cooled to −40° while 18.1 g. (0.1 mole) of ethyl β-bromopropionate was added dropwise with stirring. A thin slurry of phenylbiguanide, 17.7 g. (0.1 mole), in 40 ml. of methanol was added slowly while the temperature was maintained at −40°. On standing overnight, white crystals separated, 7.2 g. (33.6%), m.p. 241–243°, identical with a known sample of phenylbiguanide hydrobromide, m.p. 241–243°, mixed m.p. 241–243°.

The filtrate was allowed to stand for three to five days and poured into 350 ml. of 10% trichloroacetic acid. A white precipitate separated, 11.0 g. (26.6%), m.p. 138–139°,[12] the trichloroacetic acid salt of I, R = $-CH_2CH_2-O-CH_3$. The free base, 5.9 g. (90.5%), was liberated by the addition of dilute aqueous methanolic alkali, m.p. 116–118°, mixed m.p. 114–118°.[11b,12]

Acknowledgment.—We are grateful to Dr. Louis H. Freedman of the U. S. Vitamin Corporation, Yonkers, N. Y., for his generosity in allowing one of us to use the facilities of their laboratories. We would also like to thank the American Cynamid Company for a generous supply of phenylbiguanide.

BROOKLYN, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Benzidine Rearrangement. IV. Kinetics of the Rearrangement of *o*-Hydrazotoluene[1]

BY ROBERT B. CARLIN AND RAYMOND C. ODIOSO

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The spectrophotometric analytical method was used to study the rate of rearrangement of *o*-hydrazotoluene by hydrogen chloride in 95% ethanol. *o*-Tolidine was shown to be the sole rearrangement product under the imposed conditions. The rate is first order with respect to *o*-hydrazotoluene concentration, but. in contrast with the rearrangements of hydrazobenzene which are second order in acid concentration, the order of participation of acid concentration in the rate expression for the rearrangement of *o*-hydrazotoluene is 1.6. Chloride ion concentration is not involved in the rate expression. Activation energies for the process (18.7, 19.1 and 20.2 kcal./mole) were computed from measurements carried out under three sets of conditions, and an entropy of activation (−0.62 kcal./deg./mole) was calculated; but little significance is attributed to these quantities. There is a positive salt effect on the rate which is similar in magnitude with that observed in investigations of the rearrangements of hydrazobenzene. Increasing the proportion of water in the solvent causes a rate increase, but replacement of part of the ethanol by dioxane effects little change. Arguments are advanced to show that the observations resulting from this investigation can be reconciled with Hammond's proposed reaction sequence for the benzidine rearrangement.

Recent kinetic studies of the acid-catalyzed rearrangements of hydrazobenzene have demonstrated that the reaction rate is first order with respect to hydrazobenzene concentration[2–5] and second order with respect to acid concentration,[3–5] that there is a positive salt effect upon the rate[3,4] which satisfies the Brønsted–Bjerrum equation,[5] that the rate increases steadily with increasing dielectric constant in ethanol–water solutions,[5] that the reactions are subject to general acid catalysis[6] and that the simultaneous rearrangements to benzidine and diphenyline are identical kinetically and substantially free, under the chosen conditions, of side reactions such as disproportionation.[4] In an effort to observe the effects of substituents on the kinetics, a series of investigations of the rates of rearrangements of some substituted hydrazobenzenes has been undertaken. This paper reports the results of a study of the kinetics of the hydrogen chloride-catalyzed rearrangement of *o*-hydrazotoluene (2,2′-dimethylhydrazobenzene).

Using the analytical technique first described by Dewar,[2] Croce and Gettler[5] measured the rates, activation energy, PZ factor and related quantities for the transformation of *o*-hydrazotoluene by hydrogen chloride in 90% ethanol; however, the product or products of the transformation were not disclosed, and the salt and solvent effects and the order of the effect of acid concentration on the rate were not investigated. In the study reported here the spectrophotometric analytical method first used in kinetic measurements of the rearrangements of hydrazobenzene[4] was again employed, so that both the concentration of *o*-hydrazotoluene and that of *o*-tolidine (3,3′-dimethyl-4,4′-diaminobiphenyl), its sole transformation product, could be followed simultaneously. The order in which acid concentration appears in the rate expression was determined, and the salt effect and some observations related to medium effects were recorded.

The solvent chosen for most of the rate runs on *o*-hydrazotoluene was 95% ethanol, in order that the results could be compared justifiably with those from the preceding study of hydrazobenzene,[4] in which the same solvent was used. The ultraviolet extinction curves for *o*-hydrazotoluene and *o*-tolidine were determined in 95% ethanol solution (Fig. 1). Then *o*-hydrazotoluene was subjected to the action of hydrogen chloride in 95% ethanol under the same conditions which were to be used in the rate runs, and the extinction curve for the product solution was identical, within experimental error, with that of *o*-tolidine solutions. Therefore, *o*-tolidine was the sole product under the imposed conditions, and the absence of rearrangements to other isomers and of disproportionation was demonstrated. This observation contrasts with those of previous investigators,[7] who have reported that diphenyline formation and disproportionation accompany the main reaction when *o*-hydrazotoluene is boiled with concentrated hydrochloric acid. The apparent discrepancy undoubtedly can be attributed to the well known effect of change in reaction

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(1) From the D.Sc. Thesis by Raymond C. Odioso.

(2) M. J. S. Dewar, *J. Chem. Soc.*, 777 (1946).

(3) G. S. Hammond and H. J. Shine, THIS JOURNAL, **72**, 220 (1950).

(4) R. B. Carlin, R. G. Nelb and R. C. Odioso, *ibid.*, **73**, 1002 (1951).

(5) L. J. Croce and J. D. Gettler, *ibid.*, **75**, 874 (1953).

(6) M. D. Cohen and G. S. Hammond, *ibid.*, **75**, 880 (1953).

(7) E. Noelting and P. Werner, *Ber.*, **23**, 3252 (1890).

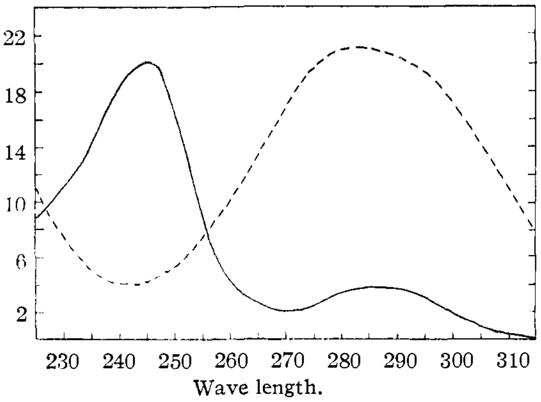

Fig. 1.—The ultraviolet absorption spectra of: —, *o*-hydrazotoluene; - - - - -, *o*-tolidine.

conditions upon the nature and proportions of the transformation products. The *o*-tolidine structure for the rearrangement product of *o*-hydrazotoluene appears to have been proved adequately,[8] and the close similarity between its extinction curve and that for benzidine[4] can be considered confirmatory evidence.

The spectrophotometric analytical method was prepared and used in the same way which had proved successful in the study of the rearrangements of hydrazobenzene.[4] The two wave lengths 245 and 285 mμ were selected for measurement of optical densities leading to the analysis of mixtures of *o*-hydrazotoluene and *o*-tolidine. These wave lengths, which correspond to the absorption maxima for the two compounds (Fig. 1), satisfy all three fundamental requirements for satisfactory analytical wave lengths.[4] Optical density *vs.* concentration plots for each component in 95% ethanol at each wave length showed that Beer's law was being obeyed in all cases; Fig. 2 shows the two plots for *o*-hydrazotoluene. The slopes of these plots yielded the extinction coefficients (Table I) which were used in the two equations from which the analytical results were computed for each mixture. The development and use of the equations based on these data followed the procedures reported in the preceding article.[4] Ten analyses by this method of known mixtures of *o*-hydrazotoluene and *o*-tolidine in which the composition varied between 20 and 80% in one component gave results having the average deviation 0.82% from the known. The method is thus substantially more accurate with these mixtures containing but two components than it was with mixtures formed by the rearrangements of hydrazobenzene, in which three components were present.

TABLE I

SPECIFIC EXTINCTION COEFFICIENTS

Compound	245 mμ	285 mμ
o Hydrazotoluene	95.0	19.0
o-Tolidine	18.6	103.0

Experimental

***o*-Hydrazotoluene.**—A vigorously stirred mixture of 120 g. of zinc dust, 68 g. of *o*-nitrotoluene and 300 ml. of methanol was treated dropwise with 250 ml. of 30% aqueous sodium hydroxide, and the mixture was boiled for several hours. Most of the methanol was removed by distillation, and the solids were collected by filtration and extracted with hot ethanol. The ethanol extracts were concentrated and treated first with 50 ml. of concentrated aqueous ammonia and then with hydrogen sulfide until the red color of the solution disappeared. The pale yellow crude *o*-hydrazotoluene (26 g., 50%), m.p. 158–162°, which crystallized from solution throughout the hydrogen sulfide treatment, was removed from time to time. Recrystallization of the crude material from petroleum ether yielded white flakes, m.p. 165°, in agreement with the reported value.[9] For spectral measurements the white material was recrystallized from petroleum ether until the extinction curve became constant.

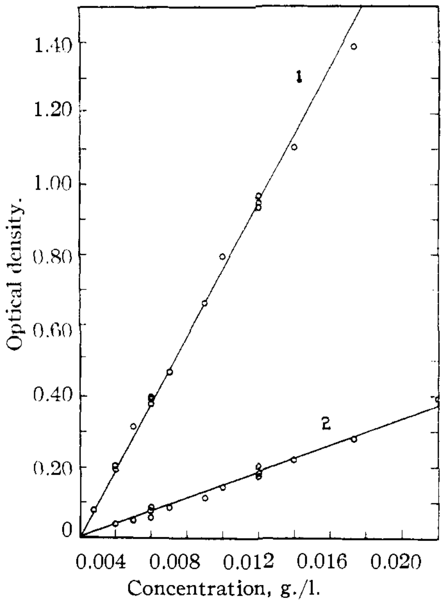

Fig. 2.—Verification of validity of Beer's law and determination of extinction coefficients for *o*-hydrazotoluene at (1) 245 mμ, and (2) 285 mμ.

o-Tolidine (Eastman Kodak Co.) was purified by allowing its benzene solution to trickle through a 12 × 1 cm. column of activated alumina and then crystallizing from benzene–petroleum ether. This process was repeated, and the white crystals, m.p. 131–132°,[10] were recrystallized until the extinction curve was constant. The **N,N′-diacetyl** and **N,N′-bis-salicylal derivatives** had the m.p's. 318–319°[11] and 202°,[12] respectively.

Dioxane was purified by the method given by Fieser.[13] Other solvents, reagents and solutions and the apparatus and experimental procedures were the same as those used in the work on hydrazobenzene.[4] Pseudo first-order rate constants were computed from the good linear plots of log (100/% unchanged *o*-hydrazotoluene) *vs.* time in minutes; 10 to 18 points determined the slope of each line. A plot of the data from a typical run (no. 11) is shown in Fig. 3.

Results

In Table II the data from 26 rate runs are listed. At least two independent runs were carried out under each of the majority of sets of experimental conditions. A comparison of runs 1–3 and 6–10 shows the effect of varying the acid concentration at constant temperature and ionic strength. A plot of log k_1 *vs.* log [HCl] using the data from

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[8] G. Schultz, G. Rhode and F. Vicari, *Ann.*, **352**, 111 (1907).

[9] H. Petriew, *Ber.*, **6**, 557 (1873).

[10] A. L. Guitermann, *ibid.*, **20**, 2016 (1887), reported the m.p. 129°.

[11] G. Schultz, *ibid.*, **17**, 463 (1884), reported the m.p. 315°.

[12] H. Schiff and A. Vani, *Ann.*, **258**, 377 (1890), reported the m.p. 202°.

[13] L. F. Fieser, "Experiments in Organic Chemistry," Second Ed., Part II, D. C. Heath and Co., New York, N. Y., 1941, p. 369.

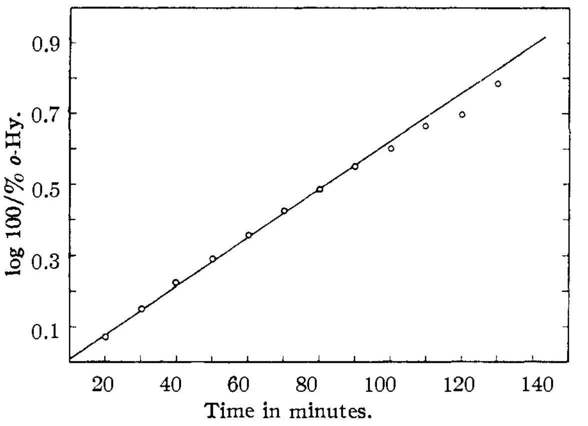

Fig. 3.—Determination of pseudo first-order rate constant for rate run no. 11.

these runs is shown in Fig. 4; the experimentally determined points correspond to a linear relationship having the slope 1.60. It is therefore clear that the rearrangement rate is not second order with respect to hydrogen chloride concentration, as is the rate of rearrangements of hydrazobenzene under identical conditions; rather, the order of involvement of acid concentration in the rate expression is 1.6 in this case. Therefore, $k_{exp} = k_1[HCl]^{1.6}$.

TABLE II

REARRANGEMENT OF *o*-HYDRAZOTOLUENE (1.18×10^{-3} *M*) BY HYDROGEN CHLORIDE

Run no.	Temp., °C.	[HCl] mole/l.	Total ionic strength[a]	$k_1 \times 10^2$, min.$^{-1}$
1	14.60	0.1020	0.1020	4.61
2	14.60	.1020	.1020	4.74
3	14.60	.1020	.1020	4.97
4	14.60	.0510	.0510	1.15
5	14.60	.0510	.0510	1.11
6	14.60	.0510	.1020	1.61
7	14.60	.0510	.1020	1.59
8	14.60	.0765	.1020	2.99
9	14.60	.0892	.1020	3.85
10	14.60	.0340	.1020	0.875
11	14.60	.0510	.0850	1.54
12	14.60	.0510	.0680	1.41
13	25.00	.0510	.0510	4.42
14	25.00	.0510	.0510	4.44
15	25.00	.1020	.1020	16.1
16	25.00	.1020	.1020	15.8
17	0.00	.1020	.1020	0.822
18	.00	.1020	.1020	.821
19	.00	.0510	.0510	.192
20	.00	.0510	.0510	.196
21[b]	25.00	.0510	.0510	13.7[b]
22[c]	25.00	.0510	.0510	4.72[c]
23	25.00	.0510	.1020	5.06
24	25.00	.0510	.1020	5.26
25	0.00	.0510	.1020	0.276
26	0.00	.0510	.1020	0.292

[a] Lithium chloride was used to increase the ionic strength of those solutions whose total ionic strength exceeds that owing to hydrogen chloride. [b] Solvent 75:25 ethanol-water. [c] Solvent 75:25 ethanol-dioxane.

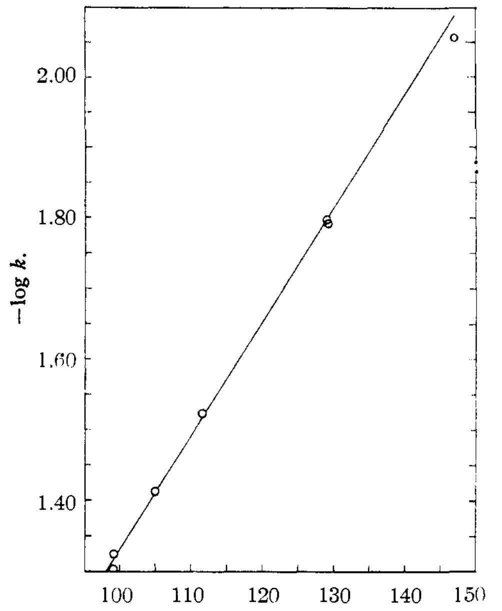

Fig. 4.—*o*-Tolidine: effect on pseudo first-order rate constant of varying acid concentration at constant ionic strength and temperature. Since slope of line = 1.60, it follows that $k_{exp.} = k_1[HCl]^{1.6}$.

It is also clear from the results of runs 1–3 and 6–10, in which chloride ion concentration as well as ionic strength were held constant, that the observed rate increase is solely a function of acid concentration. The implication thus derived that chloride ion concentration is not involved in the rate expression receives substantial support from the data from runs 4–7 and 11 and 12, in which the acid concentration and temperatures were held constant while the ionic strength was varied by the addition of lithium chloride. Although the rate increased with increasing lithium chloride concentration, the relationship was not linear with respect to chloride ion concentration, and a twofold increase in chloride ion concentration caused a rate increase of only about 50%.

Plots of log k_1 *vs.* $1/T$ afforded activation energies (E^a) under three sets of conditions, so that a qualitative evaluation of the effects on E^a of changes in acid strength and in ionic strength was possible. A plot of the data from runs 1–3 and 15–18 is shown in Fig. 5; the slope of the straight line, determined by the method of least squares, corresponds to an activation energy of 19.1 kcal./mole. Since the rate measurements from which this figure was derived were made in solutions 0.1020 *M* in hydrogen chloride which contained no other electrolyte, the value may be compared with 20.6 kcal./mole, which was the E^a value for the rearrangements of hydrazobenzene derived from rate measurements carried out in solutions of the same electrolyte and solvent composition.[4] Data from runs 4, 5, 13, 14, 19 and 20 yielded in a similar way E^a = 18.7 kcal./mole for solutions 0.0510 *M* in hydrogen chloride which contained no other electrolyte. Data from runs 6, 7 and 23–26 led to E^a = 20.2 kcal./mole for solutions 0.0510 *M* in hydrogen chloride in which the total ionic strength was made 0.1020 by addition of lithium chloride. When the value 19.1 kcal./mole for E^a and the rate constant k_{exp} ($= k_1/[HCl]^{1.6}$)

from run 15 were substituted into the equation[14]

$$k_{\text{exp}} = (ekT/h)e^{-E^{a}/RT}e^{\Delta S^{\ddagger}/R}$$

$\Delta S^{\ddagger}$ was calculated to be -0.62 cal./mole deg. This value was obtained from runs carried out in solutions of the same electrolyte and solvent composition as those from which $\Delta S^{\ddagger} = 2.9$ cal./mole deg. was computed for the rearrangements of hydrazobenzene.[4]

The E^{a} values calculated from the work reported here agree well with the figure 19 kcal./mole reported by Croce and Gettler.[5] Their value of 1.3 cal./mole deg. for $\Delta S^{\ddagger}$ may at first glance seem significantly different from ours; however, when consideration is given to the fact that their k_3 $(= k_1/[\text{HCl}]^2)$ from which presumably they computed their $\Delta S^{\ddagger}$ value is of a different nature from the $k_{\text{exp}}(= k_1/[\text{HCl}]^{1.6})$ from which our value was derived, the discrepancy has no meaning.

A comparison of the rate constants from runs 4–7 and 11 and 12, wherein the acid concentration was held constant while the ionic strength of the solutions was varied, shows that the rate of rearrangement of *o*-hydrazotoluene, like that of hydrazobenzene, is subject to a positive salt effect. When hydrazobenzene and *o*-hydrazotoluene rates derived from runs carried out in solutions of identical electrolyte and solvent composition are compared, the magnitudes of the salt effects on the two rates are found to be very similar. A plot of log k_1 *vs.* $\sqrt{\mu}$, where μ is the ionic strength, using the data from runs 4–7 and 11 and 12, is not linear, in conformity with the Brønsted–Bjerrum equation ($\log k = \log k_0 + Z_{\text{A}}Z_{\text{B}}A'\sqrt{\mu}$) but is a curve of decreasing slope. The slope of the curve in the region of the experimental points corresponding to the smallest ionic strengths (runs 4 and 5) was about 3.4. When this figure is divided by the value 1.6 calculated for A' $(= 2A/2.303)$ from the defining equation for A[15] and dielectric constant data for 95% ethanol, the quotient, which is the ion charge product $Z_{\text{A}}Z_{\text{B}}$, is found to be about 2. Because there is no assurance that the slope 3.4 used in these calculations approximates the limiting slope, and because the application of expressions derived from the Debye–Hückel limiting law to solutions of such comparatively high ionic strength in a medium of such low-dielectric constant is of doubtful validity, the significance of the value 2 for $Z_{\text{A}}Z_{\text{B}}$ is questionable. Likewise, the apparent contradiction between the value 2 obtained in this work and the value 1 from the work of Croce and Gettler[5] may have little meaning. It does seem safe to conclude from studies of the salt effect on the rate of the rearrangements of hydrazobenzene and of *o*-hydrazotoluene that the reaction in the sequence which is most responsive to changes in ionic strength involves two ions of like sign.

The solvent in run 21 was 75:25 ethanol–water and in run 22 it was 75:25 ethanol–dioxane. When the rate constant from run 21 is compared with those from runs 13 and 14, which were carried out under the same conditions of temperature, ionic strength and acid concentration, it is apparent that an increase in the proportion of water in the solvent (and consequently in the dielectric constant) causes a marked increase in the reaction rate. This observation parallels those of Croce and Gettler,[5] who studied in more detail the relationship between the rate constant and the dielectric constant in the rearrangements of hydrazobenzene in ethanol–water solutions. The rate constant from run 22 is greater than those from runs 13 and 14 by a small but significant margin. If the only effect of medium on reaction rate were that caused by changes in the macroscopic dielectric constant, then, as long as the rate increases when the solvent is changed from 95% ethanol to 75:25 ethanol–water, the rate should decrease when the change is to 75:25 ethanol–dioxane. That no such rate decrease is observed constitutes evidence that medium effects are involved other than those owing to the macroscopic dielectric constant.

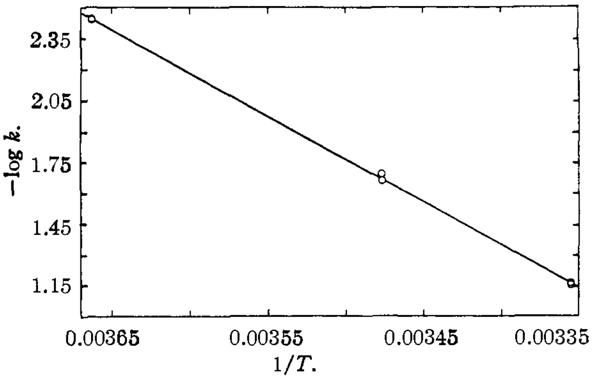

Fig. 5.—*o*-Tolidine: plot from which activation energy (E^{a}) of 19.1 kcal./mole was computed from rate measurements made in solutions 0.1020 *M* in hydrogen chloride, the only electrolyte.

In this work, as in the rearrangements of hydrazobenzene,[4] the reproducibility of the individual rate constants was considered to be the measure of precision. For nine rate constants, each of which was measured in two or more independent runs, the average deviation from the mean was 1.3%, and the greatest deviation from the mean was 2.8%. The errors thus introduced into the E^{a} and $\Delta S^{\ddagger}$ values are of the order 125 cal./mole and 0.70 cal./mole-deg., respectively[16]; consequently, the differences among the three E^{a} values derived from measurements made under varying solution conditions probably are indicative of real differences, rather than of statistical variation in observations.

Discussion

The fact that acid concentration is present to the 1.6 power, rather than to the second power, in the rate expression for the rearrangement of *o*-hydrazotoluene under the conditions imposed in this work certainly makes it unjustifiable to assume second-order dependence on acid concentration of the rates of rearrangement of all substituted hydrazobenzenes. Until enough substituted hydrazobenzenes have been examined to permit the deduction of generalizations concerning the relationships be-

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[14] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 197.

[15] E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 25.

[16] F. P Price, Jr., and L. P. Hammett, THIS JOURNAL, **63**, 2387 (1941).

tween structure and acid concentration order, the order will have to be determined for each hydrazo compound which is newly subjected to kinetic measurement.

The mixed order of acid concentration involvement in the rate expression for the rearrangement of *o*-hydrazotoluene may be interpreted in terms of the reaction sequence proposed by Hammond and Shine.[3]

$$C_6H_5NHNHC_6H_5 + H^+ \rightleftarrows C_6H_5\overset{+}{N}H_2NHC_6H_5 \qquad (1)$$

$$C_6H_5\overset{+}{N}H_2NHC_6H_5 + H^+ \rightleftarrows C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 \qquad (2)$$

$$C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 \longrightarrow H_2NC_6H_4C_6H_4NH_2 + 2H^+ \qquad (3)$$

In the preceding publication of this series[4] the expression 4 was indicated to be derivable from the reaction sequence 1–3 and the assumptions (a) that reaction 3 is slow and 1 and 2 rapidly reversible and (b) that acid concentration is effectively constant. In equation 4, $[\mathrm{Hy}]_0^{\mathrm{obs}}$ and $[\mathrm{Hy}]^{\mathrm{obs}}$ are the observed concentrations of unchanged hydrazobenzene at zero time and at time t, respectively, %Hy is the per cent. observed unchanged hydrazobenzene after time t, and K_1, K_2 and k_3 are the equilibrium and rate constants for the corresponding numbered steps in the reaction sequence. A similar expression 5 can be derived from the same reaction sequence, the constancy of acid concentration, and the assumption, based on Hammond's recent observations,[3,6] that step 2 is slow in the forward direction and step 3 rapid.

$$\ln [\mathrm{Hy}]_0^{\mathrm{obs}}/[\mathrm{Hy}]^{\mathrm{obs}} = \ln 100/\%\mathrm{Hy} = \frac{K_1K_2k_3[\mathrm{H}^+]^2}{1 + K_1[\mathrm{H}^+] + K_1K_2[\mathrm{H}^+]^2}\, t \qquad (4)$$

$$\ln [\mathrm{Hy}]_0^{\mathrm{obs}}/[\mathrm{Hy}]^{\mathrm{obs}} = \ln 100/\%\mathrm{Hy} = \frac{K_1k_2[\mathrm{H}^+]^2}{1 + K_1[\mathrm{H}^+]}\, t \qquad (5)$$

(k_2 is the rate constant for the second step). Because the third term in the denominator of the right-hand member of equation 4 is almost certainly negligibly small compared to the second term, equations 4 and 5 have the same essential form. Still another equation of the same form can be derived on the assumption that both steps 2 and 3 are slow but that the reverse of step 2 is rapid. All of these equations reduce to the form 6. It is clear from 6

$$\ln 100/\%\mathrm{Hy} = \frac{C[\mathrm{H}^+]^2}{1 + K_1[\mathrm{H}^+]}\, t \qquad (6)$$

where C is a constant, composed of equilibrium and rate constants, that if $K_1[\mathrm{H}^+] \ll 1$, then the pseudo first-order rate constant $k_1 = C[\mathrm{H}^+]^2$; but if $K_1[\mathrm{H}^+] \gg 1$, then $k_1 = C'[\mathrm{H}^+]$, so that the rate will be dependent upon the square of the acid concentration in one instance and on its first power in the other. However, should $K_1[\mathrm{H}^+]$ be of the order of unity, then an order of dependence on acid concentration between 1 and 2 might be observed. Inasmuch as the rate of rearrangement of hydrazobenzene has been shown to be second order in acid concentration in the same short range of acid concentration and under the same solution conditions which obtain when the rate of rearrangement of *o*-hydrazotoluene shows a 1.6 order of dependency on this quantity, the foregoing interpretation requires that K_1 for *o*-hydrazotoluene be greater than that for hydrazobenzene and that $K_1[\mathrm{H}^+] \cong 1$ for *o*-hydrazotoluene, while $K_1[\mathrm{H}^+] < 1$ for hydrazobenzene. Since $K_1 = K_b/K_s$, where K_b is the base dissociation constant and K_s the ionic dissociation constant for the solvent, the first requirement is that *o*-hydrazotoluene must be a stronger base than hydrazobenzene. Consideration of the polar effects of methyl groups does not make this condition appear altogether unreasonable, despite the fact that aniline is very slightly more basic in water solution ($pK_b = 9.42$) than is *o*-toluidine ($pK_b = 9.48$). The second requirement of this interpretation, that $K_1[\mathrm{H}^+] \cong 1$ for *o*-hydrazotoluene or, in other words, that K_b be within about an order of magnitude of K_s, also appears reasonable in view of Dewar's estimate that pK_b for hydrazobenzene should be about 14 (presumably in water).[2] Unfortunately, no quantitative information about K_b for any aromatic hydrazo compound appears to have been published. Thus, the occurrence of acid concentration to the 1.6 power in the rate expression for the rearrangement of *o*-hydrazotoluene can be reconciled with Hammond's reaction sequence, within the limits of the information now available.

If the postulate is correct that the 1.6 order of rate dependency on acid concentration is associated with the proximity to unity of $K_1[\mathrm{H}^+]$, then it follows that a change of acid concentration in the solutions by a factor of ten should produce a substantial change in the observed order. An attempt will be made to put this possibility to experimental test.

Attention has already been drawn to the fact that E^a and $\Delta S^\ddagger$ for the rearrangement of hydrazobenzene cannot at present be related to the activation energy and entropy for the rearrangement step in the reaction sequence.[4] The same uncertainty concerning the meaning of these quantities also is obtained in the *o*-hydrazotoluene rearrangement. Moreover, in the latter case another complication arises from the mixed order of acid concentration in the rate expression. If the interpretation of this mixed order given in the preceding paragraph is correct, then, for the rearrangement of hydrazobenzene $k_1 = C[\mathrm{H}^+]^2$, where C is derived from equation 6 while, for the rearrangement of *o*-hydrazotoluene, $k_1 = C[\mathrm{H}^+]^2/(1 + K_1[\mathrm{H}^+])$. In the former case the observed activation energy and entropy may be related to the rate and equilibrium constants which compose C, but in the latter case no such simple relationship exists. It follows, then, that because of the differing values of the order of acid concentration in the rate expressions for the two rearrangements, there is little known basis for a comparison of the two sets of E^a and $\Delta S^\ddagger$ value.

Finally, the observed positive salt effect on the rate of rearrangement of *o*-hydrazotoluene and the rate increase which occurs when the proportion of water in the ethanol–water solvent is increased are consistent with Hammond's postulate that the slow step in the reaction sequence involves the interaction of two ions of like sign.

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