

357. Kinetic Form of the Benzidine and Semidine Rearrangements.

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The rate of rearrangement of hydrazobenzene to benzidine and diphenylene in the presence of perchloric acid in 60% aqueous dioxan is correlated with Hammett acidity functions rather than with acid concentration, the dependence being quadratic at low acidities. The rearrangement thus takes place in a second conjugate acid, formed wholly by specific hydrogen-ion catalysis, *i.e.*, by two successive pre-equilibria which desolvate the two successively adding protons. This conclusion is confirmed by the unprecedentedly large acceleration which is observed when the water in the solvent is replaced by deuterium oxide. The rearrangement of 4:4'-dimethylhydrazobenzene to the *o*-semidine shows a similar quadratic dependence on acid; that is, the benzidine and semidine rearrangements have an identical kinetic form. These results delimit permissible theories of the mechanism of the benzidine and semidine rearrangements.

THE considerable body of previous work on the kinetics of benzidine rearrangements still leaves several points in a more or less uncertain state. We try here to settle some of these, in order to clear the ground for a new attack on the mechanism of these rearrangements.

(1) Kinetic Dependence of the Benzidine Rearrangement on Acidity

The first point relates to the form of the dependence on acid of the rate of this rearrangement under catalysis by a strong acid. Van Loon¹ originally recorded data in approximate agreement with the conclusion that the rate of rearrangement of hydrazobenzene, under catalysis by hydrochloric acid, is proportional to the square of the concentration of the acid. More recently, Hammond and Shine² reached this conclusion, on the basis of measurements in 75% aqueous ethanol, at what was described as constant ionic strength, sodium perchlorate being added to the hydrogen chloride to make up a constant total-electrolyte concentration of 0.4M. Carlin, Nelb, and Odioso,³ working in 95% aqueous ethanol with lithium chloride to make up the "ionic strength", obtained generally confirmatory results, and showed in addition that the product ratio, benzidine:diphenylene, is independent of the acid concentration. For the rearrangement of *o*-hydrazotoluene in similar conditions, Carlin and Odioso⁴ observed a kinetic order of 1.6 in acid, whereas for that of *m*-hydrazotoluene the order was close to 2.0. For the rearrangement of hydrazobenzene in 90% aqueous ethanol, but in otherwise similar conditions, Croce and Gettler⁵ obtained results indicating an order of about 1.85 in acid.

Concerning the main exception to an otherwise fair agreement, Carlin and Odioso point out⁴ that, if rearrangement is assumed always to take place through the second conjugate acid of the hydrazo-compound, a lower-than-second order in the catalytic acid could be understood on the basis that during reaction the storage of hydrazo-compound as its first conjugate acid is considerable: obviously if it were total, the order in acid could drop to unity. The greater basicity of *o*-hydrazotoluene than of the other hydrazobenzenes could thus be the cause of the observed low kinetic order in this case.

It may, however, be questioned whether the kinetic dependence of these rearrangements on acidity should be referred to hydrogen-ion concentration. Water is not stoichiometrically involved and it is thus possible that the relevant function of acidity is, not the acid concentration, but the Hammett function h_0 , and perhaps also the function h_+ . In water, when h_0 and $[H^+]$ diverge, h_0 always rises the faster, and in a certain range will

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, *ibid.*, 1951, **73**, 1002.

⁴ Carlin and Odioso, *ibid.*, 1954, **76**, 100, 2345.

⁵ Croce and Gettler, *ibid.*, 1953, **75**, 874.

rise somewhat similarly to $[H^+]^2$. We do not know how the acidity function of hydrogen chloride varies with concentration in any of the alcoholic media used in the foregoing investigations. Hence we do not know the region of concentration in which h_0 diverges from $[H^+]$, or resembles $[H^+]^2$, though it might well lie quite low. Thus it seems possible to overestimate on this account the kinetic order in acid. It is certain that, at concentrations of tenths molar, activity coefficients will not depend on 1:1-electrolytes simply through their concentrations, independently of their nature: at such concentrations, "ionic strength" will have no clear meaning for kinetics, and, in particular, activity coefficients will not remain constant while hydrogen chloride is replaced by sodium perchlorate or lithium chloride. A still more elementary difficulty is that we do not know above what concentrations hydrogen chloride ceases to be completely ionised in the alcoholic media, though this also probably happens at somewhat low concentrations.

FIG. 1. Rearrangement of hydrazobenzene by perchloric acid in 60% aqueous dioxan at 0°. Logarithmic plot of the rate constant versus the acid concentration. The slope of the straight line is 2.0.

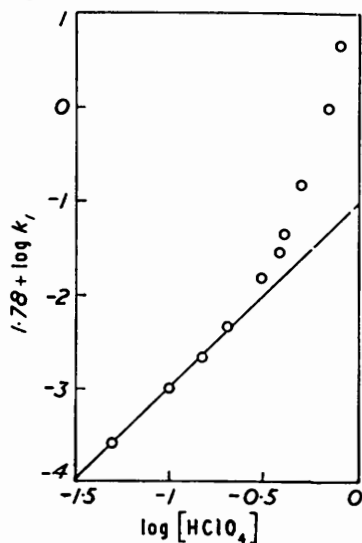
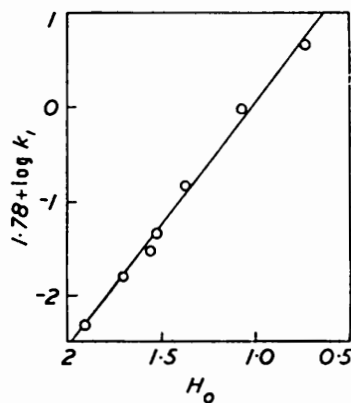


FIG. 2. Rearrangement of hydrazobenzene by perchloric acid in 60% aqueous dioxan at 0°. Plot of the logarithm of the rate constant versus Hammett's $H_0 = -\log h_0$. The slope of the line is 2.6.



Incomplete ionisation, if it were considerable, would lead to an underestimation of the kinetic order in acid.

These difficulties could be overcome by investigating the catalysis of the rearrangement by a strong acid in a medium in which its Hammett functions are known. Most acidity functions have been determined, nearly all of them h_0 functions, for mixtures of strong acids with water. But for very many organic chemical reactions, including the benzidine rearrangement, water is not a convenient, or even a practicable, solvent. As a step towards meeting this general difficulty in the investigation of acid-catalysed organic reactions, a number of tables of the function h_0 have been constructed in these laboratories for strong acids in dioxan-water mixtures. They will be published soon (by Bunton, Ley, Rhind-Tutt, and Vernon); but one of them, that relating to perchloric acid in 60% aqueous dioxan at 0°, has found service in the present investigation.

Results.—First-order rate constants for the rearrangement of hydrazobenzene under catalysis by perchloric acid in 60% aqueous dioxan at 0° are given in Table 1. Their significance is shown in Figs. 1 and 2.

As Fig. 1 shows, the rate of rearrangement at low acidities follows the square of the acid concentration to acidities above 0.1M. However, near 0.2M the rate begins to rise

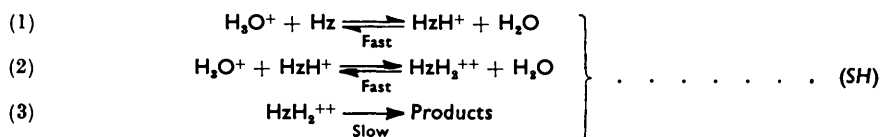
considerably faster than the square of the acid concentration. Nevertheless, as Fig. 2 shows, the logarithm of the rate continues to rise linearly with the Hammett function $H_o = -\log h_o$ up to much higher concentrations, indeed up to the highest for which rates could be measured.

TABLE 1.—*First-order rate-constants (k_1 in sec^{-1}) for the rearrangement of hydrazobenzene in the presence of perchloric acid in a mixture of 60 vols. of dioxan with 40 vols. of water at 0°.*

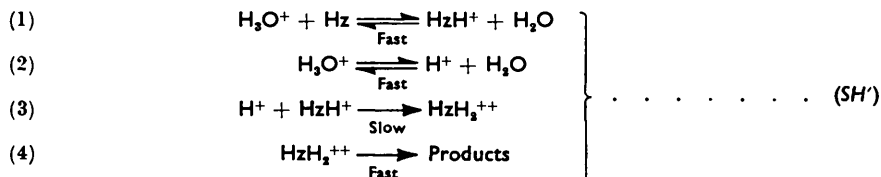
$\{[\text{HClO}_4] \text{ (M)} \dots\dots\dots$	0.050	0.101	0.151	0.200	0.304	0.383	0.406	0.500	0.700	1.000
$\{10^4 k_1 \dots\dots\dots$	0.427	1.63	3.53	7.67	25.5	47.5	74.2	248	1600	7350

Discussion.—Our results clearly substantiate previous suggestions that the rearrangement goes through the second conjugate acid of hydrazobenzene. However, several mechanisms of acid catalysis will satisfy that condition. The most worthy of consideration seem to be four, which all assume a rapid and reversible formation of the first conjugate acid of hydrazobenzene. With respect to the formation of the second conjugate acid, two of the four are mechanisms of specific hydrogen-ion catalysis, and two are mechanisms of general acid catalysis. We shall label them *SH*, *SH'*, *GA*, and *GA'*.

The first specific hydrogen-ion mechanism assumes that, not only the first conjugate acid, but also the second, are formed in rapid pre-equilibria, the slow step occurring in the rearrangement of the second conjugate acid. Writing Hz for hydrazobenzene, this mechanism may be formulated thus:



The second specific hydrogen-ion mechanism differs from the first in that it assumes the second conjugate acid to be formed by the slow addition of a pre-activated proton, that is, of one which has already escaped from its normal situation of binding in the ground state of H_3O^+ . Such pre-activation has been suggested for the protonation of carbon-carbon double bonds,⁶ and it might conceivably be needed for the protonation of such a very weak base as the first conjugate acid of hydrazobenzene. The rearrangement of the second conjugate acid would now be taken as a fast process:



With the usual assumptions underlying the kinetic use of Hammett functions,⁷ both these mechanisms lead to the approximate rate equation:

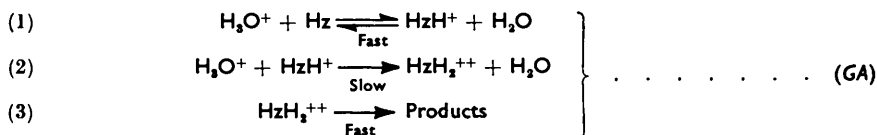
$$\text{Rate} \propto h_o h_+ [\text{Hz}] \dots\dots\dots (a)$$

The third mechanism assumes the second conjugate acid to be formed by a slow protonation effected by the ordinary solvated hydrogen ion. This mechanism is in part one of general acid catalysis, because, although the transition state contains only the proton from the first protonation, it contains the whole acid molecule, H_3O^+ , involved in

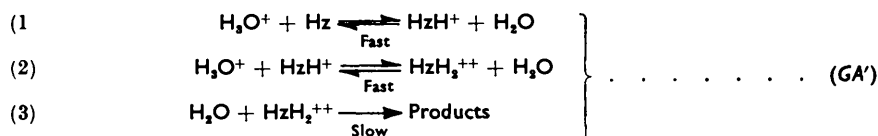
⁶ de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930.

⁷ Hammett, "Physical Organic Chemistry," McGraw-Hill, London, 1940, p. 273.

the second protonation. Here also the rearrangement of the second conjugate acid is a fast process :



The fourth mechanism assumes that the second protonation is rapid and reversible, but that the rearrangement of the second conjugate acid depends on the slow extraction of a proton, presumably from carbon, by water acting as a base. This is also general acid catalysis, because the transition state includes the equivalent of a molecule of the acid H_3O^+ , even though it has been acquired a piece at a time :



Again with the usual assumptions underlying the use of Hammett functions in kinetics, and, in particular, acceptance of the Zucker-Hammett hypothesis,⁷ both general acid mechanisms lead to the approximate rate-equation,

$$\text{Rate} \propto h_0[\text{H}_3\text{O}^+][[\text{Hz}]] \dots \dots \dots (b)$$

Thus the distinction on which the present results bear is essentially that between specific hydrogen-ion mechanisms requiring equation (a), and general acid mechanisms requiring equation (b).

This last statement requires a reservation concerning mechanism GA. For Long and Paul have suggested⁸ that, in reactions depending on slow proton-transfers from strong acids, the Zucker-Hammett hypothesis may be inapplicable, because the H_2O -portion of the solvated hydrogen ion is not sufficiently deeply implicated in the transition state to influence its activity coefficient as it influences that of the initial state. If this were so, the kinetic equation would be (a), and not (b). But if it were so, we would prefer to re-classify the reaction as one of specific hydrogen-ion catalysis, and to represent in some explicit way, perhaps somewhat as shown for reaction SH', the effective disengagement from water of the proton that is to enter the transition state. With this understanding, we may retain our classification of mechanisms into specific hydrogen-ion and general acid mechanisms, having the kinetic equations (a) and (b), respectively.

In seeking to compare our rates with equations (a) and (b), we meet the difficulty that we possess a Table of values of h_0 , but not of h_+ . That is why the conclusion, which is reached below, takes the slightly unsymmetrical form that the data exclude equation (b), but might be consistent with equation (a).

As to equation (b), we know that, as h_0 rises, $[\text{H}^+]$ drops increasingly below it. Hence equation (b) requires that the points in Fig. 2 should describe a curve bending over strongly towards the H_0 axis. This is not observed.

As to equation (a), we know that, as $[\text{H}^+]$ rises, h_0 will rise increasingly above it; and it is probable that h_+ will also rise above it, rather similarly. If any lack of proportionality between h_0 and h_+ could be neglected, so that equation (a) could be approximated to the equation,* $\text{Rate} \propto h_0^2[\text{Hz}]$, then the slope of the plot in Fig. 2 would be required to

* *Added, February 27th, 1957.*—Bonner and Lockhart (*J.*, 1957, 364) showed that for aqueous sulphuric acid H_0 and H_+ differ at most by a small constant. If the same is true of perchloric acid in aqueous dioxan, then h_+ can indeed be replaced by h_0 in eqn. (a).

⁸ F. A. Long and M. A. Paul, forthcoming paper in *Chem. Reviews*. Professor Long was very kind in allowing us to see this paper in manuscript.

be 2. In the acid concentration range 0.2—1.0M, covered in Fig. 2, the actual slope is 2.6, though at low acidities, from 0.1M downwards, as will be clear from Fig. 1, the slope must fall to 2. Now the literature contains rate data⁸ for a number of reactions that depend on single pre-equilibrium protonations; and for these reactions, linear plots, analogous to that of Fig. 2, have been obtained. The slopes are not all exactly 1, but vary from case to case, between 0.86 and 1.25. These deviations from the theoretical slope of 1 are ascribed⁸ to "specific effects," that is, to the invalidity of the assumption, inherent in the use of Hammett functions, that the ratio of the activity coefficients of two species differing in composition only by a proton is the same for all pairs of species. The fact that our slope for double protonation is rather greater than twice the largest of the slopes observed for single protonation might be due either to a steeper increase of h_+ than of h_0 with increasing acidity, or to greater specific effects in the double protonation.

The conclusion to be drawn from this work is that the benzidine rearrangement does indeed involve the second conjugate acid of hydrazobenzene, and that the relative rates of the successive processes form a pattern consistent with specific hydrogen-ion catalysis, but not with general acid catalysis. We cannot distinguish between the more conventional specific hydrogen-ion scheme labelled *SH*, and the less usual active-proton scheme labelled *SH'*.

(2) Hydrogen-isotope Dependence of the Rate of the Benzidine Rearrangement

Cohen and Hammond⁹ examined the kinetics of the rearrangement of hydrazobenzene in aqueous ethanol in the presence of acids ranging in strength from formic to cyanoacetic, in concentrations up to 2.5M, with the addition of their sodium salts, as well as of either lithium perchlorate or potassium chloride in order to make up the so-called ionic strength. They interpreted their results as pointing to general acid catalysis, although their catalytic coefficients could not be fitted to a Brønsted relation. The difficulty in interpreting such work is that the great medium changes must profoundly modify all activity coefficients.

Since Cohen and Hammond's conclusion is not that reached in the preceding Section, it seemed desirable to seek evidence by an independent method. The obvious method was the study of hydrogen-isotope effects.

On the assumption, in agreement with Cohen and Hammond, that the question of general acid catalysis could be seriously entertained only with respect to the second step of protonation, the two mechanisms which fall within the scope of such catalysis are those labelled *GA* and *GA'* in Section 1. Now Hammond and Grundemeier¹⁰ took the first step in the application of hydrogen-isotopic methods by introducing deuterium into the substrate: they showed that *para*-deuterated hydrazobenzene does not rearrange significantly more slowly than does the undeuterated compound. It follows that extraction of a benzenoid proton is not rate-controlling, *i.e.*, that mechanism *GA'* is inapplicable. Thus mechanism *GA* remains the only acceptable expression of the theory of general acid catalysis.

Between mechanism *GA*, on the one hand, and the two mechanisms, *SH* and *SH'*, of specific hydrogen-ion catalysis, on the other, a strong distinction can be drawn with respect to the expected kinetic effects of hydrogen-isotopic substitution *in the solvent*. The method is well known,¹¹ and its two simple principles are that D_3O^+ in D_2O is a stronger acid than is H_3O^+ in H_2O , and that D^+ is transferred from, or to form, D_3O^+ more slowly than is H^+ from, or to form, H_3O^+ . Thus every pre-equilibrium step involving destruction of a solvated hydrogen ion makes a reaction go faster in a deuterium than in a protium solvent, whilst every step of slow destruction or formation of a solvated hydrogen ion

⁹ Cohen and Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 880.

¹⁰ Hammond and Grundemeier, *ibid.*, 1955, **77**, 2444.

¹¹ Bell, "Acid-Base Catalysis," Clarendon Press, Oxford, 1949, p. 143.

makes a reaction go more slowly in the deuterium solvent. Recorded factors of acceleration in deuterium water for single pre-equilibrium steps are often about 2, the largest one known to us being 2.7. Factors of retardation arising from a single slow transfer can range from not much above 1, to considerably more than 2.

The following is an analysis of the effects, to be expected from a change from a protium to a deuterium solvent, on rate by each of the mechanisms set out in Section 1. The figures refer to the numbers of the stages, and the signs $>$ and \lesssim represent one-stage factors of acceleration and retardation, respectively, in the deuterium solvent :

(SH)	(1)	D > H, (2) D > H, (3) —	Overall D \gg H
(SH')	(1)	D > H, (2) D > H, (3) —, (4) —	„ D \gg H
(GA)	(1)	D > H, (2) D \lesssim H, (3) —	„ D \gtrsim H
(GA')	(1)	D > H, (2) D > H, (3) D \lesssim H	„ D > H

Evidently, the specific hydrogen-ion mechanisms *SH* and *SH'* should distinguish themselves by showing a large acceleration (*e.g.*, by a factor 4) in a deuterium solvent. The general acid mechanism *GA* should have a not much greater rate in a deuterium than in a protium solvent. The only mechanism for which an intermediate behaviour is predicted, which might have led to difficulty of identification, is mechanism *GA'*; but this has already been excluded by Hammond and Grundemeier's investigation.

Results and Discussion.—The results of our comparative measurements of the rate of rearrangement of hydrazobenzene under catalysis by perchloric acid in media made with ordinary water and with deuterium water are assembled in Table 2. They show that the reaction goes four times faster in the deuterium than in the protium solvent. This is an unprecedentedly large factor of increase, one which it would seem impossible to understand, except on the basis of two pre-equilibrium proton-transfers.

TABLE 2. Comparison of first-order rate constants (k_1 in sec.^{-1}) in the rearrangement of hydrazobenzene in the presence of perchloric acid (concn. M) in mixtures of 60 vols. of dioxan with 40 vols. of either water or deuterium oxide at 0°.

H ₂ O-dioxan		D ₂ O-dioxan		Comparison				
[HClO ₄]	10 ⁵ k_1	[DClO ₄]	10 ⁵ k_1	[Acid]	10 ⁵ k_H	10 ⁵ k_D	k_D/k_H	
0.101	1.63	0.104	6.40	0.100	1.60	5.89	3.7	
0.200	7.67	0.195	29.8	0.200	7.67	31.3	4.1	
							Mean	3.9

We conclude that the mechanism of rearrangement of hydrazobenzene in our conditions cannot be one of general acid catalysis, and is very reasonably regarded as one of specific hydrogen-ion catalysis, though we still cannot decide between mechanisms *SH* and *SH'*, *i.e.*, between pre-equilibrium proton-transfer and pre-equilibrium proton-desolvation.

(3) Kinetic Dependence of the Semidine Rearrangement on Acidity

The kinetics of the semidine rearrangement have not previously been determined, although Dewar¹² deduced from a pre-conception concerning the mechanism of benzidine and semidine rearrangements that the latter should distinguish themselves from the former in that semidine changes should show only a first-order kinetic dependence on acid. We have examined the matter in the example of the rearrangement of 4 : 4'-dimethylhydrazobenzene to the *o*-semidine, under catalysis by perchloric acid, in 60% aqueous dioxan at 0°.

¹² Dewar, *Ann. Reports*, 1951, **48**, 126.

Results and Discussion.—The reaction is fast, and we were accordingly restricted to acidities so low that there is no clear distinction between $[H^+]$, and h_0 or h_+ . Therefore we describe our results in terms of the concentration $[H^+]$. The results themselves are in Table 3, and a logarithmic plot of first-order rate constants *versus* acid concentrations is shown in Fig. 3, in which the straight line has a slope of 2.0.

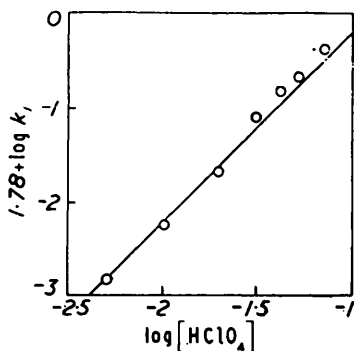


FIG. 3. Rearrangement of 4:4'-dimethylhydrazobenzene by perchloric acid in 60% aqueous dioxan at 0°. Logarithmic plot of the rate constant versus the acid concentration. The slope of the line is 2.0.

From these results it is clear that, contrary to prediction from Dewar's theory, the semidine rearrangement is, not only of first order in the hydrazobenzene, but also of second order in acid. It thus has the same kinetic form as the benzidine rearrangement.

TABLE 3. First-order rate constants (k_2 in sec^{-1}) for the rearrangement of 4:4'-dimethylhydrazobenzene in a solution of perchloric acid (M) in a mixture of 60 vols. of dioxan with 40 vols. of water at 0°.

{ $[HClO_4]$ (M)	0.0051	0.0104	0.0200	0.0309
{ $10^5 k_1$	2.33	8.93	33.3	135.5
{ $[HClO_4]$ (M)		0.0417	0.0515	0.0708
{ $10^5 k_1$		253	365	722

Although this has been checked only at low acidities, it seems likely that it will apply right up the acidity scale. The semidine rearrangement, like the benzidine rearrangement, takes place by way of the second conjugate acid of the hydrazobenzene.

This conclusion is consistent with the suggestion, contained in Brownstein, Bunton, and Hughes's proposed mechanism¹³ of benzidine and semidine rearrangements, that they pursue a common path to, and through, a rate-controlling step, becoming differentiated only later by product-determination in concurrent fast steps. Like the earlier mechanism due to Hughes and Ingold,¹⁴ this new mechanism can accommodate all the facts so far established. Accordingly an attempt is now being made experimentally to distinguish between the two ideas, through the effect of *o*- and *p*-deuteration, particularly the former, on rates and product-ratios, especially the latter.

EXPERIMENTAL

Materials.—Hydrazobenzene, m. p. 125°, and 4:4'-dimethylhydrazobenzene, m. p. 133—134°, prepared by alkaline reduction of the appropriate nitro-compounds, were crystallised from aqueous ethanol until almost colourless, and were stored in desiccators under nitrogen. Bindschedler's Green was prepared as described by Dewar.¹⁵ The solvent was prepared by mixing 60 volumes of purified dioxan with 40 of either water or deuterium oxide. Perchloric acid was made up so that its solvent content had these compositions.

Kinetic Methods.—The procedure was essentially that outlined by Dewar¹⁵ and by Hammond and Shine.² For the slower runs with hydrazobenzene, separate solutions of this

¹³ Brownstein, Bunton, and Hughes, *Chem. and Ind.*, 1956, 981.

¹⁴ Hughes and Ingold, *J.*, 1941, 608.

¹⁵ Dewar, *J.*, 1946, 777.

substance and of perchloric acid were cooled to 0°, and mixed; and then aliquot parts were withdrawn, and added to Bindschedler's Green, the excess of which was subsequently titrated with titanous sulphate. For the faster runs with hydrazobenzene, series of inverted-Y tubes were used. The solutions of hydrazobenzene and of perchloric acid were placed in the separate limbs, cooled to 0°, and mixed by tilting; and the reaction was subsequently stopped by the addition of excess of Bindschedler's Green. All runs with hydrazobenzene gave good first-order rate constants as far as the reaction was followed, in some cases to over 90% of the stoicheiometric total.

The runs with 4:4'-dimethylhydrazobenzene were affected by an appreciable reaction between the formed semidine and the dye. For this reason, only about the first 40% of reaction gave good first-order rate-constants, and it became our practice to accept the rate constants deduced from these first portions of the reaction. The procedure now was to titrate the residual hydrazo-compound with Bindschedler's Green directly.

During all these experiments the Bindschedler's Green, which is somewhat unstable in solution, was titrated at frequent intervals with titanous sulphate.

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