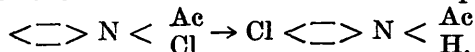


The Temperature Coefficient of the Decomposition of N-chloracetanilide.

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THE rearrangement of N-chloracetanilide to p-chloracetanilide,



in hydrochloric acid solution has often been quoted in support of the "activity rate" hypothesis of chemical kinetics, according to which the "active masses" of the Guldberg-Waage Law are to be identified with the thermodynamic activities of the reacting species rather than the ionic concentrations. In the case of a balanced reaction the thermodynamic Law of Mass Action follows directly. Because of our ignorance of the value of the activity of a single ion, however (see Taylor, 1927) the hypothesis cannot be tested directly by means of reactions between a neutral molecule and one ion. The more favourable case of a reaction between a neutral molecule and two oppositely charged ions is rarer and for this reason the rearrangement of N-chloracetanilide assumes considerable importance in the modern theory of solutions. The reaction has been studied by Rivett (1913), Harned (1918), Akerlöf (1922), and Harned and Seltz (1922), the data of the last mentioned conforming with the equation:

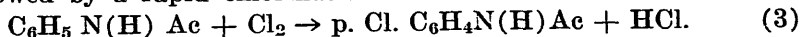
$$-d[A]/dt = k [A] \gamma_{\text{H}} \gamma_{\text{Cl}} C_{\text{H}} C_{\text{Cl}} \quad (1)$$

[A] being the concentration of N-chloracetanilide, $\sqrt{\gamma_{\text{H}} \gamma_{\text{Cl}}}$ the mean activity coefficient of hydrochloric acid and C_{H} , C_{Cl} the ion concentrations. Two disconcerting results of their investigation were the dependence of the temperature coefficient of the reaction rate on the temperature and the failure of the simple equation (1) for reactions proceeding in the presence of neutral salts. The latter difficulty has been emphasised by Belton (1930) and also by Dawson and Millet (1932), who discard the activity rate hypothesis in favour of catalysis by undissociated hydrochloric acid molecules.

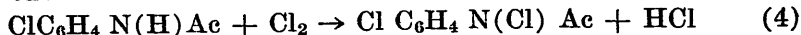
The work of Soper and Pryde (1927), however, has reopened the whole question. They have shown that the rearrangement proceeds by a slow reaction:



followed by a rapid chlorination:



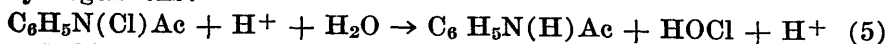
The second reaction, however, does not always occur, as the chlorine may be taken up by a molecule of p-chloracetanilide previously formed:



the chlorine attached to the nitrogen being reactive to potassium iodide in the same way as the chlorine of the N-chloranilide whose rate of decomposition is followed by addition of potassium iodide

and titration of the liberated iodine. In other words, the side-reaction (4) lowers the observed rate of rearrangement. This reaction can be avoided by the addition of an excess of an easily chlorinated substance such as phenol, p-cresol or acetanilide.

In addition, a simultaneous hydrolysis occurs, catalysed by hydrogen ions:



and this effect has to be measured by means of experiments in other acid solutions. Soper and Pryde also used the activity of the anilide rather than the concentration, the activity coefficient being determined from solubility measurements. Their results favour the activity rate hypothesis.

The following work was commenced as a study of the kinetics of a termolecular reaction in solution and particularly with the hope that the refinements introduced by Soper and Pryde would account for the variable temperature coefficient and for the failure of the activity rate hypothesis in the presence of neutral salts. Our expectations were realised with regard to the former but not with regard to the latter.

EXPERIMENTAL.

N-chloroacetanilide was prepared by the method of Barnes and Porter (1930) and its rate of decomposition followed in 0.01 *M* solution by the addition of potassium iodide to aliquot samples and titration of the liberated iodine with thiosulphate. The first series of measurements were made in hydrochloric acid solution ranging from 0.1 to 1.0 *M*, both with and without the addition of 0.03 *M* phenol. In Table I k' is the unimolecular velocity constant in the absence of phenol; the figures agree satisfactorily with those of Harned and Seltz. k_1 is the constant in presence of phenol, the data again agreeing with those of Soper and Pryde; k_2 is the velocity constant found in nitric acid solution of corresponding strength, the figures in brackets being interpolated; k is the difference ($k_1 - k_2$). Solubility measurements recorded at the foot of the table give the activity coefficient of the anilide, γ_{NCl} . Finally K is the termolecular velocity constant $k/(\gamma_{\text{NCl}}\gamma_{\text{HCl}}^2 C_{\text{H}} C_{\text{Cl}})$, γ_{HCl} being taken from the data of Randall and Young (1928). The constancy of the figures in the last column supports the activity rate hypothesis for this medium. In this paper velocity constants will be expressed with minutes and mols. per litre as units. This will facilitate comparison with other data.

TABLE I.
REACTION RATES IN HYDROCHLORIC ACID SOLUTION AT 25°.

<i>M</i> -HCl	$k' \times 10^3$	$k_1 \times 10^3$	$k_2 \times 10^3$	γ_{NCl}	K
0.1	0.48	0.51	0.0335	0.991	.0760
0.2	1.71	1.89	(0.051)	.982	.0798
0.3	3.77	4.10	0.095	.973	.0795
0.4	6.56	7.15	(0.12)	.964	.0800
0.5	10.4	11.2	0.15	.954	.0809
0.6	15.4	16.1	(0.17)	.945	.0809
0.7	20.9	21.9	(0.20)	.936	.0796
0.8	27.9	29.0	0.23	.927	.0794
0.9	36.5	37.9	(0.27)	.918	.0798
1.0	45.7	47.7	0.315	.908	.0796

SOLUBILITY OF N-CHLOROACETANILIDE
(in g. mols. per litre).

In water ..		0.01390		
	0.4M	0.7M	1.0M	
In KCl ..	0.01208	0.01092	0.00988	
KNO ₃ ..	0.01344	0.01308	0.01268	
HNO ₃ ..	0.01592	0.01774	0.01998	

Since it may be argued that the constancy of K may be fortuitous owing to the small range over which γ_{HCl} varied (0.755–0.810) experiments were conducted in more dilute acid solution with a variation of γ_{HCl} from 0.76 to 0.91, but in order to obtain reaction in a reasonable time, the experiments were conducted at 55°, with the following results.

TABLE II.
REACTION RATES IN HYDROCHLORIC ACID SOLUTION AT 55°.

$M\text{-HCl}$..	0.01	0.02	0.05	0.1	0.2	0.3
$k_1 \times 10^3$..	0.32	0.86	3.7	11.2	43.7	99.7
$k_2 \times 10^3$..	0.19	0.37	0.92	1.74	3.18	4.3
K ..	15.9	16.7	16.3	15.0	17.2	18.5

The factor $\gamma : \text{NCl}$ is negligible at these concentrations. Whilst these figures are not as accurate as those at 25° the results afford definite evidence in favour of the activity rate hypothesis.

The Neutral Salt Effect. Determinations were made of the rate of reaction in the presence of phenol, (1) at constant acid strength (0.01 $M\text{-HCl}$) and an amount of potassium chloride varying from 0.1 to 1.5 M and (2) in a solution of hydrochloric acid and potassium chloride such that the total molality was constant at 1 M , there being in this case a simple law relating the activity coefficient of the acid to its concentration (Harned, 1926).

TABLE III.
REACTION RATES IN THE PRESENCE OF NEUTRAL SALT AT 25°.

0.1 $M\text{-HCl}$ + x $M\text{-KCl}$.

[KCl]	k ₂ × 10 ³	k ₃ × 10 ³	γ : NCl	K
0.1	0.82	0.031	1.036	0.0677
0.2	1.14	.028	1.073	.0641
0.3	1.50	.025	1.119	.0615
0.5	2.06	.021	1.202	.0551
0.9	3.21	.016	1.370	.0452
1.0	3.47	.015	1.404	.0429
1.5	4.95	.012	1.598	.0343

Constant total molality of 1 M .

[KCl]	k ₂ × 10 ³	k ₃ × 10 ³	γ : NCl	K
0.	47.7	0.315	0.908	0.0796
0.25	31.7	.164	1.036	.0669
0.5	18.8	.090	1.155	.0573
0.75	8.57	.040	1.282	.0506
0.9	3.21	.0162	1.370	.0459

Although there may be some doubt as to the value of $\gamma : \text{NCl}$ in these cases, the data recorded in the above table, using the $\gamma : \text{HCl}$ values given by Harned and Åkerlöf (1926), cannot be reconciled with the activity rate hypothesis.

The Temperature Coefficient.

Separate experiments in nitric and perchloric acid solution showed that the temperature coefficient of the hydrolytic side-reaction corresponded to an energy of activation of 19,400 cal. The temperature coefficient of the main reaction is of the same order and therefore will not be affected appreciably by the side reaction.

TABLE IV.
TEMPERATURE COEFFICIENT OF THE REACTION RATE.

Solution.		15°	25°	35°	45°	55°	E
$k_1 \times 10^3$	0.3 M-HCl	.. 1.205	4.10	12.3	36.4	99.1	20,650
	0.2 M-HCl + 0.3 M KCl	.. 1.13	3.69	11.4	34.5	97.6	20,950

The energy of activation may be taken as 20,800 cal.

DISCUSSION.

According to equation (5) the hydrolytic side reaction should involve collision between anilide molecules, hydrogen ions and solvent molecules.

Application of the usual formula:

$$k_3 = \frac{N_0}{1000} \sigma^2 \sqrt{\left\{ 8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}} e^{-E/RT} \quad (6)$$

for the reaction rate in terms of molecular radii and velocities, on the assumption that reaction is caused by binary collisions of activated molecules leads to a calculated velocity constant some 1300 times larger than the observed. We may assume a probability factor of a reasonable magnitude to allow for this, but alternatively we may note that the kinetics of the reaction according to equation (5) necessitate the participation of water molecules in the binary collisions. In this respect the reaction resembles the iodination of β -phenylpropionic acid (Moelwyn-Hughes and Legard, 1933) and the decomposition of hydrogen peroxide catalysed by iodide ion (Hender and Robinson, 1933), and the equation which was found applicable in these cases should apply here:

$$k_2 = \frac{N_0}{1000} \frac{3\pi\eta\sigma}{2m_A n_W} e^{-E'/RT}$$

where N_0 is Avogadro's Number, η is the solvent viscosity, σ the mean diameter, m_A the molecular mass of one of the reacting species, n_W the number of solvent molecules per c.c. and E' is the energy of activation corrected for a viscosity variation. Although the theoretical basis of this equation may be somewhat insecure, its success in a number of applications justifies its use as an empirical indication that solvent molecules participate in the reaction. It is therefore encouraging to find that, using the corrected value $E' = 23,350$ cal. the calculated value of the velocity constant is in reasonable agreement with that found experimentally. There is, indeed, no difficulty in accounting for the kinetics of this reaction.

Turning now to a consideration of the main reaction we have two problems, (1) the neutral salt effect and (2) the temperature coefficient. If we adopt the view that the acid catalyst is for all practical purposes completely dissociated, then we can only conclude

that in the presence of neutral salts there is a "primary neutral salt effect" in a negative direction and leave a further explanation until more is known about the general question of primary salt effects. On the other hand, it has been claimed that this anomaly can be removed by assuming that catalysis is due to undissociated acid molecules. This view can be shown to be erroneous, for let K_A be the acid dissociation constant, then

$$K_A = \gamma_H \gamma_{Cl} C_H C_{Cl} / C_{HCl}$$

since the activity coefficient of the undissociated molecule may be taken as unity. The rate of reaction is now given by:

$$\begin{aligned} -d[A]/dt &= k[A] C_{HCl} \\ &= k'' [A] \gamma_H \gamma_{Cl} C_H C_{Cl} \end{aligned}$$

This view, therefore, leads to an equation identical with that which is deduced on the assumption of complete dissociation; in fact, the two postulates cannot be distinguished by experiments at a single temperature.

The temperature coefficient of the reaction may, however, distinguish between the two postulates. Before proceeding further with the argument, it will be necessary to make some assumption as to the number of ternary collisions which can occur in a given time. The number of binary collisions per c.c. per sec. is:

$$Z_{12} = n_1 n_2 \sigma^2 \sqrt{\left\{ 8 \pi R T \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}}$$

where M_1 and M_2 are molecular weights and n_1 and n_2 the number of molecules of each species per c.c.

A ternary collision will occur if at the moment of impact the third molecule is within a specific distance r of the complex formed by the first two molecules. The probability of this is $\frac{3}{4} \pi r^3 n_3$, so that:

$$Z_{123} = \frac{4}{3} \pi n_1 n_2 n_3 r^3 \sigma^2 \sqrt{\left\{ 8 \pi R T \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}}$$

where n_3 is the number of molecules of the third kind per c.c.

The number of molecules decomposing per c.c. per sec. is then:

$$-dn/dt = \frac{4}{3} \pi n_1 n_2 n_3 r^3 \sigma^2 \sqrt{\left\{ 8 \pi R T \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}} P e^{-E/RT}$$

P being an orientation factor which is probably low for trimolecular reactions. Consequently:

$$k_3 = 80 \pi \left(\frac{N_0}{1000} \right)^2 r^3 \sigma^2 \sqrt{\left\{ 8 \pi R T \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}} P e^{-E/RT}$$

The data of Stern (1904) for the polymerisation of benzaldehyde in the presence of cyanide ions are given by:

$$k_3 = 3.16 \times 10^7 e^{-13000/RT}$$

Similarly the data of Bailey (1930) on the reaction between ammonia and ethyl malonate are given by:

$$k_3 = 2.46 \times 10^8 e^{-8620/RT}$$

These reactions can be brought into line with the above equation, assuming reasonable molecular diameters, $r = \sigma = 5 \text{ \AA}$, if P is of the order of 10^5 .

These calculations have no claim to accuracy, but they serve to demonstrate that termolecular reactions in solutions can be accounted for, at least qualitatively, the point to be emphasised being that the observed rate is lower than the calculated, as would be expected in view of the peculiar orientation of molecules necessary for such reaction. The decomposition of *N*-chloracetanilide can be represented by the equation:

$$k_3 = 10^{14} e^{-20800/RT} \quad (7)$$

whereas the calculated value of the collision factor is of the order of 10^{12} . Since errors in our theory will tend to give too high a value to this collision factor, we may conclude that our results are not consistent with the hypothesis of ternary collision.

It may be, however, that reaction occurs between anilide molecules and undissociated acid molecules according to the approximate equation:

$$-d[A]/dt = k [A] C_{\text{HCl}}$$

in which case k should be capable of calculation by means of equation (6). An approximate estimate of the dissociation constant of hydrochloric acid has already been made (Robinson, 1936) and thence we may calculate the following values for C_{HCl} in 0.3 *M* solution at different temperatures whilst the experimental data for the rate of reaction gives values of k as follows:

°C	15	25	35	45	55
$C_{\text{HCl}} \times 10^8$	2.49	6.92	18.4	46.2	105
$k \times 10^4$	4.8	5.9	6.7	7.9	9.5

These velocity constants can be represented by the equation:

$$k = 8 \times 10^6 e^{-20800/RT}$$

with an experimental value for the collision factor of 8×10^6 , whilst the value for the collision factor calculated by equation (6) is of the order 10^{13} . This implies that only one in about 10^6 of the activated collisions is effective, but it is encouraging to find that the value from the experimental data is *less* than the calculated, as would be expected for a reaction of this type; indeed, Rolfe and Hinshelwood (1934) found a probability factor of 10^7 for the esterification of methyl alcohol catalysed by undissociated acetic acid molecules. We have therefore a reasonable hypothesis to account for the temperature coefficient of this reaction. We may be tempted to identify these undissociated hydrochloric acid molecules with the "ion pairs" of Bjerrum's association hypothesis, but that such is unlikely may be shown by a consideration of the energy magnitudes involved. The energy liberated when an ion pair is formed is of the order of 2 k T ,

i.e., about 1200 calories per gram-molecule (*vide* Fuoss and Kraus, 1933), whereas the undissociated molecules we are considering are formed with an absorption of about fifteen times as much heat, *i.e.*, a greater part of the apparent energy of activation is really the energy necessary for the formation of these undissociated molecules. Again, according to Harned and Ehlers, the mean diameter of the hydrogen and chlorine ions is 4.3 Å and it is doubtful if under these conditions any ion pairs can be formed. For this reason we do not believe that ion pairs function as the catalyst; but that undissociated molecules exist in very small amount, formed by means of a covalent bond in equilibrium with similar molecules in the gaseous phase.

Finally, if we adopt Brönsted's view (1922) that the rate of reaction is governed by the formation of a "critical complex," it can be shown that the neutral salt effects observed in this reaction, whilst not explicable quantitatively, are at least not inconsistent with the activity rate hypothesis. For on Brönsted's theory the rate of reaction will be given by:

$$-d[A]/dt = k_1[A]C_H C_{Cl} \gamma_H \gamma_{Cl} \frac{\gamma : NCl}{\gamma_X}$$

where γ_X is the activity coefficient of the "critical complex." The introduction of this additional factor will not influence to any serious extent the validity of the argument we have already pursued with regard to the temperature coefficient of this reaction for γ_X will not vary greatly with temperature, but its variation with the addition of neutral salts will be important. Now it will be reasonable to postulate that $\gamma_X \gamma : NCl$ will vary in a similar manner with the ionic strength of the solution; thus, without assuming identity of γ_X and $\gamma : NCl$ it is reasonable to believe that if $\gamma : NCl$ is large and positive then γ_X will also be positive and of comparatively large magnitude and *vice versa* if $\gamma : NCl$ is negative, whereas if $\gamma : NCl$ is nearly unity then γ_X also will not be far removed from unity. In the limiting case where $\gamma_X = 1$ then Brönsted's equation reduces to equation (1) with the inclusion of $\gamma : NCl$ an equation which we have substantiated in the absence of neutral salts. The coincidences of these two equations would depend therefore on the close approach of γ_X to unity in pure hydrochloric acid solution; this is probable since $\gamma : NCl$ is not far removed from unity. In potassium chloride solution however the observed values of the "constant" K in Table III diminish with increasing salt concentration which would be expected if γ_X increased with addition of salt, a hypothesis which is also probably correct since $\gamma : NCl$ undergoes a considerable increase under these circumstances. A similar behaviour was observed by Dawson and Millet in sodium chloride solution. Data have also been obtained for sodium nitrate and perchloric acid solutions, but these are not susceptible to treatment in the absence of activity coefficient data for hydrochloric acid in these solutions. We may conclude, however, that, viewed in the light of Brönsted's theory, there is nothing in these neutral salts effects which can be demonstrated to be contrary to the activity rate theory.

SUMMARY.

The rate of isomerisation of *N*-chloracetanilide by hydrochloric acid has been investigated and two side reactions taken into account. The neutral salt effect and the temperature coefficient have been studied.

The high temperature coefficient of the reaction has been shown to be consistent with catalysis by undissociated hydrochloric acid molecules.

No evidence has been found inconsistent with the activity rate hypothesis.

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