**Ornithine dipicrate** was prepared from the hydrochloride in aqueous solution, m.p. 196–197°; reported, m.p. 195.5–196.5°.[15]

**Ethyl *p*-Methoxybenzylacetamidocyanoacetate (V).**—The ester, I, 850 mg., was dissolved in 5 ml. of absolute ethanol in a 100-ml. 3-neck flask equipped with a mercury-sealed stirrer, reflux condenser and dropping funnel. A solution of 119 mg. of sodium in 5 ml. of ethanol was added and the reaction mixture was cooled to room temperature. From a graduated dropping funnel, 0.79 ml. of *p*-methoxybenzyl bromide[16] (density 1.41) was added dropwise, with cooling. After stirring for 2 hours at room temperature, the slurry was diluted with 10 ml. of water. The product, V, weighed 1.39 g. (96%), m.p. 169.5–170.5°. An analytical sample, from dilute alcohol, melted at 170.0–171.0°.

*Anal.* Calcd. for $C_{15}H_{18}N_2O_4$: C, 62.05; H, 6.25. Found: C, 62.0; H, 6.3.

Substitution of the *p*-methoxybenzyl chloride for the bromide reduced the yield of V to 85%.

***dl*-Tyrosine-2-C-14.**—The ester, V, 1.39 g., was boiled under reflux in 15 ml. of 48% hydrobromic acid for 4 hours. After distillation of the excess acid *in vacuo*, the residue was dissolved in 5 ml. of water and filtered through a charcoal bed. A slight excess of ammonium hydroxide was added and then a slight excess of acetic acid. The tyrosine, washed with water and ethanol, weighed 827 mg. (95%), dec. 303–304° (evacuated tube).

*Anal.* Calcd. for $C_9H_{11}NO_3$: C, 59.66; H, 6.12. Found: C, 59.7; H, 6.2.

A similar hydrolysis of V with concd. hydrochloric acid in a sealed tube at 160° for 3 hours also gave *dl*-tyrosine in 95% yield.

**Dibenzoyl *dl*-tyrosine**, prepared in dilute sodium hydroxide solution,[17] melted at 208–209° after crystallization from glacial acetic acid; reported m.p. 213–214°.[17]

Boston, Mass. Received September 11, 1950

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[15] N. F. Albertson and S. Archer, This Journal, **67**, 2043 (1945).

[16] H. Stephen and C. Weizmann, *J. Chem. Soc.*, 1152 (1914).

[17] R. B. Loftfield, This Journal, **72**, 2499 (1950).

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[Contribution from the Departments of Chemistry, University of Rochester and Carnegie Institute of Technology]

# The Benzidine Rearrangement. III. Kinetics of the Rearrangements of Hydrazobenzene

By Robert B. Carlin, Robert G. Nelb and Raymond C. Odioso

A spectrophotometric method of analysis has been developed by means of which the concurrent rearrangements of hydrazobenzene to benzidine and diphenyline have been followed. Rate constants and energy (20.6 kcal./mole) and entropy (2.9 e.u. at 25°) of activation have been determined for the total process; and the second order dependency of the rate on acid strength, as well as a positive salt effect on the rate, have been confirmed. The benzidine-to-diphenyline product ratio (70:30) has been shown to be independent of temperature, acid concentration and total ionic strength, within the limits investigated. The fallacy of attempting to relate observed activation energy and entropy to the rearrangement step in the reaction sequence without further information is pointed out. Evidence is presented to support the belief that the benzidine rearrangement may occur in the solid state.

## Introduction

Although a thorough kinetic study of the benzidine rearrangement has long been recognized as necessary to an understanding of this transformation, experimental difficulties have limited the number and scope of investigations in this field. Van Loon[1] followed the rate of formation of benzidine in several solvent combinations and in the presence of various acids. His results suggested that benzidine formation is first order in hydrazobenzene concentration and second order in oxonium ion concentration. In more recent work, the rate of consumption of hydrazobenzene has been followed. Biilman and Blom[2] used an electrometric method to measure the rates of rearrangements of two *p,p'*-disubstituted hydrazoanilines, but their method was not readily adaptable to studies of simpler aromatic hydrazo compounds. Dewar[3] devised a new analytical scheme which enabled him to determine rates of and Arrhenius activation energies for the rearrangements of hydrazobenzene and of three symmetrically substituted hydrazobenzenes. Recently, Hammond and Shine[4] pointed out that Dewar's interpretations of his results do not take into account the involvement of acid concentration in the rate expression. Using Dewar's analytical method, Hammond and Shine have firmly established the second order dependency of the rate of consumption of hydrazobenzene on acid concentration and have observed a positive salt effect on the rate. They have also perceived that mechanisms for the rearrangement step which have been proposed in recent years[5-8] all are based on the assumption that the rearranging species is the first conjugate acid of hydrazobenzene. It is difficult to adjust any of these formulations to accommodate the indications, derived from kinetic studies,[1,4] that the second conjugate acid undergoes rearrangement.

In no kinetic investigation thus far reported has it been possible to obtain information about both of the concurrent rearrangement reactions which occur when hydrazobenzene is treated with acids. Although it is well known that diphenyline (2,4'-diaminobiphenyl) is formed in appreciable amounts along with benzidine, limitations imposed by the analytical methods used to follow the progress of the reactions restricted all studies either to the sum of the rates of all reactions (consumption of hydrazobenzene) or to the rate of formation of benzidine alone. Thus, even though the over-all reaction is now known to be approximately second

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[1] Van Loon, *Rec. trav. chim.*, **23**, 62 (1904).

[2] Biilman and Blom, *J. Chem. Soc.*, **125**, 1719 (1924).

[3] Dewar, *ibid.*, 777 (1946).

[4] Hammond and Shine, This Journal, **72**, 220 (1950).

[5] Robinson, *J. Chem. Soc.*, 220 (1941).

[6] Hughes and Ingold, *ibid.*, 606 (1941).

[7] Hammick and Mason, *ibid.*, 638 (1946); 1938 (1949).

[8] Dewar, *Nature*, **176**, 784 (1945); *J. Chem. Soc.*, 406 (1946); "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 233–240.

order in acid concentration, the possibility could not be excluded that diphenyline formation, which occurs to a much smaller extent than benzidine formation, might be of a different order in acid without affecting the total reaction order beyond the limits of the appreciable experimental errors. The use of spectrophotometric methods of analysis appeared to offer a possible solution to the problem of following the concentrations of hydrazobenzene and its various rearrangement and disproportionation products throughout the course of the reaction. In this paper, a spectrophotometric method of analysis is described which permits concentrations of hydrazobenzene, benzidine and diphenyline to be determined at any time during the reaction. Rates of rearrangement in homogeneous solution in 95% ethanol at three temperatures are reported, the activation energy and entropy for the total process have been calculated, the second order dependency of both rearrangement reactions on hydrochloric acid concentration has been confirmed, and the positive salt effect on the over-all reaction rate, reported by Hammond and Shine,[4] has now been observed on the rates of each of the two rearrangement reactions.

In order to evaluate the feasibility of analyzing the reaction mixtures spectrophotometrically, the ultraviolet absorption spectra of benzidine, diphenyline, hydrazobenzene, azobenzene and aniline were determined through the region 220–320 mμ (Fig. 1). Redetermination of most of these curves was considered necessary because of the lack of agreement among literature reports. The spectrum of diphenyline, however, does not appear to have been published previously. When preliminary rearrangements of hydrazobenzene were carried out under the conditions to be used in the main runs and when the spectra of the reaction mixtures were examined, no evidence of significant amounts of disproportionation products (azobenzene and aniline) was found. The occurrence of an absorption band for azobenzene with a maximum near 320 mμ, in a region where the other components give comparatively weak absorption, facilitated this phase of the investigation. The analytical problem was then confined to the development of a scheme for analyzing solutions containing hydrazobenzene, benzidine and diphenyline. The analysis of a three-component mixture requires that optical densities of its solution be measured at three wave lengths. For best results, these wave lengths should be so chosen that (a) the extinction coefficients of the components differ considerably at each wave length, (b) the ratios of the extinction coefficients vary with the wave lengths chosen, and (c) steep sections of the extinction curves of the components be avoided. Examination of Fig. 1 discloses no set of three wave lengths which satisfies these conditions. Consequently, analyses of solutions of known mixtures were attempted, using several sets of more or less empirically chosen wave lengths. The best and most consistent results were obtained when analysis was based upon optical density readings taken at 245, 270 and 285 mμ. The extinction coefficients for each of the three components at each of these three wave lengths were computed from the slopes of the best straight lines derived from plots of optical density *vs.* concentration. In Fig. 2 these plots for diphenyline are shown. In all cases, the fact that the best straight line passed through the origin showed that Beer's law is obeyed. The values for the specific extinction coefficients used for analysis of the mixtures are shown in Table I.

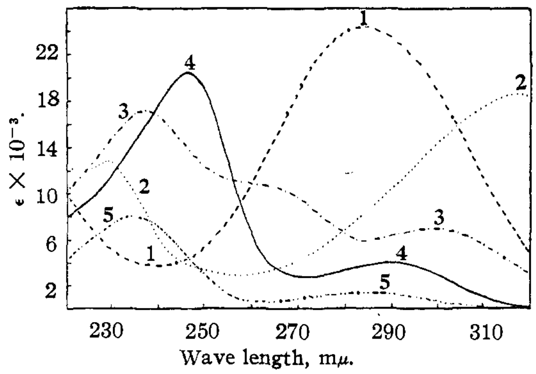

Fig. 1.—The ultraviolet absorption spectra of: 1, -------, benzidine; 2, ..........., azobenzene; 3, -.-.-.-, diphenyline; 4, ——, hydrazobenzene; 5, --·--·--, aniline.

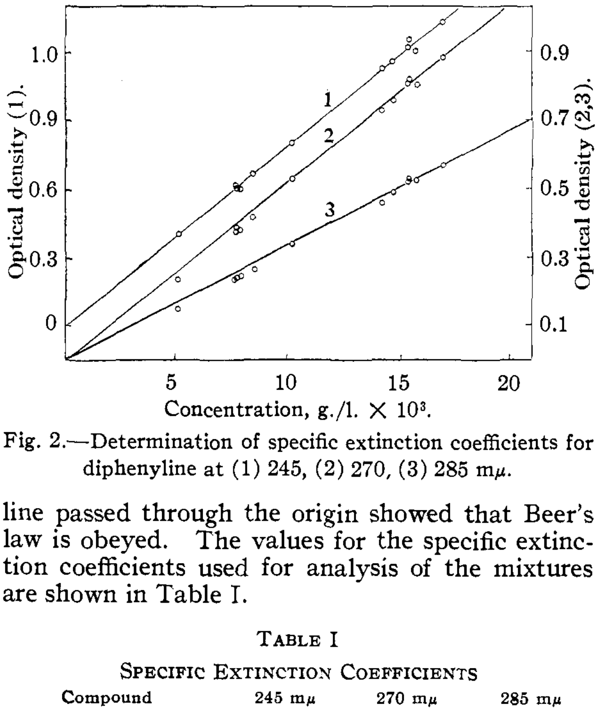

Fig. 2.—Determination of specific extinction coefficients for diphenyline at (1) 245, (2) 270, (3) 285 mμ.

TABLE I

SPECIFIC EXTINCTION COEFFICIENTS

| Compound | 245 mμ | 270 mμ | 285 mμ |
|---|---|---|---|
| Benzidine | 22.0 | 101.9 | 134.5 |
| Diphenyline | 79.2 | 52.0 | 32.2 |
| Hydrazobenzene | 110.0 | 12.9 | 19.2 |

From the equation

$$D_{245} = 22.0[\mathrm{B}] + 79.2[\mathrm{D}] + 110.0[\mathrm{Hy}]$$

(where $D_{245}$ is the optical density of the solution determined at 245 mμ, and [B], [D] and [Hy] represent the concentrations of benzidine, diphenyline and hydrazobenzene, respectively) and the two analogous equations for the optical densities at 270 and 285 mμ, [B], [D] and [Hy] were calculated for each sample. Because the results were to be used in the determination of pseudo first order rate constants, in the computation of which concentration ratios, rather than absolute concentrations, are employed, it was convenient to express them in terms of per cent. of charged hydrazobenzene, *e.g.*, $\%B = 100[B]/([B] + [D] + [Hy])$.

## Experimental[9]

**Materials.**—The "spectroscopic" **ethanol** used in the early part of this work was stock 95% ethanol which had been purified by the method of Leighton, Crary and Schipp.[10] Later, a substantial supply of stock ethanol became available which was indistinguishable from the "purified" solvent in the spectrophotometer, and substitution of this ethanol for "purified" ethanol did not affect the observed reaction rates. Hereafter, all references to "ethanol" used in the preparation of solutions to be employed in the rate runs will mean this "spectroscopic" ethanol.

**Hydrazobenzene** was purified by recrystallization from petroleum ether (b.p. 60–110°) until the absorption spectrum was constant; pure white crystals, m.p. 128°.

**Benzidine** (Eastman Kodak Co.) was dissolved in benzene and the solution decolorized by permitting it to flow through two 2-cm. columns of activated alumina and then concentrated until crystallization occurred on cooling. The product was recrystallized alternately from ethanol and from benzene until its absorption spectrum was constant; white crystals, m.p. 128°.

**Diphenyline.**—A solution of 5.12 g. of 2,4'-dinitrobiphenyl[11] in 100 ml. of benzene was treated with 0.25 g. of Adams catalyst, and the mixture shaken at room temperature for 3 hours under hydrogen at 40 lb./sq. in. The benzene solution of the product was dried ("Drierite") and treated with dry hydrogen chloride until precipitation of diphenyline dihydrochloride was complete. After drying at 80°, this material (yield 4.00 g., 75%) was dissolved in the minimum amount of distilled water and the solution was stirred vigorously as it was made just alkaline by the dropwise addition of 10% aqueous sodium hydroxide. After a day at 0°, the solution deposited 0.66 g. of white crystals, m.p. 51.5–52°. Recrystallization from petroleum ether (principally of b.p. 30–60°, with a little of b.p. 60–110°) gave white crystals, m.p. 54–54.5°. Further recrystallization changed neither the m.p. nor the absorption spectrum of this material. The m.p. 45° has been reported.[12]

*Anal.* Calcd. for $C_{12}H_{12}N_2$: C, 78.2; H, 6.6. Found: C, 78.4; H, 6.4.

**N,N'-Diacetyldiphenyline**, prepared in the usual way from diphenyline, had the m.p. 202–202.5°, in agreement with reported[12a,b] values.

**Aniline** was purified first by drying over potassium hydroxide and then by fractionation over zinc dust. The fraction selected for use had the b.p. 183°; $n^{22}D$ 1.5853.

**Azobenzene** (Eastman Kodak Co.) was recrystallized from ethanol until its absorption spectrum remained constant; red crystals, m.p. 68–68.5°.

**Ethanolic hydrogen chloride** was prepared by dissolving dry hydrogen chloride in ethanol. More concentrated solutions were diluted to about 0.32 *M* with ethanol and were standardized immediately preceding each rate run against aqueous sodium hydroxide of known concentration.

**Ethanolic Sodium Hydroxide.**—Concentrated solutions of sodium hydroxide in ethanol were filtered free of insoluble carbonates and diluted to 0.5–0.6 *M* with ethanol. These solutions were protected from atmospheric carbon dioxide during storage and were standardized before each rate run against aqueous hydrochloric acid of known concentration.

**Procedure.**—The reaction vessel was provided with a brass bearing seal stirrer and attached glass apparatus which allowed nitrogen to be supplied to the reaction mixture at all times. Before it entered the reaction zone, the nitrogen was dried, freed of oxygen and then passed through ethanolic hydrogen chloride of the same concentration and at the same temperature as that being employed in the reaction. Slightly greater than atmospheric pressure was maintained in the apparatus for use in charging solutions into the reaction vessel or in removing samples from it during the run. Stopcocks in the system were lubricated with Dow-Corning Highvac Silicone grease, of which no component absorbing radiation in the 220–320 mμ region dissolved in ethanol. Except for the 0° runs, the reaction vessel was immersed in a kerosene-bath in which the temperature was controlled to ±0.01°.

A solution of 0.0500 g. of hydrazobenzene in exactly 25 ml. of ethanol was charged into the apparatus and then diluted with sufficient ethanol or ethanolic lithium chloride so that the total volume of solution would be 200 ml. after the requisite measured amount of 0.32 *M* ethanolic hydrogen chloride was added to start the reaction. The solution was stirred and allowed to reach bath temperature before the previously thermostated ethanolic hydrogen chloride was charged. Zero time was set at the beginning of the charging of the acid. At appropriate time intervals, 1.5–2.0-ml. samples were forced under nitrogen pressure from the reaction flask into a roughly calibrated test-tube. The delivery apparatus attached to the reaction flask was so arranged that solution remaining in the delivery tube after sampling could be forced under nitrogen pressure either out of the tube or back into the reaction flask. From the test-tubes 1-ml. portions were pipetted into 25-ml. volumetric flasks which contained sufficient ethanolic sodium hydroxide to neutralize the acid and stop the reaction. The time of sampling was taken at the instant when the sample began to flow from the 1-ml. pipet. Test-tubes and pipets employed in the transfer of 0° samples were chilled before use. Within a half-hour after neutralization of the samples and dilution to the mark of the volumetric flask with ethanol, the optical densities of the solutions were measured in calibrated quartz cells at 245, 270 and 285 mμ with a Beckman quartz spectrophotometer, model DU. The concentrations of organic solutes were so adjusted that the measured optical densities were maintained within the limits 0.2–1.0, the region within which the instrument yields its maximum accuracy.[13] The proper functioning of the instrument was checked from time to time by the method of Ewings and Parsons.[14] In all cases, the sum of the analytically determined concentrations of the three components agreed within a margin of less than 5% with the known concentration of hydrazobenzene originally charged.

## Results

The pseudo first order rate constant for each run was calculated as 2.303 times the slope of the best straight line derived by plotting log (100/%Hy) *vs.* time in minutes. At least eight experimental points were used to determine the position of each line. Spectrophotometric analysis of the final products of exploratory runs at 25°, in which hydrochloric acid was about 0.1 *M*, indicated that hydrazobenzene gave 70% benzidine and 30% diphenyline under these conditions. From this, the relationships

$$\log([Hy]_0/[Hy]) = \log(100/\%Hy) = \log[70/(70-\%B)] = \log[30/(30-\%D)]$$

follow, and plots of $\log[70/(70 - \%B)]$ or of $\log[30/(30 - \%D)]$ *vs.* time should be identical with $\log(100/\%Hy)$ *vs.* time plots, as long as the 70/30 product ratio holds. Figure 3 shows the linear nature of the plots and the identity between the $\log(100/\%Hy)$ and the $\log[70/(70 - \%B)]$ functions of run 1. Although the $\log[30/(30 - \%D)]$ function is not shown in Fig. 3, it also corresponds to the same straight line. For all other rate runs, both hydrazobenzene and benzidine data were plotted in this way, and for every run the two sets of data yielded straight lines whose slopes were in satisfactory agreement. For certain ran-

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[9] Melting points are corrected.

[10] Leighton, Crary and Schipp, THIS JOURNAL, **53**, 3017 (1931).

[11] Gull and Turner, *J. Chem. Soc.*, 494 (1929).

[12] (a) Schmidt and Schultz, *Ber.*, **11**, 1754 (1878); (b) Schultz, Schmidt and Strasser, *Ann.*, **207**, 354 (1881); (c) Fischer, *Monatsh.*, **6**, 546 (1885).

[13] The Misses Virginia Fitzgerald and Mary Xerocostas prepared many of the solutions, took most of the optical density readings, and carried out some of the calculations required for the analysis of the samples.

[14] Ewings and Parsons, *Anal. Chem.*, **20**, 423 (1948).

domly chosen runs, log [65/(65 − %B)] and log [75/(75 -- %B)] were also plotted against time. In no case did either plot correspond to a straight line, and a great variation from the log (100/%Hy) *vs.* time plot was always observed. It is evident, therefore, that the figure 70% for the yield of benzidine (and 30% for diphenyline) is accurate within a margin much less than 5% *for all runs.*

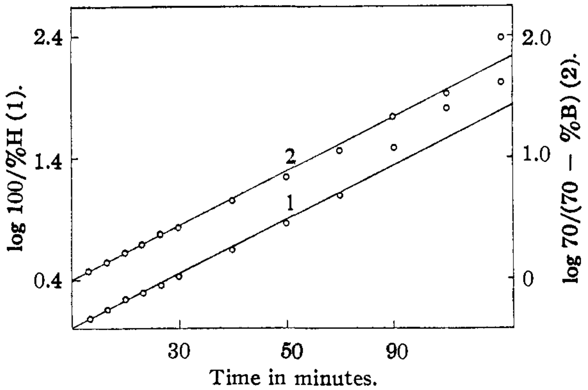

Fig. 3.—Determination of pseudo first order rate constant for Run 1 from (1) hydrazobenzene; (2) benzidine data.

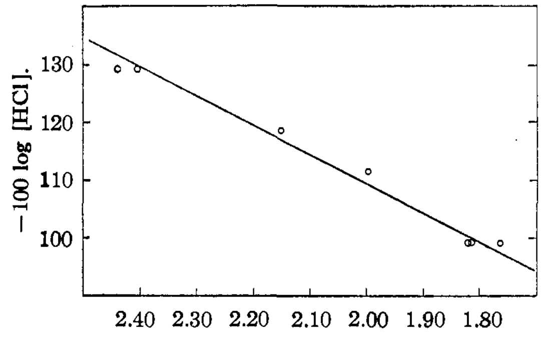

Fig. 4.—Effect of varying acid concentration at constant ionic strength and temperature. A straight line having slope 2.0 has been drawn through experimental points to show validity of equation: log $k_1$ = 2 log [HCl].

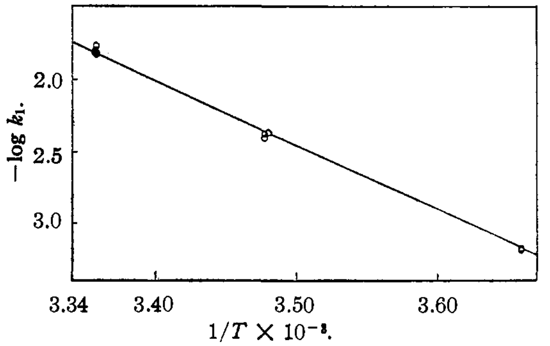

Fig. 5.—Plot from which activation energy ($E^a$) of 20.6 kcal./mole is calculated.

In Table II the results of sixteen rate runs are listed. It will be observed that at least two runs were carried out under most of the experimental conditions chosen. A comparison of the results of the first five runs and of runs 8–11 shows the effect on the rate of varying the acid concentration at constant ionic strength and temperature. This effect is shown graphically in Fig. 4, which makes apparent the second order dependency of the rate on acid concentration. A positive salt effect upon the rate is evident when the results of runs 6 and 7 are compared with those of runs 8 and 9, in which the only difference in experimental conditions was that in total ionic strength. The Arrhenius activation energy ($E^a$) for the complete process was calculated to be 20.6 kcal./mole from the slope of the good straight line plot of log $k_1$ *vs.* $1/T$ (Fig. 5), using the results of runs 1–5 and 12–16. The significance of the difference between this value and the figure 17.6, computed by Dewar from rate constants determined at two temperatures,[3] is doubtful. The effect on the observed activation energy of the greater ionic strength of Dewar's solutions might well be sufficient to account for a substantial part of the difference. Since all of the runs 1–5 and 12–16 were carried out under identical conditions of acid concentration and ionic strength, it is clear that the same value of $E^a$ is derived from this work whether the pseudo first order rate constants ($k_1$) or the "third order" rate constants ($k_3 = k_1/[\mathrm{HCl}]^2$) are used. From values of $k_3$ (from $k_1$ in sec.$^{-1}$) for any of the runs 1–5, $E^a$ and the equation[15]

$$k_3 = (ekT/h)e^{-E^a/RT}e^{\Delta S^{\ddagger}/R}$$

the observed entropy of activation ($\Delta S^{\ddagger}$) for the process was calculated to be about 2.9 e.u. at 25°.

TABLE II

| Run[a] | Temp., °C. | [HCl] mole/l. | $k_1 \times 10^3$, min.$^{-1}$ |
|---|---|---|---|
| 1 | 24.55 | 0.1020 | 33.6 |
| 2 | 24.55 | .1020 | 34.5 |
| 3 | 24.78 | .1020 | 34.5 |
| 4 | 24.78 | .1020 | 39.7 |
| 5 | 24.78 | .1020 | 34.7 |
| 6 | 24.78 | .0510 | 5.53 |
| 7 | 24.78 | .0510 | 5.49 |
| 8 | 24.78 | .0510[b] | 8.29[b] |
| 9 | 24.78 | .0510[b] | 8.96[b] |
| 10 | 24.78 | .0650[b] | 16.1[b] |
| 11 | 24.78 | .0765[b] | 23.0[b] |
| 12 | 14.72 | .1020 | 10.3 |
| 13 | 14.60 | .1020 | 10.5 |
| 14 | 14.60 | .1020 | 9.08 |
| 15 | 0.15 | .1020 | 1.54 |
| 16 | 0.15 | .1020 | 1.51 |

[a] Initial concentration of hydrazobenzene was 1.35 × $10^{-3}$ *M*, [b] Lithium chloride was added to bring total ionic strength to 0.1020.

The measure of accuracy in this work was taken to be the reproducibility of individual rate constants. Deviations from the mean of constants (Table II) measured under identical conditions ranged from 1 to 6%. Hammett's estimation of the influence of the deviation of the mean of the rate constant on the probable errors in $E^a$ and $\Delta S^{\ddagger}$[16] leads to the conclusion that a 6% probable error in $k_1$ corresponds to probable errors of about

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(15) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941, p. 197.

(16) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 122; Price and Hammett, THIS JOURNAL, **63**, 2387 (1941).

375 cal./mole and about 2.1 e.u. in $E^a$ and $\Delta S^{\ddagger}$, respectively.

## Discussion

The constancy of the benzidine-to-diphenyline ratio with varying acid concentration and temperature demonstrates that the formation of benzidine and of diphenyline both are second order in acid concentration and that, within the limits of experimental error, the observed activation energy and entropy hold for both reactions. These facts, together with the constancy of the product ratio with changing ionic strength, strongly suggest that both benzidine and diphenyline are formed by the rearrangement of the second conjugate acid of hydrazobenzene and that no essential mechanistic difference exists between the two concurrent rearrangement reactions. In agreement with the concept that the second conjugate acid of hydrazobenzene is the species undergoing rearrangement are the indications recorded by Pongratz and Scholtis[17] that N,N′-dimethylhydrazobenzene dimethiodide readily rearranges to N,N,N′,N′-tetramethylbenzidine.

Hammond and Shine[4] have indicated that the reaction sequence

(1) $C_6H_5NHNHC_6H_5 + H^+ \rightleftarrows C_6H_5NH_2{}^+NHC_6H_5$

(2) $C_6H_5NH_2{}^+NHC_6H_5 + H^+ \rightleftarrows C_6H_5NH_2{}^+NH_2{}^+C_6H_5$

(3) $C_6H_5NH_2{}^+NH_2{}^+C_6H_5 \longrightarrow H_2NC_6H_4C_6H_4NH_2 + 2H^+$

in which either reaction (2) or (3) may be rate determining, is in harmony with the kinetic observations. It is now possible to add that this sequence accounts equally well for the formation of either rearrangement product. If one assumes that the third step is slow and the first two rapidly reversible, then, in view of the fact that our method of analysis for hydrazobenzene determines the sum of the concentration of hydrazobenzene plus those of the two conjugate acids, it is possible to derive the equation

$$\ln \frac{[\mathrm{Hy}]_0^{\mathrm{obs}}}{[\mathrm{Hy}]^{\mathrm{obs}}} = \ln \frac{100}{\%\mathrm{Hy}} = \frac{K_1K_2k[\mathrm{H}^+]^2}{1 + K_1[\mathrm{H}^+] + K_1K_2[\mathrm{H}^+]^2}\, t$$

where $[\mathrm{Hy}]^{\mathrm{obs}}$ indicates the experimentally observed hydrazobenzene concentration, $t$ is time, $K_1$ and $K_2$ are the equilibrium constants for the first two reactions and $k$ is the rate constant for the third step. This equation is in accord with the kinetic measurements if: $K_1[\mathrm{H}^+] + K_1K_2[H^+]^2 \ll 1$. Since $K_2$ must be several orders of magnitude smaller than $K_1$, this expression effectively reduces to $K_1[\mathrm{H}^+] \ll 1$. Inasmuch as $K_1 = K_b/K_s$, where $K_b$ is the first base constant for hydrazobenzene and $K_s$ the ionic dissociation constant for the solvent, the requirement is that $K_b$ be no greater than $K_s$. It seems probable that this requirement is actually fulfilled; Dewar,[3] on other grounds, has estimated $K_b$ (presumably in water) to be about $10^{-14}$.

If the above reaction sequence and related assumptions are correct, then the third order rate constants measured during this investigation are given by: $k_3 = K_1K_2k$. From this, it follows that the observed value of 20.6 kcal./mole for $E^a$ is actually the sum of the activation energy for step (3) plus the heats of reaction for steps (1) and (2); and an analogous statement holds for the 2.9 e.u. value for $\Delta S^{\ddagger}$. Consequently, it is impossible to evaluate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for step (3) in the absence of information about the heats and standard entropies of reactions (1) and (2). Even if different assumptions are made regarding the reaction sequence or if a different reaction sequence is devised to account for the results of the kinetic studies, the kinetically measured $k_3$ must still be some composite of rate and equilibrium constants. Therefore, efforts to relate the observed activation energy and entropy to the rearrangement step cannot be justified until more information is available.

Some incidental observations which must be considered in relation to any proposed mechanism for the benzidine rearrangement should be recorded here. The rearrangement has been observed in the absence of any solvent. After crystalline hydrazobenzene was exposed to the action of dry hydrogen chloride at room temperature for several hours and after the powder which resulted was poured into a large excess of 20% aqueous sodium hydroxide, benzidine, identified as its disalicylal derivative, was the only product obtained. That the rearrangement occurs very rapidly in the solid state is indicated by failures to isolate any hydrochloride of hydrazobenzene.[18] A precipitate having the correct neutral equivalent (calcd., 254; found, 257) for hydrazobenzene dihydrochloride was formed instantly on addition of just two equivalents of hydrogen chloride in dry dioxane to a solution of hydrazobenzene in the same solvent. However, even when the addition of the hydrogen chloride was followed immediately by the addition of excess ammonia in dioxane, no hydrazobenzene could be recovered; only benzidine was obtained. This experiment in itself does not prove that rearrangement could not have occurred with great speed in dioxane solution before precipitation of the product hydrochloride took place. But in independent experiments, hydrazobenzene was shown to rearrange slowly enough in homogeneous solution in 50% aqueous dioxane at room temperature to permit easy measurement of rates. It does not seem likely that a change from 50% aqueous dioxane to pure dioxane would effect a nearly infinite rate increase in solution. Apparently. the intervention of solvent molecules is not necessary either to bring about the reaction or to hold portions of the molecule together while intramolecular rearrangement occurs.

Although none of the mechanisms thus far written for the rearrangement step of the benzidine transformation can readily be reconciled with the facts now available, we prefer to assemble more evidence before proposing a new mechanism.

**Acknowledgment.**—The authors wish to express their gratitude to the Research Corporation for a Frederick Gardner Cottrell Grant which supported a substantial portion of this work. The active

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[17] Pongratz and Sholtis, *Ber.*, **75**, 138 (1942).

[18] Pongratz, Bohmert-Suss and Scholtis, *Ber.*, **77**, 651 (1944), have isolated and characterized a dihydroiodide and a dihydrobromide of hydrazobenzene, both of which are stable for some time at room temperature in the solid state. They were unable to obtain a dihydrochloride "of required purity," however.

and constructive interest taken in the work by Professors W. D. Walters, J. P. Fugassi and D. S. McKinney is also acknowledged with thanks.

PITTSBURGH 13, PENNSYLVANIA RECEIVED JULY 13, 1950

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

# The Formation of Benzophenone and its Diethylketal in the Ethanolysis of Diphenyldichloromethane[1]

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A study of the ethanolysis of diphenyldichloromethane shows that benzophenone diethylketal is the reaction product only if the initial dichloride solution is very dilute or sodium ethoxide is present in the reaction medium. In solutions in which the dichloride concentration is 0.02 *M*, benzophenone is formed in quantitative yield.

A study of the kinetics of ethanolysis of the dichloride indicates that the reaction rate is first order with respect to dichloride concentration and independent of sodium ethoxide concentration. Kinetics studies of the hydrogen chloride catalyzed conversion of benzophenone diethylketal to the ketone in absolute ethanol support the assumption that the ketone formed on ethanolysis of the dichloride is produced by an acid catalyzed decomposition of the initially formed ketal.

Rate constants for the conversion of the ketal to ketone have been determined for various ethanol-water solvent mixtures. The constants reach a minimum value in a solvent which contains 15 mole per cent. water. The changes in the rate constants with changing solvent composition are explained in terms of the acidity functions of ethanol-water solutions of hydrogen chloride.

In connection with a study of solvolysis reactions of methylene chloride derivatives under way in this Laboratory an investigation of the ethanolysis of diphenyldichloromethane has been made. By spectrophotometric studies of the reaction products and by investigation of the reaction kinetics those conditions which favor the production of benzophenone as opposed to its diethylketal have been established.

**The Ethanolysis Products.**—Diphenyldichloromethane is converted in good yield in ethanol solution in the presence of excess sodium ethoxide to benzophenone diethylketal.[2] The dichloride readily undergoes hydrolysis to form benzophenone.[3] It has been shown now that at room temperature in 99.7% absolute ethanol containing no sodium ethoxide, diphenyldichloromethane reacts to form the ketal in stable condition only if the dichloride concentration of the solution is extremely small. In ethanol solutions in which the initial dichloride concentration is appreciable, benzophenone is formed.

By means of ultraviolet absorption spectrum measurements it was shown that benzophenone was formed in quantitative yield when a 0.02062 *M* solution of the dichloride in absolute ethanol stood at room temperature for 90 minutes after preparation. A sample of the resulting solution was diluted with ethanol to yield a solution ($3.30 \times 10^{-5}$ *M* with respect to concentration of the original dichloride), the spectrum of which showed the pronounced absorption maximum at 252 mμ ($d = 0.588$) characteristic of the benzophenone spectrum and lacking in that of its diethyl ketal. Figure 1 gives the absorption spectra of known samples of the ketone and ketal in ethanol.

The benzophenone concentration of the diluted dichloride solution was calculated from the expression $d = \epsilon lc$ using the measured optical density ($d$) at 252 mμ and the molecular extinction coefficient ($\epsilon = 1.74 \times 10^4$) of benzophenone at this wave length ($l$, the light path length, was 1 cm. in all experiments described in this report). The resultant value, $3.38 \times 10^{-5}$ *M*, compared favorably with the concentration assigned to the solution on the basis of the original dichloride concentration of the parent solution.

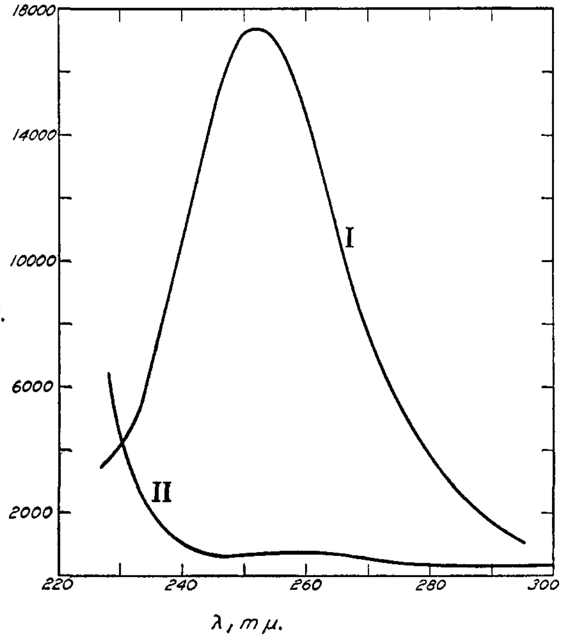

Fig. 1.—The absorption spectra of benzophenone (I) and its diethyl ketal (II) in absolute ethanol.

A very dilute solution (*ca.* $4 \times 10^{-5}$ *M*) of diphenyldichloromethane was prepared by adding 1 drop (approximately 1 mg.) of the halide to 100 ml. of absolute ethanol. The optical density at 252 mμ for this solution was initially small (0.090) and diminished as the solution stood at room temperature. The optical density readings at 230 mμ decreased rapidly with time to reach a constant value (0.196) at about 80 minutes after preparation of the solution. The absorption curve after cessation of reaction was of the same shape

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[2] Mackenzie, *J. Chem. Soc.*, **69**, 985 (1896).

[3] Kekule and Franchimont, *Ber.*, **5**, 908 (1872).