238. *Acid Catalysis in Non-aqueous Solvents. Part VII. The Rearrangement of* N-*Bromobenzanilide in Chlorobenzene.*

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The kinetics of the acid-catalysed rearrangement of *N*-bromobenzanilide have been studied in chlorobenzene solution at 25°. There is, in general, some variation of catalytic constant with acid concentration, but the catalytic constants extrapolated to zero concentration bear a simple relation to the dissociation constants in water in the case of the eight acids studied.

Previous papers in this series (Bell, *Proc. Roy. Soc.*, 1934, **143**, *A*, 1, 377; Bell and Levinge, *ibid.*, 1935, **151**, *A*, 211) have dealt with the rearrangement of *N*- into *p*-bromoacetanilide. The present paper describes similar investigations of the analogous rearrangement of *N*-bromobenzanilide. Although the general behaviour is similar in the two cases, there are quantitative differences which are of interest.

Experimental.

Preparation of Materials.—*N*-Bromobenzanilide was prepared by slowly adding ($\frac{1}{2}$ hour) a slightly warm solution of benzanilide in the minimum quantity of alcohol to an aqueous solution of hypobromous acid containing potassium bicarbonate, which was mechanically stirred and cooled in a freezing mixture during and for 1 hour after the addition (cf. Chattaway and Orton, *Ber.*, 1899, **32**, 3580; Slosson, *ibid.*, 1895, **28**, 3265; *Amer. Chem. J.*, 1903, **29**, 289). The purity of the product is considerably affected by the concentration of hypobromous acid used, a five-fold excess of N/30-acid being best. This gave an almost quantitative yield of a buff-coloured powder having about 90% of the theoretical oxidising power towards potassium iodide. The impurity present was essentially *p*-bromobenzanilide. Stock solutions were made by leaching the crude *N*-bromo-compound with a little solvent on a filter, and diluting the concentrated solution to about M/10; the *p*-bromo-compound did not dissolve. The stock solutions were kept in the dark in a desiccator, but were somewhat unstable; however, the rate of decomposition was negligible compared with even the slowest catalysed reactions measured. On standing for a long time, these solutions deposited crystals of *p*-bromobenzanilide, m. p. 198° (uncorr.) (Beilstein gives 202°).

Attempts to prepare *N*-bromobenzanilide by shaking a chloroform solution of benzanilide with aqueous hypobromous acid (cf. Chattaway, J., 1902, **101**, 816) never gave an appreciable yield.

Chlorobenzene was dried over phosphoric oxide and fractionally distilled.

The acids were pure commercial specimens used without further purification, except that monochloroacetic acid was recrystallised from benzene, phenylacetic and *m*-nitrobenzoic acids from aqueous alcohol, and acetic acid was twice frozen and the crystals separated.

Measurement of Reaction Velocity.—The acid solutions were made up by weight, and their concentrations checked by titration. The reaction mixtures were made up by volume from the stock solutions, and the catalyst concentration calculated in weight molar units, the differences in density between the various solutions being neglected. The error in this procedure is never more than a few units %, and is less than the uncertainty in the velocity measurements. The concentration of *N*-bromobenzanilide was throughout about 0·005M.

The reactions took place in vessels of the type described by Bell and Levinge (*loc. cit.*), which were covered with tin-foil to exclude light. The reaction was followed by withdrawing 2-c.c. samples at intervals and titrating the iodine liberated from potassium iodide with N/100-thiosulphate, a micro-burette being used. The titres were reproducible to 0·01 c.c. With the exception of some experiments in which the catalyst was trichloroacetic acid (see Table I), the course of the reactions was always of the first order kinetically, and was usually followed

TABLE I.

Trichloroacetic acid.

$10k_{\text{A}} = 1{\cdot}05 + 6{\cdot}0c.$

c.	10^2k.	$10k_{\text{A}}$ (obs.).	$10k_{\text{A}}$ (calc.).
0·00615	0·064	1·04	1·09
0·00860	0·097	1·13	1·10
0·0122	0·147	1·20	1·12
0·0245	0·290	1·18	1·20
0·0245	0·304	1·23	1·20
0·0368	0·474	1·29	1·27
0·0490	0·624	1·27	1·34
*0·0490	0·80	1·63	(1·34)
*0·0612	1·56	2·57	(1·42)
*0·0734	2·48	3·38	(1·49)
*0·0945	5·45	5·60	(1·62

Dichloroacetic acid.

$10^2k_{\text{A}} = 1{\cdot}53 - 1{\cdot}9c.$

c.	10^3k.	10^3k_{A} (obs.).	10^3k_{A} (calc.).
0·0264	0·382	14·5	14·8
0·0528	0·772	14·6	14·3
0·0792	1·08	13·7	13·8
0·106	1·41	13·4	13·3
0·139	1·71	12·4	12·7

Monochloroacetic acid.

$10^3k_{\text{A}} = 1{\cdot}98 - 4{\cdot}9c.$

0·0279	0·051	1·82	1·85
0·0418	0·076	1·81	1·78
0·0832	0·125	1·51	1·57
0·112	0·172	1·54	1·48
0·138	0·167	1·21	1·30
0·179	0·208	1·16	1·10
0·209	0·192	0·92	0·95

Phenylpropiolic acid.

$10^2k_{\text{A}} = 0{\cdot}60 - 1{\cdot}9c.$

c.	10^3k.	10^2k_{A} (obs.).	10^2k_{A} (calc.).
0·0232	0·124	0·54	0·56
0·0232	0·133	0·57	0·56
0·0464	0·235	0·51	0·51
0·0696	0·351	0·51	0·47
0·0696	0·305	0·44	0·47
0·0834	0·360	0·43	0·44

m-*Nitrobenzoic acid.*

$10^3k_{\text{A}} = 1{\cdot}09 - 5{\cdot}5c.$

c.	10^4k.	10^3k_{A} (obs.).	10^3k_{A} (calc.)
0·0207	0·203	0·98	0·98
0·0345	0·284	0·82	0·90
0·0345	0·334	0·97	0·90
0·0690	0·490	0·71	0·71
0·104	0·540	0·53	0·52

Acetic acid.

$10^3k_{\text{A}} = 0{\cdot}34 - 0{\cdot}16c.$

0·112	0·34	0·31	0·32
0·224	0·71	0·32	0·30
0·374	1·01	0·27	0·28
0·449	1·23	0·27	0·27
0·561	1·38	0·25	0·25

β-Chloropropionic acid.

$10^3k_{\text{A}} = 0{\cdot}53$ (mean value).

c.	10^4k.	10^3k_{A}.
0·0189	0·100	0·53
0·0756	0·390	0·52
0·0945	0·510	0·54
0·151	0·786	0·52
0·189	1·01	0·53

Phenylacetic acid.

$10^3k_{\text{A}} = 0{\cdot}56$ (mean value).

c.	10^4k.	10^3k_{A}.
0·064	0·347	0·54
0·096	0·566	0·59
0·160	0·890	0·56

* In these experiments there was a considerable deviation from a unimolecular course, there being progressive retardation as the reaction proceeded. The velocity constants given correspond to the initial rates.

over about two-thirds of its course. The velocity constants were evaluated graphically by plotting the logarithm of the titre against the time.

Results.—In Table I the concentrations are expressed as moles per 1000 g. of solution, and the velocity constants k are first-order constants with the time in minutes and decadic logarithms. The catalytic constants k_A are given by $k_A = k/c$. The equations representing the variation of catalytic constant with concentration are given before the results for each acid.

Discussion of Results.

It will be seen that for most of the acids used there is some variation of catalytic constant with acid concentration, which can be expressed as a linear dependence. This type of variation was also found for *N*-bromoacetanilide, and appears to be a general phenomenon for catalysis by carboxylic acids in non-dissociating solvents (cf. Brönsted and Bell, *J. Amer. Chem. Soc.*, 1931, **53**, 2478; and earlier papers of this series). Various possible explanations have been previously discussed, and the results described here do not throw any new light on this problem. In comparing the catalytic power of the acids with their dissociation constants we have used the catalytic constants at infinite dilution, as was done in the case of *N*-bromoacetanilide. These extrapolated values are collected in Table II, together with the dissociation constants of the acids in water at 25°. The figure shows the relation between $\log_{10} k_A$ and $\log_{10} K_A$, the full line representing the equation $k_A = 0{\cdot}0078 K_A^{0{\cdot}51}$.

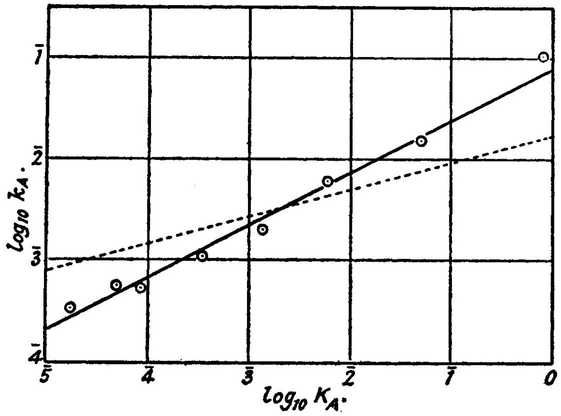

TABLE II.

Catalyst acid.	$10^4 k_A$.	K_A.	Catalyst acid.	$10^4 k_A$.	K_A.
Trichloroacetic	1050	8×10^{-1}	*m*-Nitrobenzoic	10·9	$3{\cdot}48 \times 10^{-4}$
Dichloroacetic	153	5×10^{-2}	*β*-Chloropropionic	5·3	$8{\cdot}6 \times 10^{-5}$
Phenylpropiolic	60	$5{\cdot}9 \times 10^{-3}$	Phenylacetic	5·6	$4{\cdot}88 \times 10^{-5}$
Monochloroacetic	20	$1{\cdot}38 \times 10^{-3}$	Acetic	3·4	$1{\cdot}75 \times 10^{-5}$

The general behaviour of *N*-bromobenzanilide is thus very similar to that of *N*-bromoacetanilide. There is, however, a striking difference in the exponents of the Brönsted relation, the results for *N*-bromoacetanilide at 25° (Bell, *Proc. Roy. Soc.*, 1934, **143**, *A*, 477) being represented by $k_A = 0{\cdot}017 K_A^{0{\cdot}27}$ when converted into the units used in the present paper. This equation is represented by the broken line in the figure, and it will be seen that the two lines cross; *i.e.*, with the stronger acids *N*-bromoacetanilide is transformed more slowly than *N*-bromobenzanilide, whereas with the weaker acids the reverse is the case. If we consider this fact in the light of the theoretical picture which has been advanced for proton-transfer reactions (Horiuti and Polanyi, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 505; Bell, *Proc. Roy. Soc.*, 1936, **154**, *A*, 414), it is seen that the change from one substrate to another must involve a considerable change in the *form* of the potential-energy curves concerned, and not merely in their relative height. This aspect of the problem will be dealt with more fully in another paper.

The results with the higher concentrations of trichloroacetic acid are anomalous, the sudden large increase in the catalytic constant being accompanied by poor reproducibility and departures from the unimolecular law. It seems probable that some new reaction mechanism is beginning to play a part, possibly involving free radicals and a chain mechanism. It may be noted that attempts to study the analogous transformations of *N*-bromo-ω-chloro- and *N*-bromo-ωωω-trichloro-acetanilide gave results which were throughout very erratic. It is possible that in these cases the reaction takes place predominantly by a chain mechanism. Further experiments with *N*-bromoacetanilide at 25° revealed a tendency for the catalytic constant to increase at high concentrations of trichloroacetic acid (>0·2M), though to a much smaller extent than with *N*-bromobenzanilide. These anomalies do not appear to affect the results with the lower concentrations of trichloroacetic acid, and they are not present with the other acids.

Our thanks are due to the Chemical Society for a grant.

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[*Received, May* 16*th*, 1939.]