

**467.** *Mechanism of Benzidine and Semidine Rearrangements. Part VII.\* Transitional Kinetics and Solvent-isotope Effect in Acid Rearrangement of o-Hydrazotoluene.*

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Carlin and Odioso had shown that the rearrangement of *o*-hydrazotoluene with hydrogen chloride in "95%" ethanol has the kinetic order 1.6 in acid over the acid-concentration range 0.03—0.10*N*. Using perchloric acid in "60%" aqueous dioxan as the reaction medium, we find that the order does average 1.6 in this range, though it is rising, from 1.4 to 1.8, and will continue rising to 2.0 as the acidity continues to rise to 0.25*N*. Moreover, the functional form of the change of order with acidity is in quantitative agreement with the requirements of the hypothesis, first advanced by Blackadder and Hinshelwood in explanation of Carlin and Odioso's fractional kinetic order, that two independent processes of rearrangement, one linear and the other quadratic in hydrogen-ion dependence, are here running concurrently. At acidities higher than 0.25*N*, Hammett's  $H_0$  diverges markedly from the negative logarithm of the stoichiometric acidity, and only the former is now correlated simply with rate. Using  $H_0$  values for conditions of constant total electrolyte, as adopted in kinetics in order to avoid including a general salt effect in the sought specific effect of acid, we found the plot of the specific rate against  $-H_0$  to be linear, with slope 2.2, up to 0.5*N*-acid, the limit of the kinetic investigation.

When the water in the aqueous dioxan solvent was replaced by deuterium oxide, rearrangement was faster, but by factors which increased with the kinetic order in acid, as controlled by the acidity. Thus the factor was 2.1 when the order in acid was 1.3, but was 3.5 at a higher acidity at which the order was 1.9. These results are compared with those obtained (Parts I and VI) for hydrazobenzene, 1,1'-hydrazonaphthalene, and *N*-2-naphthyl-*N'*-phenylhydrazine.

The rearrangement, over the whole range of conditions of the kinetic record, gives essentially one product, *o*-tolidine. At low acidities, disproportionation becomes a considerable competitor, and for that reason the kinetic study was not extended to acidities below 0.02*N*.

With the experience of the work of the preceding papers of the two limiting kinetic forms, and of transitional kinetics, in benzidine-type rearrangements, we returned to the original example in which transitional kinetics were discovered: in 1954, Carlin and Odioso reported<sup>1</sup> that the conversion of *o*-hydrazotoluene (2,2'-dimethylhydrazobenzene) into its sole rearrangement product, *o*-tolidine (4,4'-diamino-3,3'-dimethylbiphenyl) in 95% aqueous ethanol containing hydrogen chloride was of order 1.6 in hydrogen chloride; and further that the catalytic entity was hydrogen ion, the chloride ion having no specific effect, though neutral salts, like extra water in the solvent, increased the rate. Since then, this finding has often been discussed, but seems not to have been experimentally reviewed.

The main motive for reviewing it is that the order 1.6 in the acid was obtained from experiments at concentrations between 0.034 and 0.102*M* in hydrogen chloride, a 3-fold range apparently insufficient to disclose that the order is not, as it cannot be, a constant, but is itself a function of concentration. The authors were aware of this, and on theoretical grounds presumed that the order in acid would rise to 2 at low acidities and fall to 1 at high ones. But these suppositions remained unchecked.

Another reason for the present review was that we were in some doubt about the degree

\* Parts I—VI, preceding papers.

<sup>1</sup> Carlin and Odioso, *J. Amer. Chem. Soc.*, 1954, **76**, 100.

of dissociation of hydrogen chloride (and lithium chloride) in 95% ethanol, and therefore felt that some examination of the effect of acid concentration on rate in a more aqueous solvent would be useful.

Our work is in three parts. First, we have reinvestigated the dependence of the rate of rearrangement of *o*-hydrazotoluene on acidity, using "60%" aqueous dioxan as solvent and perchloric acid as the source of hydrogen ions. This acid-solvent system was chosen, partly because it allowed us to correlate rearrangement rates with either stoichiometric acidity or Hammett's acidity function,  $H_0$ , which had been determined for the system before this work was begun, though we have since extended such determinations, as will be later described in Part VIII. Secondly, we have examined the kinetic effect, at different acidities, and with consequential differences of kinetic form, of replacing the water in the "60%" dioxan solvent by deuterium oxide. We had established in three other examples (cf. Parts I and VI) that substitution by deuterium accelerates hydrazo-rearrangements by different factors according to the number of kinetically significant proton-transfers. Thirdly, we have, as usual, checked the composition of the products of rearrangement, formed in our conditions.

### (1) *Kinetics of the Acid Rearrangement of o-Hydrazotoluene*

(1.1) *Methods and Results.*—We report the results of a study of the kinetics of this rearrangement at 0° over a 30-fold range of acidities. We tried to extend this range much further, in particular, towards lower acidities, but were defeated because, as explained below, the reaction under study became accompanied by other difficultly controllable modes of decomposition of the hydrazo-compound, which we could reduce but not satisfactorily eliminate. However, the limited range of acidities over which we could get reliable acid-rearrangement rates proved sufficient to establish the kinetic nature of the process, even on the internal evidence, as well as in the light of the evidence we now have of alternative limiting kinetics, and of transitional kinetics, in other cases. The 30-fold acid-range has been covered in three series of kinetic experiments over different, partly overlapping, sub-ranges, and in different salt conditions. Because of these differences, the series differ in the ways in which acidity has to be reckoned for the purposes of correlation with reaction rate.

The rearrangement was as usual followed by observation of the disappearance of hydrazo-compound. The alternative method of its destruction, which we expected to have to take precautions against, was its disproportionation to fission amines and azo-compound. This side-reaction was estimated by spectroscopic determination of *o*-azotoluene. However, it did not arise to an appreciable degree in any of the series of runs of which we record the rate-constants in Table 1. We believe that these rates do relate exclusively to the intended reaction of acid-catalysed rearrangement.

At acidities between  $10^{-2}$  and  $10^{-3}N$  in perchloric acid, *i.e.*, acidities lower than any included in Table 1, disproportionation did occur, often to non-reproducible extents. By excluding peroxides and atmospheric oxygen, we could limit it, generally to under 5%, as calculated on the measured azotoluene; but we could not eliminate it. The main difficulty was, however, that appreciable disproportionation was associated with rates of disappearance of hydrazo-compound which were irreproducibly high to apparently excessive extents, bearing no simple relation to the amounts of disproportionation as calculated from determinations of formed azotoluene, assuming a straightforward stoichiometry of disproportionation. We concluded that these rates were subject to an uncertainty of interpretation; and we did not undertake any experiments at the still lower acidities requiring buffers.

For the three series of kinetic experiments which we quote, it was established that the rearrangement was always of first-order in the substrate. Not only did the individual runs show kinetics of that form, but also runs, conducted in conditions identical except

for differences in the initial concentration of the substrate, gave identical first-order rate-constants in substrate. This matter established, we were able to compare rates generally, as is done below, in the form of first-order rate-constants in the substrate. These rate-constants, and the relevant stoichiometric and Hammett measures of acidity, are given in Table 1.

TABLE 1.

First-order rate-constants,  $k_1$  in  $\text{sec}^{-1}$ , of rearrangement of *o*-hydrazotoluene, usually in initial concentration of 0.004M, in "60%" aqueous dioxan containing perchloric acid at 0.0°.

Series A: Added lithium perchlorate: $\mu = ([\text{HClO}_4] + [\text{LiClO}_4]) = 0.1$ .								
$10^3[\text{HClO}_4]$ .....	16	27	35	44	61	78	100	
$10^3k_1$ .....	0.0066	0.0120	0.0168	0.0253	0.0449	0.0692	0.106	
Series B: No added salt: $\mu = [\text{HClO}_4]$ .								
$10^3[\text{HClO}_4]$ .....	100	200	240	260	290	330	400	480
$H_0$ ( $\mu$ unadjusted) *	2.37	2.03	1.92	1.87	1.80	1.72	1.57	1.41
$10^3k_1$ .....	0.116	0.685	1.05	1.50	3.47	4.00	11.9	18.9
Series C: Added lithium perchlorate: $\mu = ([\text{HClO}_4] + [\text{LiClO}_4]) = 0.5$ .								
$10^3[\text{HClO}_4]$ .....	50	100	150	200	300	400	500	
$H_0$ ( $\mu = 0.5$ ) *	—	2.02	1.87	1.76	1.62	1.47	1.34	
$10^3k_1$ .....	0.209	0.694	1.42	2.53	4.75	11.6	21.4	

\* Values from Part VIII (forthcoming).

(1.2) *Lower Acidities in the Presence of Salt.*—In Series A, the concentration of perchloric acid ran from 0.02 to 0.10N, and lithium perchlorate was added to make up the total electrolyte to 0.1M throughout. This salt was introduced in order to standardise the kinetic effect of ionic strength, and so to avoid including such a general effect in the sought specific effect of hydrogen ions. The whole of this sub-range lies below the threshold at which, in "60%" aqueous dioxan, the  $H_0$  function ceases to parallel the negative logarithm of the hydrogen-ion concentration. Hence we may legitimately use the stoichiometric acidity for correlation with reaction rate in this Series.

When the logarithms of the specific rates were plotted against those of the hydrogen-ion concentrations, the points of Fig. 1 were obtained, which lie on a curve slowly steepening to higher acidities. Its slope rises from 1.4 at  $[\text{H}^+] = 0.025$  to 1.8 at  $[\text{H}^+] = 0.100\text{N}$ . If one did put a straight line through the points over that acidity range, its slope would be 1.6, the slope obtained by Carlin and Odioso in a similar acidity range, though in a different solvent; but the deviations would obviously be systematic.

There is more internal evidence of the correctness, and of the significance, of the curvilinear plot, despite the smallness of the acid range. According to the explanation which Carlin and Odioso<sup>1</sup> gave of the non-integral order which they observed, the apparent order should fall with increasing acidity. The present experimental plot shows an order rising with acidity. This could be understood, if the two separately established limiting forms of benzidine-type rearrangement, those with linear and quadratic dependence on hydrogen ions, were here in action concurrently, as, indeed Blackadder and Hinshelwood did suggest,<sup>2</sup> before the separate existence of the two forms had been experimentally demonstrated. The concurrent rates would then be additive, as in the kinetic law (3)

$$k_1 = -(\text{d}[\text{Hydz}]/\text{d}t)/[\text{Hydz}] = k_2[\text{H}^+] + k_3[\text{H}^+]^2 \quad (3)$$

(cf. Part V) (Hydz = hydrazo-compound), and the plot of  $k_1[\text{H}^+]^{-1}$  against  $[\text{H}^+]$  should be a straight line, giving an axial intercept  $k_2$  and having a slope  $k_3$ . As Fig. 2 shows, this plot is indeed linear. From the line, one can read back how the order in acid ought, if equation (3) is valid, to rise with acidity along the curve of Fig. 1.\* We thus find that

\* At any acidity the apparent order in acid is less than two by the ratio of the intercept to the height of the line in Fig. 2.

<sup>2</sup> Blackadder and Hinshelwood, *J.*, 1957, 2898.

at  $[H^+] = 0.025N$ , the order in acid should be 1.50, at  $[H^+] = 0.050N$ , it should be 1.67, and at  $[H^+] = 0.100N$ , it should be 1.80, figures all in satisfactory agreement with those read from Fig. 1 itself. The rate-constants of the component reactions, as evaluated from Fig. 2, are  $k_2 = 0.21 \times 10^{-3} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ l.}$ , and  $k_3 = 8.5 \times 10^{-3} \text{ sec.}^{-1} \text{ mole}^{-2} \text{ l.}^2$ , these values applying to the conditions, including the ionic strength, set up in Series A.

(1.3) *Higher Acidities in the Absence of Salt.*—Bunton, Ingold, and Mhala's study<sup>3</sup> of the rate of rearrangement of hydrazobenzene in "60%" aqueous dioxan containing moderate and large concentrations of perchloric acid showed that the logarithm of the specific rate was correlated linearly with the logarithm of the stoichiometric acidity up to

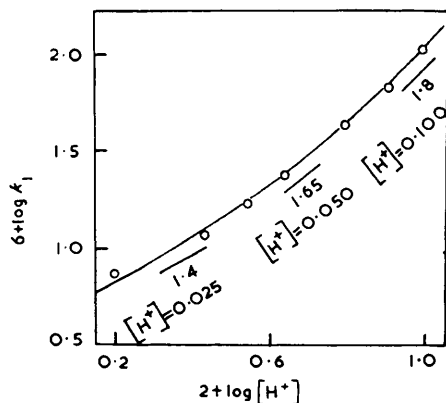


FIG. 1.

FIG. 1. Plot of the logarithm of the specific rate of rearrangement of *o*-hydrazotoluene in "60%" aqueous dioxan at 0° against that of the concentration of perchloric acid in the range 0.02—0.10N, with lithium perchlorate added to the ionic strength 0.10M. (The figures against the short straight lines show how the slope of the curve rises with increasing acidity.)

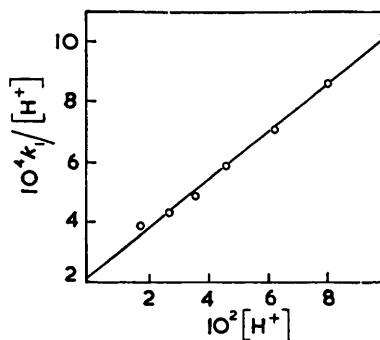


FIG. 2.

FIG. 2. Plot demonstrating that the curve in Fig. 1 is fitted by equation (3):  $k_1/[H^+]$  is plotted against  $[H^+]$ .

about 0.25N-acid, thereafter diverging from linearity very strongly. However, the logarithm of the rate continued to be correlated linearly with the  $H_0$  function from 0.2N to the limit (1.0N-perchloric acid) reached in the experimental investigation. In our Series B, the concentration of perchloric acid ran from 0.1 to 0.5N, and hence above the limit of useful rate-correlations with stoichiometric acidity. We therefore expected to have to correlate rate with acidity as given by  $H_0$  values. The upper limit of concentration, 0.5N, was a practical one, set by the highest rates that could be measured by our kinetic technique.

No lithium perchlorate was added in these experiments. This was because, when they were performed, the only available  $H_0$  values for perchloric acid in "60%" aqueous dioxan were those of Bunton, Ley, Rhind-Tutt, and Vernon,<sup>4</sup> which applied to that acid-solvent system in the absence of salts. We did subsequently revise and extend their  $H_0$  scale for the system, plotting to lower acidities, and tracing  $H_0$ , not only in the absence, but also in the presence of salt, as will be described later in Part VIII. But, although we now treat the rates of Series B with the aid of these new  $H_0$  data, we must still choose, from among the several  $H_0$  scales now available, that one which applies in the absence of salt. Since in the kinetic experiments of Series B ionic strength was not standardised, but rose with acidity, we do inevitably include an ionic-strength effect along with the sought specific effect of acidity. As all benzidine rearrangements, including the present one, have

<sup>3</sup> Bunton, Ingold, and Mhala, *J.*, 1957, 1906.

<sup>4</sup> Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.

large and positive salt effects, any apparent kinetic order in acid, that we may derive from the results of Series B, will be raised spuriously by the general ionic-strength effect.

The result of the correlation, made as described, between the logarithm of the specific rates of Series B, and the relevant  $H_0$  values, is in Fig. 3. The correlation is linear to the limit of acidity reached, and the slope of the line is 2.4. From this we can conclude only that, in the range of acidity represented, the order in hydrogen ion is in the general neighbourhood of 2. We do not suggest that the whole of this excess of the slope over 2 is due to the included ionic-strength effect; but a part of it almost certainly is, as will appear more clearly below. The remaining difference may be ascribed to one or more of those factors, to be mentioned in Part VIII, which could cause such a slope to depart from an integral value, even when the order in hydrogen ion, if given by molecularity, would be exactly integral.

(1.4) *Higher Acidities in the Presence of Salt.*—In the runs of Series C, we do seek to standardise general salt effects at the higher acidities. This recently performed series of

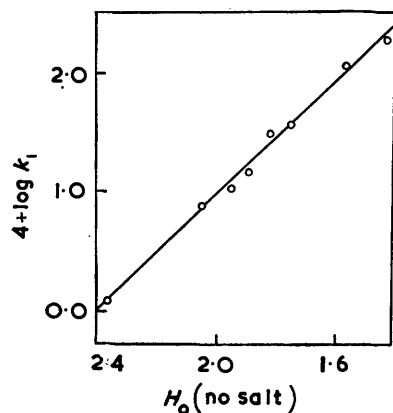


FIG. 3. Plot of the logarithm of the specific rate of rearrangement of *o*-hydrazotoluene in "60%" aqueous dioxan at 0° in the presence of perchloric acid in the range 0.1—0.5N, against the Hammett acidity  $H_0$ , in the absence of salts. (The slope of the line is 2.4.)

runs was planned along with the scheme of work to be reported in Part VIII, on further determinations of Hammett acidities of perchloric acid in "60%" aqueous dioxan. The opportunity was taken to plot the  $H_0$  function for the acid-solvent system, not only in the absence of added salts, but also in the presence of enough added lithium perchlorate to make up certain fixed concentrations of total electrolyte. One of these fixed concentrations was 0.5M; and this value was chosen in order to make it worth while to carry through a series of kinetic runs on the rearrangement of *o*-hydrazotoluene in "60%" dioxan containing perchloric acid in concentrations running up to 0.5N (the practical limit of our kinetic technique), with the same fixed concentration, similarly made up, of total electrolyte. This planned series of runs is our present Series C, in which the perchloric acid is taken from 0.05 to 0.5N, and lithium perchlorate is added to ionic strength 0.5M.

According to previous experience of the rearrangement of hydrazobenzene under the influence of perchloric acid in "60%" aqueous dioxan, we should expect the first 5-fold portion of this 10-fold acid-concentration range, *i.e.*, from 0.05 to 0.25N-perchloric acid, to allow correlation of the measured rates with stoichiometric acidities. This first part of Series C would then constitute a continuation of Series A, apart from the upward shift in rates arising from the salt effect. When the logarithms of the specific rates of Series C were plotted against the logarithms of the stoichiometric acidities, a curve was obtained which is shown as Curve I in Fig. 4. Over the first 5-fold part of its acid-concentration range, this curve does slowly steepen quite similarly to the curve for Series A in Fig. 1, though, in the last 2-fold part of the range, one sees a marked change of character. Where the acid concentrations in Series A and C overlap, as the last 2-fold part of the range of

Series A does with the first 2-fold part of the range of Series C, the curves of Fig. 1 and Fig. 4 are exactly parallel, though with a vertical shift, arising from the 6.5 times higher rates at the larger ionic strength of Series C than of Series A. As before, the slope slowly mounts from 1.65 at  $[H^+] = 0.05$  to 1.8 at  $[H^+] = 0.10N$ , in this overlapped region. But now, going beyond the limit of Series A, the slope of the curve for Series C continues smoothly to rise to 2.0 at  $[H^+] = 0.25N$ . Thereafter, much more sudden steepening occurs, the slope rising to 3 over the last 2-fold increase in acid concentration.

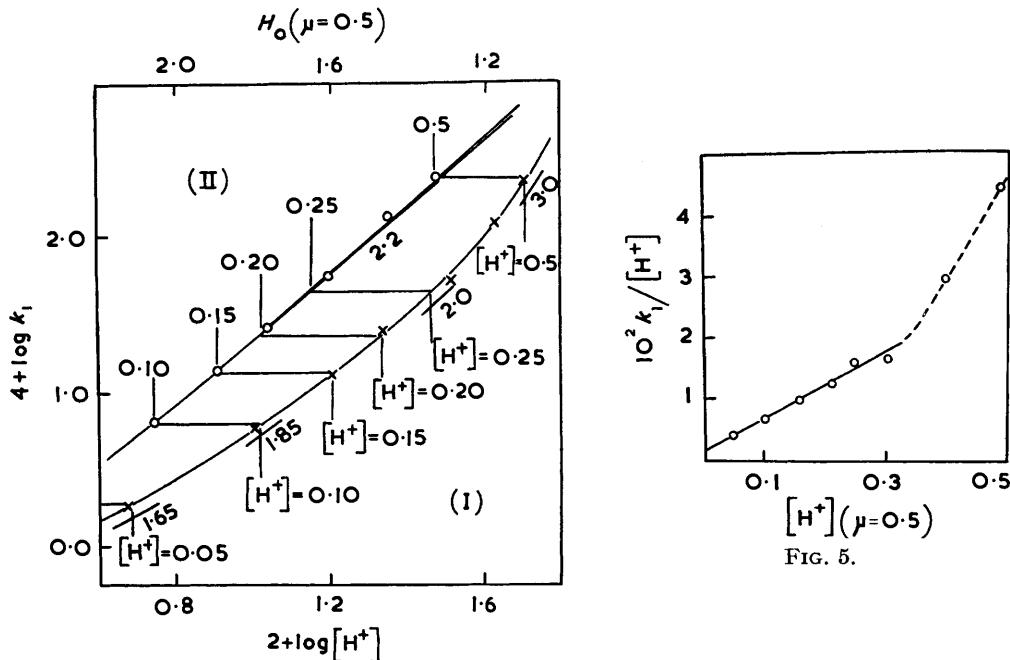


FIG. 4.

FIG. 4. Rearrangement of *o*-hydrazotoluene in "60%" aqueous dioxan at  $0^\circ$  with perchloric acid in the range 0.05–0.5N and with constant total electrolyte made up to 0.5M with lithium perchlorate; plot of the logarithm of the specific rate against (I) the logarithm of acid concentration, and (II) Hammett's function  $H_0$  in the same salt conditions. (Curve I is to be read with the lower axis of abscissae, and curve II with the upper. These acidity scales are displaced from each other in the diagram, but some tie-lines have been introduced to mark a few identical acidities. The short straight lines below curve I record the progress of its rising slope. The almost linear curve II has the limiting slope 2.2.)

FIG. 5. Plot demonstrating that the part of curve I in Fig. 4 which represents the first 5-fold portion of its total range of acid concentration is fitted by equation 3, whilst the part of curve I which corresponds to the last 2-fold portion of the acid range is not so fitted:  $k_1/[H^+]$  is plotted against  $[H^+]$ .

We assume that the slow curvature up to  $[H^+] = 0.25N$  results from the change of kinetic order as expressed in equation (3) for concurrent reactions linear and quadratic in hydrogen ions. We assume that the much sharper curvature at higher acidities arises from the entry of another factor, *viz.*, the change of direction, at about  $[H^+] = 0.25N$ , of the Hammett function  $H_0$  of the acid-solvent system, relative to the negative logarithm of the stoichiometric acidity.

Support for these interpolations is obtained by plotting the results, as in Fig. 5, in such a way as to test the range of validity of equation (3). The plot of  $k_1/[H^+]$  against  $[H^+]$  is a straight line up to  $[H^+] = 0.25N$ . From this line, we can read back that curve I in Fig. 3 should have the slope 1.67 at  $[H^+] = 0.05$ , the slope 1.79 at  $[H^+] = 0.10$ , and the

slope 1.91 at  $[H^+] = 0.25N$ , figures all in good agreement with the slopes given by the curve in Fig. 3. We can evaluate the rate constants of the component integral-order reactions. They are  $k_2 = 1.4 \times 10^{-3} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ l.}$ , and  $k_3 = 53 \times 10^{-3} \text{ sec.}^{-1} \text{ mole}^{-2} \text{ l.}^2$ . These rate constants, which apply to total electrolyte set at  $\mu = 0.5$ , are both about 6.5 times larger than those given in Section 1.2 above, which apply to  $\mu = 0.1M$ .

In order to deal with the rates at acidities above the limit of usefulness of acid concentrations, we must have recourse to the  $H_0$  values. On plotting the logarithms of the specific rates against the  $H_0$  values for the acidity and salt conditions, we obtain in curve II in Fig. 4, a straight line of slope 2.2, from the experimental upper limit of acidity 0.5N-down to 0.2N-acid. Below that, down to 0.1N-acid, the lower limit of our knowledge of the relevant  $H_0$  function, the slope falls off just perceptibly to 2.1 or slightly less. Such a slight tailing in that region of acidity would be expected from the appreciable incursion there of the component process involving linear hydrogen-ion dependence. However, the limit of slope at high acidities is quite firmly 2.2.

When we compare the curve of Fig. 3, in which ionic strength effects remain uncorrected, with curve II of Fig. 4, for which they are standardised, and, one hopes, eliminated, we see that such standardisation has brought down the high-acidity slope of the plot of the logarithm of the specific rate against  $-H_0$  from 2.4 to 2.2. This is as far as we have so far gone towards establishing that the idealised order in acid, as given by molecularity in hydrogen ions, does settle to an asymptote of 2 at high acidities. The residual difference from 2.0 may have several causes of which two could be evaluated by further work. First, the  $H_+$  function for the acid-solvent system, if determined, would allow rates in which two protons are transferred, high-acid rates in the present case, to be compared, as they should be, with  $H_0 + H_+$  rather than with  $2H_0$ . Secondly, the  $H_0$  and  $H_+$  functions would be more suitable to the present purpose, if they were determined at the kinetic temperature  $0^\circ$ , rather than at the customary  $20^\circ$  of indicator measurements. But there would still remain other possible causes of deviation, of which the methods of evaluation are unknown to us.

### (2) *The Kinetic Effects of Solvent Deuterium*

It was shown by Bunton, Ingold, and Mhala,<sup>3</sup> and is confirmed in Parts I and VI (preceding), that, on replacing the water in "60%" aqueous dioxan by deuterium oxide, the rates of acid-catalysed hydrazo-rearrangement in the dioxan solvent are increased. The rate of rearrangement of 1,1'-hydrazonaphthalene, for which the kinetic order in acid is 1.0, is thus increased by the factor 2.3, that of hydrazobenzene, for which the order is 2.0, is increased by the factor 4.8, and that of *N*-2-naphthyl-*N'*-phenylhydrazine, which has various orders in acid depending on the acidity, is increased by various factors, which rise with the kinetic order and the acidity.

In the rearrangement of *o*-hydrazotoluene we have another reaction of which the kinetic order in acid changes with the acidity. This gave the opportunity to collect some further data on the relation between the kinetic effect of solvent deuterium and the kinetic dependence of the rearrangement on acid, without changing the nature of the substrate.

The results of some experiments on these lines are in Table 2. It is found that at a somewhat low acidity, at which the order in acid is 1.3, the acceleration due to solvent deuterium is by the factor 2.1; but that, at a higher acidity, at which the order is 1.9, the acceleration is by the factor 3.5. Thus, the relation between the kinetic order in acid and the accelerating effect of solvent deuterium is generally similar to that observed for the rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine, and is in qualitative accord with the major difference between the isotope effects shown by the rearrangements of 1,1'-hydrazonaphthalene and hydrazobenzene. However, the acceleration factor for a particular kinetic order does seem to be a little smaller in the example of *o*-hydrazotoluene than in any of the other examples, *e.g.*, 1.9 as estimated for order 1.0 in acid, instead of 2.2 or 2.3.

TABLE 2.

Comparison of first-order rate-constants,  $k_1$  in  $\text{sec.}^{-1}$ , of rearrangement of *o*-hydrazotoluene in the presence of perchloric acid in mixtures of 60 vol. of dioxan with 40 vol. of either water or deuterium oxide at  $0.0^\circ$ .

[HClO <sub>4</sub> ] or [DClO <sub>4</sub> ]	[LiClO <sub>4</sub> ]	System	Order in acid	$10^3 k_1$	Found	$k_D/k_H$	Corr. 1 <sup>e</sup>	Corr. 2
0.01	0.1	H	1.28 <sup>c</sup>	0.0037	} 2.1	2.1	2.1	2.1
0.01	0.1	D <sup>a</sup>	1.28 <sup>c</sup>	0.0078				
0.29	—	H	1.92 <sup>d</sup>	3.45	} 3.3	3.4	3.4	3.5
0.286	—	D <sup>b</sup>	1.92 <sup>d</sup>	11.4				

<sup>a</sup> The D<sub>2</sub>O contained 98.9 atoms % of D in its hydrogen. <sup>b</sup> The D<sub>2</sub>O contained 98.2 atoms % of D in its hydrogen. <sup>c</sup> From equation (3) and Fig. 2. <sup>d</sup> From equation (3) and Fig. 5. <sup>e</sup> Corrected to identical acidities. Corrected to isotopically pure D<sub>2</sub>O.

### (3) Products of the Rearrangement

Carlin and Odioso found<sup>1</sup> that in their solvent, 95% ethanol, this rearrangement leads to the *pp'*-ring-coupled product, *o*-tolidine, exclusively. We have obtained the same result in our solvent, "60%" aqueous dioxan, at all acidities from 0.02N to 0.5N. In experiments at several acidities over the range for which rates are recorded, recoveries of 99% or better of this diamine were obtained. Spectroscopic examinations revealed no other product. Paper-chromatographic studies of residues did, however, show that a second diazotisable amine was formed, though only in traces. No carbazole derivative could be detected by chemical separations supplemented with chromatography.

At lower acidities, and especially in the presence of adventitious peroxides or of molecular oxygen, appreciable amounts (units %) of *o*-azotoluene were produced. This material was spectroscopically determined. It was not proved that *o*-toluidine was formed concurrently, and hence the stoichiometry of disproportionation of the hydrazo-compound remains unknown.

### EXPERIMENTAL

*o*-Hydrazotoluene.—In our hands, Cohen's method<sup>5</sup> (described by him for hydrazobenzene) was the best of the three methods we tried. Vogel's method<sup>6</sup> (as described for hydrazobenzene) and Carlin and Odioso's procedure<sup>1</sup> were less suitable. Our starting substance, *o*-nitrotoluene, was shown by vapour-phase chromatography to be substantially pure, and, in particular, free from *meta*- and *para*-isomers. In applying Cohen's procedure for its reduction by zinc dust in alkaline aqueous ethanol, we found it important to follow him in so adding the zinc that the exothermic process goes as quickly and vigorously as possible: otherwise reduction may not go through completely to the hydrazo-stage. The hydrazo-product, precipitated by water, and subsequently extracted from the zinc and zinc oxide with ethanol, was crystallised thrice from ethanol and washed with light petroleum (Found: C, 79.4; H, 7.9. Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>: C, 79.2; H, 7.6%).

Like *N*-1-naphthyl-*N'*-phenylhydrazine (Part V), this hydrazo-compound had a highly variable decomposition temperature, which seemed unconnected with analytically detectable impurities. Carlin and Odioso give<sup>1</sup> m. p. 165°. Our many preparations had decomposition points, varying with the preparation, from 135° to 160°, as taken in tubes at heating rates from 1° to 2° per minute; and the sample giving 160°, when re-examined with the Kofler hot-bench, again gave 160°, so showing that the heating rate was not highly critical.

By every chemical test, all these samples were pure. They were entirely homogeneous under paper-chromatography with our usual solvent systems. Their ultraviolet absorption spectra were identical with one another, and with the spectrum recorded by Carlin and Odioso for *o*-hydrazotoluene.<sup>1</sup> All samples had 99.5% or better of the theoretical reducing power towards Bindschedler's Green. All samples gave 99% or more of the single rearrangement product, *o*-tolidine, the absorption spectra of the recovered samples of which agreed accurately with one another, and with the spectrum recorded by Carlin and Odioso<sup>1</sup> for *o*-tolidine.

<sup>5</sup> Cohen, "Practical Organic Chemistry," Macmillan, London, 1949, p. 162.

<sup>6</sup> Vogel, "Practical Organic Chemistry," Longmans Green, London, 1956, p. 632.



In slowly heated tubes, decomposition was observed under magnification to start with the formation of one or two red spots (azo-compound?), which then spread rapidly. It seems possible that sub-analytical traces of adventitious impurities (*e.g.*, dust) determine the temperature of a local nucleating process.

*Kinetics.*—The reaction mixture was quenched with Bindschedler's Green, the excess of which was titrated with titanous chloride; visual end-point determinations were not upset by the residual faint blue colour. In the runs of Series A, and at lower acidities, samples were withdrawn from a bulk of reaction-solution maintained under nitrogen, the solvent having been previously freed from peroxides and oxygen. In fast runs, such as those of Series B and C, and the last two in Table 2, the inverted-Y-tube method was employed.

The formation of *o*-azotoluene was followed spectrophotometrically, by using the extinction coefficient, 670 at 456  $m\mu$ , obtained from authentic *o*-azotoluene (prepared by oxidation of the hydrazo-compound with Bindschedler's Green).

*Products.*—The ultraviolet absorption spectra of products, obtained over the range of conditions of Table 1, were all identical with Carlin and Odioso's recorded spectrum<sup>1</sup> of *o*-tolidine. By the usual gravimetric separation, this compound was recovered as its sulphate in 99% yield or better. No carbazole was found. However, traces were found of a second diazotisable amine, which had  $R_F$  0.60 on paper chromatography with formamide-cyclohexane.

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