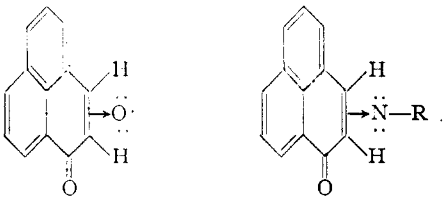
tron distribution implied by so-called π-bond structures for either the epoxides[8a] or the ethylenimines[8b] as have been offered by others would not suggest the low level of hyperconjugation in these molecules and thus such pictures are not very useful in describing the properties of these compounds.



π-bond structures

On the other hand our findings may be offered as strong verification for the usefulness of the previously[2,9] suggested molecular orbital pictures of such structures. It is now seen that the requirement of proper orientation of the π-orbital bearing carbons attached to the three-ring carbons must be rather critically met if appreciable three-ring hyperconjugation is to take place. Our studies of these steric factors are being continued.

Acknowledgment.—A portion of the work described here was done under a grant to one of us from the National Science Foundation, Research Grant NSF-G57.

Experimental

Preparation and Purification of Materials.—The perinaphthenone-7 for these experiments was prepared by the method of Fieser and Hershberg[10] and recrystallized several times from methanol and then from benzene and petroleum ether mixtures; m.p. 153.5–154.5°.

8,9-Epoxyperinaphthanone-7 was prepared by the method described by Fieser and Newton[5] and purified by chromatographing on activated alumina to free the crude product from considerable amounts of perinaphthenone-7. The material was deposited on the column from a solvent mixture of four parts of 60–70° boiling petroleum ether and three parts of benzene. The column was developed with a mixture of two parts of benzene to one part of petroleum ether and then the purple and brown colored bands eluted with pure benzene. The lowest band was purple in color and eluted as a pale yellow solution. This first eluate contained all of the desired pure 8,9-epoxyperinaphthanone-7. It formed pale yellow needles on recrystallization from benzene and petroleum ether, m.p. 123–124°. The brown colored band eluted as a bright yellow solution and was shown to consist mainly of perinaphthenone-7.

Perinaphthanone-7 was prepared by the method of Fieser and Gates,[11] m.p. 84°.

Absorption Spectra.—The *ultraviolet-visible* absorption spectra were determined at about 25° using 2,2,4-trimethylpentane (Spectro Grade, Eastman Kodak Co.) 10^{-4} molar solutions and a Beckman model DU photoelectric quartz spectrophotometer employing 10-mm. silica cells; see Fig. 1. The *infrared* absorption spectra were determined at about 25° using Nujol mulls of the compounds and a Perkin-Elmer recording infrared spectrophotometer Model 21 by Dr. H. S. Gutowsky of the University of Illinois; see Fig. 2.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Benzidine Rearrangement. Kinetics and Temperature Coefficients of the Rearrangements of Hydrazobenzene and Certain Substituted Hydrazobenzenes[1]

BY LOUIS J. CROCE AND JOSEPH D. GETTLER

RECEIVED DECEMBER 20, 1951

The rates of rearrangement of hydrazobenzene and a number of substituted hydrazobenzenes have been determined. A positive linear salt effect has been established, dielectric constant effects have been studied and energies and entropies of activation have been obtained. The effect of substituents has been shown to influence the energies and entropies of activation in a linear fashion. The rate has been shown to be second order with respect to the hydrogen ion concentration.

Introduction

Relatively few kinetic studies of the benzidine rearrangement have been made up to the present time. Van Loon[2] studied the rate of formation of benzidine in several mixed solvents and in the presence of various acids. His results indicated that the rearrangement is first order with respect to the hydrazobenzene concentration and second order with respect to the hydrogen ion concentration. Bulman and Bloom[3] obtained the rate of rearrangement of two *p,p'*-disubstituted hydrazoanilines by measuring the rate of their disappearance using a potentiometric method. Dewar,[4] using a chemical method involving the reduction of a dye, obtained the rates, the temperature coefficients and thermodynamic quantities of hydrazobenzene and three symmetrically substituted hydrazobenzenes. Recently, Hammond and Shine[5] indicated that Dewar's interpretations of his results do not consider the effect of acid concentration in the rate expression. Hammond and Shine using the analytical method of Dewar firmly established the second-order dependency of the rate of rearrangement on the oxonium ion concentration and they observed a positive salt effect on the rate. These authors propose the reaction sequence

$$C_6H_5NHNHC_6H_5 + H^+ \rightleftarrows C_6H_5N^+H_2NHC_6H_5 \qquad (A)$$

$$C_6H_5N^+H_2NHC_6H_5 + H^+ \rightleftarrows C_6H_5N^+H_2N^+H_2C_6H_5 \qquad (B)$$

$$C_6H_5N^+H_2N^+H_2C_6H_5 \longrightarrow H_2NC_6H_4C_6H_4NH_2 + 2H^+ \qquad (C)$$

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[1] This paper is based in part on a thesis submitted by Louis J. Croce to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Evans Research and Development Corporation, New York, N. Y.

(2) J. P. Van Loon *Rec. trav. chim.*, **23**, 62 (1904).

(3) E. Bulman and J. H. Bloom, *J. Chem. Soc.*, **125**, 1719 (1924).

(4) M. J. S. Dewar, *ibid.*, 777 (1946).

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They have observed that the recent mechanisms[6–9] proposed for the benzidine rearrangement are all predicated on the assumption that the rearranging entity is the first conjugate acid of the hydrazobenzene. It is difficult to apply any of these mechanistic formulations to accommodate the indications derived from rate studies[1,4] that the second conjugate acid undergoes rearrangement. Ingold[10] has recently proposed a mechanism involving a simultaneous heterolytic cleavage and rearrangement of the second conjugate acid. This latter mechanism is virtually identical with the previously considered reaction sequence (A), (B), (C) where (C) is the rate-controlling step.

Carlin, Nelb and Odioso[11] using a spectrophotometric method of analysis studied the concurrent rearrangement of hydrazobenzene to benzidine and diphenyline. Rate constants, temperature coefficients and thermodynamic quantities were determined for the total process. The second-order dependency of the rate on the oxonium ion concentration as well as the positive salt effect on the rate was substantiated. The benzidine-to-diphenyline ratio was determined and was found to be independent of temperature, acid concentration and the total ionic strength, within the experimental limits investigated.

In the present paper, the method of analysis was essentially that used by Dewar[4] and Hammond and Shine.[5] The rates of rearrangement were determined by measuring the consumption of hydrazobenzene or its substituted derivatives. The method depends upon the principle that hydrazobenzene and its substituted derivatives are instantaneously and quantitatively oxidized by Bindschedler's Green, an indamine dye.

Rates of rearrangement in homogeneous solution in water–ethanol mixtures of various percentages and in various oxonium ion concentrations are reported. Salt effects, dielectric effects and activation energies and entropies have been determined for hydrazobenzene and for some eight substituted hydrazobenzenes. The second-order dependency of the rearrangement on the acid concentration has been confirmed, the linear nature of the salt effect has been established. It has also been shown that in the case of the substituted hydrazobenzenes the substituent exerts an effect on both the energy and entropy factors in the rate expression,

Experimental

Materials.—Hydrazobenzene and the substituted hydrazobenzenes were prepared from the corresponding azo compounds. This procedure was followed because the commercially available nitro compounds contain varying percentages of isomers. The stable azo compounds are also easier to purify than the unstable hydrazo compounds. The azo compounds after purification gave sharp melting points agreeing within a degree or less of those reported in the literature. The melting points are given in parentheses after each compound in the following paragraphs,

All the symmetrical azo compounds were prepared by the method described in reference 12 which involves the reduction of a nitro compound using zinc and sodium hydroxide. The following azo compounds were prepared in this manner; 2,2′-dimethylazobenzene (55°)[13a]; 3,3′-dimethylazobenzene (55°)[13b]; 2,2′,3,3′-tetramethylazobenzene (111°)[13b]; 2,2′-dimethoxyazobenzene (153°)[13c]; 3,3′-dimethoxyazobenzene (74°)[13d]; 2,2′-diethoxyazobenzene (131°)[13e]; 3,3′-dichloroazobenzene (101°)[13f]; 3,3′-diaminoazobenzene (57°).[13g] Azobenzene (68°) (Eastman Kodak Co.) is commercially available in a high degree of purity,

The unsymmetrical azo compounds were prepared by condensation of nitrosobenzene and the substituted anilines in glacial acetic acid.[14a] Two unsymmetrical ethers, 2-methoxyazobenzene (41°)[14a] and 2-ethoxyazobenzene (44°)[14b] were prepared by this procedure.

Hydrazobenzene (131°), 2,2′-dimethylhydrazobenzene (165°)[15a] and 2,2′,3,3′-tetramethylhydrazobenzene (150°)[15d] were prepared by the catalytic reduction of the corresponding azo compounds. Approximately $^1/_{20}$th of a mole of azo compound was dissolved in 250 cc. of absolute ethanol and 400 mg. of palladium catalyst (5% on activated charcoal) added. The hydrogenations were performed at room temperature with a hydrogen pressure of approximately two atmospheres. The hydrogen uptake is rapid and the reaction complete in about 20 minutes as indicated by the pressure remaining constant. The catalyst was removed by filtration and washed with hot ethanol. Water was added to the yellow filtrate containing the hydrazobenzene. A white precipitate of the hydrazobenzene appeared immediately and the mixture, consisting of precipitate and solution, was placed in a freezing mixture to obtain the maximum yield. The hydrazobenzene obtained was pure white in color. The absence of traces of alkali improves the stability of hydrazobenzene because the oxidation is base catalyzed.[16]

The symmetrical hydrazo ethers, 2,2′-dimethoxyhydrazobenzene (102°),[17a] 2,2′-diethoxyhydrazobenzene (89°)[17b] and 3,3′-dimethoxyhydrazobenzene (60°)[4] were prepared by alkaline reduction with zinc and sodium hydroxide and isolated by the procedure given by Hickinbottom.[18] The compounds were white, crystalline and the melting points were identical to those in the literature.

The reduction of azo compounds with zinc and ammonia at 50°[19a] is milder than the procedure using sodium hydroxide and zinc. The hydrazo compounds formed are easier to isolate and are obtained in greater yield by this method. The unsymmetrical ethers, 2-methoxyhydrazobenzene (75°) and 2-ethoxyhydrazobenzene (66°)[14d] were prepared by this method in addition to 3,3′-dimethylhydrazobenzene,[19b] 3,3′-diaminohydrazobenzene (151°)[19c] and 3,3′-dichlorohydrazobenzene (95°).[13f] The 2-methoxyhydrazobenzene was not reported in the literature. *Anal.* Calcd. for $C_{13}H_{14}ON_2$: N, 13.08. Found: N, 13.11.[19d]

Bindschedler's Green was prepared by the method of Wieland.[20] The dye is isolated as the deep red zinc chloride double salt. The determined equivalent weight was found to be 264.

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[9] M. J. S. Dewar, *Nature*, **176**, 784 (1945); *J. Chem. Soc.*, 406 (1946).

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[20] H. Wieland, *Ber.*, **48**, 1087 (1915),

Lithium chloride, reagent grade (Merck & Co., Inc.) containing less than 1% impurity was dried in an oven at 120° for a day and cooled in a desiccator. The salt was weighed as rapidly as possible due to its hygroscopic nature and placed in ethanol–water mixtures to provide ionic strength variation for the determination of salt effects.

Anhydrous ethanol was prepared from the commercially available "anhydrous" ethanol by the procedure of Smith.[21]

Titanous chloride reagent of approximately 0.01 N was prepared by the procedure described by Cumming, Hopper and Wheeler.[22] Thirty cc. of 20% titanous chloride (Amend Drug Co.) was boiled with 250 cc. of concentrated hydrochloric acid. The acid solution was dissolved in 4.5 l. of oxygen-free distilled water and the system kept under an atmosphere of nitrogen to prevent extreme changes in the normality of the titanous chloride. The titanous chloride solution was standardized by titration with a standard ferric ammonium sulfate solution using potassium thiocyanate as an indicator.[23] The ferric ammonium sulfate solution was obtained by oxidation of a standard solution of ferrous ammonium sulfate (Mohr's salt) with potassium permanganate until a faint red color persisted. A solution of ferric alum was prepared by dissolving 70 g. of ferric alum in 5 l. of distilled water and acidifying with sulfuric acid. This solution was standardized using the titanous chloride solution and stored for the subsequent standardization of titanous chloride samples. The titanous chloride reagent was restandardized at least three times a week or prior to each run.

A solution of sodium hydroxide was prepared and standardized by the method given by Pierce and Haenisch.[24] This solution was used to standardize the ethanolic hydrogen chloride mixtures and also to check the acid normality of each run to prevent variations in experimental conditions.

Preparation of Solutions.—The ethanol solutions were prepared on a weight per cent. basis. This method reduces the errors inherent in volumetric procedures and facilitates the determination of dielectric constants which are reported in the literature on a weight per cent. basis. Experimental conditions can easily be reproduced by this procedure. A given weight of acid was added to a given weight of water in the preparation of the ethanolic hydrogen chloride solutions. Five mixtures were prepared for various phases of the work and they were 70, 75, 80, 85 and 90% by weight of ethanol.

The lithium chloride solutions were prepared by dissolving the calculated amount of lithium chloride in one liter of the ethanolic hydrogen chloride solution. Aliquots of this solution were then removed and used for ionic strength variations for studying salt effects. All solutions were kept a maximum of two weeks and then discarded because of the formation of oxidation products.

Apparatus and Equipment.—Three different thermostats were used to produce the operating temperatures of −5°, 0, 9, 25 and 36°. The 0 and −5° temperatures were obtained by ice–water and ice–water–salt mixtures, respectively. The 9°, the 25° and 36° thermostats were all of conventional design.

The thermometers used in all thermostats were subdivided in tenths of degrees and could be estimated to 0.02°. The exact operating temperature was determined by standardizing the thermometers used at the operating temperatures. A Bureau of Standards calibrated thermometer was used for standardization.

All flasks and pipets used to prepare the samples and withdraw aliquots from the reaction flask were calibrated. The weights used in weighing samples of the hydrazobenzenes were also calibrated.

A calibrated automatic buret was used to store and deliver the titanous chloride reagent which was maintained under an atmosphere of nitrogen.

The nitrogen used to obtain an oxygen-free atmosphere was the oil-pumped grade which contained approximately 0.3% impurities. The low oxygen content made it unnecessary to pass the gas through a special purification system.

Titrations with titanous chloride solutions were conducted under a nitrogen atmosphere using conventional type of apparatus. The apparatus used was identical to the one described by Kolthoff and Sandell.[25]

The reaction flasks were thin-walled solubility bottles of approximately 250-cc. capacity. They were fitted with a ground glass stopper which prevented loss of solvent on prolonged standing.

Procedure.—The calculated weight of hydrazobenzene was dissolved in a known volume of ethanol–water solution. The solutions were placed in the thermostats at least an hour and a half before mixing and usually in the permanent thermostats a day before use. At zero time 100 cc. of ethanolic hydrogen chloride solution was added to the solution of hydrazobenzene. At suitable intervals, aliquots were removed and pipetted into erlenmeyer flasks containing 50 cc. of standardized Bindschedler's Green solution. The oxidation of the remaining hydrazobenzene was instantaneous and quantitative. The excess dye was immediately titrated with titanous chloride solution under a stream of nitrogen. The dye samples were unstable and were titrated at half-hour intervals and the normalities recorded. By plotting the normality as a function of time a curve was obtained which gave the exact normality of the dye when the aliquot was removed.

Results

The benzidine rearrangement is first order with respect to the concentration of the rearranging hydrazo compound.[4,5] Although the rate of this reaction is dependent on the square of the concentration of the acid catalyst, the fact that the catalyst is present in considerable excess during the reaction places this rearrangement in the pseudo first order class.

In order to establish a basis of comparison for the rates reported in this paper, the authors thought it desirable to obtain rates for the rearrangement of hydrazobenzene under experimental conditions somewhat comparable to those used by previous investigators.[4,11]

The rate constants were determined by measuring the concentration of hydrazobenzene remaining at convenient intervals of time. The usual first-order rate expression was expanded to

$$t = \frac{2.303}{k}\log_{10}a - \frac{2.303}{k}\log_{10}(a - x) \qquad (1)$$

where $(a - x)$ is equal to the volume of the dye required to oxidize the remaining hydrazobenzene. A plot of log $(a - x)$ against t yielded a straight line. The slopes of these straight lines were calculated by the method of least squares. The values of k were obtained by dividing 2.303 by the slope of the experimentally determined lines. Whenever the rate of rearrangement of a particular hydrazobenzene permitted it, the experimental run was carried to at least 60% completion and most experiments involved the plotting of 7 to 8 experimentally determined points. Figure 1 contains the resultant plot of the data for experimental run no. 3.

Table I includes data for the rearrangement of hydrazobenzene under varying experimental conditions including varying ionic strength and dielectric constant.

The accuracy of the results can best be indicated by the reproducibility of duplicate experimental de-

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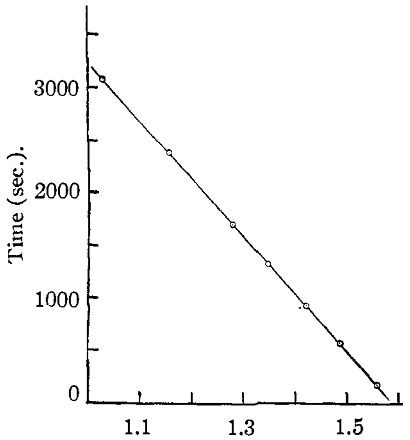

log cc. of dye used.

Fig. 1.—Rearrangement of hydrazobenzene; data from experimental run 3.

terminations. In Table I the pairs of runs 1 and 2 or 3 and 4 represent identical experimental conditions. The average deviation between both members of each pair is approximately 1.5%. The average deviation of comparable experiments reported by Dewar[4] is very much in agreement with our result while the average deviation of the method of Carlin[11] exhibits a range of 1 to 6%.

TABLE I

KINETIC DATA FOR HYDRAZOBENZENE (0.005 *M*)

Run No.	t, °C.	Acid, N	LiCl, N	μ	Ethanol, wt. %	$k \times 10^5$, sec.$^{-1}$
1	0.0	0.0931	....	0.0931	70	2.68
2	0.0	.0931	....	.0931	70	2.61
3	25.0	.0931	....	.0931	70	42.0
4	25.0	.0931	....	.0931	70	40.8
5	25.0	.0839	0.0092	.0931	70	36.3
6	25.0	.0525	.0406	.0931	70	14.8
7	25.0	.0263	.0768	.0931	70	4.64
8	25.0	.0525	....	.0525	70	12.1
9	25.0	.0525	.0275	.0800	70	13.8
10	25.0	.0525	.0125	.0650	70	12.8
11	25.0	.0931	....	.0931	80	29.6
12	0.0	.0931	....	.0931	80	2.18
13	25.0	.0931	....	.0931	60	73.3
14	0.0	.0931	....	.0931	60	,7.32
15	25.0	.0931	....	.0931	65	54.0
16	25.0	.0931	....	.0931	75	34.6

Hammond[5] and Carlin[11] have established the dependency of the specific rate constant on the square of the acid concentration. Both of these investigators employed solutions of constant ionic strength but varying acid concentration. The present paper reports experiments performed to study the effect of constant ionic strength and varying oxonium ion concentration. The experimentally determined values are included in Table II.

TABLE II

DEPENDENCE OF *k* ON ACID CONCENTRATION

Run no.	HCl, N	μ	$k \times 10^4$	k/c^2_{HCl}
3	0.0931	0.0931	4.20	0.0485
5	.0839	.0931	3.63	.0515
6	.0525	.0931	1.48	.0537
7	.0263	.0931	0.46	.0672

The values of k/c^2_{HCl} reported in Table II show a range of 4.85×10^{-2} to 6.72×10^{-2} while values of k/c^2_{HCl} reported by Hammond[1] show a range of 3.78 to 7.48. The fact that k/c^2_{HCl} is sensibly a constant indicates a third order constant or equivalently that the reaction is second order with respect to hydrogen ion concentration. Carlin[11] likewise found that a plot of log k values against the log HCl yielded a collection of points which approximated to a straight line of slope equal to 2.

A positive salt effect was observed.[26] The Debye–Hückel theory is applied to reaction kinetics by inserting the limiting law

$$-\log_{10} f_i = AZ_i^2\sqrt{\mu} \qquad (2)$$

into the Brönsted general velocity equation

$$k' = k_0' \left(f_A f_B / f_x\right) \qquad (3)$$

The resultant equation is known as the Brönsted–Bjerrum equation and may be written in the form

$$\log k' = \log k_0' + Z_A Z_B A'\sqrt{\mu} \qquad (4)$$

A plot of log k' against $\sqrt{\mu}$ should yield a straight line with slope $Z_A Z_B A'$. The value of A' is equal to $2A/2.303$ and may be obtained from activity coefficient data in the range of the ionic strength variations. Runs 6, 8, 9, 10 of Table I indicate the variation of k as a function of ionic strength. Figure 2 shows graphically this variation. The slope of the line in Fig. 2 was equal to 1.115 and A' was calculated to be 1.192. From this information the value of the charge product, $Z_A Z_B$, was found to be +0.935 which is virtually unity.

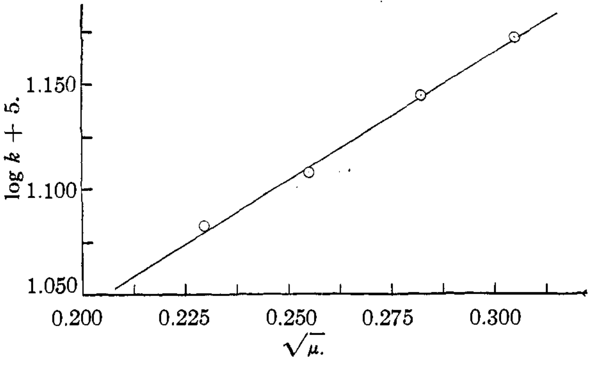

Fig. 2.—Dependence of the rate on ionic strength.

The effect of varying dielectric constant upon the rate constant furnishes a means of arriving at the identity of the ions involved in the reaction. The Brönsted–Christiansen–Scatchard equation

$$\ln k' = \ln k'_{\substack{\kappa=0\\ D=\infty}} \frac{-Z_A Z_B \epsilon^2}{DkTr} + \frac{Z_A Z_B \epsilon^2}{DkT} \times \frac{\kappa}{1 + a_i\kappa} \qquad (5)$$

ϵ = electronic charge
k = Boltzmann constant
T = temperature
D = dielectric constant of medium
r = radius of complex ($r_A + r_B$)
a_i = the distance of closest approach of the ions
Z_A, Z_B = charge on ions A and B
κ = $\sqrt{(4\pi\epsilon^2/DkT)\Sigma n_i Z_i^2}$

interprets the effect of the dielectric constant of a solvent on the rate constant.

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[26] E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 71–80.

Table III includes data indicating the effect of the dielectric constant on the specific rate constant.

TABLE III

EFFECT OF DIELECTRIC CONSTANT ON THE RATE (25°)

[HCl] = 0.0931 *N*; [hydrazobenzene] = 0.005 *M*

Ethanol wt. %	D	$1/D \times 10^3$	$k \times 10$ sec.$^{-1}$	$\log k + 5$
80	32.8	3.05	2.96	1.4713
75	35.4	2.82	3.46	1.5391
70	38.0	2.63	4.20	1.6232
65	40.7	2.46	5.40	1.7324
60	43.4	2.30	7.33	1.8651

A plot of these data appears in Fig. 3. Ideally, the variation in *k* with variation in *D* should follow a linear course. However, the results of the present investigation indicate that the rate is much faster than it should be at low values of *D*.

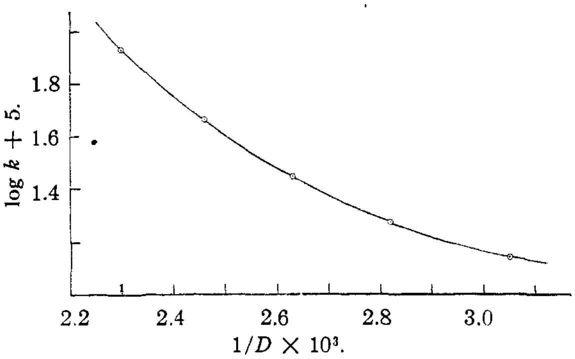

Fig. 3.—Effect of dielectric constant on the rate.

This behavior is found in mixed solvents of dielectric constants of less than forty. Similar behavior has been reported for the reaction of the divalent negative tetrabromophenolsulfonthalein ion and the univalent negative hydroxide ion.[27]

The explanation suggested[28] for this behavior is that the molecules of water are preferentially oriented around the ionic species. The concentration of water is greater in the vicinity of the ions and hence the dielectric constant will be increased making for larger specific rate constants.

It is apparent from equation (5) that oppositely charged ions will give a positive slope and ions with the same charge will give a negative slope. The slope of the line in Fig. 3 is negative and indicates a reaction between ions of like charge.

The activation energy and other thermodynamic quantities were calculated for hydrazobenzene. The experimental data for runs 1, 2, 3 and 4 were employed to determine the activation energy using the Arrhenius equation

$$\log_{10} k = \log_{10} PZ - \frac{E}{2.303\, RT} \qquad (6)$$

A plot of $\log_{10} k$ against $1/T$ appears in Fig. 4. The slope of the best straight line passing through the experimental points was calculated. The activation energy was calculated as were the other thermodynamic quantities. The values obtained were: E = 18 kcal., $PZ = 5.0 \times 10^{11}$ $\Delta S^* = 7.0$ e.u.

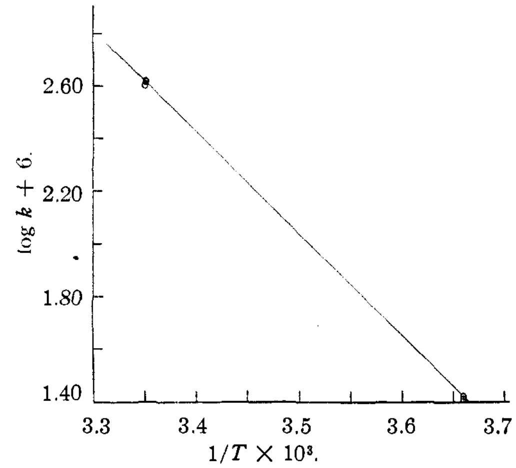

Fig. 4.—Plot of log *k versus* 1/*T* for hydrazobenzene.

The second phase of the research was concerned with the reactivity of various substituted hydrazobenzenes. Eleven substituted compounds were chosen for study. Experimental conditions were chosen so that measurable rates were obtained for the majority of the compounds. To accomplish this an acidity of 0.0675 *N* and a percentage of alcohol of 90% was selected for "standard" experimental conditions. Two compounds, the symmetrical ortho dimethoxy and diethoxy ethers, had immeasurably rapid rates under the chosen conditions and every attempt to obtain measurable rates by decreasing the acidity and temperature was fruitless. An opposite behavior was exhibited by 3,3'-dichlorohydrazobenzene and 3,3'-diaminohydrazobenzene. Although in the case of these two compounds, the acidity was quadrupled and the temperature was increased sensibly, the reactions were still extremely slow. Rate constants were, nevertheless, obtained. However, the specific rate constants and activation energies cannot be compared to the other data because the conditions are not identical. The data for the compounds studied under identical experimental conditions appear in Table IV.

The compounds follow no regularly defined sequence in which the activation energy or the *PZ* term remains constant. The substituent effect can usually be detected by changes in the activation energy if the *PZ* factor remains constant. The only apparent correlation that can be obtained from the tabulated data is that the activation energy and the *PZ* factor both increase in a regular order with change of the substituent. When this type of behavior is observed it has been found that in many cases a plot of *E* against log *PZ* is approximately linear.[29] The data from Table IV were used to construct Fig. 5. The curve is roughly linear and therefore excludes any reliable conclusions as to the electromeric effect, steric effect or inductive effect of the substituents. The most valid observation is that groups that increase the electron den-

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[27] E. S. Amis and V. K. LaMer, THIS JOURNAL, **61**, 905 (1939).

[28] S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 432.

[29] C. N. Hinshelwood, "The Kinetics of Chemical Change," Clarendon Press, Oxford 1940, pp. 258-261.

TABLE IV

KINETIC DATA FOR HYDRAZOBENZENE AND SUBSTITUTED HYDRAZOBENZENES (0.005 M), (0.067 N ACID)

Compound	t, °C.	k_1, sec.$^{-1}$	$k_2 = k_1/[\mathrm{HCl}]^2$	PZ	E, kcal.	ΔH^*, kcal.	ΔS^*, e.u.
2-Methoxyhydrazobenzene	9.0	3.07×10^{-3}	6.74×10^{-1}	6.4×10^{7}	10	13	−25
	0.0	1.54×10^{-3}	3.39×10^{-1}				
	−5.0	1.08×10^{-3}	2.37×10^{-1}				
2-Ethoxyhydrazobenzene	9.0	3.60×10^{-3}	7.90×10^{-1}	1.3×10^{9}	12	14	−19
	0.0	1.79×10^{-3}	3.93×10^{-1}				
2,2′,3,3′-Tetramethylhydrazobenzene	9.0	3.76×10^{-3}	8.25×10^{-1}	6.8×10^{12}	17	19	− 1.7
	0.0	1.41×10^{-3}	3.10×10^{-1}				
3,3′-Dimethylhydrazobenzene	25.0	1.41×10^{-3}	3.10×10^{-1}	8.5×10^{12}	18	21	− 1.3
	9.0	2.44×10^{-4}	5.36×10^{-2}				
2,2′-Dimethylhydrazobenzene	25.0	1.19×10^{-3}	2.62×10^{-1}	3.1×10^{13}	19	22	1.3
	9.0	1.81×10^{-4}	3.97×10^{-2}				
	0.0	6.12×10^{-5}	1.35×10^{-2}				
3,3′-Dimethoxyhydrazobenzene	25.0	4.44×10^{-4}	9.77×10^{-2}	6.5×10^{13}	20	23	2.8
	9.0	6.41×10^{-5}	1.41×10^{-2}				
Hydrazobenzene	25.0	1.35×10^{-4}	2.96×10^{-2}	4.0×10^{12}	19	22	− 2.8
	9.0	2.11×10^{-5}	4.63×10^{-3}				
	0.0	6.87×10^{-6}	1.47×10^{-4}				

sity of the ring or the position adjacent to the nitrogen will give an increased rate of reaction.

The investigations of the present paper have revealed an apparent inconsistency in some results reported by Dewar.[4] In his paper, he reports the rate of rearrangement of *m*-hydrazoanisole to be approximately twice as great as the rate of rearrangement of hydrazobenzene under identical experimental conditions. However, later in the same paper he specifies the following order for the rates of these compounds: *o*-hydrazoanisole >> hydrazobenzene > *m*-hydrazoanisole, which is clearly inconsistent with his experimentally determined values. Furthermore, our experimental results agree with his experimental findings with respect to the relative order of the rates of hydrazobenzene and *m*-hydrazoanisole. A second conclusion of Dewar's is at variance with some of our results. Dewar maintains that the entropies of activation for the compounds investigated by him are approximately equal. Our entropies of activation listed in Table IV exhibit a considerable range of values. This range is so large that it cannot be ascribed to experimental error.

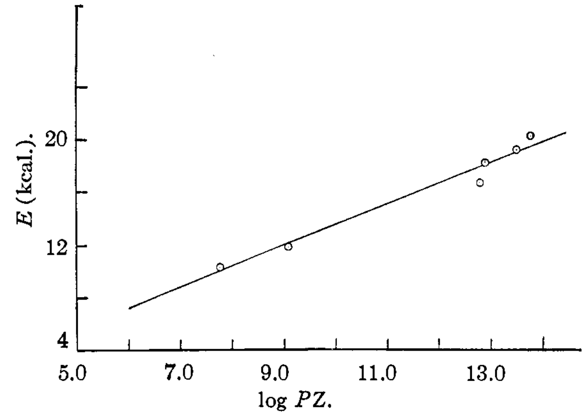

Fig. 5.—Plot of activation energy *versus* log PZ for substituted hydrazobenzenes.

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