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

2,2′-Dimethoxyhydrazobenzene

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The effect of pressure on the rate of acid-catalyzed rearrangement of 2,2′-dimethoxyhydrazobenzene in 85 vol% aqueous-ethanolic solution was studied under the conditions of 5～25°C, 1～2,000 kg/cm². As a result, it was confirmed that the rearrangement and the disproportionation reactions concurred and both were of first order with respect to the concentration of hydrogen ion. It was found that the rearrangement reaction was strongly accelerated but the disproportionation retarded by pressure, so it was thought that each reaction of rearrangement and of disproportionation passed through the different transition state.

Considering the activation parameters, *i.e.* $E_1^* = 10.0$ kcal/mole, $\Delta S_1^* = -24$ e.u., $\Delta V_1^* = -12$ cc/mole for rearrangement and $E_2^* = 14.4$ kcal/mole, $\Delta S_2^* = -11$ e.u., $\Delta V_2^* = 5$ cc/mole for disproportionation reaction, the reaction schemes were discussed.

Introduction

In the previous study of the effect of pressure on the rate of rearrangement of 2,2′-dibromohydrazobenzene, it was observed that a reaction of first order with respect to HCl (one-proton mechanism) and a reaction of second order (two-proton mechanism) concurred, and the former was strongly but the latter was slightly accelerated by pressure[1]. Considering the apparent activation parameters of these two mechanisms, it was suggested that the second protonation might be a rate-determining step, and if not so, two transition states of one-proton and two-proton mechanism might have forms different from each other.

At this time, for the purpose of promoting a better understanding for the transition state of one-proton mechanism, we studied the effect of pressure on the rate of rearrangement of 2,2′-dimethoxyhydrazobenzene which had electron-releasing substituents in contrast with bromine and had been reported to follow one-proton mechanism[2].

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1) a : J. Osugi, M. Sasaki and I. Onishi, *This Journal*, **36**, 100 (1966)
b : J. Osugi, M. Sasaki and I. Onishi, *ibid.*, **39**, 57 (1969)
2) D. V. Banthorpe and A. Cooper, *J. Chem. Soc.*, (B) **1968**, 605

Experimentals

Materials

2,2′-Dimethoxyhydrazobenzene (B) was synthesized[3] by the reduction of 2-nitroanisole with zinc dust and sodium hydroxide, being recrystallized from ethanol to get white crystal, mp. 102°C. Red crystal of 2,2′-dimethoxyazobenzene (A) was obtained by the oxidation of 2,2′-dimethoxyhydrazobenzene in ethanolic alkaline solution, mp. 153°C. White crystal of 3,3′-dimethoxybenzidine (P) was prepared by the recrystallization of commercial E. P. reagent (Tokyo Kasei Ltd) from water, mp. 131°C. 2-Methoxyaniline (D) was prepared from commercial G. R. reagent of 2-methoxyaniline hydrochloride and sodium hydroxide, and distilled in vacuum at 133°C.

Procedure

As the rate of rearrangement of (B) was very fast, the reaction medium of monochloroacetate buffer solution was employed to keep hydrogen ion concentration constant. Aqueous monochloroacetic acid solution of 0.666 mole/*l* (a) and aqueous solution of sodium hydroxide of 0.665 mole/*l* (b) were stocked. The reaction medium was prepared from (a), (b), water, and ethanol so as to get available concentration; 85 vol% for ethanol, 0.05 for the ionic strength. The rate of rearrangement was measured under the conditions of 5～25°C, 1～2,000 kg/cm², pH=3.51～5.15. The initial concentration of (B) was around 2×10^{-4} mole/*l* all over the kinetic runs. At this time, hydrogen ion concentrations at the ordinary atmospheric pressure were measured by means of a pH-meter but those at high pressure were estimated on the assumption that the effect of pressure on the pK_a of monochloroacetic acid (4.34 at the ordinary atmospheric pressure at 5°C) was almost the same as that of acetic acid[4].

The reaction products were analyzed by means of thin layer chlomatography using silica-gel and chloroform. 3,3′-Dimethoxybenzidine, 2,2′-dimethoxyazobenzene and 2-methoxyaniline were detected by color spots after the ultraviolet irradiation on the thin layer.

Table 1 R_f-value and color of spots after UV irradiation on the thin layer of silica-gel

	(P)	(A)	(D)
R_f	0.16	0.58	0.48
color	gray-brown	yellow	violet-brown

The experimental apparatus both at the atmospheric and high pressure was the same as reported previously[1].

After an appropriate time interval, the reacting solution was taken out and diluted with aqueous ethanolic solution of sodium hydroxide to stop the reaction. The reaction was pursued by analyzing

3) P. Starke, *J. Prakt. Chem.*, 59, 205 (1899)
4) S. D. Hamann, "Physico-Chemical Effect of Pressure", p. 151 Butterworths Scientific Publication, London (1957)

each component (B), (P), (A), and (D) from the measurement of the absorbances at 235, 250, 305, and 340 mμ. Molecular extinction coefficients used for the analysis are shown in Table 2.

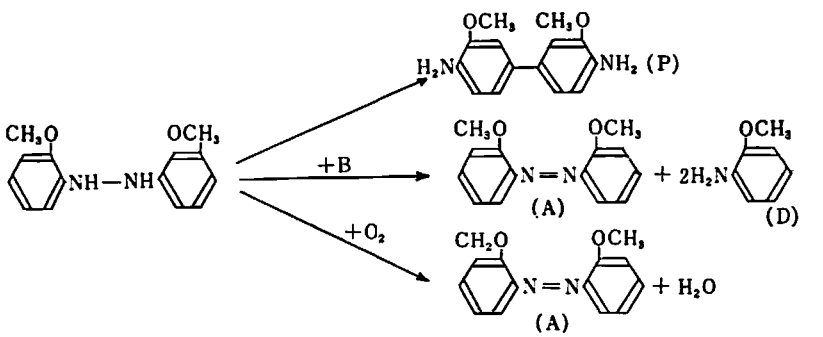
Table 2 Molecular extinction coefficients ($\varepsilon \times 10^{-3}$)

Compound	235mμ	250mμ	305mμ	340mμ
(B)	13.99	19.61	0.855	0.080
(P)	8.78	6.12	19.27	1.71
(A)	8.58	6.51	8.67	9.92
(D)	7.40	2.39	0.40	0.008

Results and Considerations

The oxidation reaction occurred together with the rearrangement because the studies were performed in aerated solutions as reported previously[1]. Furthermore, the formation of 2-methoxyaniline was confirmed and this fact suggests that the disproportionation reaction also takes place concurrently.

The following reaction scheme as postulated by Banthorpe[2] may be considered to be most appropriate, which the present work supports as discussed in the later section.



The rate of disappearance of B was of first order with regard to the concentration of B, as shown in Figs. 1 and 2.

$k_{\Delta P}$ and $k_{\Delta D}$ are calculated from the slopes of the straight lines obtained by plotting $(\Delta[P]/\Sigma) \times \log([B]_0/[B])$ and $(\Delta[D]/\Sigma) \times \log([B]_0/[B])$ against time,* respectively (Figs. 1, 2). And when $k_{\Delta P}$'s were plotted against the concentration of hydrogen ion, the straight lines passing through an origin were obtained as shown in Fig. 3. The ratios of $k_{\Delta P}/k_{\Delta D}$ were independent of the concentration of hydrogen ion, their numerical values being shown in Table 3. Therefore, both the rearrangement and disproportionation are first order with respect to the concentration of hydrogen ion.

* If the increases of P, A, and D in the reaction time are defined by $\Delta[P]$, $\Delta[A]$ and $\Delta[D]$, the quantities of the rearranged, disproportionated and oxidized can be indicated by $\Delta[P]$, $\Delta[D]$ and $\Delta[A]-(1/2)\Delta[D]$. The sums of the concentration $\Sigma(=\Delta[P]+\Delta[D]+\Delta[A]-(1/2)\Delta[D])$ and [B] were kept constant at any time during the reaction. $[B]_0$ shows the initial concentration of B.

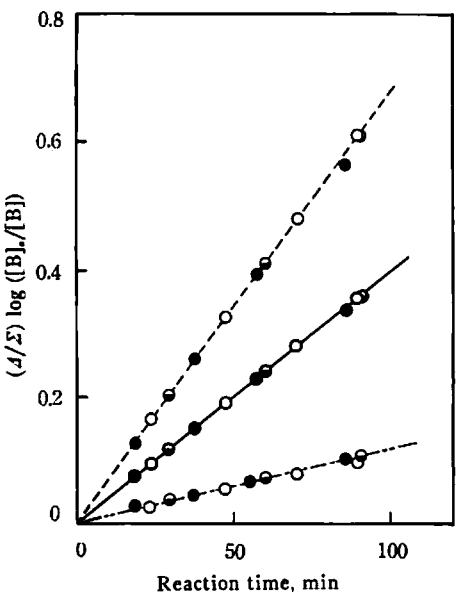


Fig. 1 First order plot (25°C, 1 kg/cm², $pH=4.47$)
The ordinate represents,
----: log([B]₀/[B])
——: (Δ[P]/Σ) log ([B]₀/[B])
--—: (Δ[D]/Σ) log ([B]₀/[B])
Initial concentration of B(mole/l):
●: 3.26×10^{-4} ○: 2.56×10^{-4}
◒: 28.3×10^{-4}

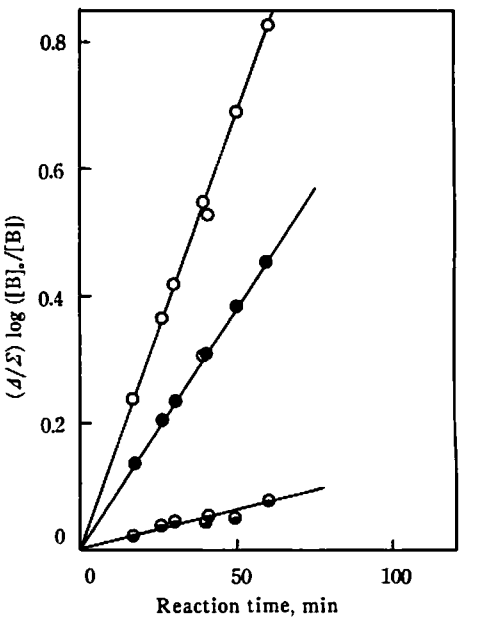


Fig. 2 First order plot (25°C, 700 kg/cm², $[B]_0=3\times10^{-4}$ mole/l, $pH=4.47$)
The ordinate represents,
○: log ([B]₀/[B])
●: (Δ[P]/Σ) log ([B]₀/[B])
◒: (Δ[D]/Σ) log ([B]₀/[B])

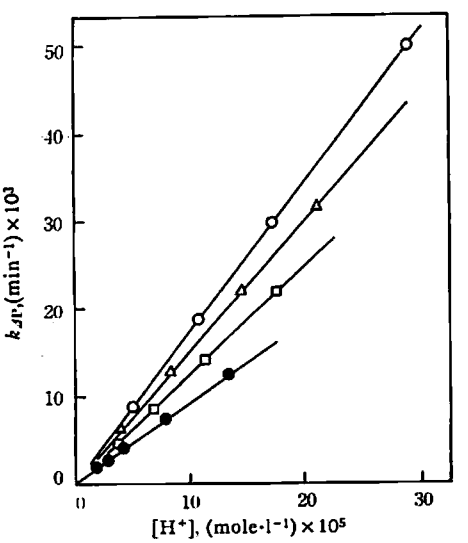
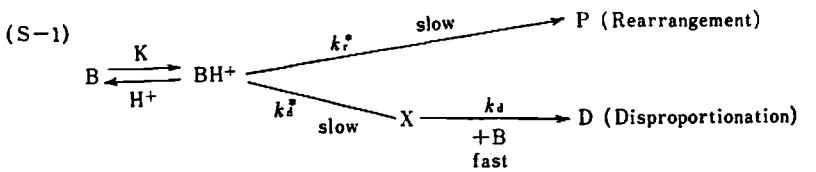


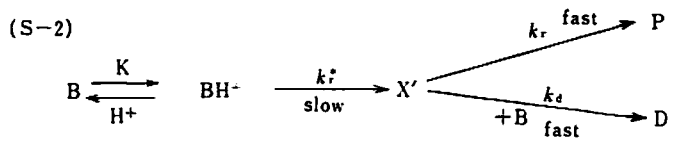
Fig. 3 Relationship between $k_{\Delta P}$ and $[H^+]$ (5°C) pressure (kg/cm²):
●: 1 □: 700 △: 1,400
○: 2,000

Table 3 The ratio of $k_{\Delta D}$ to $k_{\Delta P}$

Temperature, °C	1 kg/cm²	700 kg/cm²	1,400 kg/cm²	2,000 kg/cm²
5	0.19	0.12	0.09	0.07
10	0.23	0.16	0.11	0.09
15	0.25	0.16		0.09
20	0.31	0.21		
25	0.32	0.20		

Under the validity of this kinetic order, two mechanisms may be postulated as follows:





As the disproportionation is first order with respect to both $[H^+]$ and [B], the second molecule of B cooperates after the rate-determining step.

In the case of mechanism (S–1), the rate equations can be written as follows:

$$\frac{d[P]}{dt} = k_r^* K[H^+][B], \tag{1}$$

$$\frac{d[D]}{dt} = k_d^* K[H^+][B], \tag{2}$$

$$\frac{\Delta[D]}{\Delta[P]} = \frac{k_d^*}{k_r^*}. \tag{3}$$

Therefore, the ratio of $\Delta[D]/\Delta[P]$ is independent of the concentration of B.

On the other hand, in the case of mechanism (S–2), the ratio of $(d[D]/dt)/(d[P]/dt)$ will vary in proportion to the concentration of B as follows:

$$\frac{d[P]}{dt} = \frac{k^* k_r K[H^+][B]}{k_r + k_d[B]}, \tag{4}$$

$$\frac{d[D]}{dt} = \frac{k^* k_d K[H^+][B]^2}{k_r + k_d[B]}, \tag{5}$$

$$\frac{d[D]/dt}{d[P]/dt} = \frac{k_d}{k_r}[B]. \tag{6}$$

As [B] is dependent on the reaction time, (d[D]/dt)/(d[P]/dt) should vary with the reaction time if (S–2) scheme was appropriate.

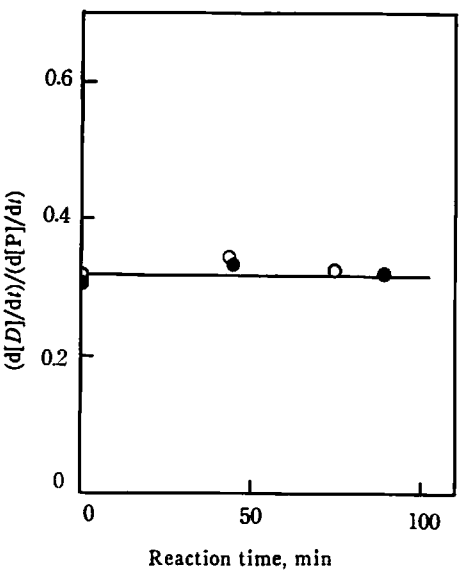


Fig. 4 Relationship between (d[D]/dt) /(d[P]/dt) and reaction time (25°C, 1 kg/cm², pH=4.47, half-value period 45 min)
[B]$_0$(mole/l):
●: 28.3×10^{-4} ○: 3.26×10^{-4}

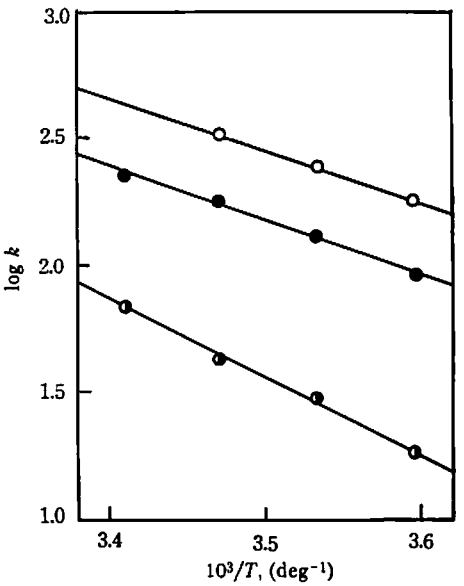
As shown in Fig. 4 though the initial concentrations of B are changed about 10 times, under the conditions of 25°C, pH=4.47 and atmospheric pressure, the term questioned above is nearly constant. Therefore, it is believed that each of rearrangement and disproportionation may be controlled by the different rate-determining step. Then, the values of $k_{\Delta P}$ and $k_{\Delta D}$ should be the apparent rate constants of rearrangement and disproportionation, respectively.

Plotting the values of $k_{\Delta P}$ against [H$^+$] (Fig. 3), the real rate constant of rearrangement k_1 are obtained, as shown in Table 4.

Table 4 Rate constants for rearrangement k_1 (l·mole^{-1}·min^{-1})

Temperature, °C	1 kg/cm²	700 kg/cm²	1,400 kg/cm²	2,000 kg/cm²
5	92	124	150	172
10	128	171	218	237
15	172	222		324
20	220	301		
25	270	363		

From the dependences of k_1 upon temperature (Fig. 6), the activation parameters were obtained and summarized in Table 5, compared with the results reported previously[1].



Fis. 5 Dependence of the rate constants on temperature
Rearrangement; ●: 1kg/cm²
○: 2,000kg/cm²
Disproportionation; ◑: 1 kg/cm²

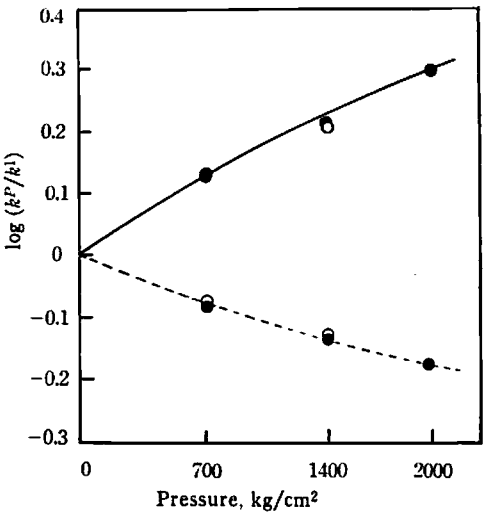


Fig. 6 Dependence of the rate constants on pressure
—— Rearrangement
--- Disproportionation
●: 5°C ○: 10°C

Table 5 Activation parameters for one-proton mechanism of rearrangement

Substituents	Pressure P, kg/cm²	Volumes of activation $\Delta V^{\ddagger}$, cc/mole	Energies of activation $E^{\ddagger}$, kcal/mole	Entropies of activation $\Delta S^{\ddagger}$, e.u.
2 CH_3 2′ CH_3 (†)	1	− 2.5	20.9	0.6
	3,000		21.6	3.3
2 Br 2′ Br (†)	1	−10.7	16.3	−34
	3,000		13.2	−41
2 CH_3O 2′ CH_3O	1	−12	10.0	−23.6
	2,000		8.9	−26.0

† In the two compounds, 2,2′-dimethyl- and 2,2′-dibromohydrazobenzene, rearrangement proceeds through one-proton and two-proton mechanisms but only the one-proton mechanism of those are compared here.

The rate constants of one-proton mechanism for three compounds were summarized in Table 6 together with the results reported by Ingold *et al.*

The rates of rearrangement undergo the influence of the electrostatic characters of substituents; the stronger the electro-attractive inductive effect is, the slower the rate of the rearrangement. But even the qualitative tendency of the activation parameters cannot be compared with electrostatic character of the substituents. The volumes of activation in Table 5, it may be only stated, are predominantly controlled by the energy of activation rather than the entropy of activation.

Table 6 Rate constants of one-proton mechanism for rearrangement

Substituents	Reaction medium†	Ionic strength	Temperature °C	$k_1 \times 10^5$ $l \cdot mole^{-1} \cdot sec^{-1}$
2 CH_3O 2′ CH_3O	85% E	0.05	25	450,000(present work)
	60% D	0.1	0	154,000(Banthorpe)[2]
2 CH_3 2′ CH_3	96% E	0.02	25	1,000(authors)[1a]
	60% D	0.5	0	140(Banthorpe)[5]
2 Br 2′ Br	85% E	1.8	25	0.27(authors)[1b]
	60% D	1.0	25	8(Banthorpe)[6]

† Where E and D represent ethanol and dioxan, respectively.

As for the volume of activation, provided that the volume change of pre-equilibrium is negative, about -5 cc/mole,[1a)7)] it seems probable that the distance between the adjacent two nitrogen atoms unfolded asymmetrically is not so long (5～7 Å) as presumed by Ingold[8)] and that the solvation should occur so strong as to compensate the increase of volume accompanying the stretching of the N : N bond. Namely, the transition state of one-proton mechanism should be a strongly solvated, polar and/but compact one and these facts are also probably suggested by a large negative value of entropies of activation. The above mentioned features do not appear in the case of 2,2′-dimethylhydrazobenzene, perhaps because the solute-solvent interaction is somewhat different from the other cases due to different reaction medium (96% aqueous ethanol).

If the disproportionation reaction accompanies the rearrangement according to the scheme (S–1), equation (3) is valid. And moreover, the kinetically observed rate constants, k_1 (rearrangement) and k_2 (disproportionation) can be defined as

$$k_1 = k_r{}^*K\,, \quad k_2 = k_d{}^*K\,, \quad k_2 = k_1(\Delta[D]/\Delta[P])\,. \tag{7}$$

The rate constants derived from equation (7) are summarized in Table 7.

Table 7 Rate constants of disproportionation k_2 in $l \cdot mole^{-1} \cdot min^{-1}$

Temperature, °C	1 kg/cm²	700 kg/cm²	1,400 kg/cm²	2,000 kg/cm²
5	18	15	14	12
10	30	27	24	21
15	43	36		29
20	68	63		
25	86	73		

From the temperature and pressure dependences of these rate constants various activation parameters can be derived as follows;

5) D. V. Banthorpe, C. K. Ingold and J. Roy, *J. Chem. Soc.*, **1962**, 2436
6) D. V. Banthorpe, C. K. Ingold and M. O'Sullivan, *J. Chem. Soc.*, **(B) 1968**, 624
7) E. Walley, *Trans. Faraday Soc.*, **55**, 798 (1959)
8) D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, **1964**, 2864

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$E_2^* = 14.4$ kcal/mole

$\Delta S_2^* = -10.7$ cal/mole·deg

$\Delta V_2^* = +5$ cc/mole

Although the results are somewhat obscure, it is assumed that the distance between two nitrogen atoms will stretch in the transition state considering the positive value of ΔV_2^*. Anyway, the reaction mechanism of disproportionation has been little studied and is quite ambiguous, although the investigation of the pressure effects would be expected to light some aspects on elucidating the reaction mechanism.

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