463. *Mechanism of Benzidine and Semidine Rearrangements. Part III.* Kinetics and Products of Acid Rearrangement of 2,2'-Hydrazonaphthalene.*

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The acid rearrangement of 2,2'-hydrazonaphthalene proceeds somewhat more slowly than those of the 1,1'- and the 1,2'-isomer. It follows approximately, but not exactly, the same kinetics. In " 60—70% " aqueous dioxan, with perchloric acid in the range 10^{-2}—10^{-1}N, the formal kinetic order in acid is 1·15. It is suggested that transitional kinetics are just beginning to emerge in this example. The solvent effect on the rate in a series of dioxan–water mixtures is qualitatively similar to that of the rearrangement of hydrazobenzene in a series of ethanol–water mixtures (Croce and Gettler), despite the difference of kinetic form, if in both cases we relate the free-energy of activation of the reaction to the dielectric constant of the medium. It is suggested that the rearrangements develop their characteristic polarity after uptake of the necessary number of protons, whether one or two. The products of the rearrangement of 2,2'-hydrazonaphthalene are the diamine (I) and the carbazole (II), along with traces of an unidentified amine, but no disproportionation products. Increasing the acidity above the kinetic range appears to shift the product proportions away from carbazole and towards diamine. At a sufficient acidity, no carbazole is formed. This finding is hypothetically linked with the suggested incursion of transitional kinetics.

As the next step in exploration of the range of application of the new rate law for benzidine rearrangements, that established in the foregoing papers in the examples of 1,1'- and 1,2'-hydrazonaphthalene as involving a linear dependence of the rate on hydrogen ions, we studied the rearrangement of 2,2'-hydrazonaphthalene.

This compound has been described before, but the earlier preparations,[1,2] reported as having m. p.s between 140° and 165°, contained large proportions of the products of its rearrangement. It was first obtained in a pure state by Krolik and Lukashevich,[3] whose work has been confirmed by Shine,[4] and now by ourselves. The pure hydrazo-compound has m. p. 130° (decomp.).

(1) *Kinetic Form of the Acid-catalysed Rearrangement of 2,2'-Hydrazonaphthalene.*—In aqueous organic solvents at acidities in the centinormal range, the absolute rates of rearrangement of the three hydrazonaphthalenes in like conditions stand in the order, $1,1' > 1,2' > 2,2'$; but the differences are moderate, a single power of ten sufficing to cover the series. For this reason, we pre-supposed that the rearrangement of the 2,2'-compound would resemble in its detailed kinetics the rearrangements of the 1,1'- and the 1,2'-isomer. It does show a general, but not an exact, resemblance.

In " 60% " aqueous dioxan at 0°, in the presence of 0·01—0·05N-perchloric acid the rearrangement of 2,2'-hydrazonaphthalene, initially present in concentration 0·004M or less, followed a first-order rate law in the individual runs. Moreover, the initial rates of different runs at the same acidity but with different initial concentrations of the hydrazo-compound were proportional to those initial concentrations. The same two things were true of a series of runs in " 70% " aqueous dioxan at 0° in the presence of 0·05—0·20N-perchloric acid. On this evidence, we concluded that the rearrangement was of first order in substrate, and that we could express the dependence of its rate on other variables in terms of first-order rate-constants.

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* Parts I and II, preceding papers.

[1] Hantzsch and Schmiedel, *Ber.*, 1897, **30**, 82.

[2] Meisenheimer and Witte, *Ber.*, 1903, **36**, 4113.

[3] Krolik and Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, 37.

[4] Shine, *J. Amer. Chem. Soc.*, 1956, **78**, 4807.

In order to investigate the variation of the rate with the concentration of perchloric acid, we arranged the runs in series, in each of which the concentration of the catalysing acid was varied from run to run, but the total electrolyte concentration, *i.e.*, the formal ionic strength, was made up with added lithium perchlorate to a constant value for the series. Two such series are represented in Table 1. One relates to reaction in " 60% " aqueous dioxan at 0°, with the acid running from 0·01 to 0·06N, and a constant ionic strength of 0·06; the other applies to the slower solvent " 70% " aqueous dioxan at 0°, and to the higher acidity range 0·05—0·20N, the ionic strength now being 0·20.

TABLE 1.

First-order rate-constants, k_1, in sec.$^{-1}$, of rearrangement of 2,2'-hydrazonaphthalene, initially 0·004M, in dioxan–water mixtures at 0·0° in the presence of perchloric acid and lithium perchlorate.

Series A: Medium: dioxan 60 vol. % + water 40 vol. %.
$\mu = ([HClO_4] + [LiClO_4]) = 0·06$M.

$10^3[HClO_4]$ ...	10	10	12·5	15	15	20	20	30	40	50	60
10^3k_1	3·59	3·70	4·39	5·24	5·25	8·06	8·64	13·2	16·5	23·0	28·6

Series B: Medium: dioxan 70 vol. % + water 30 vol. %.
$\mu = ([HClO_4] + [LiClO_4]) = 0·20$M.

$10^3[HClO_4]$	50	70	80	100	150	200
10^3k_1	10·2	15·2	18·4	24·6	37·0	50·5

A plot of the logarithm of the first-order rate-constant against the logarithm of the acid concentration for each of these series is shown in Fig. 1. Each plot gives a straight line of slope about 1·15. Thus the nearest integral order in acid is unity, and, as a broad result, it can be stated that the kinetics of the rearrangement of 2,2'-hydrazonaphthalene in aqueous dioxan in the 10^{-2}—10^{-1}N-acid range are approximately of the linear-hydrogen-ion type of equation (1) in Part I, already exemplified for the rearrangements of 1,1'- and 1,2'-hydrazonaphthalene in like conditions.

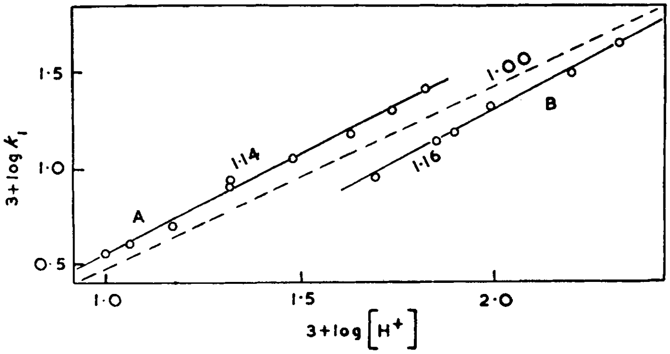

FIG. 1. Plots of the logarithm of the first-order rate-constant of rearrangement of 2,2'-hydrazonaphthalene against the logarithm of the hydrogen-ion concentration at a fixed ionic-strength in dioxan–water mixtures at 0·0°.

Series	Aqueous dioxan	μ	Slope
A	" 60% "	0·06	1·14
B	" 70% "	0·20	1·16

The broken line is drawn to the theoretical slope of 1·00.

On the other hand, it appears from Fig. 1 that the deviation of the observed slopes from the theoretical slope of unity exceeds the casual error. We think the most likely cause of systematic error is that the kinetics themselves are beginning to show transitional character. The manifestation is slight enough to make the case a difficult one for detailed investigation, and, having on hand more tractable examples of transitional kinetics, we did not pursue that matter in the present case.

(2) *Solvent Effect on the Rate of Rearrangement of* 2,2′-*Hydrazonaphthalene.*—Croce and Gettler [5] examined the solvent-dependence of the rate of rearrangement of hydrazobenzene, using as solvents a range of ethanol–water mixtures. They were, of course, here dealing with a rearrangement which follows the quadratic hydrogen-ion kinetics of equation (2) in Part I. On plotting the logarithm of the first-order rate-constant at a constant acidity against the reciprocal of the dielectric constant of the medium, they obtained a curve which rose and steepened towards low values of the reciprocal of the dielectric constant, *i.e.*, towards high water contents.

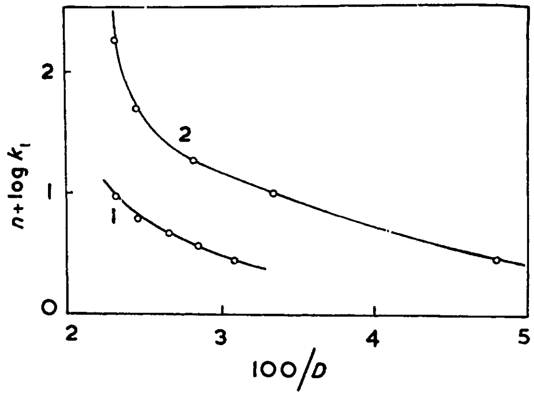

FIG. 2. Solvent-dependence of the rates of rearrangement of hydrazo-compounds at constant acidity.

(1) Hydrazobenzene in ethanol–water mixtures with [HCl] = 0·093N at 25° (Croce and Gettler).

(2) 2,2′-Hydrazonaphthalene in dioxan–water mixtures with [$HClO_4$] = 0·020N at 0°.

The logarithm of the first-order rate-constant is plotted against the reciprocal of the dielectric constant (*D*) of the medium. For curve (1), $n = 4$; and for curve (2), $n = 3$.

We have examined the solvent-dependence of the rate of rearrangement of 2,2′-hydrazonaphthalene in a range of dioxan–water mixtures. As the kinetics of this reaction are approximately of the linear-hydrogen-ion form expressed by equation (1) in Part I, we ought not necessarily to expect correspondence with Croce and Gettler's results. However, maintaining a constant acidity, we observed the variations of rate with medium-composition shown in Table 2; a plot of the logarithm of the rate-constant against the reciprocal of the dielectric constant of the medium rose and steepened towards low values of the reciprocal, *i.e.*, towards high water contents. Croce and Gettler's curve for the rearrangement of hydrazobenzene, and ours for that of 2,2′-hydrazonaphthalene, are shown together in Fig. 2.

TABLE 2.

First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of 2,2′-hydrazonaphthalene in the presence of 0·020N-perchloric acid in dioxan–water mixtures at 0·0°.

Dioxan (vol. %)	70	60	55	50	48
Dielectric constant	20·4	30·0	35·0	40·0	42·0
10^3k_1	1·89	7·65	15·9	44·5	166

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[5] Croce and Gettler, *J. Amer. Chem. Soc.*, 1953, **75**, 874.

The reason for making this type of plot is that the electrostatic energy of interaction of any one distribution of charges, however complicated, with any other, in a medium having a dielectric constant effective for the interaction is inversely proportional to the dielectric constant. Thus, if the free-energy of activation of a reaction of high polarity consists of medium-independent terms plus electrostatic terms dependent on the medium only through a constant, which we hypothetically identify with the macroscopic dielectric constant, then we might expect the logarithm of the rate to be linearly related to the reciprocal of the latter constant. This assumed relation appears in all the usual electrostatic rate equations.

However, there are various reasons why the assumption that a macroscopic dielectric constant is effective for a local molecular interaction is unlikely to be true. One is that electrical saturation of the dielectric in the strong fields near solute charges will exhaust the power of the medium to reduce interaction energies as it can reduce them when the fields are weak. Another is that in most local situations, the solvent medium does not occupy the whole field of interaction of the charges. Both these factors have been discussed in relation to equilibrium phenomena, notably acid strengths,[6,7] and the same treatments could obviously be applied to rate problems. However, neither factor can be dominating in the present problem; for either would selectively reduce the potency of high macroscopic dielectric constants for weakening local interaction energies; and, since, over the range of experiments considered, high macroscopic dielectric constants are associated with high reaction rates, either factor should selectively reduce the higher rates. This would cause a deviation having a curvature opposite to that common to the curves in Fig. 2 from the idealised linear relation between the logarithm of the rate and the reciprocal of the dielectric constant.

A possible cause of deviations of the curvature illustrated is one already suggested by Croce and Gettler, *viz.*, that the components of the mixed solvent become locally separated, the more strongly solvating, presumably the water, concentrating towards solute changes. This would make a small water content act as though it were greater, the more so when water is scarce than when water is plentiful. Since, in the range of experiments considered, low water contents are associated with low reaction rates, the kinetic effect of this factor would be selectively to raise the lower rates, and thus to produce curvatures such as Fig. 2 illustrates in the relations between the logarithm of the rate and the reciprocal of the dielectric constant. The steepness of the dioxan–water curve at the higher water contents suggests that local phase separation is occurring in this region, *i.e.*, final breakdown of hydrogen-bonding, as in salting-out, between the dioxan and the water.

It is implicit in this explanation that the transition states of rearrangement of hydrazobenzene and 2,2′-hydrazonaphthalene are more strongly solvated than are their respective initial states. If this conclusion applied only to the rearrangement of hydrazobenzene, it would occasion no surprise, and would probably be ascribed provisionally to the concentration in the transition state of two protonic charges, which in the initial state were spread between separate hydrogen ions. However, this interpretation cannot be applied to the rearrangement of 2,2′-hydrazonaphthalene, in which, to a first approximation, there is only one net positive charge on the transition state, and only one hydrogen ion in the initial state. The interpretation is thus inapplicable generally, and we should conclude that neither monoprotonation nor diprotonation of the hydrazo-substrate gives to the benzidine rearrangement the strong increment of polarity characteristic of the process. This excess of polarity, of which there is much evidence from both salt and solvent effects, must therefore in either case arise through some heterolytic process subsequent to protonation.

Croce and Gettler have claimed[5] that by application of Debye's limiting law the salt effects in the acid rearrangement of hydrazobenzene in 7 : 1 w/w ethanol–water (lithium

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[6] Ingold, *J.*, 1931, 2179.

[7] Kirkwood and Westheimer, *J. Chem. Phys.*, 1938, **6**, 306.

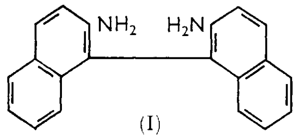
chloride being the salt), as well as the dependence of the rate on the composition of ethanol–water mixtures, can be interpreted, the former effects quantitatively, on the basis that the reaction develops its polarity by bringing together two like charges in the rate-controlling step. We doubt the applicability of the limiting ionic-strength law to the solvent at the concentrations of lithium chloride used; and we have to take account of the newly disclosed circumstance that very similar salt and solvent effects apply to the acid rearrangements of the hydrazonaphthalenes, where only one net positive charge can be present in the transition state. Hence we adhere to the conclusion stated in the preceding paragraph.

(3) *Products of Rearrangement of* 2,2′-*Hydrazonaphthalene.*—Meisenheimer and Witte [2] reported 2,2′-diamino-1,1′-binaphthyl (I) as the only product formed by the acid-catalysed rearrangement of 2,2′-hydrazonaphthalene. Jacobson [8] confirmed this finding. The diamine (I) has often been preparatively produced by reactions, such as the acid reduction of 2-nitronaphthalene [9] or of 2,2′-azonaphthalene,[10] which must have involved the formation and rearrangement of the hydrazo-compound.

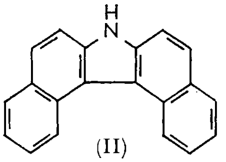
We found three products. The chief one was, indeed, the diamine (I). Next in importance was 3,4:5,6-dibenzocarbazole (II). This substance, like the diamine, is well known. We confirmed the identity of our carbazole product, by making it independently by cyclisation of the diamine with boiling 2N-sulphuric acid. We also confirmed that the carbazole (II) is not formed from the diamine (I) under the conditions in which, in our experiments, the two compounds are concurrently produced by rearrangement. Our third product (III), formed in small amount, sometimes mere traces, was not fully identified, but was a diazotisable amine with a sparingly soluble sulphate. Presumably it was either an isomeric diaminobinaphthyl or an aminodinaphthylamine (of semidine type). If it is a diaminobinaphthyl, an internuclear linking at position 3 must be involved, and it is relevant that Hodgson, Habeshaw, and Murti have shown [11] that acid reduction of 2,2′-azonaphthalenes in which the 1,1′-positions are substituted (by Cl or Br) does lead to 3,3′-linked binaphthyls.

Jacobson [8] reported no semidines, and no disproportionation products, *i.e.*, no azonaphthalene and no naphthylamine. We also could find no signs of disproportionation.

Shine and Trisler have recently reported [12] that the neutral rearrangement at 80° of 2,2′-hydrazonaphthalene in ethanol yields about 80—85% of the diamine (I) and 15—20% of the carbazole (II), along with small proportions of 2,2′-azonaphthalene. They found the last-named product to be formed much more extensively in the slower thermal rearrangements of the hydrazo-compound in non-hydroxylic solvents, such as acetone, dioxan, and tetrahydrofuran.



(I)



(II)

The results of our analyses of the products of rearrangement of 2,2′-hydrazonaphthalene at 0° in two aqueous organic solvents and at three acid concentrations are in Table 3. The determinations of the different products are by gravimetric separation and are independent, as in Part I (preceding).

Table 3 shows an apparent trend towards the production from 2,2′-hydrazonaphthalene

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[8] Jacobson, *Annalen*, 1922, **427**, 142; **428**, 76.

[9] Cumming and Ferrier, *J.*, 1924, **125**, 1111.

[10] Kuhn and Goldfinger, *Annalen*, 1929, **470**, 190.

[11] Hodgson, Habeshaw, and Murti, *J.*, 1947, 1390.

[12] Shine and Trisler, *J. Amer. Chem. Soc.*, 1960, **82**, 4054.

TABLE 3.

Proportions of products of rearrangement of 2,2′-hydrazonaphthalene in aqueous organic solvents acidified with perchloric acid at 0·0°.

Solvent	[HClO$_4$]	Diamine (I)	Products (%) Carbazole (II)	Amine (III)
" 60% " aqueous dioxan *	0·05	92·0	6·0	—
,, ,, ...	0·10	93·3	5·4	0·08 ‡
,, ,, ...	0·30	95·8	4·7	—
" 95% " Aqueous ether–ethanol † ...	0·10	92·3	6·2	1·2

* Mixture of dioxan 60 vol. with water 40 vol.
† Mixture of ether 47·5, ethanol 47·5, and water 5 vol.
‡ Result of an independent larger-scale experiment.

of an increased proportion of the diamine (I), and a decreased proportion of the carbazole (II), as the concentration of the acid catalyst is increased. A similar trend was found in Part II (preceding) for the rearrangement of 1,2′-hydrazonaphthalene, and the spread of the figures was in that case greater in relation to the analytical error than it is in the present case. Because of this indirect support, we considered that the trend shown in Table 3 is real.

This was subsequently confirmed in the semi-quantitative way used to check a similar (more lightly based) suspicion in Part I (preceding), by measuring the dibenzocarbazole produced in rearrangement at very much higher acidities than those for which the kinetics had been demonstrated. These results are in Table 4. The analyses are quantitative, but their correlation with acidity is not, because the half-lives of reaction are either of the same order of magnitude as, or smaller than, the time taken to mix aqueous acid into the initial solutions of hydrazo-compound in dioxan containing less than the ultimate amount of water. Thus, considerable amounts of rearrangement must have occurred during the mixing, and hence at lower acidities than those eventually provided, which are recorded in Table 4. However, the qualitative result is clear: with a sufficient acidity, no carbazole at all is formed. This allows us to understand why Jacobson, whose product examinations were thorough, found no carbazole.[8] His method was to reduce the azonaphthalene by stannous chloride in hydrochloric acid, allowing the hydrazo-derivative to rearrange, as it would within a second or less, in the acid in which it was produced. By this technique, the hydrazo-compound would, of course, feel the full effect of the acidity provided.

TABLE 4.

Proportions of dibenzocarbazole (II) formed by rearrangement of 2,2′-hydrazonaphthalene (initially 0·008M) in " 60% " aqueous dioxan at 20° in the presence of high concentrations of acid.

Acid	[Acid]	Carbazole (II) (%)	Acid	[Acid]	Carbazole (II) (%)
HClO$_4$	0·6	4·5	HClO$_4$	2·4	2·0
HClO$_4$	1·2	4·0	HCl	4·5	0·0

We explain these results in the same way as the comparable ones of Parts I and II, *viz.*, by assuming that the mechanism involving double protonation is entering increasingly towards higher acidities, and that this mechanism produces no carbazole.

EXPERIMENTAL

Preparation.—2-Naphthalenediazonium chloride was reduced with sodium sulphite to 2,2′-azonaphthalene,[1] by following the details given by Cohen and Oesper.[13] The azo-compound was purified by chromatography on alumina with benzene, and crystallised from benzene; it had m. p. 209—210° (lit., 208—209°). It was reduced with zinc and ammonium chloride,[3] by the method described in detail in Part II for the analogous reduction. The resulting 2,2′-hydrazonaphthalene, m. p. 130° (decomp.; rate of heating 1° per min.), agreed in its properties

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[13] Cohen and Oesper, *Ind. Eng. Chem. Analyt.*, 1936, **8**, 306

with the descriptions given by Krolik and Lukashevich [3] and by Shine,[4] and was chromatographically pure. It is less easily oxidised by air to the azo-compound than are the isomeric hydrazo-compounds described in Parts I and II.

Kinetics.—The general methods were as described in Parts I and II. In this case, as in that of Part II, the products of rearrangement did not form coloured titanium complexes, and hence the end-points of titration of the excess of Bindschedler's Green with titanous chloride were determined visually, rather than electrometrically.

Products.—The method of gravimetric separation described in Part I was applied. In the first step, the precipitation of insoluble sulphates, only very small amounts of such (0·1—1%) were obtained. Chromatography showed that they consisted mainly of a primary aromatic amine of unknown constitution, together with a little 2,2′-diamino-1,1′-binaphthyl, which is isolated in bulk later, but is evidently here co-precipitated to a small extent. The unknown amine, developed on the paper chromatogram with *p*-dimethylaminobenzaldehyde, appeared as a yellow spot. Developed by diazotisation with nitrous gases, it remained invisible, but on subsequent coupling with *N*-1-naphthylethylenediamine, it formed a purple spot. The second step of separation yielded the neutral 3,4:5,6-dibenzocarbazole, which was here obtained chromatographically pure and on crystallisation successively from ethanol and benzene–ligroin had m. p. 158° (lit., 156—158°). The third step, the isolation of bases with soluble sulphates, gave 2,2′-diamino-1,1′-binaphthyl, also obtained chromatographically pure and, after crystallisation from ethanol, with m. p. 190° (lit., 189—191°). This amine, on being boiled for 2 hr. with 2N-sulphuric acid, gave 3,4:5,6-dibenzocarbazole, shown to be identical with the carbazole obtained in the rearrangement by comparison of their infrared spectra.

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