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THE EFFECT OF PRESSURE ON THE RATE OF THE BENZIDINE REARRANGEMENT VII

Substitution Effects and Related Kinetic Discussions

BY ICHIRO ONISHI

The benzidine rearrangement is a general term for the acid-catalyzed rearrangement of aromatic hydrazo-compounds (B) to benzidine (P), diphenylene (D) or semidine (S).

From the facts that the only form of benzidine obtained from the rearrangement of unsymmetrical hydrazo-compound (ab form) is unsymmetrical (ab form), and that the products obtained from the rearrangement of the mixture of two symmetrical hydrazo-compounds (aa form and bb form) are symmetrical, it is believed that the so-called benzidine rearrangement is an intramolecular rearrangement¹⁾.

Over a 38-year period ever since the intramolecularity of the benzidine rearrangement was confirmed, active controversies for the reaction mechanisms, especially for the transition states, have been repeated.

For some kinds of hydrazo-compounds, the disproportionation reaction, which has nothing to do with the rearrangement, concurs with the rearrangement, and kinetically it can be seen that the rate of the disproportionation reaction is of first order with respect to the concentration of hydrazo-compound and acid, just as in the case of the rearrangement^{2,3)}.

In order to obtain some information about the reaction mechanism and the transition state by studying the effect of pressure on the rate of the rearrangement, the reactions of 2, 2'-dimethoxy-⁴⁾, 2-methoxy-2'-methyl-⁵⁾, 2, 2'-dimethyl-⁶⁾, 2-chloro-2'-methyl-⁷⁾ and 2, 2'-dibromohydrazobenzene⁸⁾ were studied under ordinary and high pressures.

The reaction order in acid

Although it is common in all cases that the rate of the rearrangement is of first order with respect to the concentration of hydrazo-compound (B), the reaction order in acid varies with the substituents introduced into the aryl ring. The rate of the rearrangement of unsubstituted hydrazobenzene is of second order with respect to the concentration of acid. However, it has been found that, though the ratio of the two products of benzidine (P) to diphenylene (D) is independent of the acid concentration, the yield of benzidine slightly decreased from 76% to 72%⁹⁾ by changing the reaction solvent from

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- 1) C. K. Ingold and H. V. Kidd, *J. Chem. Soc.*, 1933, 984
- 2) D. V. Banthorpe and A. Cooper, *ibid.*, (B), 1968, 605
- 3) D. V. Banthorpe, A. Cooper and C. K. Ingold, *ibid.*, (B), 1968, 609
- 4) J. Osugi, M. Sasaki and I. Onishi, *This Journal*, 40, 39 (1970)
- 5) J. Osugi and I. Onishi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, 92, 702 (1971)
- 6) J. Osugi, M. Sasaki and I. Onishi, *This Journal*, 36, 100 (1966)
- 7) J. Osugi and I. Onishi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, 92, 131 (1971)
- 8) J. Osugi, M. Sasaki and I. Onishi, *This Journal*, 39, 57 (1969)

60% aqueous dioxane to 100% ethanol. This fact indicates that the productforming step is influenced by the dielectric constant of the medium.

Since Carlin and Odioso discovered in 1954 the unintelligible fact that the rate of the rearrangement of 2, 2'-dimethylhydrazobenzene is 1.6 order with respect to the acid concentration¹⁰⁾, attention has been paid to the problem of the benzidine rearrangement and various interpretations to this fact have been offered by Carlin and Odioso, Hinshelwood¹¹⁾ and Dewar¹²⁾.

Thereafter, in the re-examination made by Ingold in 1962¹³⁾ or by the present author in 1966⁶⁾, and also in the present author's recent studies for the rearrangement of 2, 2'-dibromo-⁸⁾ and 2-chloro-2'-methylhydrazobenzene⁷⁾, it was observed that the reaction order in acid increased continuously with the increase of the acid concentration, and further, a good linearity was obtained by plotting the ratio of the apparent rate constant to the acid concentration against the concentration of the acid. Therefore, it was confirmed from these facts that two different reactions concurred in the rearrangement; one was of first order with respect to the acid concentration (one-proton mechanism) and the other was of second order (two-proton mechanism).

Figs. 1 and 2 illustrate the dependency of the apparent rate constants k_{app} of the rearrangement of 2-chloro-2'-methylhydrazobenzene upon the concentration of the acid.

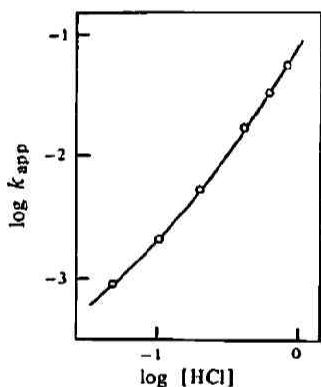


Fig. 1 The dependency of the apparent rate constants of the rearrangement of 2-chloro-2'-methylhydrazobenzene upon the acid concentration at 20°C, under ordinary pressure in 85vol% aqueous ethanolic solution

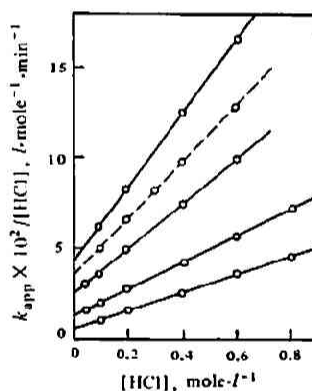
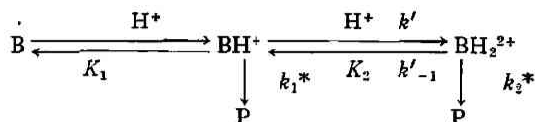


Fig. 2 The dependency of the apparent rate constants of the rearrangement of 2-chloro-2'-methylhydrazobenzene upon the acid concentration in 85vol% aqueous ethanolic solution
Temperature: 30°C, 25°C, 20°C, 15°C, from top to bottom
Pressure: — 1 kg/cm²,
..... 2,000 kg/cm²

- 9) D. V. Banthorpe, E. D. Hughes, C. K. Ingold and J. Roy, *J. Chem. Soc.*, 1962, 3294
- 10) R. B. Carlin and R. C. Odioso, *J. Am. Chem. Soc.*, **75**, 100 (1953)
- 11) D. V. Blackadder and S. C. Hinshelwood, *J. Chem. Soc.*, 1957, 2898
- 12) M. J. S. Dewar, "Theoretical Organic Chemistry, Kekule Symposium", p. 195, Butterworth, London (1959)
- 13) D. V. Banthorpe, C. K. Ingold and J. Roy, *J. Chem. Soc.*, 1962, 2436



$$-d[\text{B}]/dt = k_{\text{app}}[\text{B}] = \{k_1[\text{H}^+] + k_2[\text{H}^+]^2\}[\text{B}],$$

$$k_{\text{app}}/[\text{H}^+] = k_1 + k_2[\text{H}^+],$$

$$k_1 = k_1^*K_1, \quad k_2 = k_2^*K_1K_2 \quad \text{or} \quad k_2 = k'K_1, \quad k'/k'_{-1} = K_2.$$

In the above scheme and equations, k_1 refers to one-proton mechanism and k_2 to two-proton mechanism. Table 1 illustrates the reaction order in acid for the rearrangement and the rate constants k_1 ($l \cdot \text{mole}^{-1} \cdot \text{min}^{-1}$) and k_2 ($l^2 \cdot \text{mole}^{-2} \cdot \text{min}^{-1}$) at 25°C. under the ordinary pressure in 85 vol% aqueous ethanolic solution.

Table 1 The reaction orders in acid and the rate constants of the rearrangement

Substituents	Reaction order	k_1 ($l \cdot \text{mole}^{-1} \cdot \text{min}^{-1}$)	k_2 ($l^2 \cdot \text{mole}^{-2} \cdot \text{min}^{-1}$)
2 OCH ₃ , 2' OCH ₃	1	270	
2 OCH ₃ , 2' CH ₃	1	72	
2 CH ₃ , 2' CH ₃	1~2	3.51	70
2 Cl, 2' CH ₃	1~2	0.0235	0.127
2 Br, 2' Br	1~2	0.00016	0.00023
2 I, 2' I	1 *)		

*) Cited from Banthorpe and O'Sullivan's data in 60% aqueous dioxane¹⁴⁾.

The transition states and the volumes of activation

The reactions of one-proton mechanism occur in two opposite cases: one is when the electron donative substituent (methoxy or methyl) is introduced into the aryl ring, and the other is when the electron attractive substituent of halogen (bromine or iodine) is introduced. This means that the reactions of one-proton mechanism are strongly influenced by the electrostatic character of the substituents. As shown in Table 1, the stronger the electron donating effect, the greater the rate of the rearrangement, and the stronger the electron-attracting effect, the slower the reaction.

According to the polar transition state theory by Ingold¹⁵⁾, in the case of one-proton mechanism, after the first protonation on the a-ring, the stronger the electron donation of the substituent of the b-ring and the stronger the electron affinity of NH₂⁺ of the a-ring, the easier the electron displacement from NH to NH₂⁺. It is considered that the heterolytic and ionic fission is facilitated without any help of the second protonation.

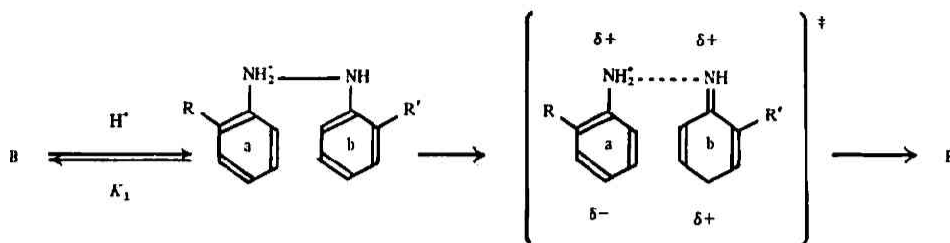
After the heterolytic fission, each ring is stabilized by resonances and both rings come near to each other in consequence of the localized positive and negative charges appearing on the rings, and

14) D. V. Banthorpe and M. O'Sullivan, *J. Chem. Soc.*, (B) 1968, 627

15) D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *ibid.*, 1964, 2864

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the rearrangement reaction comes to an end to produce benzidine and diphenylene.

As shown in Table 2, in which the volumes of activation of one-proton and two-proton mechanisms obtained by the author are summarized, the negative values of the volumes of activation for one-proton mechanisms are obtained. As the volume changes of pre-equilibrium of the protonation are to be about $-5 \text{ cm}^3/\text{mole}^{16)}$, these transition states are presumed to be so strongly solvated and polar as to sufficiently overcome the volume increase resulting from the $\text{NH}_2^+:\text{NH}$ bond fission after protonation. Therefore, it is concluded that Ingold's "polar transition state" must be supported.

For the two-proton mechanisms, as the second protonation breaks the asymmetry of $\text{NH}_2^+:\text{NH}$, the possibility of the homolytic fission is caused. Since the volume changes of pre-equilibrium of the addition of two protons are presumed to be about $-10 \text{ cm}^3/\text{mole}^{16)}$, it may be considered that the transition states of two-proton mechanisms are less solvated and less polar than postulated by Ingold.

Table 2 The volumes of activation of the rearrangement in 85 vol% ethanolic solution at 25°C under ordinary pressure

Substituents	$\Delta V^\ddagger_1 \text{ cm}^3/\text{mole}$ (one-proton)	$\Delta V^\ddagger_2 \text{ cm}^3/\text{mole}$ (two-proton)
2 OCH ₃ , 2' OCH ₃	-12	
2 OCH ₃ , 2' CH ₃	-8.5	
2 CH ₃ , 2' CH ₃	-2.5	-7.2
2 Cl, 2' CH ₃	-6.8	-3.2
2 Br, 2' Br	-10.7	-0.4

The product forming step and the intermediate

As for the elimination of the ring hydrogen atoms, since no hydrogen isotopic effect was observed for the rearrangement of hydrazo-compounds, it is obvious that the hydrogen atoms of the ring still keep the stable bonds in its transition state¹⁷⁾. That is, the hydrogen atoms of the rings have to be eliminated in the step after passing the transition state and this fact is consistent with the result of

16) E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959)

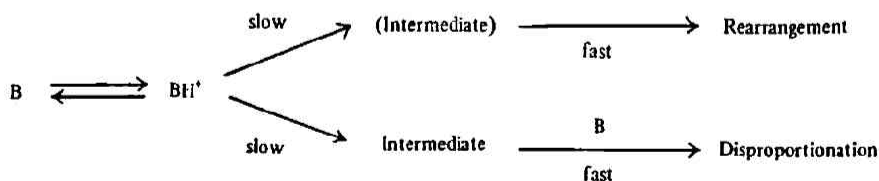
17) D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, **1962**, 3299; **1962**, 3308

the solvent effect on the rearrangement as described above⁹⁾.

As previously reported in the rearrangement of 2, 2'-dimethoxyhydrazobenzene¹⁾, the disproportionation reaction which produced 2, 2'-dimethoxyazobenzene and 2-methoxyaniline occurred concurrently. At that time, two experimental facts were observed; one is the fact that the rate of the disproportionation reaction is of first order with respect to the concentration of hydrazo-compound (B) and acid, respectively as in the case of the rearrangement, and the other is the fact that the ratio of the rate of benzidine formation ($d[P]/dt$) to that of aniline formation ($d[An]/dt$) were kept constant. Therefore, from the viewpoint of the stoichiometry, in the disproportionation reaction, it is considered as follows: the former indicates the fact that the second hydrazo-molecule must participate in the fast step after passing the rate-determining step, and the latter suggests that the disproportionation reaction and the rearrangement reaction pass through the separate rate-determining steps each other, and one intermediate has to exist after the rate-determining step in the disproportionation reaction.

Various controversies on the benzidine rearrangement are tentatively separated in two opinions; one is Ingold's polar transition state theory in which the reaction proceeds in one step without any intermediate, where the product's skeleton is almost constructed in the transition state, and the other is Dewar's π -complex theory which includes the π -complex intermediate capable of the free rotation of the both rings, although his early π -complex theory was kinetically inconsistent with the experimental results and was thereafter corrected many times.

Recently it has been discovered that *p*-semidine is formed in the rearrangement of 4-methoxyhydrazobenzene, even if no heavy metallic ion exists^{2,3)}. If the reaction mechanism is to be considered including the *p*-semidine formation, the polar transition state theory which requires the fission of N: N and simultaneous attraction through the long distance between nitrogen and 4'-carbon, is not probable. And further, from the standpoint of intramolecularity, it seems probable that a kind of intermediate in which both rings are held together parallel by the weak π -electronic force may be existent, because the hydrogen atoms of the benzene rings are kept rather fixed in the transition state. Therefore, the rearrangement reaction may pass through a kind of π -complex intermediate after passing the polar transition state, though no accurate evidences for this intermediate cannot be found.



For instance, the solvent effect on the rearrangement of hydrazobenzene described above⁹⁾—that the yield of benzidine decreased by changing the reaction solvent from 60% aqueous dioxane to 100% ethanol—may be explained by the assumption that the repulsion between NH_2^+ and NH_2^+ of each ring of a kind of π -complex intermediate favors the free rotation of both the rings, by decreasing the

dielectric constant of the medium¹⁸⁾. And the pressure effect on the rearrangement of hydrazobenzene —that the yield of benzidine is increased with increasing pressure— can be in accord with the interpretation that the pressure hinders the free rotation of each ring in π -complex intermediate¹⁹⁾.

The linear free energy relationship

The reactions of the ortho-substituted compounds depart from Hammett's rule. As reported previously⁵⁾⁷⁾, by taking account of the steric effect of the substituents, a good linearity of slope of 1.00 was obtained between the logarithms of the rate constants of the rearrangement of one-proton mechanism and the values of ρK_a of the corresponding ortho-substituted anilinium ions.

The rate constants of one-proton mechanism k_1 ($l\text{-mole}^{-1}\text{min}^{-1}$) and of two-proton mechanism k_2 ($l^2\text{mole}^{-2}\text{min}^{-1}$) are indicated as follows,

$$k_1 = k_1^* K_1, \quad k_2 = k_2^* K_1 K_2. \quad (1)$$

Assuming that the equilibrium constants of the protonation on the hydrazo-compounds, K_1 and K_2 , are proportional to the equilibrium constants of the protonation on the corresponding ortho-substituted free aniline, K_1 and K_2 , equation (1) becomes as follows,

$$k_1 = k_1^* \rho K_1, \quad k_2 = k_2^* \rho' K_1 K_2, \quad (2)$$

where ρ and ρ' are proportional constants. In one-proton mechanism, assuming that the heterolytic fission occurs after the first protonation on the a-ring, the rate constant of the rate-determining step, k_1^* , is proportional to the ease of the electron displacement from un-protonated b-ring to a-ring, that is, proportional to the electron density of NH of b-ring, or to the basicity of b-ring, accordingly to the equilibrium constant K_2 of the protonation on the corresponding ortho-substituted free aniline. Therefore, equation (2) becomes as follows,

$$k_1 = \rho \alpha K_1 K_2, \quad (3)$$

where $k_1^* = \alpha K_2$, and α is a proportional constant.

As $\log K_1$ or $\log K_2$ is equal to ρK_{a1} or ρK_{a2} , equations (2) and (3) are rewritten as follows,

$$\log k_1 = \log(\rho \alpha) - \rho K_{a1} + \rho K_{a2}. \quad (4)$$

$$\log k_2 = \log(\rho' k_2^*) + \rho K_{a1} + \rho K_{a2}.$$

The electron displacement results from the electro-neutral NH and not from NH_2^+ of the protonated b-ring. The electron displacement or the electron density of the electro-neutral NH is not proportional to the equilibrium constant K_2 itself which collectively comprises the effects of polarity, of resonance and of steric hindrance. Therefore, if the electron density is assumed to be correlated with the value of $(\rho K_{a2} + \gamma E_s)$ which is obtained by deducting from the value of ρK_{a2} the steric effect that hinders the protonation, the rate constant of one-proton mechanism is indicated as follows.

$$\log k_1 = \log(\rho \alpha) + \rho K_{a1} + \rho K_{a2} + \gamma E_s, \quad (6)$$

18) L. C. Snyder, *J. Am. Chem. Soc.*, **84**, 340 (1962)

19) J. Osugi and T. Hitouji, *This Journal*, **34**, 88 (1964)

where E_s is Taft's steric factor²⁰⁾ and γ was determined, using the rate constants k_1 for 2, 2'-dimethoxy- and 2, 2'-dibromohydrazobenzenes, to be 1.51.

Fig. 3 illustrates the plotting of the logarithms of the rate constants of one-proton and of two-proton mechanisms, $\log k_1$ and $\log k_2$, against the value of $(\rho K_{a1} + \rho K_{a2} + \gamma E_s)$ or $(\rho K_{a1} + \rho K_{a2})$. As a result, in the case of one-proton mechanism, a good linearity of slope of 1.00 is obtained, and the coefficient of correlation is 0.999.

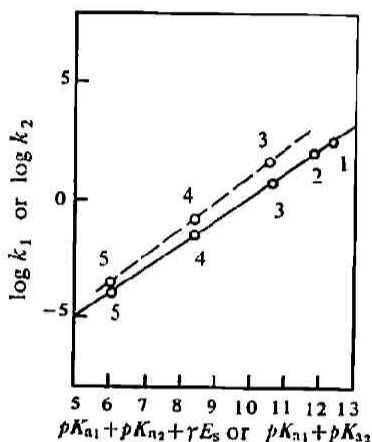


Fig. 3 The linear free energy relationship under ordinary pressure at 25°C in 85vol% aqueous ethanolic solution

- one-proton,
- - - two-proton
- 1: 2,2'-dimethoxy-,
- 2: 2-methoxy-2'-methyl-,
- 3: 2, 2'-dimethyl-,
- 4: 2-chloro-2'-methyl-,
- 5: 2, 2'-dibromohydrazobenzene

From the facts described above, Ingold's polar transition state theory that the heterolytic fission is facilitated by the electron displacement from the b-ring after the protonation on the a-ring, is supported.

For the two-proton mechanism, the mean slope of 1.22 is obtained, although this value is not reliable because of the scantiness of the data, and it slightly increases with the increase of ρK_a . Therefore, it is presumed that the N:N fission embraces a slightly heterolytic character, and the polarity of the transition state increases with the increase of the electron donative effect of the substituents. And these characters are consistent with the results obtained for the volumes of activation of the two-proton mechanisms.

Summary

Through the studies of the effect of pressure on the rate of the benzidine rearrangement, it was confirmed that the polar transition state will be supported, although it is somewhat less polar in the case of the two-proton mechanism. The remaining work for the overall description of the reaction mechanism of the benzidine rearrangement is to ascertain the existence and the character of an inter-

20) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reaction", p. 268, John Wiley and Sons, Inc., New York and London (1963)

mediate.

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