362. *Acid Catalysis in Non-aqueous Solvents. Part VIII. The Rearrangement of* N-*Chloroacetanilide in Chlorobenzene Solution at* 100°.

By R. P. Bell and P. V. Danckwerts.

The catalysed transformation of *N*-chloroacetanilide into *o*- and *p*-chloroacetanilide has been studied in chlorobenzene solutions of carboxylic acids at 100°. Under these conditions the transformation is subject to general acid catalysis, as distinct from the specific mechanism involving free chlorine which operates in catalysis by hydrogen chloride. The course of each reaction is autocatalytic, but the initial rates are related in a simple way to the concentration and dissociation constant of the catalysing acid. The transformations of *N*-chloroacetanilide, *N*-bromoacetanilide, and *N*-iodoformanilide are compared, and an explanation is suggested for the autocatalytic behaviour of the chloro-compound.

Many kinetic measurements have already been made on the catalysed transformation of *N*- into *o*- and *p*-chloroacetanilide, the catalyst being in almost every case a hydrogen halide in a solvent containing water. Under these conditions the transformation undoubtedly takes place by a specific mechanism involving free halogen; this is shown by a large amount of kinetic evidence (summarised by Orton, *Brit. Assoc. Reports*, 1910, 85), and also by recent measurements with radio-active chlorine as an indicator (Olson, Porter, Long, and Halford, *J. Amer. Chem. Soc.*, 1936, **58**, 2467; 1937, **59**, 1613). On the other hand, it has been shown in previous papers of this series that the rearrangement of *N*-iodoformanilide (Bell and Brown, J., 1936, 1520), *N*-bromoacetanilide (Bell, *Proc. Roy. Soc.*, 1934, *A*, **143**, 377), and a number of other *N*-bromoanilides (Bell and Lidwell, this vol., p. 1096) is catalysed by carboxylic acids and phenols in non-dissociating solvents, and that no mechanism involving free halogen can be operative in these catalyses (Bell, J., 1936, 1154). It is therefore of interest to discover whether general acid catalysis of this kind can also take place in the transformation of *N*-chloroacetanilide. Rivett (*Z. physikal. Chem.*, 1913, **82**, 202) found that very slow transformation took place in aqueous solutions of sulphuric and other acids, but this can be attributed to small amounts of hydrogen chloride formed by hydrolysis. Earlier experiments had also shown that no measurable reaction took place with carboxylic acids in chlorobenzene at room temperatures. However, it had been found that *N*-iodoformanilide is rearranged about 500 times as fast as *N*-bromoacetanilide under the same conditions of catalyst and temperature; hence the analogous rearrangement of *N*-chloroacetanilide might well be undetectable except at higher temperatures. In the present paper measurements were carried out at 100°, with the result that general catalysis was established in this case also.

EXPERIMENTAL.

Materials.—*N*-Chloroacetanilide, prepared from acetanilide and sodium hypochlorite solution saturated with sodium bicarbonate, was recrystallised from aqueous acetic acid and left in a desiccator over soda-lime until the smell of acetic acid had disappeared. The amount of iodine liberated from potassium iodide corresponded to a purity of at least 99%.

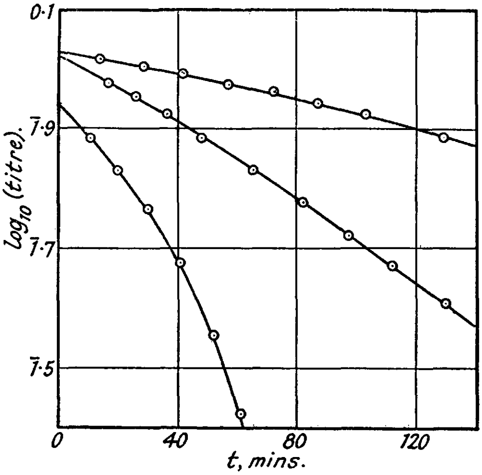
Chlorobenzene was dried over phosphoric oxide and fractionally distilled, being collected within a range of 0·5°.

The acids used were mostly commercial specimens of established purity, but dichloroacetic acid was fractionally distilled, and chloroacetic acid recrystallised from benzene.

Measurement of Reaction Velocity.—The reactions were carried out in vessels of the type previously described (Bell and Levinge, *Proc. Roy. Soc.*, 1935, *A*, **151**, 211) immersed in a steam-bath. The temperature sometimes varied by as much as 0·5°, but this is not important, since the kinetic results are not of high accuracy. The concentration of anilide was about M/200 throughout, and the reaction was followed by extracting about 2 g. of reaction mixture from time to time, adding it to a weighed flask containing acidified potassium iodide solution, and estimating the iodine liberated by weight titration with N/100-thiosulphate. These titrations could be carried out with a reproducibility of better than 0·5% provided that the conditions were carefully standardised, and it was found that the best end-points were obtained with N/10-potassium iodide containing N/2-acetic acid.

When the logarithm of the titre was plotted against the time, straight lines were not obtained, almost all reactions showing a marked acceleration. This is illustrated by Fig. 1, which shows portions of three typical experiments. The velocity constants recorded were taken from the initial slopes of these plots. The accelerating effect appeared to depend on the time rather than on the extent of the reaction, and the initial slopes were therefore more difficult to obtain in the slower reactions. A large number of titrations (not shown in Fig. 1) were therefore carried out near the beginning of the reaction, and the errors are probably not greater than ± 10% at the worst.

Fig. 1.



Solutions of *N*-chloroacetanilide in chlorobenzene without the addition of any acid showed no change in titre after being kept at 100° for several days.

Results.—In the following tables, *c* is the acid concentration in g.-mols. per 1000 g. of solution, *k* the initial first-order velocity constant with decadic logarithms and the time in minutes, and k_A the value of k/c extrapolated to $c = 0$. In addition to the results recorded, attempts were made to study catalysis by trichloroacetic and phenylpropiolic acids, but in both cases the results were very erratic, possibly owing to slight decomposition of these acids at 100°.

c.	$10^4 k$.	$10^4 k/c$.	*c*.	$10^4 k$.	$10^4 k/c$.	*c*.	$10^4 k$.	$10^4 k/c$.
Dichloroacetic acid : $10^4k_A = 50$.			*o*-Nitrobenzoic acid : $10^4k_A = 47$.			Chloroacetic acid : $10^4k_A = 11$.		
0·499	43	86	0·156	7·3	47	0·466	6·6	14
0·360	24	66	0·116	5·0	43	0·244	3·0	12
0·239	17	71	0·069	3·5	51	0·118	1·2	10
0·125	7·0	56	0·047	2·2	47	0·116	1·5	13
0·097	5·7	59						
m-Nitrobenzoic acid : $10^4k_A = 2·6$.			Phenylacetic acid : $10^4k_A = 2·1$.					
0·430	2·9	6·7	1·043	4·7	4·5	0·456	1·6	3·5
0·316	1·6	5·0	0·929	3·8	4·1	0·258	0·6	2·3
0·194	1·0	5·1	0·695	2·1	3·0	0·247	0·9	3·6
0·112	0·40	3·6	0·519	1·6	3·1			

DISCUSSION.

The General Catalytic Effect.—The above data show clearly that the rearrangement of *N*-chloroacetanilide is catalysed by carboxylic acids at 100°, and that there is a general correlation between the strength of the acid and its catalytic power. In order to make a quantitative comparison we shall use the extrapolated values of k_A given above. Their accuracy is low, partly because of the errors in the individual velocity constants, and partly because of the difficulty in extrapolating to infinite dilution. The collected values are given below, together with the dissociation constants (K) of the acids in water at 25°.

Acid	Dichloroacetic	*p*-Nitrobenzoic	Chloroacetic	*m*-Nitrobenzoic	Phenylacetic
$10^6 K$	5200	640	150	35	5·2
$10^4 k_A$	50	47	11	2·6	2·1

Fig. 2 shows a plot of $\log_{10}k_A$ against $\log_{10}K$. It is seen that a relation of the type $k_A = GK^x$ is approximately obeyed, the slope of the line drawn in the figure being 0·6. There is little information about the dissociation constants of acids in water at 100°, but it seems likely that their use would somewhat increase the value of x.

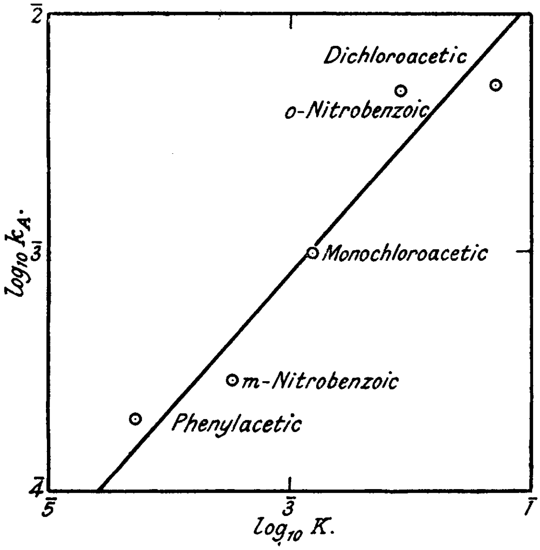
It is of interest to consider together the results for the chloro-, bromo-, and iodo-anilides. A direct comparison of the rates is not possible, since in the first case the data are for 100°, and in the last two for 25°. However, we can make a rough estimate of the rate at 25° for *N*-chloroacetanilide by making an assumption about the energy of activation.

With dichloroacetic acid as the catalyst E is 13,800 cals. for N-bromoacetanilide (Bell, *Proc. Roy. Soc.*, 1934, *A*, **143**, 377) and we shall take $E = 18,000$ cals. for the much slower reaction of N-chloroacetanilide. This gives the following figures for the three anilides at 25°.

Anilide.	x.	Relative rate.
N-Chloroacetanilide	0·6	1
N-Bromoacetanilide	0·3	1×10^3
N-Iodoformanilide	0·2	4×10^5

It is clear that the increase in rate is accompanied by a decrease in the exponent of the Brönsted relation. It is of interest to consider the bearing of this result on the interpretation of proton-transfer reactions in terms of potential-energy curves (cf. Polanyi and Horiuti, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 505; Bell, *Proc. Roy. Soc.*, 1936, *A*, **154**, 414). The decrease in x corresponds to a smaller angle of intersection for the two potential-energy curves representing the binding of the proton. A small change in x could be attributed to a relative displacement of the energy minima of the two curves without any change in their form, but the large changes observed in this series must be connected with a change in the shape of the potential-energy curve which represents the attachment of a proton to the anilide. Other evidence for this change of shape has already been brought forward (Bell and Lidwell, *loc. cit.*), and it may be noted that in the present case an increased proton affinity corresponds to a steeper potential-energy curve: this is in agreement with the general relation which exists between the force constants and binding energies of a series of similar links.

FIG. 2.



The Autocatalytic Behaviour.—As has already been mentioned, the course of the reactions was always strongly autocatalytic. The following additional observations are of assistance in interpreting this behaviour. (*a*) The addition of pure *o*- and *p*-chloroacetanilide had no effect upon the initial rate, though it accentuated the accelerating effect. (*b*) When a solution in which the reaction had gone to completion (catalyst, dichloroacetic acid) was extracted with a small quantity of water, no chloride ion could be detected when silver nitrate was added to the extract; however, when the experiment was repeated with much more concentrated N-chloroacetanilide (M/2), chloride ion was detected. (*c*) In presence of approximately 10^{-4} N-hydrogen chloride in chlorobenzene, the rearrangement of N-chloroacetanilide takes place at 100° with a velocity constant of $1{\cdot}7 \times 10^{-3}$, *i.e.*, faster than almost all of the other reactions measured. Hydrogen chloride of this concentration could not be detected by extracting with water and testing with silver nitrate. (*d*) No change can be detected if N-chloroacetanilide is heated to 100° with *o*- and *p*-chloroacetanilide in chlorobenzene solution without the addition of any catalyst.

On the basis of these observations we suggest that the acceleration observed in the kinetic experiments is due to catalysis by very small amounts of hydrogen chloride formed by the slow reaction

$$C_6H_5{\cdot}NClAc + C_6H_4Cl{\cdot}NHAc \longrightarrow C_6H_5NAc{\cdot}NAc{\cdot}C_6H_4Cl + HCl$$

this action being itself catalysed by acids. The observed acceleration could be accounted for if less than 1% of the N-chloroacetanilide reacts in this way.

PHYSICAL CHEMISTRY LABORATORY, BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.

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