461. *Mechanism of Benzidine and Semidine Rearrangements. Part I. Kinetic Dichotomy: Kinetics, Solvent-isotope Effect, and Products of Acid Rearrangement of* 1,1′-*Hydrazonaphthalene.*

By D. V. BANTHORPE, E. D. HUGHES, and Sir CHRISTOPHER INGOLD.

The established quadratic dependence on hydrogen-ion concentration of the rate of the acid-catalysed rearrangements of hydrazobenzene, and of a number of its simpler derivatives, is conceived as characterising one limiting kinetic form of a range of forms belonging to this group of rearrangements as a whole. The first example of the anticipated second limit, that involving linear dependence of the rate on hydrogen ions, is here established, over a range of 10^4 in hydrogen-ion concentration, in the rearrangement of 1,1′-hydrazonaphthalene in " 60% " aqueous dioxan. The change in kinetic type from the benzene to the naphthalene derivatives is associated with a change in solvent isotopic effect; for, whilst replacement of the water in the medium by deuterium oxide accelerates the rearrangement of hydrazobenzene by 4·7 times, it accelerates that of 1,1′-hydrazonaphthalene by only 2·3 times. Both rearrangements are accelerated by salts and by extra water. There are signs of an incipient change of kinetic form in the rearrangement of 1,1′-hydrazonaphthalene in a much more nearly anhydrous solvent.

The sole products of the acid-catalysed rearrangements of 1,1′-hydrazonaphthalene are 4,4′-diamino-1,1′-binaphthyl. 1,1′-diamino-2,2′-binaphthyl, and 1,2:7,8-dibenzocarbazole. No 2,4′-binaphthyl, no semidines, and no disproportionation products could be detected. In the kinetically investigated and similar conditions, the proportions of rearrangement product are independent of acidity, and of ionic strength; they are slightly dependent on temperature, and considerably so on medium composition. At much higher acidities the proportion of dibenzocarbazole formed falls to low values. The products of disproportionation, 1,1′-azonaphthalene and 1-naphthylamine, are formed under non-acidic and basic conditions. A number of erroneous accounts of 1,1′-hydrazonaphthalene and of its reactions are corrected in the course of this work.

(1) *Introduction to a Group of Papers*

(1.1) *Approach.*—For a number of general reactions, it has emerged that the most important step in the elucidation of mechanism was the establishment of two limiting kinetic forms, and of the conditions under which a shift will occur from one form to the other. The two kinetic forms of nucleophilic aliphatic substitution, the two of elimination and of aromatic nitration, and the larger number of electrophilic chlorination and of reactions, such as diazotisation, which depend on nitrosation, provide examples enough to justify a similar approach to the mechanism of the benzidine rearrangement.

When we took up this matter there was already in the literature an indication that the reaction might have two limiting kinetic forms. One kinetic form had been established in a sufficient number of examples to justify the presumption that it was widespread. On the other hand, there was one well documented record of an appreciable departure from this kinetic form, to one less simple, which might conceivably represent a transitional situation.

In the first few papers of this group we shall establish in several examples the second limiting kinetic form of the benzidine rearrangement. Then we shall show that the suspected transitional case was correctly so diagnosed, and we shall describe other transitional cases. Moreover, we shall establish the conditions in which, in such cases, the kinetic form can be shifted towards either limit.

As in some of the prior studies of mechanism mentioned in the first paragraph, a frame will thus have been provided on which evidence of various dependent kinds can be carried.

Such evidence will relate to the dependence on kinetic form of product composition, and to solvent and salt effects on the rate. It will relate also to effects of isotopic substitution, in the solvent and in the substrate, on rates and product-compositions. A body of evidence will thus be built up, which will support the discussion of mechanism offered in a later paper of this series.

Equation (1) represents the limiting rate-law which it will be our first concern to establish and generalise. Equation (2) expresses the known rate-law to which we assign the status of the complementary limiting law (Hydz = hydrazo-compound):

$$\text{Rate} \propto [\text{Hydz}][\text{H}^+] \qquad (1)$$

$$\text{Rate} \propto [\text{Hydz}][\text{H}^+]^2 \qquad (2)$$

(1.2) *Background.*—The known rate-law (2) was indicated in the early work of van Loon [1] on the rearrangement of hydrazobenzene, and was firmly established in that example by Hammond and Shine.[2] Using 75% aqueous ethanol as solvent, they observed a strong positive salt effect. Carlin, Nelb, and Odioso [3] confirmed these findings, adding the point that the product ratio, benzidine : diphenyline (4,4′- : 2,4′-diaminobiphenyl) = 70 : 30, is independent of acidity, ionic strength, and temperature. Croce and Gettler [4] reconfirmed the kinetic findings over the solvent range 60—90% aqueous ethanol, noting the accelerating effect of water. They extended their work to a number of substitution products of hydrazobenzene.

Carlin and Odioso [5] made the discovery, which became motivating in our work, that the rearrangement of 2,2′-dimethylhydrazobenzene in 95% aqueous ethanol is of order 1·6 in acid, though it is stoicheiometrically simple, yielding only *o*-tolidine (4,4′-diamino-3,3′-dimethylbiphenyl). They looked for other examples of such behaviour. However, the rearrangement of 3,3′-dimethylhydrazobenzene [6] in similar conditions, which was equally simple stoicheiometrically, yielding only *m*-tolidine (4,4′-diamino-2,2′-dimethylbiphenyl), had a kinetic order of 2·0 in acid, so following the original rate-law (2). Furthermore, the same law applied, as Carlin and Wich established,[7] to the reaction of 4,4′-dimethylhydrazobenzene, though the products were now the *ortho*-semidine, *pp*′-azotoluene, and *p*-toluidine, in proportions, 40 : 20 : 40, which were shown to be independent of acidity, ionic strength, the water content of the aqueous-ethanolic solvent, and the temperature. However, the statement is on record,[8] though without supporting data, that the conversions of 4-chloro-4′-methyl- and 4-chloro-4′-t-butyl-hydrazobenzene into unstated products in aqueous ethanol are of order 1·5—1·6 in acid.

As to the rearrangement of hydrazobenzene itself under the standard rate-law (2), some further results have been established, which, after confirmation or extension, or both, we shall employ as reference points in comparisons of behaviour under the two limiting rate-laws. One is that in 60% aqueous dioxan, for which the acidity function H_0 of perchloric acid has been determined [9] (but not, unfortunately, the function H_+*), the concentration-order of 2·0 in acid, as observed at low concentrations of perchloric

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* Bonner and Lockhart have shown [10] that, for sulphuric acid in water, H_0 and H_+ are parallel functions at high acidities. But they might not be at lower; because Dr. M. W. Fuller (forthcoming paper) has determined H_- for perchloric and hydrochloric acid in water, and finds that H_0 and H_- are parallel at high acidities but not at lower.

[1] Van Loon, *Rec. Trav. chim.*, 1904, **23**, 62.
[2] Hammond and Shine, *J. Amer. Chem. Soc.*, 1950, **72**, 220.
[3] Carlin, Nelb, and Odioso, *J. Amer. Chem. Soc.*, 1951, **73**, 1002.
[4] Croce and Gettler, *J. Amer. Chem. Soc.*, 1953, **75**, 874.
[5] Carlin and Odioso, *J. Amer. Chem. Soc.*, 1953, **75**, 100.
[6] Carlin and Odioso, *J. Amer. Chem. Soc.*, 1953, **75**, 2345.
[7] Carlin and Wich, *J. Amer. Chem. Soc.*, 1958, **80**, 4023.
[8] Dewar and McNicol, *Tetrahedron Letters*, 1959, No. 5, 22.
[9] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.
[10] Bonner and Lockhart, *J.*, 1957, 364.

acid and expressed in rate-law (2), correlates at high concentrations of acid with a linear relation,[11] having a slope of 2·6, between the logarithm of the rate and the function $-H_0$. This comparison allows us to correlate in other cases rates and their dependence on acidity over a wide range of acidities. A second recorded result [11] is that *para*-deuteration of hydrazobenzene does not alter either the rate of its rearrangement or the ratio of the products. We shall confirm this finding and extend it to deuteration in other positions, so establishing a set of results for substrate deuteration, which can be compared with those obtained on investigating the same phenomenon in rearrangements under the alternative kinetic law. The third previous result [12] is that transfer of the rearrangement of hydrazobenzene to a deuterium solvent, from dioxan–H_2O to dioxan–D_2O, enhances the rate, and does so by the unprecedented factor of above 4. This result also we shall confirm, and use for similar comparative purposes.

(2) *Kinetics of Rearrangement of* 1,1′-*Hydrazonaphthalene*

(2.1) 1,1′-*Hydrazonaphthalene.*—This substance is not unequivocally characterised in the literature: its recorded descriptions are consistently inconsistent, various m. p.s from 130° to 280°, having been assigned to it.[13-19] The main reason for the disagreement is that the compound rearranges more rapidly than has been assumed, and often did rearrange, partly or wholly, under the conditions of its intended production. Krolik and Lukashevich,[17] whose methods we have followed, first described it correctly, as having m. p. 136°. We have shown by column and paper chromatography that, for example, materials of the recorded m. p.s 153° and 274°, prepared by published methods, consist largely of rearrangement products, but that the material of m. p. 136° is a single substance. By oxidising it with ethanolic alkali to 1,1′-azonaphthalene, and with oxygen to 1,1′-azoxynaphthalene, both well characterised substances, we have satisfied ourselves that the compound is indeed 1,1′-hydrazonaphthalene.

(2.2) *The Kinetic Conditions.*—The rearrangement of this substance was followed in " 60% " aqueous dioxan (a mixture made from 60 vol. of dioxan and 40 vol. of water) at 0·0°. The analytical measurement was of the disappearing substrate. Owing to the high rates, our upper limit of hydrogen-ion concentration was 0·05M, the half-time of reaction being then 8 sec. Thus, the region of acidity in which Hammett's H_0 departs widely from the negative logarithm of the hydrogen-ion concentration, the region above about 0·25M-hydrogen ions in this medium, was not even remotely approached. As to lower limits of acidity, we could, without buffers, take the hydrogen-ion concentration down to about 0·0002M, and, with the aid of buffers, carry the hydrogen-ion activity to about 0·000005M.

(2.3) *Order in* 1,1′-*Hydrazonaphthalene.*—In all these conditions, the rate of disappearance of this compound is of first order in the compound. This was shown by the kinetic forms of the runs, and by their identical specific rates, at common acidities and ionic strengths with different initial concentrations of the substrate. It became our practice to record the rates of runs as first-order rate-constants in the substrate, and to relate these figures to the acidity and other factors of the medium composition.

(2.4) *Order in Perchloric Acid.*—Several series of runs were carried out, with perchloric acid as the source of hydrogen ions, and with added lithium perchlorate to make up a constant ionic strength within each series. The molar proportion of water in the medium was high enough to allow us to assume that the acid and salt were almost completely

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[11] Bunton, Ingold, and Mhala, *J.*, 1957, 1906.
[12] Hammond and Grundemeier, *J. Amer. Chem. Soc.*, 1955, **77**, 2444.
[13] Nietzki and Goll, *Ber.*, 1885, **18**, 3252.
[14] Hepworth, *J.*, 1920, **117**, 1004.
[15] Cumming and Steel, *J.*, 1923, **123**, 2464.
[16] Cumming and Dowie, *J.*, 1933, 133.
[17] Krolik and Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, 37.
[18] Beringer, Farr, and Sands, *J. Amer. Chem. Soc.*, 1953, **75**, 3984.
[19] Večera, Petranek, and Gasparič, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1603.

dissociated at our concentrations. It is not certain that their activity coefficients will depend only on the formal ionic strength of the solution throughout our concentration range; but at least the variation in the activity coefficients with changing acid : salt ratio at constant concentrations of total electrolyte, should be smaller for hydrogen and lithium perchlorates than for most other acid–salt pairs. In one of our series, we replaced the perchlorates by hydrogen and lithium chlorides; and the kinetic results were nearly the same as interpolation showed that they would have been had we retained perchlorates throughout. The runs of which rate-constants are recorded in Table 1 are arranged in successive series, A—D, in which the ionic strength, common within the series, was progressively reduced, and the acidity, varying within the series, was taken in successively more dilute ranges. In runs C and D we had to measure initial rates for a reason that will appear below.

Fig. 1 contains a plot, for each of these four series, of the logarithm of the first-order rate-constant against the logarithm of the hydrogen-ion concentration. The plots are

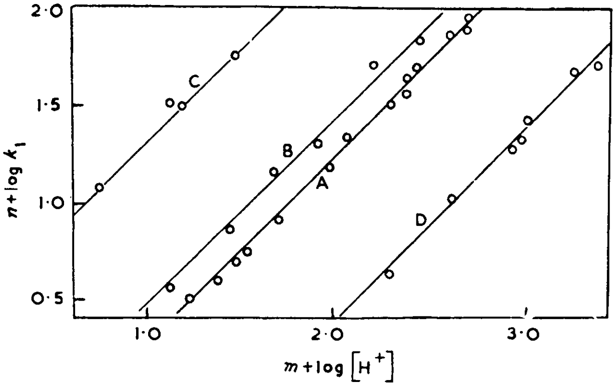

FIG. 1. Plots of the logarithm of the first-order rate-constant (k_1 in sec.$^{-1}$) of rearrangement of 1,1′-hydrazonaphthalene against the logarithm of the hydrogen-ion concentration (M) in " 60% " aqueous dioxan at 0·0° and at the ionic strengths given.

Series	m	n	μ	Slope
A	4	3	0·0500	1·02
B	4	4	0·0160	1·03
C	4	5	0·0050	1·00
D	6	5	0·0028	1·01

TABLE 1.

First-order rate-constants, k_1, in sec.$^{-1}$, of rearrangement of 1,1′-hydrazonaphthalene, initially 0·004M, in " 60% " aqueous dioxan at 0·0°

Series A: μ = [HClO$_4$ + LiClO$_4$] = 0·0500M.

10^3[HClO$_4$]	2·00	3·20	4·50	5·00	7·00	10·0	12·0
10^3k_1	3·35	4·63	7·08	7·63	11·6	16·3	21·7
10^3[HClO$_4$]	15·0	18·0	20·0	25·0	30·0	32·0	—
10^3k_1	27·1	28·9	33·6	45·3	49·6	54·6	—

Series B: μ = [HClO$_4$ + LiClO$_4$] = 0·0160M.

10^3[HClO$_4$]	1·00	2·00	4·00	6·00	10·0	16·0	—
10^3k_1	0·319	0·600	1·50	2·06	5·00	5·67	—

Series C: μ = [HCl + LiCl] = 0·0050M.

10^3[HCl]	0·36	0·80	1·00	2·00	—
10^3k_1	0·096	0·301	0·283	0·518	—

Series D: μ = [HClO$_4$ + LiClO$_4$] = 0·0028M.

10^3[HClO$_4$]	0·05	0·20	0·40	0·80	0·90	1·00	2·00	2·80
10^3k_1	0·0072	0·042	0·095	0·170	0·190	0·240	0·54	0·59

linear, with slopes of unity to within the experimental error. This result establishes rate-equation (1) in this first example.

Comparison between the series provides evidence of a strong positive salt effect. Thus the rate-constants at equal acidities are 7 times greater, whilst the ionic strength is 18 times greater, in series A than in series D. Evidently the plots would not have been linear, and their average slopes would have been greater than unity, had not the precaution been taken of keeping ionic strength constant within the several series.

The main difficulty with these measurements arose at the lower acidities, where, at a certain point in a run, the accumulating basic rearrangement products begin to destroy an appreciable fraction of the catalysing acid, so causing a fall in rate, and thus limiting the proportion of the run that remained useful for the purpose of evaluating rate-constants. We therefore sought to extend our useful range of acidity by the employment of buffers.

(2.5) *Order in Buffered Hydrogen Ion.*—The use of buffers for setting hydrogen-ion activity raised several questions concerning the technique and meaning of measurements of pH in " 60% " aqueous dioxan. The matter of standardising, in terms of concentration, measurements of pH made in a uniform way, was dealt with by showing that pH-meter readings in the range 1·5—5·5, so made in this medium at 20°, of solutions of perchloric acid, were almost unaffected by additions of lithium perchlorate up to concentrations 0·2M, and were uniformly 0·18 unit below the values of $-\log [H^+]$, as calculated on the assumption, which we believe to be substantially valid, that this acid is completely dissociated over this range of conditions. This result is consistent with Dole's finding [20] that, at constant water-activity, a condition that should be closely satisfied in these experiments, the errors created in the potential of a glass electrode by a constant proportion of a non-aqueous co-solvent are independent of pH. It follows that pH-meter readings will directly reproduce pH differences in a series of buffers, and that the individual pH values can be brought to the scale of perchloric acid concentrations by applying the uniform correction noted.

It has been observed by Grunwald and Purlee [21] that glass electrodes reach equilibrium only slowly in the presence of large proportions of non-aqueous solvents. We found that, in " 60% " aqueous dioxan at 20°, our electrode potential became steady enough during the first two minutes to yield an apparent pH which was definite to within the precision with which the meter could be read, but that the apparent pH then fell slowly over about an hour to another, more strictly steady value. However, the difference between the two values was independent of pH, so that either could be used, and converted, with a suitable uniform correction, to correspond to perchloric acid concentrations as explained above. A similar situation prevailed with respect to the temperature of measurement of pH. In contrast to its low temperature-coefficient in water, the glass electrode has a somewhat large temperature-coefficient in " 60% " aqueous dioxan. But the differences between pH readings made at 0° and at 20° were independent of pH within the range of our experiments. Thus, any constant temperature within this range could be used when comparing a series of buffers with respect to pH, and the individual measurements could be converted into terms of concentration of perchloric acid by an appropriate uniform correction. Of course, the approximate nature of these empirical corrections would be expected to introduce a certain systematic error, but our impression was that this was inconsiderable in the presence of the casual errors, the general scatter being over an interval of about 0·1 pH unit.

In each buffer series a constant ionic strength was maintained. The concentrations of buffer materials were made sufficient to allow never less than 40% and usually 70% or more of each run to be used, despite the low hydrogen-ion concentrations, for the evaluation of first-order rate constants. We have used acetate buffers, made from sodium acetate and hydrochloric acid, with added lithium perchlorate to make up the ionic

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[20] Dole, *J. Amer. Chem. Soc.*, 1932, **54**, 3095.

[21] Grunwald and Purlee, *J. Amer. Chem. Soc.*, 1957, **79**, 1366.

strength. We have also used a phthalate buffer, made from potassium hydrogen phthalate and hydrochloric acid, and a phosphate–citrate buffer, from sodium dihydrogen phosphate and citric acid. The results obtained by these methods are recorded in Table 2, and some plots based on them are shown in Fig. 2.

The slopes of the plots of the logarithm of the rate-constant against the pH are -1 to within the experimental error, which is rather greater here than in the runs without buffers recorded in Section 2.5. However, the runs in buffers again establish equation (1) as the kinetic law governing the rearrangement of 1,1′-hydrazonaphthalene in " 60% " aqueous dioxan. The combined effect of the runs without and with buffers is to establish that law over a 10^4-fold range of hydrogen-ion concentrations.

The runs in buffers again show the strong positive salt effect. Rates for a given acidity are about six times as great in series E, and about twice as great in series F, as in series G or H: in series E and F, the ionic strength is six and three times as great, respectively, as in series G and H.

The runs in buffers incidentally show the absence or unimportance of general acid-catalysis. The catalytic effect of acetic acid molecules in the 0·1M-region of concentration is inappreciable in comparison with the effect of hydrogen ions in their lowest buffer-regulated concentrations.

TABLE 2.

First-order rate-constants, k_1, in sec.$^{-1}$, of rearrangement of 1,1′-hydrazonaphthalene, initially 0·004M, in the presence of hydrogen-ion buffers in " 60% " aqueous dioxan at 0·0°.

Series E: Acetate buffers, μ = 0·160M.

pH at 20°	2·12	2·38	3·25	4·19	5·29
10^3k_1 at 0°	8·53	3·67	0·454	0·144	0·0134

Series F: Acetate buffers, μ = 0·080M.

pH at 20°	2·58	3·00	3·05	3·42	3·42	3·96	4·42	4·66	4·66
10^3k_1 at 0°	0·794	0·324	0·320	0·170	0·203	0·0502	0·0158	0·0123	0·0069

Series G: Phthalate buffer: μ = 0·025M.

pH at 20°	2·36	2·80	3·09	3·16	3·21	4·12
10^3k_1 at 0°	0·930	0·361	0·182	0·210	0·124	0·0115

Series H: Phosphate–citrate buffer: μ = 0·025M.

pH at 20°	3·40	3·64
10^3k_1 at 0°	0·112	0·0400

(2.6) *Kinetic Effect of Salts.*—The existence of strong positive salt effects in this reaction is clear from both the groups of experiments summarised in Sections 2.4 and 2.5. The following further experiments were undertaken in order to determine whether any large part of these salt effects arose from specific participation by salt anions in the transition state of the reaction, which is undoubtedly a cationic transition state apart from any such intervention by an anion. The runs of this group were made with a common concentration 0·001M of perchloric acid as the source of hydrogen ions, and a common concentration 0·001M of each of a series of uni-univalent salts, or 0·00033M of a uni-bivalent salt, so to make up a common ionic strength of 0·002M. We judged these salt concentrations to be large enough to disclose any important specific effects of the kind sought, without bringing in to any considerable degree effects of ion-aggregation in the salts. As will be seen in Table 3, the rates measured in the presence of all the salts thus investigated were essentially the same. We conclude that the observed salt effects in this reaction are non-specific, and presumably represent electrostatic interaction between the charges of the ambient ions and the excess polarity acquired by the reaction in its transition state.

(2.7) *Solvent Effects on Rate.*—A general qualitative study of these effects led to a

TABLE 3.

Effect of salts, added to a common ionic strength of 0·002M, on the initial first-order rate-constant, k_1 in sec.$^{-1}$, of rearrangement of 1,1′-hydrazonaphthalene initially 0·004M, in the presence of 0·001M-perchloric acid, in " 60% " aqueous dioxan at 0·0°.

Salt	10^3k_1	Salt	10^3k_1	Salt	10^3k_1	Salt	10^3k_1
LiCl	0·20	Li_2SO_4............	0·22	NH_4Cl............	0·22	Na_2SO_4	0·19
LiBr...............	0·24	$LiClO_4$............	0·21	NaCl	0·19	$NaClO_4$	0·21
LiI	0·23	NH_4NO_3.........	0·21	$NaO_3S{\cdot}Ph$	0·23		

specific quantitative one. First, solutions of 1,1′-hydrazonaphthalene in the anhydrous solvents, ether, dioxan, acetone, and acetonitrile have the property that additions of hydrogen chloride in the same solvent cause immediate precipitation of the products of rearrangement of 1,1′-hydrazonaphthalene. These rearrangements, which we assume to be heterogeneous, are much too fast to be followed kinetically, even at —50°. In a mixture of 90 vol. % of dioxan with 10 vol. % of water, some precipitation of products occurs, but it is less immediate and complete. However, the rearrangement is still very fast.

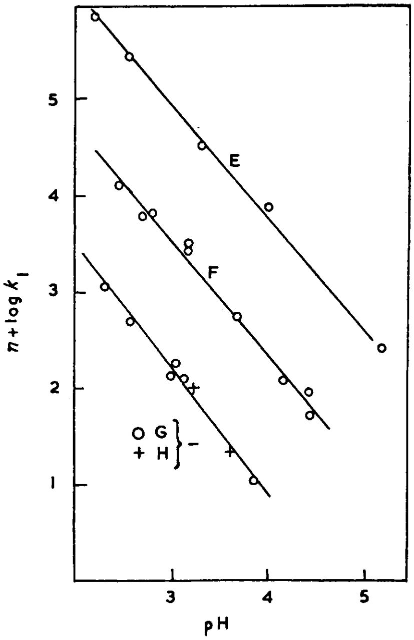


FIG. 2. Plots of the logarithm of the first-order rate-constants (k_1, in sec.$^{-1}$) of rearrangement of 1,1′-hydrazonaphthalene in " 60% " aqueous dioxan at 0·0° against the pH at 20°, at the ionic strengths specified.

Series	n	μ	Slope
E	8	0·160	—0·90
F	7	0·080	—0·96
G	6	0·025	—1·12
H(+)	6	0·025	

In solvents in which the solutes remain dissolved, that is, dry ethanol and various aqueous organic solvents, the considerably smaller rates of rearrangement at a common acidity stand in the following order: 100% ethanol > 95% acetonitrile > 95% ethanol > 95% 2-ethoxyethanol > 95% acetone > 40% dioxan > 70% dioxan (the percentages describe the proportions by volume of the organic components of the solvents, the other component being water). The rates in ethanol are large, but within a power of ten of being measurable in the presence of 0·01M-acid at 0°. The kinetic measurements discussed in Sections 2.4 and 2.5 are for 60% dioxan, and so belong to the " slow " end of the solvent series. We report some rate measurements below, which, on being compared with those of Section 2.4, show that rates at a common acidity in the relevant solvents stand in the order (ether 47·5% + ethanol 47·5% + water 5%) > (dioxan 60% + water 40%), the percentages being again by volume. We shall describe the former solvent below as " 95% ether–ethanol."

A curious situation is here revealed. In sufficiently aqueous solvents, the reaction becomes retarded when the water is taken out, as on going from " 40% " to " 70% " dioxan, *i.e.*, from 60% to 30% of water. In this range, the polar co-solvent, water, has a positive kinetic effect, consistently with the positive salt effect found in " 60% " dioxan and described in Sections 2.4 and 2.5. On the other hand, when the water content is sufficiently reduced, the reaction becomes accelerated on its more complete removal, as on going from " 95% " to " 100% " ethanol. Also, the order of the solvents used in 95% concentration, *i.e.*, with 5% of water, gives the impression that a highly polar solvent is not now a clear advantage to the reaction. The general picture thus created seems to be one of solvent polarity in two countervailing roles, which impinge at different thresholds of polarity. The opposing effects might, for example, be on protonation, and on a decomposition of a protonated product. Hence the suggestion arises that, if we could carry over our kinetic investigation from where we have done it, namely, at the " slow " end of the solvent series, to the " fast " end, we might observe a change of kinetic form, presumably from first-order dependence on acid according to equation (1), as established in Sections 2.4 and 2.5, towards the second-order dependence, described by equation (2) and already well illustrated in the rearrangements of other hydrazo-compounds (cf. Section 1.1).

We have obtained some support for this idea by rate measurements in a rather faster solvent, though at somewhat low acidities. To establish the point thoroughly in this example would be a difficult task, because the rates in the solvents of most interest are inconveniently great, and it is not necessarily a useful counter-measure to reduce acidity; for that might only suppress a rate quadratic in acid more strongly than one which is linear, as it certainly would if the two component rates were additively associated, so making disclosure of a rate of quadratic form all the more difficult. However, steering a compromise course, we have measured some rates of rearrangement of 1,1'-hydrazonaphthalene in " 95% ether–ethanol " at millinormal acidities and at 0°. The acid was perchloric acid, and, as usual, a common electrolyte concentration was set with added lithium perchlorate. The resulting first-order rate-constants are in Table 4.

TABLE 4.

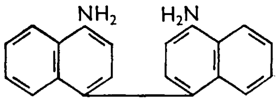
First-order rate-constants, k_1 in sec.$^{-1}$, of rearrangement of 1,1'-hydrazonaphthalene, initially 0·004M, in a mixture of 47·5 vol. % of ether, 47·5 vol. % of ethanol, and 5 vol. % of water at 0·0°.

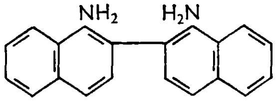
$\mu = [HClO_4] + [LiClO_4] = 0{\cdot}002$M.

$10^3[HClO_4]$	0·5	1·0	1·5	2·0	2·0
10^3k_1	0·25	0·81	1·23	1·89	1·97

Over the range covered in these experiments, the linear plot of the logarithm of the rate-constant against the logarithm of the acid concentration has a slope of 1·4. We tentatively regard the kinetic situation thus disclosed as a transitional one, such as will be more fully illustrated in some following papers, between the limiting kinetic forms expressed in equations (1) and (2). The present range of concentrations and rates is, of course, too limited to show the deviation from logarithmic linearity that this interpretation implies. In order to demonstrate this, we should have to measure rates at acidities ranging more widely, but in comparable salt conditions; which could not be maintained in a solvent, such as this, wherein ionic aggregates are formed so easily that ionic strength has not much meaning.

(2.8) *Solvent Isotope Effect on Rate.*—Bunton, Ingold, and Mhala [11] examined the effect on the rate of the benzidine rearrangement of replacing H_2O by D_2O in the " 60% " aqueous dioxan used as solvent. This was in the example of the rearrangement of hydrazobenzene, which follows the kinetics of equation (2). They observed a 4-fold acceleration. An acceleration in a deutero-solvent of an acid-catalysed reaction is always taken to signify pre-equilibrium proton-transfer, rather than slow proton-transfer. But such accelerations are usually about 2-fold, the highest previously recorded factor being 2·7. The observed 4-fold acceleration was taken to mean that the two protons shown by equation (2) to be involved, are both fully transferred in the transition state.


(I)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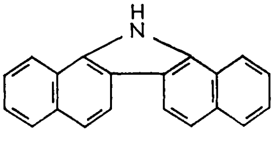
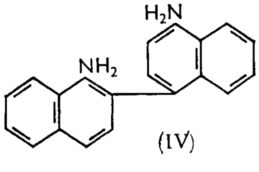
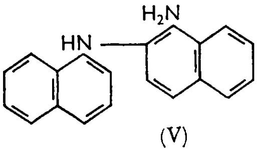
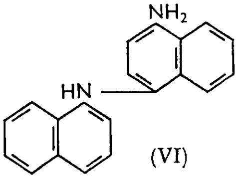

(III)


(IV)


(V)


(VI)

To us, this result was an important standard of comparison and we started therefore by repeating the work. We confirmed the unprecedented magnitude of the acceleration, obtaining, indeed, the slightly larger factor 4·7, as against Bunton, Ingold, and Mhala's 4·1, under similar conditions. Whilst the cause of this difference, which is about twice the expected experimental error, is unexplained, it does not affect the contrast now to be noted. This is that the effect of the same change of medium on the rearrangement of 1,1'-hydrazonaphthalene, which follows the kinetic law of equation (1), is an acceleration, but by the entirely normal factor of 2·3. The figures are in Table 5. From them we conclude that kinetic form and solvent-isotope effect in the benzidine rearrangement can be correlated on the uniform basis that each involved proton acts as if fully transferred.

TABLE 5.

Comparisons of first-order rate-constants, k_1 in sec.$^{-1}$, in the rearrangement of hydrazobenzene and 1,1'-hydrazonaphthalene in the presence of perchloric acid in mixtures of 60 vol. of dioxan with 40 vol. of either water or deuterium oxide at 0·0°.

Dioxan–H_2O *		Dioxan–D_2O *†		Comparison			
[$HClO_4$]	10^3k_1	[$DClO_4$]	10^3k_1	[Acid]	10^3k_H	10^3k_D	k_D/k_H
Hydroazobenzene							
0·1915	0·0805	0·1925	0·391	0·200	0·0882	0·423	4·8
0·1915	0·0806	0·1925	0·378	0·200	0·0883	0·408	4·6
1,1-*Hydrazonaphthalene*							
0·0100	9·90	0·0100	23·0	0·010	9·90	23·0	2·3

* As calculated with full allowance for the details of the ways in which the solutions were made up, the dioxan–H_2O contained 23·8 mol. %, and the dioxan–D_2O 23·9 mol. % of dioxan.

† The deuterium oxide used contained 97·8% of its hydrogen atoms in the form of deuterium. We have not attempted to correct the rates for the effect of the small content of protium oxide.

(3) *Products of Rearrangement of* 1,1'-*Hydrazonaphthalene*

(3.1) *Qualitative Account of Rearrangement Products.*—Two of these were first described by Nietzki and Goll [13] (whose original, so-called, 1,1'-hydrazonaphthalene must have consisted largely of them), and were later identified synthetically by Vesely.[22] They were the naphthidine (I) (4,4'-diamino-1,1'-binaphthyl), and the dinaphthyline (II), (1,1'-diamino-2,2'-binaphthyl). In Jacobson's comprehensive table of products of acid-catalysed

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[22] Vesely, *Ber.*, 1905, **38**, 136.

rearrangements of hydrazo-compounds,[23] they are listed as the only products from 1,1′-hydrazonaphthalene. Večera, Petranek, and Gasparič have, however, reported[19] the chromotographic detection, in the products of rearrangement of this substance, under catalysis by hydrochloric acid, not only of the two substances mentioned, but also of the third possible diaminobinaphthyl (IV), the two possible aminodinaphthylamines producible by semidine rearrangements, (V) and (VI), and the two disproportionation products, 1,1′-azonaphthalene and 1-naphthylamine, all in comparable quantities, as judged from the paper chromatogram.

In conditions similar to those of our kinetic runs, but also broadened to include a rather wider range of aqueous solvents, higher acidities, and higher temperatures than could conveniently be used in kinetic measurements, we always found just three products, *viz.*, the naphthidine (I), the dinaphthyline (II), and a substance not previously obtained, or even detected, as a product of the acid-catalysed rearrangement, *viz.*, 1,2:7,8-dibenzocarbazole (III).* The three products are formed in comparably important quantities, and together they account for the whole of the rearranged material. It was verified that the carbazole (III) is not formed from the dinaphthyline (II) under the conditions in which the compounds are produced together by rearrangement; though the carbazole can be produced by cyclisation of the dinaphthyline under other conditions, *viz.*, at much higher acidities and temperatures. In none of these rearrangements did we detect any of Večera, Petranek, and Gasparič's other rearrangement or disproportionation products—not even when we used their chromatographic methods. Incidentally, these methods displayed quite obviously the carbazole (III), which they did not find. We are at a loss to account for these discrepancies. As to disproportionation products, we further showed spectroscopically, by absorption at 400 mμ, that the proportion of formed 1,1′-azonaphthalene could not amount to 1%.

(3.2) *Qualitative Account of Disproportionation Products.*—In non-acidic and basic conditions, 1,1′-azonaphthalene and 1-naphthylamine are produced. They were identified chromatographically, and the former spectroscopically, but no quantitative material balance including both of them was completed.

In aqueous dioxan, the disproportionation products arise in the presence of basic salts, and, even in weakly acid media, in the presence of sufficient amounts of salts with basic anions, a circumstance which sets a limit of pH to the use of buffers, and, at higher pH values, a limit of buffer concentrations, in the kinetic study of the rearrangement.

In the reactions of hydrazobenzene and its simpler derivatives, the various parallel rearrangements and the disproportionation all appear to share a common acid-catalysis.[3,7,11] We might, then, expect the rearrangements and disproportionation of 1,1′-hydrazonaphthalene to share a common acid-catalysis; and they may do, but we cannot prove it , because the fraction of disproportionation under acid-catalysis is undetectably small. On the other hand, disproportionation has a high sensitivity to basic catalysis, a sensitivity which it does not share with rearrangement.

The disproportionation of 1,1′-hydrazonaphthalene can also be observed in conditions that do not depend on added solute bases, for example, in " 60% " aqueous dioxan or in aqueous ethanol at 25°. Inasmuch as Blackadder and Hinshelwood have shown[25] that the oxidation of hydrazobenzene by molecular oxygen in aqueous ethanol is catalysed by cupric and other metal ions, we examined our disproportionation for this possibility, by testing the substrate for such ions, by de-ionising the water by means of a resin, by operating in the presence of ethylenediaminetetra-acetic acid, and by adding the ash

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* This carbazole has, however, been obtained by Shine and Snell[24] by the thermal rearrangement of 1,1′-hydrazonaphthalene, *i.e.*, by heating it in ethanol without an acid catalyst (to be reported in Part XII, forthcoming).

[23] Jacobson, *Annalen*, 1922, **424**, 76.
[24] Shine and Snell, *Chem. and Ind.*, 1957, 707.
[25] Blackadder and Hinshelwood, *J.*, 1957, 2904.

obtained from a large quantity of the substrate—all with negative results. The reaction in "60%" aqueous dioxan occurs with peroxide-free dioxan, in the absence of oxygen and light, and without additives of any kind. In aqueous ethanol, it occurs when the ethanol has never been exposed to light since its purification, a necessary precaution, because a little light causes purified ethanol to develop some impurity detectable with dithizone. The disproportionation in the absence of anything but substrate and solvent was followed by spectroscopic measurement of formed 1,1′-azonaphthalene, of which about 1% a day is produced at 25° in "60%" aqueous dioxan. We suppose that these experiments may be illustrating the basic catalysis of disproportionation, the water in the solvent now being the responsible base.

When the water was omitted, with all other precautions maintained, *i.e.*, in anhydrous peroxide-free dioxan in the absence of oxygen and in the dark, no reaction occurred at 25°. But when a trace of oxygen was admitted, a slow disproportionation set in. We suppose that this proceeds by some homolytic mechanism, perhaps allied to the mechanism of the thermal rearrangements to be discussed in Part XII (forthcoming).

(3.3) *Quantitative Study of the Rearrangement Products.*—The products were determined mainly by a gravimetric scheme, which was in some degree supplemented by quantitative, infrared and ultraviolet spectroscopy and by chromatography. The proportions of

TABLE 6.

Proportions of the naphthidine (I), dinaphthyline (II), and dibenzocarbazole (III) formed in the rearrangement of 1,1′-hydrazonaphthalene in acidified aqueous organic solvents.

H_2O (vol. %)	Temp.	[$HClO_4$]	Additives	Products (%)			
				I	I	III	Total
Medium: dioxan 60 vol. + water 40 vol.							
40	0°	1·30	—	59·5	20·1	18·8	98·4
,,	,,	0·50	—	61·3	19·5	19·6	100·4
,,	,,	0·20	—	63·8	18·0	15·0	96·8
,,	,,	0·10	—	61·9	—	—	—
,,	,,	0·080	—	60·0	20·1	18·6	98·7
,,	,,	0·050	$LiClO_4$ to $\mu = 0{\cdot}1$	59·4	21·2	20·2	100·7
,,	,,	0·050	,, ,,	60·7	—	—	—
,,	,,	0·025	,, ,,	60·2	—	—	—
,,	,,	0·010	,, ,,	61·8	—	—	—
,,	,,	0·010	—	59·8	20·8	20·6	101·2
			Means	60·8	20·0	18·8	99·6
,,	25°	1·30	—	64·8	20·0	12·3	97·1
,,	,,	1·10	—	64·0	24·3	12·6	100·9
,,	,,	0·50	—	66·8	18·2	14·7	99·7
,,	,,	0·30	—	63·2	23·1	14·0	100·3
,,	,,	0·20	—	64·0	20·4	15·8	100·2
			Means	64·5	21·2	13·8	99·5
,,	0°	—	Acetate, pH 3·5	58·2	24·0	17·2	99·4
,,	,,	—	,, pH 2·4	60·5	18·2	20·6	99·3
,,	,,	—	$CH_3{\cdot}CO_2H$, 0·3M	60·9	22·8	16·1	99·8
			Means	59·9	21·7	18·0	99·6
Medium: ether 47·5 vol. + ethanol 47·5 vol. + water 5 vol.							
5	0°	0·20	—	59·3	18·8	27·6	105·7
,,	,,	0·05	—	57·2	20·2	27·4	104·8
,,	,,	0·05	—	57·7	19·9	26·0	103·6
			Means	58·1	19·6	27·0	104·7
Media: Various mixtures of dioxan and water.							
60	20°	0·05	—	67·9	17·9	16·0	101·8
50	,,	,,	—	67·2	14·4	19·5	101·1
40	,,	,,	—	64·5	13·4	18·4	96·3
30	,,	,,	—	63·1	16·7	20·1	99·9
20	,,	,,	—	62·6	13·1	24·9	100·6
10	,,	,,	—	51·8	16·2	28·5	96·6

products were shown to be independent of the concentration of the substrate, and their dependence, or lack of it, on other variables is illustrated in Table 6.

All analyses were independent, and most of them added up to 100% to within the errors of method. However, this remark needs qualifying with respect to the buffered runs, *i.e.*, those of the last three lines of the first section of Table 6. In these uniquely, substantial amounts (1·6—3·5% as estimated spectroscopically) of 1,1′-azonaphthalene were formed, notably in the tails, such as would be irrelevant to our kinetic measurements, of runs taken for product determinations to at least ten half-lives. As to the other disproportionation product, 1-naphthylamine, we could find it chromatographically but had not a convenient method for its quantitative determination in small amounts.* Therefore we assumed that the redox products are formed in equivalence, and subtracted twice the equivalent of azo-compound formed from the amount of hydrazo-compound taken, in order to obtain the amount that is rearranged. The assumption of equivalence might not be correct,[7] but our determinations of rearrangement products, calculated to that basis, do add up almost to 100%.

These results show that, over the range of conditions investigated, and to within the limits of error, the proportions of rearrangement products are independent of acidity and ionic strength, have only a small dependence on temperature, and have a considerable dependence on medium composition. The tendency is towards the production of less naphthidine and more dibenzocarbazole in the less aqueous media.

(3.4) *Proportions of Dibenzocarbazole at High Acidities.*—Though the proportions of the rearrangement products of 1,1′-hydrazonaphthalene are independent of acidity in the range of the experiments of sub-section (3.3), we had indirect reasons for suspecting that at higher, perhaps much higher, acidities than those at which we could follow the kinetics of rearrangement, the proportion of dibenzocarbazole would fall and perhaps vanish. Some experiments were made, which are reported in Table 7, and they tend to confirm this idea.

These experiments are described separately from those of Section (3.3) because those were quantitative in the usual sense, whereas these are quantitatively reproducible but not quantitatively significant. The reason is that, at the present high acidities, the half-life of reaction, a small fraction of a second, is smaller than the time taken to mix the initial solutions. A solution of the acid in water was quickly added with high-speed stirring to a solution of the hydrazo-compound in dioxan containing less water than the eventual proportion of 40% by volume of the final solution. Much of the hydrazo-compound must rearrange while the mixture is being made, and hence at acidities lower than the nominal acidities given in Table 7, lower by a greater margin when the nominal acidities are higher. The trend is clearly towards low carbazole production at high acidities, and the figures must under-estimate this actual effect of acidity on product-composition.

TABLE 7.

Proportions of dibenzocarbazole (III) formed in the rearrangement of 1,1′-hydrazonaphthalene (0·008M) in "60%" aqueous dioxan at 20° in the presence of high concentrations of acid.

Acid	[Acid]	Additive	[Additive]	Carbazole (III) (%)
$HClO_4$	1·3	—	—	17·0
,,	2·4	—	—	9·6
HCl	2·5	—	—	9·7
,,	,,	$SnCl_2$	0·01	10·1
,,	4·5	—	—	3·8, 3·5

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* Its ultraviolet spectrum is too much like those of the naphthidine and dinaphthyline to be useful. This spectral similarity presumably arises because twisting at the internuclear bond in binaphthyl[26] largely cuts out internuclear conjugation.

[26] Harris and Mellor, *Chem. and Ind.*, 1961, 557, 1082.

One motive for doing these experiments was to try to understand why earlier investigators of the rearrangement obtained no carbazole. They usually reduced the azo-compound with stannous chloride at high acidities, and allowed the hydrazo-derivatives to rearrange as formed. There is, of course, no mixing problem here, and the hydrazo-compound, as formed, will feel the full effect of the acidity provided. Hence, it seems very likely that the proportions of formed carbazole would be quite small. The Table shows that the presence of stannous chloride makes no difference to the proportion in which the carbazole is formed.

However, there is one discrepant statement in the literature. Cohen and Oesper [27] had reduced 1,1′-azonaphthalene with stannous chloride in " 60% " aqueous ethanol at 100° in the presence of 3·8M-hydrogen chloride, and had obtained no carbazole (except by subsequent cyclisation of the formed 1,1′-diamino-2,2′-binaphthyl). Hodgson and Habeshaw [28] report that, in repeating this work, they obtained 40% of carbazole in the reduction. In our hands, their procedure gave only a few units per cent of the carbazole; and this small amount must have been produced by rearrangement, because we confirmed that acid cyclisation of the diamine is much too slow to be made responsible. If the carbazole formed by rearrangement is removed, more can be produced by boiling the remaining rearrangement products in the acid medium for long periods (hours). The rearrangement itself is, of course, instantaneous in the conditions, and we can only assume that Hodgson and Habeshaw applied some heating which has escaped the record.

(3.5) *Attempts to Isolate a Protonated Intermediate.*—A number of claims to mono- and di-protonated salts of unrearranged hydrazobenzene, including coloured salts regarded by Dewar as π-complexes,[29] have been made [30-35] and refuted.[3,35] We have seen no signs of coloured salts in this or any other case. We made a long series of attempts to obtain salts of 1,1′-hydrazonaphthalene by precipitation from aprotic solvents, but we obtained only rearranged substances. We have tried following rearrangements in a recording ultraviolet spectrophotometer, in order to see if any intermediate with a characteristic absorption would be detected, but again with negative result.

EXPERIMENTAL

Materials.—Alumina used in the following preparations was dried at 200° for 12 hr. 1,1′-Azonaphthalene was prepared from naphthalene-1-diazonium chloride by use of sodium sulphite.[27] Purified by chromatography on alumina with benzene, and subsequent crystalisation first from aqueous ethanol and then from benzene, it had m. p. 190—191° (Found: C, 85·4; H, 5·3. Calc. for $C_{20}H_{14}N_2$: C, 85·2; H, 4·9%). 1,1′-Hydrazonaphthalene was prepared essentially by Krolik and Lukashevich's method.[17] The only modification was that the solution in benzene obtained after reduction with zinc and ammonium chloride was poured into water, and then the washed benzene solution was evaporated to a small bulk at 20°, the hydrazo-compound being later precipitated by addition of light petroleum (b. p. 40—60°). Purified by repeated solution in benzene and re-precipitation with light petroleum, it had m. p. 135—136° (decomp.; rate of heating 1° per minute). Stored over phosphoric oxide in an atmosphere of oxygen-free nitrogen, it remained colourless for several months. Titration with Bindschedler's Green indicated 99·5% purity (Found: C, 84·4; H, 6·0. Calc. for $C_{20}H_{16}N_2$: C, 84·5; H, 5·6%). The compound was shown to be homogeneous by chromatography on silica gel with dimethylformamide, and on paper with formamide and cyclohexane. The

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

[28] Hodgson and Habeshaw, *J.*, 1947, 77.

[29] Dewar, *J.*, 1946, 777; " Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, p. 239.

[30] Wieland, *Ber.*, 1912, **45**, 492 (footnote).

[31] Orelkin, Ryskaltschuk, and Aizikovitsch, *J. Gen. Chem. U.S.S.R.*, 1931, **1**, 696.

[32] Pongratz and Scholtis, *Ber.*, 1942, **75**, 138.

[33] Pongratz, Bohmert-Suss, and Scholtis, *Ber.*, 1944, **77**, 651.

[34] Cohen and Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 880.

[35] Krolik and Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, 229; 1953, **93**, 663.

materials of higher m. p. described in the literature as 1,1′-hydrazonaphthalene were similarly shown to consist largely of rearrangement products. Our compound was characterised by quantitative oxidation with alcoholic alkali to 1,1′-azonaphthalene, and with oxygen in ethanol to 1,1′-azoxynaphthalene.

Commercial samples of Bindschedler's Green being analytically useless, this compound was prepared by Wieland's method[36] as modified by Cohen and Hammond.[34] Our preparations (equiv., 256) had a useful life of about 3 months. After that, some slow decomposition set in, as could be told by a deterioration of the end-points of titrations with hydrazo-compounds. Indeed, at this stage, two end-points were beginning to be detectable potentiometrically.

Solvents were purified by standard methods. Dioxan was freed from peroxide and degassed. Ether was freed from peroxide. Ethanol, distilled water, and de-ionised water were degassed. Generally, solvents were stored under oxygen-free nitrogen and in the dark.

The rearrangement products are all well-known substances. We prepared them for study of their spectroscopic and chromatographic properties, and properties of solubility useful for quantitative separation, by a medium-scale rearrangement of 1,1′-hydrazonaphthalene. 4,4′-Diamino-1,1′-binaphthyl, crystallised successively from ethanol and benzene, had m. p. 200° (lit., 202°) (Found: C, 84·2; H, 5·8. Calc. for $C_{20}H_{16}N_2$: C, 84·5; H, 5·6%). 1,1′-Diamino-2,2′-binaphthyl, similarly purified, had m. p. 279° (lit., 281°) (Found: C, 83·7; H, 5·6%). 1,2:7,8-Dibenzocarbazole, crystallised successively from acetic acid and benzene, had m. p. 225° (lit., 221°) (Found: C, 89·6; H, 4·9. Calc. for $C_{20}H_{13}N$: C, 89·9; H, 4·9%). All these compounds were chromatographically pure.

Chromatographic Methods.—It was routine to check all preparations, separations, and analyses by paper chromatography, by the methods of Večera, Petranek, and Gasparič.[19] The paper had to be impregnated for at least three days with 10% formamide-in-ethanol before reproducible R_F values could be obtained. The chromatograms were developed with cyclohexane. Both the sprays recommended by those authors were employed, but the more useful one in this investigation, applied after the chromatogram had been diazotised with nitrous gases, was of the coupling component, *N*-1-naphthylethylenediamine, which gave blue-purple dyes with the diazotised primary amines. The dibenzocarbazole gave a yellow spot with the nitrous gases, but did not couple.

Kinetic Methods.—The runs were followed by back-titration of an added excess of Bindschedler's Green with 0·01M-titanous chloride in hydrochloric acid. The latter was stored under nitrogen in an automatic burette, and the titrations were done under oxygen-free nitrogen. Samples at 0° were removed with a jacketed pipette, and for the faster runs inverted Y-tubes were used.* Visual observation of the end-point was hindered in the presence of rearrangement products by the development of a strong orange colour, due, no doubt, to their involvement in titanium complexes. For this reason potentiometric detection was developed, employing either a platinum–tungsten, or, more usually, polarised platinum electrode-system, and the dead-stop method. In the latter case, the end-point potential, which did not usually coincide with zero galvanometer reading, was determined by blank runs, with the Bindschedler's Green alone, in which the end-point could be observed visually as well as

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* The composition of the so-called "60%" aqueous dioxan was slightly different, according to the kinetic method. When samples were to be withdrawn from a bulk of reaction solution, the reaction was started by dissolving the substrate in a mixture of 60·0 ml. of dioxan and 20·0 ml. of water at 20°, cooling to 0°, and adding 20·0 ml. of the aqueous acid already at 0°. With all volumetric and temperature corrections made, this produced an aqueous dioxan solvent, 60·7% by weight in dioxan. When inverted Y-tubes were used, 8·0 ml. of the substrate solution, made up as above from 60 ml. of dioxan and 20 ml. of water, were measured at 0° into one limb of a tube, and 2·0 ml. of the aqueous acid at 0° were measured into the other. The volumes cited are nominal, and were accurately determined by normal methods of calibration. With all corrections made, this solvent was calculated to be 60·5% by weight in dioxan. Because of the slight difference of solvent composition, the same kinetic technique was used throughout any one kinetic series of runs.

These remarks apply generally to the papers of this Series, except where special comment is made on the preparation of reaction solutions. In some of the papers, rates, all obtained by the inverted Y-tube method, are compared with Hammett's H_0 values, as derived from indicator measurements, also in so-called "60%" aqueous dioxan. In reality, the medium for the indicator measurements was again a little different, being 60·8% by weight in dioxan. The last difference is insignificant in this context, especially having regard to the difference of temperature between the rate measurements (0°) and the indicator measurements (20°).

[36] Wieland, *Ber.*, 1915, **48**, 1087.

potentiometrically. It was essential to flame the electrodes after each determination. Potentiometric equilibrium was at best attained somewhat slowly near an end-point, times of several seconds, even up to 20 sec., between drops being necessary. Attempts to sharpen the end-points and hasten the titrations, by working at low acidities or in buffers,[37] were unsuccessful.

The Bindschedler's Green solution was made up about 1 hr. before use, in order to allow the initial fast loss of oxidising power to spend itself. Throughout all but quite short runs, blank titrations were performed on the Bindschedler's Green solution every half-hour, so that a curve could be constructed from which the equivalent titration of the oxidising agent could be read for the time of each point of the kinetic run.

The titanous chloride solution was standardised with ferric ammonium sulphate. We found titanous sulphate in sulphuric acid an unsatisfactory reagent, as its use led to drifts of electrode potential near the end-point.

Product Analyses.—The principal method, though it was supplemented by others, was that of gravimetric analysis. The details differed according to the degree of acidity of the run, and the solvent.

For runs with less than 0·1N-perchloric acid in " 60% " aqueous dioxan, the reaction of about 0·15 g. of 1,1′-hydrazonaphthalene in 50 ml. of the medium was completed, and then 0·7 ml. of 2N-sulphuric acid was added, and the solution was left at 0° overnight. The naphthidine sulphate (Found: BH_2SO_4/B, 1·34. Calc.: 1·34) was filtered off, washed with ether, dried at 110°, and weighed. The filtrate was diluted to 600 ml. with 0·8N-aqueous sulphuric acid, and left at 0° for 2 hr. The precipitated dibenzocarbazole was filtered off, washed with water, dried at 110°, and weighed. The filtrate from this was made alkaline with sodium hydroxide, then kept for some time at 0°, and the dinaphthyline was filtered off, washed with water, dried at 110°, and weighed. It was verified by blank analyses, supported by paper chromatography, that the precipitations were complete, that no co-precipitations occurred, and that no interconversions of products occurred in any of the conditions used.

For runs with $>$0·1N-perchloric acid in " 60% " aqueous dioxan, the difficulty had to be met that the naphthidine sulphate is then appreciably soluble. The procedure here was to dilute directly the solution of the finished run to 600 ml. with 0·8N-aqueous sulphuric acid, and so to precipitate the naphthidine sulphate and the dibenzocarbazole together. This mixture was collected, washed with a minimum of cold water, dried, and weighed; then the carbazole was washed out with ether, and the naphthidine sulphate was weighed. Finally, the dinaphthyline was recovered and weighed as before.

For runs in the ether–ethanol solution, the procedures were the same, except that the layer of ether was evaporated after the dilution to 600 ml., and before filtration of the dibenzocarbazole, or the mixture containing this carbazole.

1,1′-Azonaphthalene was determined by ultraviolet spectrometry, by using the band maximum at 400 mμ, having ε 1·60 × 10^4: there was always less than 1% of it, except in some buffer runs, as noted in Section 3.3. Even here, the concurrently formed 1-naphthylamine was not precipitated with the dinaphthyline, though it was seen as an oily turbidity in the aqueous mother-liquor. 1-Naphthylamine was estimated semi-quantitatively by paper chromatographic separation: the formamide was washed out with water, the spot was eluted with acid, and the product of its diazotisation and coupling was estimated in the absorptiometer.

The ultraviolet absorption spectra of the substrate and its rearrangement products are too similar to permit three- or four-component analyses by spectrophotometry at three or four wavelengths, after the pattern of Carlin, Nelb, and Odioso's work[3] on the rearrangement products of hydrazobenzene. Also, the spectra of the coupling products of the primary bases seemed too similar to provide a convenient basis for analytical work. However, it was possible to determine the dibenzocarbazole to about ±2%, calculated on the amount of it, in the presence of the naphthidine and the dinaphthyline, by using the circumstance that the absorption of the first-named substance rises, whilst those of the others are mainly falling, towards longer wavelengths between about 240 and 300 mμ. The dibenzocarbazole was determined by this method in some cases. The extinction coefficients are in Table 8. They apply to the free bases, because it was found that, for some unelucidated reason, the protonated primary bases do not obey Beer's law.

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[37] Kolthoff and Robinson, *Rec. Trav. chim.*, 1936, **45**, 169.

The naphthidine was independently estimated by infrared spectroscopy. This substance has an absorption frequency at 13·1 μ, by means of which it can be determined to within about ±4%, calculated on the amount of it, in the presence of the other rearrangement products.

TABLE 8.

Extinction coefficients in ethanol at 20°.

	245 mμ	270 mμ	288 mμ
4,4′-Diamino-1,1′-dinaphthyl	$3{\cdot}31 \times 10^4$	$3{\cdot}54 \times 10^3$	$4{\cdot}21 \times 10^3$
1,1′-Diamino-2,2′-dinaphthyl	$4{\cdot}09 \times 10^4$	$1{\cdot}83 \times 10^4$	$1{\cdot}14 \times 10^4$
1,2 : 7,8-Dibenzocarbazole	$1{\cdot}29 \times 10^4$	$3{\cdot}02 \times 10^4$	$8{\cdot}32 \times 10^4$

The procedure was to collect the total rearrangement products after basification, and to examine spectrally a dioxan solution of the dried solids, making comparison with corresponding spectra of artificially prepared mixtures of the three rearrangement products.

Paper chromatography was used as a supplementary check on analytical figures applying to the primary amines. The method was to elute the appropriate spots, add cyclohexane, wash out the formamide with water, dilute the organic solution, and measure the ultraviolet spectra of the bases.

Attempts to Isolate a Protonated Intermediate.—Adding solutions of hydrogen chloride and of hydrogen bromide in ether and in dioxan immediately precipitated solids at −70° to +20° from solutions of 1,1′-hydrazonaphthalene in the same solvents. The solids had compositions between those of mono- and di-acid salts, but were mixtures of the rearrangement products and of their salts. On basification they gave materials, in which chromatography and infrared spectra indicated only the rearrangement products. Furthermore, the originally precipitated solids did not reduce Bindschedler's Green, and no azo-compound was produced when they were treated either with aqueous bases, or with non-aqueous ones such as ammonia in dioxan or potassium ethoxide in ethanol. Similar experiments were tried with hydrogen chloride in benzene, nitrobenzene, nitromethane, acetonitrile, acetone, dimethylformamide, and dimethyl sulphoxide. If there was an immediate precipitate, it was collected and basified, and the bases were tested as described above; and, if there was not, a non-aqueous base was added at once, and the basic products were collected and tested. Again, they consisted exclusively of rearrangement products; and, in particular, no azonaphthalene was obtained, though less than 1% of it would have been easily detected. The precipitates and the solutions were colourless or almost so: no signs were seen of highly coloured salts (cf. refs. 29, 31).

The work described in Parts I, II, and III of this series was supported by the Directorate of Chemical Science, U.S. Air Force Office of Scientific Research.

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[*Received, October 30th,* 1961.]