XX.—*The Conversion of* N-*Chloroacetanilide into* p-*Chloroacetanilide by Hydrogen and Chlorine Ions.*

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THE theory that the velocity of a chemical reaction in a homogeneous liquid system is determined by the activities of the chemical species concerned has met with some measure of success in certain cases, such as the inversion of sucrose (Jones and Lewis, J., 1920, **117**, 1120; Moran and Lewis, J., 1922, **121**, 1613; Scatchard, *J. Amer. Chem. Soc.*, 1923, **45**, 1580) and the catalytic decomposition of hydrogen peroxide by bromine–bromide solutions (Livingston and Bray, *ibid.*, p. 2048; Livingston, *ibid.*, 1926, **48**, 53). On the other hand, the velocities of some reactions appear to be adequately expressed in terms of the concentrations of the reactants. The velocity of hydrolysis of ethyl acetate catalysed by hydrochloric acid, considered by Harned and Pfanstiel (*ibid.*, 1922, **44**, 2194) to be determined by an activity relationship, has recently been found by Dawson and Lowson (J., 1928, 2146) to be proportional to the concentration of the acid over a range 0·0002—0·2*M*, through which the activity coefficient of the hydrogen ion falls by 14%. The velocity of the mutarotation of glucose in water is proportional to the concentration of glucose up to 0·6*M*, and the deviations up to five times this concentration are not great (Hudson and Dale, *J. Amer. Chem. Soc.*, 1917, **39**, 320). According to the theory of reaction velocity in solutions developed by Brönsted (*Z. physikal. Chem.*, 1922, **102**, 169; 1925, **115**, 337), the above conflicting views are special cases of a more general velocity equation which involves the activity coefficients of the reactants and of an intermediate complex. A well-known example of a reaction in which the rate is proportional to the activities of the reactants is the conversion of *N*- into *p*-chloroacetanilide, which occurs in the presence of hydrogen and chlorine ions. It is shown below, however, that the activity theory of reaction rate is of only limited application in this case, and that it breaks down completely when the concentrations of hydrogen and chlorine ions are not equal.

This reaction, which apparently follows a unimolecular course, takes place in two stages (Orton and Jones, *Brit. Ass. Rep.*, 1910, 85):

$$\mathrm{Ph{\cdot}NClAc} + \mathrm{H^{\bullet}} + \mathrm{Cl'} \rightleftharpoons \mathrm{Ph{\cdot}NHAc} + \mathrm{Cl_2} \quad . \quad . \quad . \quad . \quad (a)$$

$$\mathrm{Ph{\cdot}NHAc} + \mathrm{Cl_2} \longrightarrow \mathrm{C_6H_4Cl{\cdot}NHAc} + \mathrm{H^{\bullet}} + \mathrm{Cl'} \quad . \quad . \quad . \quad (b)$$

and only in the presence of both hydrogen and chlorine ions, either ion alone being ineffective. The first stage, being slow compared with the second, determines the velocity of the change. The specific velocity was found by Harned and Seltz (*J. Amer. Chem. Soc.*, 1922, **44**, 1476) to be proportional to the product of the activities of the hydrogen and the chlorine ions; at constant temperature their results were satisfactorily represented by the relation

$$K = k_1/a_{\mathrm{H}}{\cdot}a_{\mathrm{Cl'}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k_1 is the experimentally determined unimolecular velocity coefficient, $a_{\mathrm{H}^{\cdot}}$ and $a_{\mathrm{Cl}'}$ are the activities of the respective ions, and K is a constant varying only with temperature. This expression was modified by Soper and Pryde (J., 1927, 2761), who found that better agreement was obtained when the theoretically justified equation

$$K = k_1/a_{\mathrm{H}^{\cdot}}a_{\mathrm{Cl}'}f_{:\mathrm{NCl}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

was employed, $f_{:\mathrm{NCl}}$ being the activity coefficient of the *N*-chloroacetanilide. If the velocity of the change is proportional to the activities of the reacting substances, then we may write

$$v = Ka_{\mathrm{H}^{\cdot}}a_{\mathrm{Cl}'}a_{:\mathrm{NCl}} = Ka_{\mathrm{H}^{\cdot}}a_{\mathrm{Cl}'}C_{:\mathrm{NCl}}f_{:\mathrm{NCl}}.$$

The measured velocity coefficient is given by $k_1 = v/C_{:\mathrm{NCl}}$, and consequently $K = k_1/a_{\mathrm{H}^{\cdot}}a_{\mathrm{Cl}'}f_{:\mathrm{NCl}}$. Thus, on this basis the equation employed by Soper and Pryde, rather than that of Harned and Seltz, should be applicable.

In both these investigations the reaction was carried out in the presence of pure hydrochloric acid, in which case the hydrogen- and the chlorine-ion concentrations are necessarily equal. It would appear possible by varying independently the concentration of the two ions, by the addition of acids or of chlorides, to test the applicability of the above equation over a wider range. Measurements of the effect of neutral salts have been made by Rivett (*Z. physikal. Chem.*, 1913, **82**, 201; **85**, 113), but the concentration terms in which they are expressed render them unsuited for the test of an activity theory of reaction rate. The reaction has therefore been investigated in the presence of mixtures of hydrochloric acid with sodium chloride and with perchloric acid over a wide concentration range.

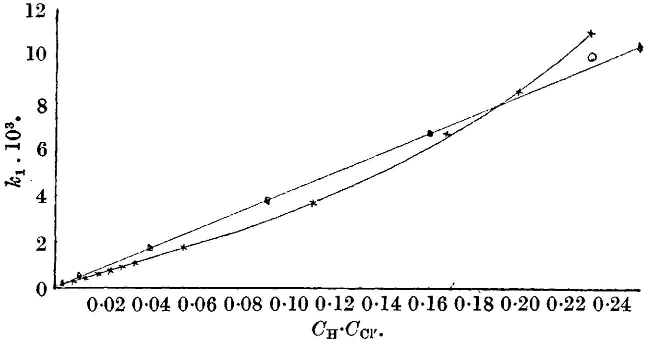
EXPERIMENTAL.

To a solution of *N*-chloroacetanilide, together with the required amount of sodium chloride or perchloric acid, was added the appropriate quantity of pure hydrochloric acid of known strength, both solutions having been first kept for some time at the temperature of reaction—in all cases 25° (± 0·02°). The reaction was then followed iodometrically : at definite times samples were removed and treated with potassium iodide solution and the liberated iodine was titrated with *N*/130-thiosulphate.

A complication is introduced by the *N*-chlorination of the anilides formed (Soper, *J. Physical Chem.*, 1927, **31**, 1193), such products reacting with potassium iodide with liberation of iodine. This takes place only to a small extent, and its obviation by the presence of a chlorine acceptor is difficult in salt solutions of high concentration, in which salting-out effects are considerable. Further, in the more dilute solutions, it was not possible to obtain reproducible results on employing *p*-cresol as such an acceptor. Hydrolysis of the *N*-chloroacetanilide also occurs to a small extent as a side reaction, the result of which is to introduce a small error in a direction opposite to that caused by *N*-chlorination. No attempt has been made here to apply a correction for either of these effects, which tend to annul each other, for it may be shown that the maximum error introduced thereby is of the order of 3%, which is only little greater than the possible experimental error and is too small to invalidate the general conclusions reached.

The velocity coefficients were calculated from the unimolecular equation $k_1 = 1/t \,.\, \log T_1/T_2$, where T_1 and T_2 are two successive titres and t is the time interval between them. For each reaction a good constant was obtained. In order to avoid errors due to lack of homogeneity and to increase in temperature on mixing, some time was allowed to elapse between the addition of hydrochloric acid and the initial titration. The specific rate of reaction of *N*-chloroacetanilide and pure hydrochloric acid at 25° was found to be in agreement with the results of Harned and Seltz (*loc. cit.*), whose values have been used in plotting K_1 against $C_{H}{\cdot}C_{Cl'}$ for pure hydrochloric acid in Figs 1. and 2.

FIG. 1.



⊡ *Pure* HCl. × 0·05*N*-HCl + NaCl. ⊙ 0·48*N*-HCl + 4*N*-$NaNO_3$.

Rate of Reaction in Hydrochloric Acid–Sodium Chloride Mixtures.—The rate of reaction was measured in mixtures in which the concentration of hydrochloric acid was kept approximately constant whilst that of sodium chloride was progressively increased. Table I gives the values of the unimolecular velocity coefficient (k_1) in mixtures in which the concentration of hydrochloric acid (C_{HCl}) varied only between 0·050 and 0·053*M*, while that of sodium chloride (C_{NaCl}) varied from 0·1 to 4·2*M*. Concentrations throughout are expressed in terms of mols. of solute per 1000 g. of water. The product of the ionic concentrations of hydrogen and chlorine ions ($C_{H^\cdot}C_{Cl'}$) is also given, these being calculated on the basis of complete electrolytic dissociation.

TABLE I.

(1) C_{NaCl}.	(2) C_{HCl}.	(3) $C_{H^\cdot}C_{Cl'}$.	(4) $k_1 . 10^4$.	(5) f_{HCl}.	(6) $f_{:NCl}$.	(7).*	(8).*	(9).*
—	0·05	0·0025	1·25	0·860	—	0·0500	0·0676	—
0·10	0·05	0·0075	3·04	0·804	1·04	0·0405	0·0627	0·0603
0·201	0·0502	0·0126	4·55	0·778	1·08	0·0361	0·0598	0·0554
0·302	0·0504	0·0178	6·05	0·765	1·12	0·0340	0·0582	0·0520
0·404	0·0505	0·0229	7·63	0·759	1·16	0·0333	0·0579	0·0497
0·505	0·0506	0·0281	9·17	0·757	1·21	0·0326	0·0570	0·0471
0·608	0·0507	0·0334	10·8	0·758	1·26	0·0323	0·0563	0·0448
1·021	0·0510	0·0547	17·6	0·785	1·47	0·0322	0·0522	0·0355
2·074	0·0519	0·110	37·0	0·945	2·19	0·0336	0·0376	0·0172
3·152	0·0525	0·168	67·0	1·216	3·25	0·0399	0·0269	0·0083
3·697	0·0528	0·198	85·0	1·402	4·02	0·0429	0·0217	0·0054
4·249	0·0531	0·229	110·0	1·628	4·91	0·0480	0·0182	0·0037

* Cols. 7, 8, and 9 give the values of $k_1/C_{H^\cdot}C_{Cl'}$, $k_1/C_{H^\cdot}C_{Cl'}f^2_{HCl}$, and $k_1/C_{H^\cdot}C_{Cl'}f^2_{HCl}f_{:NCl}$, respectively.

In Fig. 1 these values are compared with those obtaining in pure hydrochloric acid solutions. It will be observed that for the latter the velocity coefficient varies linearly with the product $C_{H^\cdot}C_{Cl'}$ over the concentration range employed, while in the presence of increasing sodium chloride concentration, the corresponding curve first lies below and then, at higher concentrations, above that for the pure acid. A similar behaviour is shown in the case of reactions carried out with a higher concentration of hydrochloric acid, again with progressive addition of sodium chloride. The values of the unimolecular velocity coefficients obtained in these reactions are given in Table II, and the relation between them and the product of the concentrations of the hydrogen and chlorine ions is shown in Fig. 2. The curve obtained is similar in general form to that found for mixtures of 0·05*M*-hydrochloric acid with sodium chloride.

TABLE II.

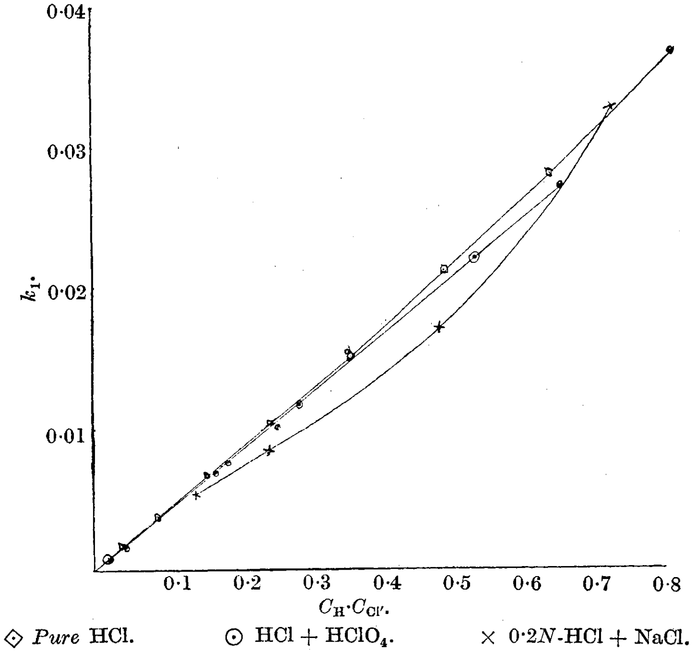
C_{NaCl}.	C_{HCl}.	$C_{H^\cdot}C_{Cl'}$.	$k_1 . 10^3$.	$f_{:NCl}$.	$k_1/C_{H^\cdot}C_{Cl'}$.	$k_1/C_{H^\cdot}C_{Cl'}f^2_{HCl}$.
0·499	0·202	0·142	5·03	0·765	0·0354	0·0607
1·007	0·204	0·247	8·47	0·806	0·0343	0·0529
2·110	0·207	0·481	17·2	0·992	0·0358	0·0458
3·244	0·210	0·725	32·7	1·307	0·0451	0·0264

In order to test the applicability of equation (2), *i.e.*, of the simple activity theory of reaction rate, a knowledge is required of the activities of hydrochloric acid and of the activity coefficient of *N*-chloroacetanilide in the systems investigated. The mean activity coefficients of hydrochloric acid in sodium chloride solutions are given with sufficient accuracy by an equation proposed on empirical grounds by Harned and Brumbaugh (*J. Amer. Chem. Soc.*, 1922, **44**, 2729), *viz.*,

$$\log f_{\mathrm{HCl}} = \alpha c - \beta\mu^{\alpha'} + \alpha''(\mu - c),$$

in which α, α', α'', and β are constants, c is the molar concentration of hydrochloric acid, and μ the ionic strength of the solution. The values of f_{HCl} calculated from this expression are given in col. 5 of Table I. The activity of the hydrochloric acid is given by

FIG. 2.



◇ *Pure* HCl. ⊙ $\mathrm{HCl} + \mathrm{HClO_4}$. × 0·2$N$-HCl + NaCl.

$$a_{\mathrm{HCl}} = a_{\mathrm{H}} \cdot a_{\mathrm{Cl'}} = f^2_{\mathrm{HCl}} C^2_{\pm} = f^2_{\mathrm{HCl}} C_{\mathrm{H}} \cdot C_{\mathrm{Cl}}$$

where $C_{\pm}$ is the mean molality of the ions.

The activity coefficients of the chloroamide were determined by solubility measurements in sodium chloride solutions of concentrations between 0·1 and 4M. The N-chloroacetanilide was shaken in a thermostat for some time with a sodium chloride solution of known strength, and a sample rapidly withdrawn through a plug of cotton-wool, by means of a pump. The sample was weighed, and the amount of N-chloroacetanilide present estimated iodometrically. From these data its solubility in mols. per 1000 g. of water is calculable. It may be assumed that the presence of $0{\cdot}05M$-hydrochloric acid would have but little effect on the solubility in comparison with the concentrations of sodium chloride employed. The activity coefficient of the chloroamide in solution is given by m_0/m_s, where m_0 is the solubility in pure water, and m_s that in the salt solution. The activity coefficients found in this way are given in col. 6 of Table I. Incidentally, it may be mentioned that the function, $\log f_{:NCl}$, varied linearly with the ionic strength of the solution up to a value $\mu = 4{\cdot}3$.

The numerical values of the expression $k_1/C_{H}\cdot C_{Cl'}f^2_{HCl}$, given in col. 8 of Table I, are seen to fall throughout with increasing sodium chloride concentration, the value in $4{\cdot}3M$-sodium chloride solution being only one-third of that in $0{\cdot}1M$-solution. For comparison, the values of $k_1/C_{H}\cdot C_{Cl'}$ are given in col. 7. Over the same concentration range, the activity coefficient of the *N*-chloroacetanilide increases from 1·04 to 4·91, and consequently the values of the expression $k_1/a_{H}\cdot a_{Cl'}f_{:NCl}$ (col. 9) fall still more rapidly than those of (1). If the velocity of reaction were proportional to the activities of the reacting substances, this expression should be constant at constant temperature; hence the simple activity theory does not apply when sodium chloride is present. A similar divergence is found in the case of more concentrated hydrochloric acid solutions. The values of $k_1/C_{H}\cdot C_{Cl'}f^2_{HCl}$ fall rapidly, and although no numerical data are available, on account of the difficulties involved in the determination of solubilities in hydrochloric acid–sodium chloride mixtures, the activity coefficients of the chloroamide in such solutions would doubtless increase and produce a still greater decrease in the value of expression (2) than in that of (1).

On the basis of Brönsted's theory of the velocity of chemical reactions in solutions, the formation of a critical complex between hydrogen ions, chlorine ions, and chloroamide might be assumed. This would give for the velocity of reaction

$$v = KC_{H}\cdot C_{Cl'}C_{:NCl}f_{H}\cdot f_{Cl'}f_{:NCl}/f_{:NCl,HCl} \quad . \quad . \quad . \quad . \quad (3)$$

where $f_{:NCl,HCl}$ is the activity coefficient of the critical complex. If it be assumed that this magnitude varies with the ionic strength of the solution in the same way as does $f_{:NCl}$, this expression becomes

$$v = KC_{H}\cdot C_{Cl'}C_{:NCl}f_{H}\cdot f_{Cl'} = Ka_{H}\cdot a_{Cl'}C_{:NCl},$$

according to which expression (1) should be constant, but this has been found not to be the case. The numerical values of the terms in equation (3) are known, with the exception of the activity coefficient of the complex. The value of $f_{:NCl,HCl}/K$ is thus calculable, and is found to increase 16-fold over the concentration range of Table I. Up to a concentration of 1M-sodium chloride, however, this increase is 70%, which might be regarded as a possible (although abnormal) increase for the activity coefficient, but it is found that its logarithm does not bear a linear relation to the ionic strength of the solution, as was found to be the case for N-chloroacetanilide itself. A further possibility is the formation of a singly charged complex between the chloroamide and either hydrogen or chlorine ions. This leads to an expression for the velocity $v = KC_{H^{\cdot}}.C_{:NCl}f_{H^{\cdot}}.f_{:NCl}/f_{:NCl,H^{\cdot}}$, but this does not lead to a constant value of K if similar variation of the activity coefficients of the positively charged ions is assumed. A similar result is obtained if Cl' is substituted for $H^{\cdot}$ in the above equation. It therefore appears to be impossible to formulate an expression, based on the formation of a critical complex by the reactants, which shall agree with the experimental results.

A comparison of the curves obtained with mixtures of hydrochloric acid and sodium chloride, and those of hydrochloric acid alone or with perchloric acid (described below) indicates that the sodium ion exerts some effect on the rate of reaction. In this connexion it is of interest to consider the effect of neutral salts not containing chlorine ions on the velocity coefficient. It was found that with 0·05M-hydrochloric acid, the addition of 4M-sodium nitrate produced no sensible increase in the value of k_1, but that with 0·48M-acid and 4M-nitrate ($C_{H^{\cdot}}.C_{Cl'} = 0{\cdot}23$) a slight increase in rate resulted. The latter point is plotted in Fig. 1. This behaviour might be expected if the reaction were of Brönsted's Type 0, in which little salt action is found. The action of sodium chloride is to produce first a slight negative, and then a positive salt effect, and in one case of the reaction types described by Brönsted (*loc. cit.*), the kinetic activity factor (F) possesses a value first less and then greater than unity (Type 1·1). This, however, involves the formation of a doubly charged complex, but it would appear difficult to formulate a mechanism of the reaction on this basis.

The Rate of Reaction in Hydrochloric–Perchloric Acid Mixtures.—In the experiments described above, the concentration of the chlorine ion was varied over a wide range in comparison with that of the hydrogen ion. By the addition of perchloric acid, which may be regarded as completely dissociated in solution, the concentration of the hydrogen ion may be made much greater than that of the chlorine ion. The experimental procedure was identical with that for sodium chloride solutions. In each case a good unimolecular velocity coefficient was obtained and these are given in Table III together with the corresponding concentration data.

TABLE III.

C_{HCl}.	C_{HClO_4}.	$C_{H^{\cdot}}C_{Cl'}$.	$k_1 . 10^4$.
0·05	0·0935	0·0072	3·2
0·051	0·201	0·0132	5·3
0·101	0·0713	0·0173	7·3
0·051	0·347	0·0203	7·8
0·052	0·792	0·0442	16·6
0·404	0·0187	0·171	69·5
0·404	0·0570	0·187	76·4
0·408	0·217	0·255	101·2
0·410	0·297	0·289	117·0
0·423	0·836	0·533	220·0
0·429	1·093	0·653	270·0

The relation between the specific velocity of reaction and the product of the ionic concentrations is given in Fig. 2. It shows that within the range investigated (up to $C_{H^{\cdot}}C_{Cl'} = 0{\cdot}65$), the unimolecular velocity coefficient varies linearly with the product of the molal concentrations of the hydrogen and chlorine ions. The velocity would then be represented by $v = KC_{H^{\cdot}}C_{Cl'}C_{:NCl}$. There appears, then, to be no need to introduce the activity theory of reaction rate in this case, the velocity of reaction being proportional to the concentrations of the reacting substances. This result would be in agreement with Brönsted's theory of reaction velocity only if the kinetic activity factor (F) showed no variation over the concentration range considered, but it is probable that the activity coefficient, f_0, of an uncharged molecule would decrease by about 12% in an acid solution of $\mu = 1{\cdot}5$.

Summary.

The rate of conversion of *N*- into *p*-chloroacetanilide in the presence of (1) hydrochloric acid–sodium chloride and (2) hydrochloric acid–perchloric acid mixtures has been measured over a wide concentration range.

In series (1) the specific rate bears no relation to the activities of the reactants, showing that the activity theory of reaction rate is only of very limited applicability to this reaction. Reaction mechanisms involving the formation of a charged complex, according to the views of Brönsted, also gave no agreement with the experimental data. In mixtures of series (2) the specific rate is proportional to the molal concentrations of hydrogen and of chlorine ions.

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