Acid Catalyzed Intramolecular Rearrangement. III.[1,2] The Benzidine Rearrangement and Kinetics of *o*-Substituted Hydrazobenzene[3]

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Recent kinetic studies of the acid-catalyzed rearrangement of hydrazobenzene have demonstrated that the reaction rate is first order with respect to the hydrazobenzene concentration[4-8] and second order with respect to the acid concentration,[6-8] and the there is a positive salt effect upon the rate.[6,7] The product ratio of benzidine and diphenyline has been shown to be independent of the temperature, the acid concentration, and the total ion strength.

The present authors wish in this paper to report their data on the benzidine rearrangement and the kinetics of the hydrogen chloride-catalyzed rearrangement of 2, 2′-hydrazobenzenedicarboxylic acid, undertaken in order to obtain highly-purified 3, 3′-benzidinedicarboxylic acid as a monomer in the cyclopolycondensation reactions.[9] To our knowledge no kinetic studies of the ortho-substituent effect on the acid-catalyzed rearrangement of 2, 2′-hydrazobenzenedicarboxylic acid have been carried out. The rates of rearrangement were determined in 75% aqueous ethanol by measuring the consumption of 2, 2′-hydrazobenzenedicarboxylic acid using the titration method, in which 2,2′-hydrazobenzenedicarboxylic acid are instantaneously and quantitatively oxidized by Bindschedler's Green.[6,8,10] It will be shown in this paper that *o*-substituents exert an effect on the rate of rearrangement and that this effect depends upon the basicity of the hydrazo group of hydrazobenzene derivatives; 3, 3′-benzidinedicarboxylic acid will be found to be the sole rearrangement product under the imposed conditions.

Experimental

2, 2′-Hydrazobenzenedicarboxylic Acid. This is prepared by the alkaline reduction of *o*-nitrobenzoic acid with zinc and sodium hydroxide. The colorless crystalline product is recrystallized from ethanol until it is nearly colorless; mp 205°C (uncor.) (lit. 205°C).[11] The structure is confirmed by a study of the infrared spectrum. (Found: C, 61.38; H, 4.48; N, 10.25%.)

Bindschedler's Green. This is prepared by the method reported by Wieland,[12] isolated as a green, crystalline solid. The molecular weight is determined to be 264. The calculated amount of a standard solution of the dye is reduced by a weighed sample of 2, 2′-hydrazobenzenedicarboxylic acid.

Titanous Chloride Solution. A titanous chloride reagent of approximately 0.01 N is prepared by the procedures of Knecht[13] and Treadwell and Hall.[14]

Procedure. The procedure outlined by Hammond[6] and Dewar[5] was followed. The calculated amount of 2, 2′-hydrazobenzenedicarboxylic acid is dissolved in 75 m*l* of anhydrous ethanol, the mixture is diluted to 100 m*l* with distilled water, and 100 m*l* of an ethanolic hydrogen chloride solution is added to the solution of 2, 2′-hydrazobenzenedicarboxylic acid at zero time. 10 m*l* aliquots are removed at suitable intervals and pipeted into 25 m*l* of a solution (approximately 0.02 N) in Bindschedler's Green. The excess dye is immediately titrated with a titanous chloride solution under a stream of nitrogen. The values of the blank are plotted against the time, and the value at the time of back titration is read off the graph.

Preparation of 3, 3′-Benzidinedicarboxylic Acid by the Benzidine Rearrangement of *o*-Nitrobenzoic Acid. 3, 3′-Benzidinedicarboxylic acid is prepared from *o*-nitrobenzoic acid by reduction with zinc in a sodium hydroxide solution, followed by benzidine rearrangement with concentrated hydrochloric acid. The reaction conditions and results are given in Table 1. Crude 3, 3′-benzidinedicarboxylic acid was purified by hydrochloric acid and sodium acetate to give a light yellow solid (mp 300°C (decomp)) in a 82.7% yield. The infrared spectrum (KBr) has absorptions at 3460 cm^{-1}, 3440 cm^{-1} (N–H), and 1670 cm^{-1} (carbonyl). Found: C, 61.53; H, 4.53; N, 10.12%.

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Table 1. Synthesis of 3, 3′-benzidinedicarboxylic acid

Expt. No.	Reduction in aq. NaOH solution					
	Benzoic acid, M	Zn g	Concn. %	Vol. m*l*	Temp. °C	Time hr.
1	0.2	33.4	35.0	100	100	4
2	0.2	33.4	35.0	100	100	14
3	0.4	66.8	35.0	200	100	4.5
4	0.4	66.8	35.0	200	100	5
5	2.28	488.0	35.0	2000	100	10
6	0.2	50.0	35.0	200	100—105	5
7	0.4	80.0	35.0	250	100	5

Calcd for $C_{14}H_{12}O_4N_2$: C, 61.76; H, 4.44; N, 10.29%.

2, 2′-Hydrazotoluene. This was prepared by the catalytic reduction of 2, 2′-azotoluene[8] (mp 163°C (lit. 165°C[8])), which is used for the pK_a measurement by means of the potentiometric titration. The structure is confirmed by the characteristic absorption of the NH group at 3360 cm^{-1} in the infrared spectrum. Found: C, 79.16; H, 7.58; N, 13.14%, mol wt, 213. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20%; mol wt, 212.

Results and Discussion

Table 1 summaries the data obtained from the preparation of 3, 3′-benzidinedicarboxylic acid under various experimental conditions in a variety of zinc, sodium hydroxide, and hydrochloric acid concentrations in a benzidine rearrangement. Table 1 reveals that the optimum reaction conditions are found in runs 6 and 7, in which both the higher concentration of hydrochloric acid and the higher temperature are indispensable for the formation of 3, 3′-benzidinedicarboxylic acid in a high yield. The benzidine rearrangement is first order with respect to the concentration of the rearrangement hydrazo compound.[5-8] The rate for the rearrangement of 2, 2′-hydrazobenzenedicarboxylic acid was measured under experimental conditions comparable to those used by previous investigators.[5-7] The experimental results are shown in Fig. 1. From the rate equation, the pseudo-first-order rate constant is determined to be depicted in Fig. 2. The data for the rearrangement of 2, 2′-hydrazobenzenedicarboxylic acid, hydrazobenzene, and 2, 2′-hydrazotoluene are summarized in Table 2. The rate of rearrangement was found to be in the following decreasing order:

$$k_{CH_3} > k_H > k_{COOH}$$

The benzidine rearrangement is well known to be acid-catalyzed, and decrease in the basicity of hydrazobenzenes might be reasonably expected to decrease the rate of the rearrangement. Thus, the

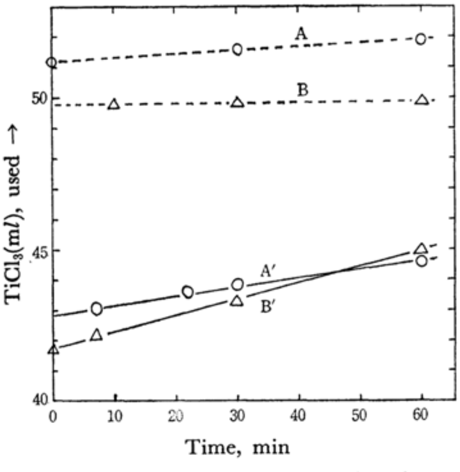

Fig. 1. Rearrangement of 2, 2′-hydrazobenzenedicarboxylic acid at 0°C and 25°C.

A : --○-- Dependence of the effect of Bindschedler's Green on time at 0°C.
B : --△-- Dependence of the effect of Bindschedler's Green on time at 25°C.
A′: —○— The value of back titration of the sample at 0°C.
B′: —△— The value of back titration of the sample at 25°C.

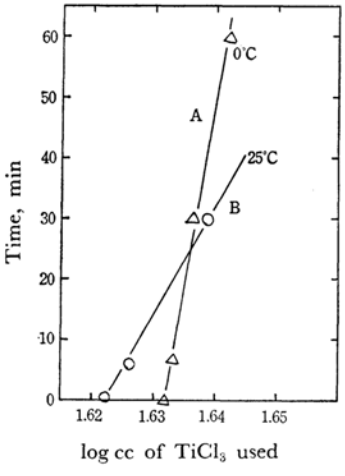

Fig. 2. Determinatian of pseudo first order rate constant of 2, 2′-hydrazobenzenedicarboxylic acid at 0°C and 25°C.

—△— at 0°C —○— at 25°C

FROM *o*-NITROBENZOIC ACID BY BENZIDINE REARRANGEMENT

Rearrangement in concn. HCl solution				Yield, %		
Concn. %	Vol. m*l*	Temp. °C	Time hr	3, 3′-Benzidine dicarboxylic acid	2, 2′-Azobenzene dicarboxylic acid	2, 2′-Hydrazo-benzene-dicarboxylic acid
20	100	20	0.5	—	40.4	—
20	100	50	0.5	—	—	—
35	500	80	0.5	—	47.8	—
35	200	100	0.5	40.4	—	—
35	3000	100	1.0	82.8	2.8	—
35	100	100	1.0	92.0	—	—
35	300	100	1.0	91.0	—	—

TABLE 2. KINETIC DATA FOR 2, 2′-HYDRAZOBENZENEDICARBOXYLIC ACID AND COMPARISON OF THE RATE OF REARRANGEMENT WITH OTHER *o*-SUBSTITUTED HYDRAZOBENZENE

Compound	Concentration M	Temp. °C	Ethanol wt%	[HCl] mol/*l*	$k_1\times10^4$ sec^{-1}	Lit.
2, 2′-Hydrazobenzene-dicarboxylic acid	1×10^{-2}	0	75	0.0712	0.050[a]	this work
	1×10^{-2}	25	75	0.0836	0.205[a]	this work
Hydrazobenzene	1×10^{-2}	0	75	0.196	2.48[a]	6)
	5×10^{-3}	25	75	0.0931	3.46[a]	8)
2, 2′-Hydrazotoluene	1.18×10^{-3}	25	75	0.0510	22.8[b]	10)

a) Measured by titration.
b) Measured by spectrophotometric analytical method.

above sequence is apparently well explained by the polar effect of substituents.

Generally the ortho substituent exerts a steric effect as well as polar effect. In an attempt to estimate the contribution of these effects to the rate, the activation energy, E, and other thermodynamic quantities were calculated from the experimental data in Table 2. The following kinetic data are obtained for 2, 2′-hydrazobenzenedicarboxylic acid: $E=9.1$ kcal, $\Delta H^*=8.9$ kcal, $\Delta S^*=-40$ e. u. and $k=2.93\times10^{-3}\ l^2\ \mathrm{mol}^{-2}\ \mathrm{sec}^{-1}$ at 25.0°C. The value of k was obtained by dividing k_1 by the square of the concentration of hydrogen chloride. Kinetic data for hydrazobenzenes in a 90% alcoholic solution were reported by Price and Gettler. The abnormally low entropy of activation for 2, 2′-hydrazobenzenedicarboxylic acid suggests the importance of the steric effect of *o, o*′-carboxyl groups and, perhaps, a substantial change in the mechanism of the reaction.

The basicity of hydrazobenzene, 2, 2′-hydrazotoluene, and 2, 2′-hydrazobenzenedicarboxylic acid was determined by the ultraviolet absorption method, varying the pH of the solvent, and by the potentiometric titration method in an ethanol-water solution. The experimental results are summarized in Table 3; the pK_a: values are in the range of 2.53 to 2.62 and are in the following order, which is in good agreement with the results of the rate of rearrangement: 2, 2′-hydrazobenzenedicarboxylic acid < 2, 2′-hydrazobenzene < 2, 2′-hydrazotoluene. The ortho-substituent effect is observed in the experimental results of the product-orientation of *o*-substituted hydrazobenzene derivatives. The data in Table 4 show that *o*-substituted hydrazobenzene gives a benzidine derivative as the sole product; that it exerts a striking effect on the product orientation is confirmed by the fact that no semidine nor diphenyline type was produced in the benzidine rearrangement.

TABLE 3. pK_a VALUES FOR HYDRAZOBENZENE DERIVATIVES

Cmpound	pK_a
Hydrazobenzene	2.53
2, 2′-Hydrazotoluene	2.62
2, 2′-Hydrazobenzenedicarboxylic acid	2.51

* Determined by the potentiometric titration method in an aqueous alcoholic solution.

Dowar claimed, in view of his pi-complex mechanism, that the electron-releasing effect of methyl substituents causes this preference of products in *o, o*′-hydrazotoluene.[15] Our results do not agree with Dewar's suggestion. Ortho substituents in

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[15] M. J. S. Dewar, "Molecular Rearrangements," Vol. I, ed. by P. de Mayo, Interscience Publishers, New York (1963), p. 340.

TABLE 4. PRODUCT ORIENTAION OF *o*-SUBSTITUTED HYDRAZOBENZENE

Compound	Benzidine type %	Semidine type %	Diphenyline type %	Lit.
Hydrazobenzene	70	—	30	7)
	60	trace	40	*
2, 2′-Hydrazotoluene	83	—	—	**
2, 2′-Hydrazobenzene-dicarboxylic acid	92	—	—	this work

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** K. Konishi and N. Kuroki, "The Chemistry of Synthetic Dyes," Maki Co., Tokyo (1958), p. 68.

the benzidine rearrangement exert more subtle effects than had been expected.

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