THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 34, NO. 2, 1964

THE EFFECT OF PRESSURE ON THE RATE OF THE BENZIDINE REARRANGEMENT

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The rate of the acid-catalysed rearrangement of hydrazobenzene in aqueous ethanol (95 wt.% EtOH) has been measured at pressures up to 5,000 atmospheres. The reaction is slightly slowed by high pressures and the proportion of benzidine is increased, but not to so high degree. The results indicate that the rearrangement goes through a cyclic transition state, in which at least two partial bonds are predominant.

Introduction

The term "benzidine rearrangement" will in general be employed to embrace the acid-catalysed conversion of aromatic hydrazo-compounds to both diaminobiaryls and aminobiarylamines. But, occasionally, the same term is used to imply the conversion of hydrazobenzene to benzidine, that is, to 4, 4′-diaminobiphenyl only.

In 1863, Hofmann¹⁾ first observed the conversion of hydrazobenzene into benzidine under the influence of acids. The positions of its amino-groups were established later by Schultz²⁾. In 1878, Schmidt and Schultz³⁾ noted the formation, along with benzidine, of the so-called diphenyline (2,4′-diaminobiphenyl).

As to the mechanism, Tichwinsky's⁴⁾ and Stieglitz's⁵⁾ theories, which assumed homolytic and heterolytic dissociation, respectively, were first promulgated in 1903. In both, it was assumed that the hydrazo-compound was dissociated into two fragments, whose centres became transferred to *p*, or *o*′-positions.

But, since Wieland⁶⁾ showed that the tetraarylhydrazines, which are dissociated in solution into free radicals, do not undergo the benzidine change and the non-crossing of the rearrangement products was observed by Ingold⁷⁾ and Whealand⁸⁾, these ideas were dismissed. Then it became accepted that

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(*Received March 20, 1965*)

1) Hofmann, *Proc. Roy. Soc.*, **12**, 576 (1863)
2) G. Schultz, *Annalen*, **174**, 227 (1874)
3) H. Schmidt and G. Schultz, *Ber.*, **11**, 1754 (1878)
4) Tichwinsky, *J. Russ. Phys. Chem. Soc.*, **35**, 666 (1903)
5) Stieglitz, *Amer. Chem. J.*, **29**, 62 (1903)
6) H. Wieland, *Annalen*, **392**, 127 (1912)
7) C. K. Ingold and H. V. Kidd, *J. Chem. Soc.*, 984 (1933)
8) D. H. Smith, G. W. Whealand and J. R. Schwartz, *J. Am. Chem. Soc.*, **74**, 2282 (1952)

the benzidine rearrangement was intramolecular.

Up to 1950, three theories have been developed with reference to the mechanism of the benzidine rearrangement.

The first theory was suggested by Hughes and Ingold in 1941[9]. This theory assumes highly polar transition state, whose bonds are mainly, though not wholly, electrovalent.

The second was suggested by Dewar in 1946[10]. In this theory, the rearrangement is assumed to go through a protonated intermediate, in which the original *N–N* bond is replaced by a delocalized covalency, called a "pi-bond", between the aromatic rings. Pi-bond thus holds the rings in parallel planes and is replaced by a localized interatomic bond to lead to the rearrangement products.

The third assumes a homolytic splitting of the protonated hydrazo-molecule into radical intermediates, which are restrained by a solvent cage.

Up to 1950, all theories assumed acid catalysis by one added proton. But, in 1950, Hammond and Shine[11] observed that the rearrangement of hydrazobenzene is of second-order in hydrogen ions and thereafter theories were modified to accomodate the second added proton.

Experimental

Materials Hydrazobenzene, benzidine, azobenzene and lithium chloride from Nakarai Chem. Co. were used for this work. Benzidine was recrystallized alternately from ethanol and from benzene.

Apparatus The high-pressure equipment is shown in Fig. 1. The glass hypodermic syringe, which contained the reaction solution, was put into the cylindrical pressure vessel, and pressure was

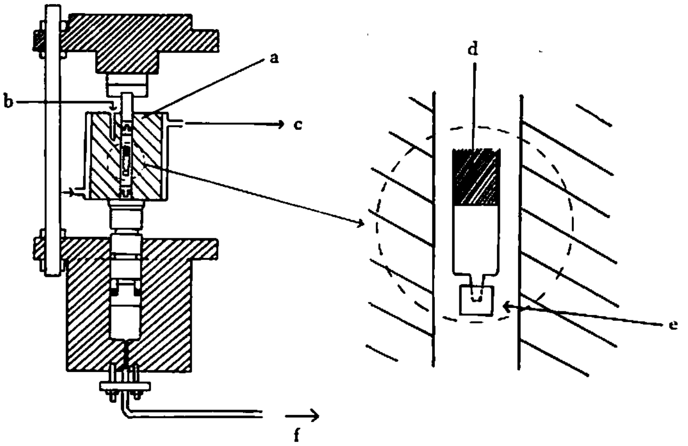

Fig. 1 The high pressure equipment. a, pressure vessel; b, thermocouple; c, thermostatted water; d, glass syringe; e, Tefron; f, to plunger pump

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9) T. R. Hughes and C. K. Ingold, *J. Chem. Soc.*, 220 (1946)

10) M. J. S. Dewar, (a), *J. Chem. Soc.*, 406 (1946); (b), *J. Chem. Soc.*, 777 (1946)

11) G. S. Hammond and H. J. Shine, *J Am. Chem. Soc.*, **72**, 220 (1950)

generated through the intensifier by means of a plunger-pump. The reaction temperature was kept constant by allowing the thermostatted water to circulate around the pressure vessel and was measured by an iron-constantan thermocouple.

Analysis At 1 atm runs, it is well known that the rearrangement of hydrazobenzene in solution free from oxygen produces only benzidine and diphenyline and a spectrophotometric method has been developed by Carlin[12] to follow these three components. In this work, the same spectrophotometric method was employed in order to analyse the reaction mixtures. The values for the specific extinction coefficients used for analysis of the mixtures are shown in Table 1.

Table 1 Specific extinction coefficients

Compound	245 mμ	270 mμ	285 mμ	320 mμ
Hydrazobenzene	109.3	16.3	23.5	9.6
Benzidine*	22.3	105.3	137.0	23.8
Diphenyline	79.2	52.0	32.2	14.3
Azobenzene	17.7	24.7	52.2	103.6

* The values for diphenyline were cited from Carlin's.

From the equation

$$D_{245}=109.3\,[H_y]+22.3\,[B]+79.2\,[D]$$

(where D_{245} is the optical density of the solution determined at 245 mμ and $[H_y]$, $[B]$ and $[D]$ represent the concentrations of hydrazobenzene, benzidine and diphenyline, respectively) and the two analogous equations for the optical densities at 270 and 285 mμ, $[H_y]$, [B] and $[D]$ were calculated for each sample. At high pressure runs, the reaction solution was not free from oxygen on account of experimental difficulty. Thus the oxidation to azobenzene, along with the rearrangement, occurred. The same spectrophotometric method was used in order to follow these four components. From the equation

$$D_{245}=109.3\,[H_y]+22.3\,[B]+79.2\,[D]+17.7\,[A]$$

(where $[A]$ represents the concentration of azobenzene) and the three analogous equations for the optical densities at 270, 285 and 320 mμ, the concentrations of four components were calculated.

Procedure The thermostatted hydrazobenzene solution and hydrogen chloride solution of known concentrations were mixed in the reaction tube, which was flushed with argon. This reaction was rapidly put into the hypodermic syringe.

The hypodermic syringe was put in the pressure vessel and was pressurized. After an appropriate time, pressure was withdrawn and the reaction solution was removed and pipetted into 50 m*l* volumetric flask, which contained sufficient ethanolic sodium chloride to neutralize the acid and stop the reaction. Within half an hour after neutralization and dilution, the optical densities of the solution were measured at 245, 270, 285 and 320 mμ.

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12) R. B. Carlin, R. G. Nelb and R. C. Odioso, *J. Am. Chem. Soc.*, 73, 1002 (1951)

Results

At 1 atm runs, no evidence of significant amount of oxidation product (azobenzene) was found. From the equations, therefore,

$$\ln\frac{[H_y]_0}{[H_y]}=\ln\frac{[H_y]_0}{[H_y]_0-(k_{1D}/k_{1B}+1)[B]}=\ln\frac{[H_y]_0}{[H_y]_0-(k_{1B}/k_{1D}+1)[D]}=k_1t \qquad (k_1=k_{1B}+k_{1D})$$

(where k_{1B} represents the rate constant of conversion to benzidine and k_{1D} that to diphenyline), the first-order rate constant k_1 can be calculated, since the rate constant ratio k_{1B}/k_{1D} can be determined from the product ratio $[B]/[D]$ ($k_{1B}/k_{1D}=[B]/[D]$). Plots of $\log([H_y]_0/[H_y])$ *vs.* time and $\log\left(\frac{[H_y]_0}{[H_y]_0-(k_{1D}/k_{1B}+1)[B]}\right)$ *vs.* time are shows in Fig. 3.

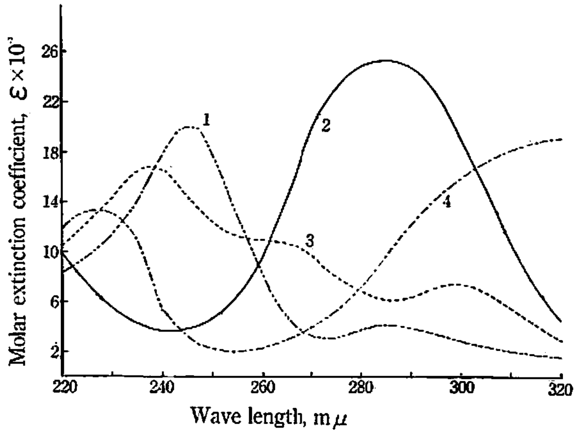

Fig. 2 The ultraviolet absorption spectra of : 1, –··–··–··–, hydrazobenzene ; 2, ————, benzidine ; 3, ..., diphenyline ; 4, –·–·–·–, azobenzene

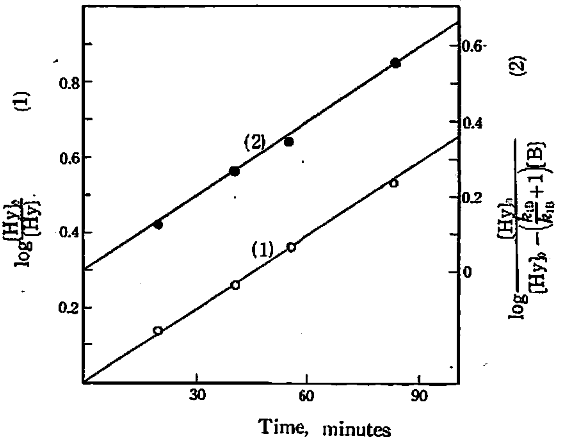

Fig. 3 Ditermination of the first-order rate constant from hydrazobenzene data (1) ; From benzidine data (2)

The two sets of the data yields straight lines whose slopes are in satisfactory agreement. Kinetic data at 1 atm runs are summarized in Table 2. A comparison of the results of runs at 25°C shows the effect on the rate of varying the acid concentration at constant ionic strength and temperature. This effect is shown graphically in Fig. 6. A straight line with slope 2.0 is drawn through experimental points to show the validity of the equation: $\log k_1 = \log k_3 + \log[\mathrm{HCl}]$.

Table 2 Kinetic data for hydrazobenzene (2.60×10^{-3}M) at 1 atm

Run no.	Temp. (°C)	HCl (mole/l)	$k_1 \times 10^3$ (min^{-1})	k_2 ($=k_1/[\mathrm{HCl}]^2$) (l^2 mole^{-2}min^{-1})
12	25.0	0.0923	30.9	3.63
27	25.0	0.0923	29.0	3.45
21	25.0	0.0791*	20.2	3.23*
22	25.0	0.0655*	14.9	3.47*
23	25.0	0.0524*	11.5	4.19*
24	25.0	0.0459*	7.08	3.36*
25	25.0	0.0459*	7.69	3.65*
			mean value	3.57
17	15.0	0.0923	7.89	0.92
28	15.0	0.0924	7.64	0.90
29	15.0	0.0792*	6.49	1.03*
30	15.0	0.0660*	5.02	1.11*
31	15.0	0.0527*	2.58	0.93*
32	15.0	0.0462*	2.37	1.12*
			mean value	1.00
20	3.0	0.0923	1.67	0.196
33	3.0	0.0792*	1.31	0.209*
34	3.0	0.0660*	1.00	0.229*
35	3.0	0.0527*	0.612	0.221*
36	3.0	0.0462*	0.340	0.159*
			mean value	0.214
50	20.0	0.0460*	3.98	1.89*

* Lithium chloride was added to bring total ionic strength to 0.0923.

In the last column of Table 2, the "third-order" rate constants calculated by using the above equation are listed. In Fig. 7, the plot of logarithm of the average values of k_3's *vs.* $1/T$ is shown. From the slope of this straight line, the Arrhenius activation energy (E_a) was calculated to be 20.8 kcal/mole, which is in agreement with the figure 20.6, computed by Carlin[12].

At high pressure runs, the reaction solution was not free from oxygen. Thus the oxidation, along with the rearrangement, occurred.

But as shown in Fig. 4, while the rearrangement products increase with time, the oxidation product ceases to be formed at an early stage (within 1.5 hour). Therefore, it is thought that only the rearrangement procedes at the later stage. As shown in Fig. 5, the plot of $\log\left(\frac{[H_y]_0}{[H_y]}\right)$ *vs.* time yields a straight line except at an early stage. The first-order rate constant was obtained from the slope of this straight line.

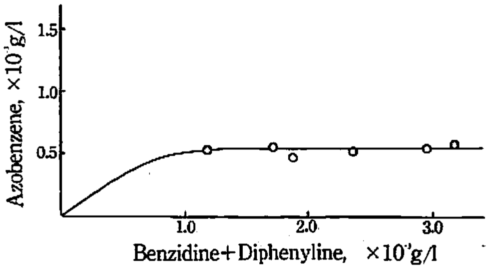

Fig. 4 Variation of azobenzene formation with respect to time at 20°C and 2000 atm

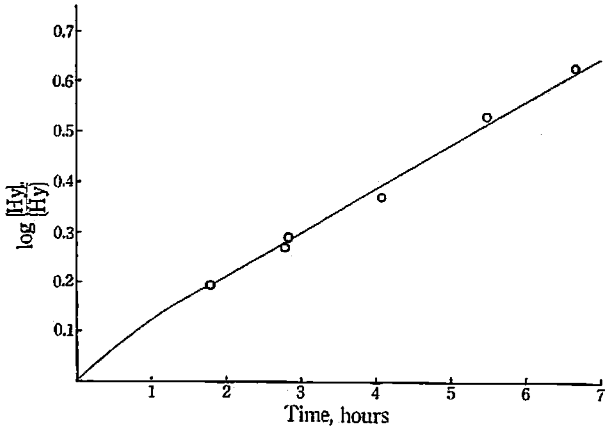

Fig. 5 Plot of $\log\frac{[Hy]_0}{[Hy]}$ vs. time for run at 20°C and 2000atm

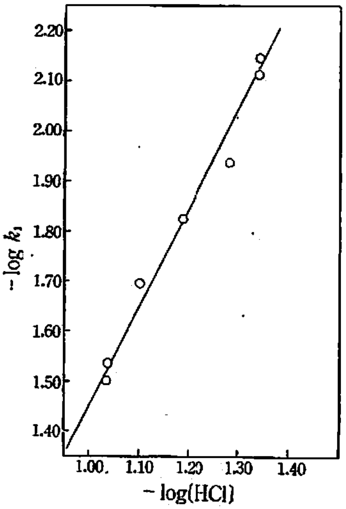

Fig. 6 The effect of varying acid concentration at constant ionic strength and temperature at 25°C and 1 atm

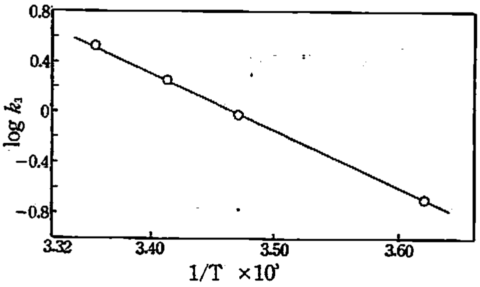

Fig. 7 Plot from which activation energy (E^a) of 20.8 kcal./mole is obtained at 1 atm

The results at high pressure runs are listed in Table 3.

The plot of $\log((k_1)_p/(k_1)_1)$ *vs.* P at 20°C is shown in Fig. 8 and from this plot, the activation volume $\Delta V^{\ne}$ is estimated to be 1.5±0.5 cc/mole.

In Table 4, the portions of benzidine and diphenyline formed at each pressure are listed.

Table 3 Kinetic data for the high pressure reactions (HCl=0.0460M)

Temp. (°C)	Pressure (atm)	$k_1 \times 10^3$ (min^{-1})	$(k_1)_p/(k_1)_1$
25.0	1	7.39	1.0
	3,000	6.32	0.85
20.0	1	3.98	1.0
	1,000	3.72	0.94
	2,000	3.40	0.85
	3,000	3.39	0.85
15.0	1	2.37	1.0
	3,000	2.04	0.86

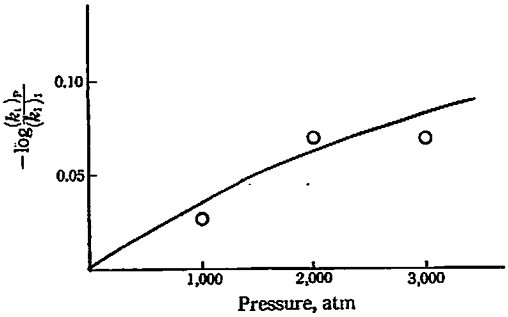

Fig. 8 Plot of log $(k_1)p/(k_1)_1$ *vs* pressure at 20°C

Considerations

The experimental results indicate that the rearrangement of hydrazobenzene is of second-order in hydrogen ions. This is in agreement with the following reaction sequence suggested by Hammond and Shine[11], which consists of three elementary processes,

$$C_6H_5\text{-}NH\text{-}NH\text{-}C_6H_5+H^+ \underset{K_1}{\rightleftharpoons} C_6H_5\text{-}NH_2^+\text{-}NH\text{-}C_6H_5,$$

$$C_6H_5\text{-}NH_2^+\text{-}NH\text{-}C_6H_5+H^+ \underset{K_2}{\rightleftharpoons} C_6H_5\text{-}NH_2^+\text{-}NH_2^+\text{-}C_6H_5,$$

$$C_6H_5\text{-}NH_2^+\text{-}NH_2^+\text{-}C_6H_5 \underset{k'_3}{\longrightarrow} \text{Products}+2H^+$$

where K_1 and K_2 are the equilibrium constants for the first two reactions and k'_3 is the rate constant for the third step.

If one assumes that the third step is rate-determining and the first two rapid and reversible[13], then, in view of the fact that the method of analysis for hydrazobenzene determines the sum of the concentration of hydrazobenzene plus those of the two conjugate acids, the experimentally observed first-order rate constant k_1 is

$$k_1=\frac{k'_3K_1K_2[H^+]^2}{1+K_1[H^+]+K_1K_2[H^+]^2}.$$

K_1 and K_2 are not known. But if one assumes $K_1[H^+]+K_1K_2[H^+]^2 \ll 1$, the equation

$$k_1 \cong k'_3K_1K_2[H^+]^2$$

will be derived and is in accord with the kinetic measurements.

Neglecting the effect of pressure on the activity coefficient of the acid catalyst[14], the equation

$$\frac{d\ln k_1}{dP}=-\frac{\Delta_1V}{RT}-\frac{\Delta_2V}{RT}-\frac{\Delta_3V^{\ddagger}}{RT}$$

will be derived (where Δ_1V and Δ_2V represent the volume changes of the first two reactions and $\Delta_3V^{\ddagger}$ the activation volume of the the third step).

From this, it follows that the observed value of $\Delta V^{\ddagger}$ is the sum of Δ_1V, Δ_2V and $\Delta_3V^{\ddagger}$, that is,

$$\Delta V^{\ddagger}=\Delta_1V+\Delta_2V+\Delta_3V^{\ddagger}.$$

The volume changes of the first two reactions, which the solvated hydrogen ions spread in the original system are transfered to hydrazobenzene molecule and its first conjugate acid, will be fairly small in the solvent[15].

Ingold[13] has indicated that a polar transition state is in harmony with their observations. In his transition state, one ring posesses two approximate units of positive charge and the other ring is like an aniline molecule.

Because of the easy flexibility of the C–N–N–C chain, the positive para-charge in one ring is attracted toward the centre of the negative charges in the other ring to yield the rearrangement products.

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13) C. K. Ingold, *J. Chem. Soc.*, 2864 (1964)

Seeing that while the N–N bond is extensive, partial bonds are formed in the *p*, *p'*-positions and in the *p*, *o'*-positions and the charges are spread in the aniline-like molecule, $\Delta_3 V^{\neq}$ will be not so large.

Thus the small positive value of $\Delta V^{\neq}$ seems to be in harmony with the above cyclic transition state.

It is seen from Table 4 that the proportion of benzidine is slightly increased with increasing pressure. This is naturally expected from the view that the pressure retards the large extension of the *N–N* bond and the relative displacements of the two rings.

Table 4 The proportions of benzidine and diphenyline formed at each pressure (20°C)

Pressure (atm)	Benzidine %	Diphenyline %	Benzidine %/Diphenyline %
1	69.0	31.0	2.3
1,000	72.3	27.7	2.6
2,000	72.2	27.8	2.6
3,000	72.6	27.4	2.6
5,000	73.6	26.4	2.7

Table 5

Pressure (atm)	k_3 (min^{-1})$=k_1/[H^+]^2$	ΔH (Kcal/mole)	ΔS (e.u.)
1	3.57	20.2	+3.6
3,000	2.99 (at 25°C)	18.5	−2.4

The discussion mentioned above is also supported by the values in Table 5 calculated from the figures in Table 3.

From Table 5, the reaction rate is retarded, in spite of the low activition energy, because of the entropies of activation which are not large but their sign is different. These are coincident with the transition state mentioned above.

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14) R. T. Harris & K. E. Weale, *J. Chem. Soc.*, 953 (1956)

15) E. Whalley, *Trans. Farad. Soc.*, 55, 798 (1959)