

Acid Catalysis in Non-Aqueous Solvents

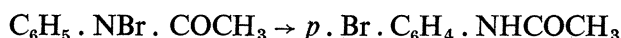
II—The Rearrangement of N-bromacetanilide in Chlorobenzene Catalysed by Trichloroacetic Acid

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INTRODUCTION

It was shown in a previous paper* that the reaction



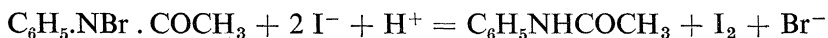
is catalysed by a number of acids in non-dissociating solvents, and follows a unimolecular course. A few measurements at 15° and 25° C gave temperature coefficients of 2.0–2.4 per 10°, corresponding to heats of activation of about 12,000–15,000 calories per gram-molecule, and it was shown that on this assumption only a small fraction of the collisions involving sufficient energy result in reaction. The present paper describes a more detailed study of the temperature coefficient of catalysis by trichloroacetic acid in chlorobenzene solution, in the course of which new features in the kinetics of the reaction were discovered.

EXPERIMENTAL

The preparation of N-bromacetanilide has been previously described (I). It was kept as a chlorobenzene solution approximately N/10 in a flask covered with tin-foil in a desiccator. The chlorobenzene was dried over phosphorus pentoxide and fractionally distilled. It was stored in a container protected from the air by mercury seals and a phosphorus pentoxide tube, and when required it was expelled by dry air. The trichloroacetic acid was dried in a vacuum desiccator, and titration showed it to be better than 99.5% pure. The solutions of trichloroacetic acid were kept in a desiccator, and their concentration determined by weight titration. The reactions took place in the type of vessel shown in fig. 1, of about 35 cc capacity. They were immersed in the thermostat to the level shown by the dotted line in fig. 1, thus preventing any distillation of solvent into the cap, and were protected from the light by a coat of tin-foil. The ground joint was kept sealed with mercury during reaction.

* Bell, 'Proc. Roy. Soc.,' A, vol. 143, p. 377 (1934), referred to subsequently as (I).

From time to time about 2 cc of the reaction mixture was pipetted out and run into a weighed flask containing potassium iodide solution and dilute acetic acid. The iodine liberated according to the equation



was titrated as before (I) with N/500 thiosulphate solution, a 2 cc micro-burette being used for the most dilute solutions. It has been previously shown (I) that solutions of N-bromacetanilide in chlorobenzene are stable in the dark for several years at room temperature. In order to test their

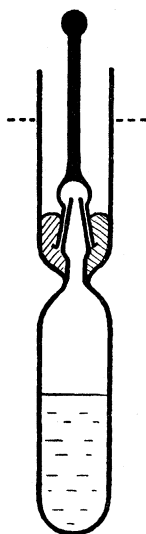


FIG 1

stability (in the absence of catalyst) under the experimental conditions used here, approximately N/100 solutions were kept at 100° for six hours in the reaction vessels described. Titration before and after showed that no decrease in the concentration of N-bromacetanilide had taken place, and this was found to be so for all the samples used. Similar experiments in sealed tubes gave very erratic results, varying from no change at all to complete disappearance of the N-bromacetanilide after 6 hours at 100°. It is possible that the operation of sealing introduces small quantities of catalyst (e.g. HCl) by decomposition of the chlorobenzene vapour. It was also found that the introduction of mercury into the reaction vessel led to fairly rapid disappearance of the N-bromacetanilide at 100°, accompanied by the formation of a solid product on the surface of the mercury. It is therefore important in measurements of catalysis to avoid contamination by mercury from the seal, but it is clear

that there will otherwise be no appreciable "spontaneous" change in the temperature range 35°–65° studied here.

The catalysed reactions followed a unimolecular course in every case, and the constants given correspond to the equation

$$k = - \frac{d \log_{10} x}{dt},$$

where x is the concentration of N-bromacetanilide present, and t is the time in minutes. The constants were calculated by plotting the logarithm of the titre (per gram solution) against the time, and measuring the slope of the straight line thus obtained. The other symbols in the following tables are :—

c_A = concentration of trichloroacetic acid in moles per litre.

c_B = initial concentration of N-bromacetanilide in moles per litre.

$\alpha = k/c_A$, the catalytic constant.

TABLE I—35° C

 $c_A = 0.0135$ (average)*

$c_B \times 10^3$	$k \times 10^2$	α
1.43	2.51	1.81
2.10	2.06	1.50
3.14	1.90	1.39
3.50	1.75	1.27
3.75	1.60	1.18
3.90	1.60	1.18
5.57	1.41	1.06
7.94	1.25	0.94

 $c_A = 0.0230$

$c_B \times 10^3$	$k \times 10^2$	α
0.74	5.00	2.09
1.65	4.40	1.85
2.20	3.92	1.70
2.99	3.80	1.62
3.40	3.31	1.44
5.20	2.98	1.32
7.94	2.62	1.18

TABLE II—45° C

 $c_A = 0.00365$

$c_B \times 10^3$	$k \times 10^3$	α
4.53	6.99	1.91
8.34	5.21	1.43
11.99	4.35	1.19
26.35	3.71	1.02

 $c_A = 0.00450$

$c_B \times 10^3$	$k \times 10^3$	α
2.09	14.6	3.19
2.33	12.6	2.76
3.06	11.3	2.48
3.78	9.9	2.19
5.02	10.1	2.19
5.85	8.62	1.90
7.82	6.95	1.56
10.3	6.92	1.57

* In this and all succeeding tables, the value of c_A in each set varied by a few per cent. in different tests. These variations were taken into account in calculating the values of α , but are not reproduced in the tables.

TABLE III—50° C

$$c_A = 0.00780$$

$c_B \times 10^3$	$k \times 10^2$	α
0.733	4.14	5.30
1.40	3.76	4.82
2.06	3.13	4.01
2.68	3.41	4.38
3.61	2.75	3.53
4.31	2.75	3.52
5.51	2.68	3.45

$$c_A = 0.0300$$

$c_B \times 10^3$	$k \times 10^2$	α
0.741	18.1	6.00
1.35	15.6	5.20
2.08	16.3	5.45
2.60	14.0	4.70
4.23	13.2	4.44
5.06	15.0	5.09

TABLE IV—65° C

$$c_A = 0.00810$$

$c_B \times 10^3$	$k \times 10^2$	α
0.71	11.2	13.7
1.35	9.6	11.8
1.91	9.8	12.1
2.12	8.7	10.7
2.80	8.65	10.7
3.56	7.25	9.0
4.22	7.1	8.8

$$c_A = 0.0170$$

$c_B \times 10^3$	$k \times 10^2$	α
0.88	24.0	14.1
1.02	22.0	12.9
1.74	22.0	12.9
2.00	20.5	12.1
2.44	19.4	11.4
4.23	19.4	11.4
5.67	16.9	9.9

$$c_A = 0.0254$$

$c_B \times 10^3$	$k \times 10^2$	α
0.82	33.3	13.9
1.48	31.0	12.3
2.03	30.1	12.0
2.96	29.7	11.7
3.31	29.8	11.8
4.52	26.1	10.4

TABLE IV—(continued)

$c_A = 0.0380$		
$c_B \times 10^3$	$k \times 10^3$	α
0.71	56.6	14.7
1.42	52.6	13.0
2.12	52.2	13.6
2.79	49.4	13.0
4.22	47.0	12.4
5.57	43.0	11.4

DISCUSSION

It will be seen immediately from the above tables that for a given concentration of acid, the velocity constant obtained varies considerably with the initial concentration of N-bromacetanilide. Since the concentration of N-bromacetanilide varies during the course of each experiment, we should expect to find a considerable drift in the value of k as the reaction proceeds. If such a drift is present at all, it is certainly very much less than would be anticipated, as the following sample set of figures shows.

TABLE V—35° C

$c_A = 0.0133$		
Time Hours	Titre cc N/500 thio- sulphate/gm	$k \times 10^3$
0	7.94	—
6.42	6.72	1.13
9.17	6.19	1.18
10.38	5.98	1.18
23.17	4.03	1.27
26.92	3.58	1.28
30.17	3.41	1.21

During this reaction the concentration of N-bromacetanilide changes from 0.0079 to 0.0034: a change of this magnitude in the initial concentration would cause a change of about 50% in k (cf. Table I).

This behaviour may be interpreted by supposing that both N-bromacetanilide and its isomer *p*-bromacetanilide exert approximately equal retarding effects on the reaction. Since the sum of their concentrations is constant in any given reaction mixture, this will lead to a unimolecular velocity constant which varies with the initial concentration. This view

is supported by some experiments in which *p*-bromacetanilide was added initially.

Within the experimental error, the effect of the added *p*-bromacetanilide was found to be the same as that of an equivalent change in the initial concentration of N-bromacetanilide.

For a study of the molecular statistics of the reaction it is desirable to eliminate this retarding effect, which can be done if it is possible to extrapolate the values of α to zero initial concentration of N-bromacetanilide. It was found empirically that for a given temperature and acid concentration the results could be expressed in the form

$$\frac{1}{\alpha} = \frac{1}{\alpha_0} + \beta c_B, \quad (1)$$

where β is a constant, and by plotting $1/\alpha$ against c_B , α_0 can be obtained fairly accurately by extrapolating to $c_B = 0$. The results for different acid concentrations at the same temperature gave on extrapolation the same value of α_0 , but the value of β was found to decrease with increasing acid concentration. All the results at one temperature can be expressed at least approximately by the equation

$$\frac{1}{\alpha} = \frac{1}{\alpha_0} + \gamma \frac{c_B}{c_A}, \quad (2)$$

where γ is a constant depending only on the temperature. This equation was finally used for evaluating α_0 , $1/\alpha$ being plotted against c_B/c_A and $1/\alpha_0$ obtained by extrapolation. Table VII gives the final values of α_0 at 35, 45, 50, and 65° C.

TABLE VII

t °C	35	45	50	65
α_0	2.17	4.00	5.87	14.5

By plotting $\log_{10} \alpha_0$ against $1/T \times 10^3$ a straight line is obtained, showing that the Arrhenius equation is obeyed within the experimental error. The slope of the straight line gives 12,800 cal for $A + \frac{1}{2} RT$, and hence **12,500 cal** for the true heat of activation A .

The observed reaction velocity may now be compared with the results of the simple collision theory. Converting to the units used here (moles per litre, hours, and decadic logarithms) this theory gives for the catalytic constant

$$\alpha_0 = 4.50 \times 10^{27} T^{\frac{1}{2}} \sigma^2 \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{\frac{1}{2}} e^{-A/RT}, \quad (3)$$

where σ = distance of closest approach of reacting molecules (cm)

M_1, M_2 = molecular weights of reacting molecules.

Putting $\sigma = 4 \times 10^{-8}$, this expression gives at 35°C , $\alpha_0 = 2.6 \times 10^4$, while the observed value is 2.2. The reaction thus takes place about 10^4 times as slowly as predicted by the simple collision theory. It is unlikely that this low-collision efficiency is due to deactivation by solvent molecules, since it was previously found (I) that the reaction velocity was of the same order of magnitude in eight solvents of different types. It does, however, appear reasonable to attribute the slowness of the reaction to a purely spatial steric effect. The factor of 10^{-4} is considerably smaller than has usually been assumed possible for such an effect, but it can easily be shown to be plausible. Thus the experimental data for the simple reaction $\text{H} + \text{H}_2$ lead to a steric factor of about 0.1, and a still lower value has been obtained theoretically by Pelzer and Wigner.* It might thus easily reach a value of 0.01 in the reaction between a hydrogen atom and a complicated organic molecule, and the corresponding factor for reaction between two large organic molecules (as in the present case) would be $(0.01)^2 = 10^{-4}$; such considerations are of course based on very simplified models, but they serve to indicate the order of magnitude to be expected for such factors.

It is more difficult to obtain a satisfactory explanation of the retarding effect exerted by *N*-bromacetanilide and *p*-bromacetanilide. The similarity in the effects of the two isomers is paralleled by the measurements of Chapman† on the Beckmann change of oxime ethers, where the reaction was found to be accelerated to an equal extent by the oxime ether and its transformation product. A similar behaviour has been observed in the decomposition of nitril chloride.‡

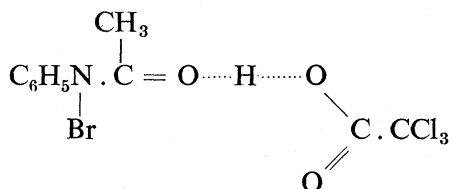
There are several alternative interpretations of a positive catalytic effect; but it is more difficult to account for the retarding effect observed in the present case. A change of medium can give rise to either positive or negative catalytic effects (by modifying either the activation energy or the conditions of orientation), but this type of influence could hardly give rise to such large effects in dilute solution, particularly as the velocity is little affected by change of solvent. Negative catalytic effects can usually be explained by assuming either the termination of a chain mechanism or the removal of one of the reactants by compound formation. There is no evidence for a chain mechanism in the present reaction, and such an

* 'Z. phys. Chem.,' vol. B 15, p. 445 (1932).

† 'J. Chem. Soc.,' p. 1550 (1934).

‡ Schumacher and Sprenger, 'Z. phys. Chem.,' vol. B 14, p. 413 (1931).

explanation is improbable on account of the low collision efficiency found. As regards compound formation, it has been shown by Weissberger and Högen* and by Weissberger and Fasold† that trichloroacetic acid probably forms compounds in solution with a large number of carbonyl compounds, and thus might be expected to do so with both N-bromacetanilide and *p*-bromacetanilide. The compound with the former can be written as



where the dotted line indicates the abnormal double co-valency of hydrogen.[‡]

In this compound the trichloroacetic acid will have largely lost its catalytic powers on account of the binding of the hydrogen, but the migration of the bromine can still take place by the agency of a free trichloroacetic acid molecule. These assumptions suffice to account for the retarding effect of N-bromacetanilide and *p*-bromacetanilide, the unimolecular course of the reaction, and the falling off of the effect with increasing acid concentration.

Bairstow and Hinshelwood⁵ have observed that in the decomposition of propionic aldehyde catalysed by iodine the course of the reaction indicates a considerable retardation by the propionic aldehyde itself, which they account for by assuming that the activated complex (X) may be specifically deactivated by collision with an aldehyde molecule. This interpretation can be applied to the present case, provided that it is assumed that N-bromacetanilide and p-bromacetanilide have equal deactivating powers. Then if x_B and x_C are the concentrations of B and C at any stage of the reaction,

Rate of formation of X = $k_1 c_A x_B$

$$, \text{ deactivation of X} = k_2 c_X (x_B + x_C) = k_2 c_X c_B$$

formation of C = $k_3 c_X$

giving for the rate of reaction in the steady state

$$\alpha = \frac{1}{c_A x_R} \frac{dx_C}{dt} = \frac{k_3 k_1}{k_3 + k_2 c_R}, \quad (4)$$

* 'Z. phys. Chem.,' vol. 156, p. 321 (1931).

† 'Z. phys. Chem.,' vol. 157, p. 65 (1931).

† Cf. Sidgwick, 'Ann. Rep. Chem. Soc.' (1934).

§ 'Proc. Roy. Soc.,' A, vol. 142, p. 77 (1933).

which is of the same form as equation (1). Similarly, equation (2) may be obtained by assuming that the rate of formation of C is proportional to the product of c_X and c_A . Unfortunately, however, this type of explanation is not legitimate, since if the molecules B and C can bring about the destruction of X, the principle of microscopic reversibility demands that they shall also take part in its formation. From a slightly different point of view, if k_3 becomes zero, then the above treatment leads to equilibrium relations between A, B, and C which are at variance with the law of mass action. The assumption of compound formation thus seem to afford the most probable explanation of the effects observed, though independent experimental evidence would be desirable.

It may be noted that the conclusions of the previous paper (I) are not materially altered by these considerations. In most of the reactions with trichloroacetic acid studied in (I), the value of c_B/c_A was so small that the retarding effect was probably less than 10%. The value of α_0 for trichloroacetic acid at 15° extrapolated from the results in Table VII is 0.48, while the previous value (not allowing for the retarding effect) was 0.41. With the other acids employed, compound formation is likely to take place to a smaller extent than with trichloroacetic acid. The statement in (I) that the reaction is unaffected by *p*-bromacetanilide was based on experiments with monochloroacetic acid.

SUMMARY

Measurements have been made at 35, 45, 50 and 65° C of the velocity of rearrangement of N-bromacetanilide in chlorobenzene solution, catalysed by trichloroacetic acid.

The catalytic constant is independent of acid concentration, but decreases with increasing concentrations of N-bromacetanilide and *p*-bromacetanilide.

By extrapolating the results to zero initial concentration of N-bromacetanilide, the molecular statistics of the unretarded reaction were investigated. Of collisions possessing the necessary energy, only about one in every 10^4 leads to reaction. This factor may reasonably be interpreted as due to a purely spatial effect.

Various hypotheses are discussed for explaining the retarding effect of N-bromacetanilide and *p*-bromacetanilide. It is probably caused by compound formation between these compounds and trichloroacetic acid.
