\bullet][\text{Cl}']$ and K/K_0 which, according to equation (3), should be constant.

TABLE III.

Reaction velocity in pure hydrochloric acid solutions ($\mu = c$).

μ (c).	$k \,.\, 10^3$.	$k/[\text{H}^\bullet][\text{Cl}']$.	$\log K/K_0$.	K/K_0.	$kK/K_0[\text{H}^\bullet][\text{Cl}']$.
0·1005	0·467	0·0462	0·135	1·365	0·0631
0·2014	1·718	0·0424	0·173	1·49	0·0631
0·3028	3·755	0·0410	0·181	1·52	0·0622
0·4042	6·66	0·0408	0·186	1·535	0·0627
0·506	10·4	0·0406	0·186	1·535	0·0613
0·608	15·05	0·0407	0·182	1·52	0·0618
0·711	21·04	0·0416	0·173	1·49	0·0620
0·814	28·0	0·0423	0·163	1·455	0·0616
0·918	36·6	0·0435	0·151	1·415	0·0616
1·022	46·5	0·0445	0·137	1·37	0·0610
					Mean 0·0620

In the matter of the relation between the hydrogen- and chlorine-ion concentrations and of the magnitude of the product $[\text{H}^\bullet][\text{Cl}']$, the three series of solutions in the above tables show very considerable differences, but they have a common characteristic in that the total concentration of electrolyte varies continuously. In the first series this variation is provided by the addition of a foreign electrolyte, *i.e.*, with no common ion, and in the second by the addition of a chloride, whilst in the third the increase in the total electrolyte concentration is the result of an increase in the concentration of the acid itself. In all cases the value of $k/[\mathrm{H}^{\bullet}][\mathrm{Cl}']$ passes through a minimum and the same result has also been obtained when the chlorine-ion concentration is kept constant by the use of a fixed concentration of hydrochloric acid and the hydrogen-ion concentration is increased by the addition of successive quantities of perchloric acid (compare Belton, *loc. cit.*).

The results justify the conclusion that the variation of $k/[\mathrm{H}^{\bullet}][\mathrm{Cl}']$ is due to the influence of the ionic environment on the degree of ionisation of hydrochloric acid, and support the view that the transformation of *N*-chloroacetanilide in such solutions is directly due to the catalytic action of undissociated hydrogen chloride, the concentration of which for a given value of the product $[\mathrm{H}^{\bullet}][\mathrm{Cl}']$ depends on the ionic environment. In accordance with this, the velocity of the change may be expressed by $v = k$ [*N*-chloroamine][HCl].

It is significant that the influence of ionic environment on the ionisation of weak and strong acids can be represented by the same formula which adapts itself quite simply to the case when the solvent contains a mixture of electrolytes. The formula combines an expression for the interionic force effects and for those which are involved in the salting-out action of electrolytes.

In view of the fact that the chloroamine transformation is frequently cited as an example of a reaction whose velocity is determined by the thermodynamic activities of the reactants, it may be well to emphasise the point that the observed reaction velocities in salt solutions containing hydrochloric acid are totally inconsistent with the activity-rate hypothesis. The apparent agreement between this hypothesis and the observed results for pure hydrochloric acid solutions would seem to be fortuitous in the light of the observations recorded in this paper.

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