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

2-Methoxy-2′-methylhydrazobenzene

BY ICHIRO ONISHI

The effect of pressure on the rate of the acid-catalyzed rearrangement of 2-methoxy-2′-methylhydrazobenzene in an aqueous ethanolic solution of 85 vol % was studied under the condition of 15~30°C and 1~1,500 kg/cm^2. It was observed that the rearrangement was of first order with respect to the concentration of hydrogen ion and was accelerated by pressure.

Comparing the activation parameters obtained, *i.e.* $E^{\ddagger}=15.1$ kcal/mole, $\Delta S^{\ddagger}=-9.4$ e.u., $\Delta V^{\ddagger}=-8.5$ cm^3/mole for one-proton mechanism, with those previously obtained, it was concluded that the transition state of one-proton mechanism was strongly solvated, polar and compact.

For this one-proton mechanism, by correcting the pK_a values for the steric effect of ortho-substituents, a good linear free energy relationship between the rate constants and pK_a of ortho-substituted anilinium ions was obtained.

Introduction

As reported previously[1] when the effect of pressure on the rate of the acid-catalyzed rearrangement of 2-chloro-2′-methylhydrazobenzene was studied with unsymmetrical introduction of two substituents of different polarity, it was observed that two different reactions concurred: one is of first order with respect to the acid concentration (one-proton mechanism) and the other is of second order (two-proton mechanism), and that the former was strongly accelerated by pressure. It was suggested that a good linearity between the logarithm of the rate constants of the rearrangement and the pK_a values of anilinium ions was obtained, by correcting pK_a of ortho-substituted anilinium ion for the steric effect of substituents. In connection with the above fact, in the case of 2-chloro-2′-methylhydrazobenzene, the reaction follows the one-proton mechanism when the first protonation occur in less basic 2-chloroaniline moiety. In this paper, in order to obtain further information for an unsymmetrical compound and to confirm the linear free energy relationship, the rates of the rearrangement of 2-methoxy-2′-methylhydrazobenzene and 2, 2′-dimethylhydrazobenzene were studied under ordinary or high pressure.

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[1] J. Osugi and I. Onishi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **92**, 131 (1971)

Experimentals

Materials

Dichloroacetic acid was purified by the distillation in a vacuum (26 mmHg, 102°C)[2], and G. R. grade ethanol was used. 2-Methoxy-2′-methylazobenzene (A) was synthesized from 2-anisidine and 2-nitrosotoluene according to the literatures[3][4], and red crystal (mp.=72°C) was obtained by the recrystallization from ethanol[*]. 2-Methoxy-2′-methylhydrazobenzene (B) was prepared by the reduction of (A) with zinc dust and ammonium chloride, by using Banthorpe's method[5] as reported previously. White crystal (mp.=84°C) was obtained by the recrystallization from ethanol[*]. 3-Methoxy-3′-methylbenzidine (P) was obtained by the rearrangement of (B) and was recrystallized from ethanol. Light violet crystal (mp.=81°C) was obtained[*].

In Table 1 and Fig. 1 the molecular extinction coefficients in the range of ultra-violet obtained from the specific absorption spectrum for each compound are summarized. The results of elementary

Table 1 Molecular extinction coefficients, $\varepsilon \times 10^{-3}$, in 85 vol% ethanol

Compound	245 mμ	285 mμ	340 mμ
(B)	20.10	5.19	—
(P)	5.74	20.95	0.93
(A)	7.51	5.15	7.66

Table 2 Elementary analysis and molecular weight of (A)

	C (%)	H (%)	N (%)	Molecular weight
Calc.	74.30	6.24	12.38	226.3
Obs.	74.77	6.28	12.48	227.0

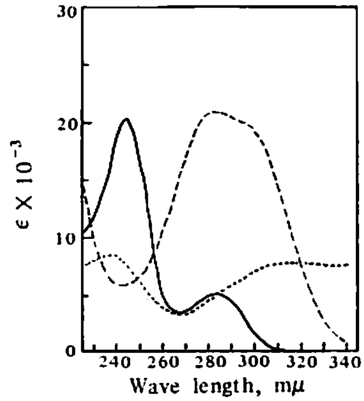

Fig. 1 Molecular extinction coefficients in 85 vol % aqueous ethanolic solution

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2) James T. Harris, Jr. and Marcus E. Hobbs, *J. Am. Chem. Soc.*, **76**, 1420 (1954)
3) R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, **2**, 68 (1937)
4) Y. Ogata and Y. Takagi, *J. Am. Chem. Soc.*, **80**, 3591 (1958)
5) D. V. Banthorpe and A. Cooper, *J. Chem. Soc.*, (B), **1968**, 605
*) These are probably new compounds and there are no literatures for the melting points.

analysis and the molecular weight of (A) are listed in Table 2.

Procedure

As the rate of the rearrangement of (B) was fast, the buffer solution of dichloroacetic acid and its salt was employed as the reaction medium in order to keep the concentration of hydrogen ion constant. The aqueous solutions of dichloroacetic acid of 0.667 mole/*l* (a) and of sodium hydroxide of 0.667 mole/*l* (b) were stocked. The reaction medium was prepared by diluting a mixture of (a), (b) and water with ethanol so as to get the fixed concentration; 85 vol% for ethanol and 0.05 for the ionic strength. The rate of the rearrangement was measured under the condition of 10~25°C, 1~1,500 kg/cm^2, $pH=2.81\sim 4.06$. The hydrogen ion concentrations at atmospheric pressure were determined using a *pH* meter (Hitachi-Horiba F-5) and those at high pressure were estimated on the assumption that the effect of pressure on the value of pK_a of dichloroacetic acid (3.56 at 25°C under atmospheric pressure) was similar to that of acetic acid[6]. Fig. 2 illustrates the relationship between the logarithm of the ratio of the concentrations of dichloroacetic acid and of its salt and the *pH* observed at 25°C under atmospheric pressure.

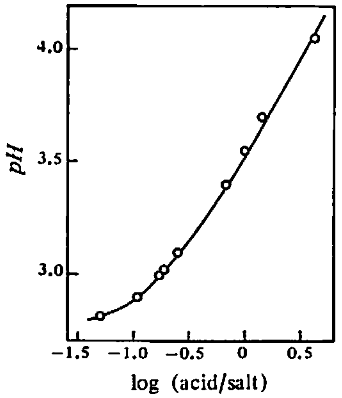

Fig. 2 The dependency of *pH* values on log (acid/salt)

Both the experimental procedure and the apparatus were the same as reported previously[1].

After an appropriate time interval, the reaction solution was taken out and was diluted with aqueous ethanolic solution of sodium hydroxide in order to stop the reaction. The reaction was followed by analyzing each component (B), (P) and (A) from the measurement of the absorbances at 245, 285 and 340 mμ. Although the reaction solution was neutralized to stop the reaction after a long reaction time interval and was developed on the thin layer of silica-gel by using chloroform, neither 2-anisidine nor 2-toluidine were detected, so no disproportionation reaction might occur. Therefore, as mentioned above, the absorbances in the range of ultra-violet were measured at three wave lengths of 245, 285 and 340 mμ.

In the previous study of 2, 2'-hydrazotoluene, the solvent was 95 vol% aqueous ethanolic solution. In order to confirm the linear free energy relationship, it is necessary to compare under the same experimental conditions, so in this study 2, 2'-hydrazotoluene was re-examined using 85 vol% aqueous ethanolic solution at 25~34.5°C in atmospheric pressure.

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6) S. D. Hamann, "Physico-Chemical Effects of Pressure", p. 151, Butterworths Scientific Publication (1957)

Results and Discussions

As the dissolved oxygen was not removed from the reaction solution, the oxidation reaction concurred with the rearrangement. But a good linearity was obtained by plotting $\{\Delta[P]/(\Delta[P]+\Delta[A])\}\log([B]_0/[B])$ against the reaction time. The apparent rate constants of the rearrangement k_{app} were obtained from the slopes of lines, $\Delta[P]$ and $\Delta[A]$ indicating the increase of the concentrations of (P) and (A), respectively, and $[B]_0$ indicating the initial concentration of (B). As shown in Figs. 3 and 4, straight lines were obtained by plotting the apparent rate constants k_{app} against the concentration of hydrogen ion. Therefore, the rate of the rearrangement of (B) was of first order with respect to the concentration of hydrogen ion (one-proton mechanism). The rate constants of the rearrangement obtained are given in Table 3.

$$B \xrightleftharpoons{H^+ \qquad K_1} BH^+ \xrightarrow{\qquad k_1^* \qquad} P$$

$$k_{app}=k[H^+]=k_1^*K_1[H^+]\,.$$

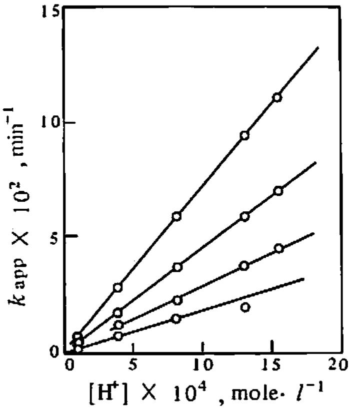

Fig. 3 Relationship between the apparent first order rate constants of rearrangement and the hydrogen ion concentrations under atmospheric pressure Temperature: 25°C, 20°C, 15°C, 10°C from top to bottom

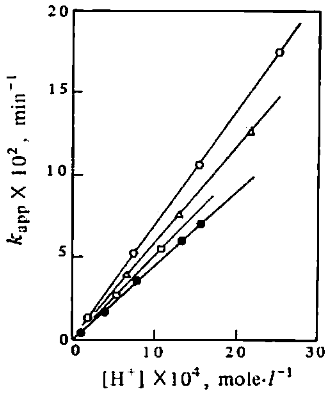

Fig. 4 Relationship between the apparent first order rate constants of rearrangement and the hydrogen ion concentrations at 20°C Pressure: 1,500, 1,000, 500, 1 kg/cm^2 from top to bottom

Figs. 5 and 6 illustrate the dependency of the rate constants on temperature and pressure, respectively. The activation parameters for the rearrangement summarized in Table 4 were obtained from these figures.

In the case of 2, 2′-hydrazotoluene, as reported previously[7], the rate constants of the rearrange-

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[7] J. Osugi, M. Sasaki and I. Onishi, *This Journal*, **36**, 100 (1966)

Table 3 The rate constants of the rearrangement of 2-methoxy-2′-methylhydrazobenzene ($\mu = 0.05$)

Temperature (°C)	Pressure (kg/cm²)	k (l·mole⁻¹·min⁻¹)
10	1	18.5
	1,500	28.0
15	1	28.8
	1,500	44.8
20	1	45.2
	500	52.0
	1,000	59.5
	1,500	70.4
25	1	72.0
	500	84.6
	1,000	98.0
	1,500	113.4

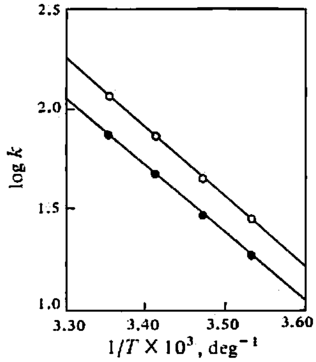

Fig. 5 Dependency of the rates of the rearrangement on temperature

○: 1,500, ●: 1 kg/cm²

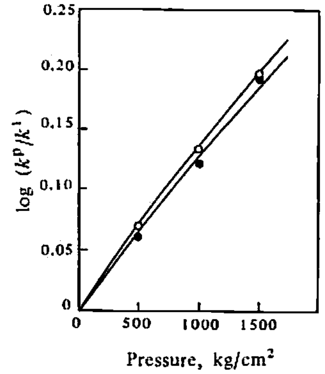

Fig. 6 Dependency of the rates of the rearrangement on pressure

○: 25°C, ●: 20°C

Table 4 The activation parameters for the rearrangement of 2-methoxy-2′-methylhydrazobenzene at 25°C

$\Delta V^{\neq}$ (cm³·mole⁻¹)	Pressure (kg·cm⁻²)	$E^{\neq}$ (kcal·mole⁻¹)	$\Delta S^{\neq}$ (e. u.)
−8.5	1	15.1	−9.4
	1,500	15.5	−7.1

$\Delta\Delta V^{\neq}/\Delta T = -0.073$, $\Delta\Delta S^{\neq}/\Delta P = 0.064$

ment of one-proton and two-proton mechanism were obtained by plotting the ratios of $k_{app}/[H^+]$ against $[H^+]$, as illustrated in Fig. 7. Rate constants and the activation parameters are summarized in Table 5.

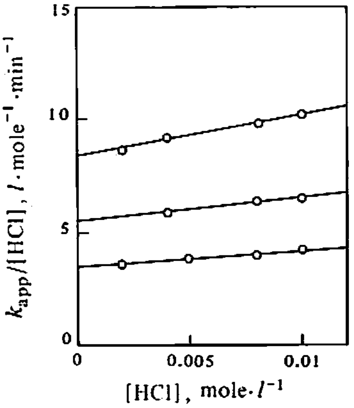

Fig. 7 Relationship between the apparent first order rate constants of rearrangement and the hydrogen ion concentrations under atmospheric pressure
Temperature: 34.5°C, 29.5°C, 25°C, from top to bottom

Table 5 The rate constants and the activation parameters for the rearrangement of 2, 2′-hydrazotoluene (μ= 1.00)

Temperature (°C)	One-proton k_1 (l·mole^{-1}·min^{-1})	Two-proton k_2 (l^2·mole^{-2}·min^{-1})
25.0	3.51	70.0
29.5	5.52	110
34.5	8.40	190

	$E^{\ddagger}$ (kcal·mole^{-1})	$\Delta S^{\ddagger}$ (e. u.)
One-proton	18.3	−4.6
Two-proton	19.0	3.6

As shown in Table 4, the volume of activation, −8.5 cm^3/mole, is also negative just as those obtained for other one-proton mechanisms: −2.5 cm^3/mole for 2, 2′-dimethyl-7), −10.7 cm^3/mole for 2, 2′-dibromo-8), −12 cm^3/mole for 2, 2′-dimethoxy-9), −6.8 cm^3/mole for 2-chloro-2′-methylhydrazobenzene1), regardless of the electrostatic character of the substituents. Since the volume changes of pre-equilibrium of the protonation are presumed to be about −5 cm^3/mole10), these transition states of one-proton mechanism are considered to be so strongly solvated and polar as to sufficiently overcome the volume increase resulting from the fission of NH_2^+: NH after protonation. Therefore, it is concluded that Ingold's "polar transition state" must be supported11).

As for a linear free energy relationship, it was indicated in the previous report1) that a good linearity between the logarithm of the rate constants of one-proton mechanism of 2, 2′-disubstituted-hydrazo-compounds and $pK_{a1}+pK_{a2}+\gamma E_s$ of free anilinium ions was obtained, where E_s and γ in the correctional term are Taft's steric factor and a proportional constant, respectively.

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8) J. Osugi, M. Sasaki and I. Onishi, *This Journal*, **39**, 57 (1969)
9) J. Osugi, M. Sasaki and I. Onishi, *ibid.*, **40**, 39 (1970)
10) E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959)
11) D. V. Banthorpe, E. D.Hughes and C. K. Ingold, *J. Chem. Soc.*, **1964**, 2864

In the case of 2-methoxy-2′-methylhydrazobenzene, the rearrangement reaction is only the one-proton mechanism, although it is an unsymmetrical compound. Even if the protonation occurs either on the methoxy side or on the methyl side, the reaction is the one-proton mechanism.

Two rings of unsymmetrical hydrazo-compounds are divided into two parts: (a) and (b), and if the equilibrium constant of the protonation on the rings (a) and (b) are expressed by K_1 and K_2, respectively, and if the rate constant of the rate-determining step of the fission after the protonation on the rings (a) and (b) are expressed by k_1^* and k_2^*, respectively, the rate constant of the rearrangement is indicated as follows,

$$k=k_1^*K_1+k_2^*K_2. \qquad (1)$$

In this case, the larger the electron density of un-protonated NH and the stronger the basicity of un-protonated aniline ring, the easier the electron displacement from NH to NH_2^+, and the more facilitated the fission between the rings. Although the basicity of un-protonated NH or the equilibrium constant of the protonation on NH of the mono-cationic hydrazo-molecule in which the already protonated NH_2^+ exists adjacently, is not identical with the equilibrium constant of the protonation on the electro-neutral hydrazo-molecule, K_1 or K_2 itself1)12)13), if the equilibrium constant of the protonation on NH of the mono-cationic hydrazo-molecule and that of electro-neutral hydrazo-molecule are presumed to be proportional to each other, the rate constants of the rate-determining steps are expressed as follows,

$$k_1^*=\alpha K_2, \qquad k_2^*=\alpha K_1, \qquad (2)$$

where α is the proportional constant.

But strictly speaking, as the electron displacement is from NH to NH_2^+ and is not from NH_2^+ to NH, the electron displacement or the electron density of electro-neutral NH is not proportional to the equilibrium constant, K_1 or K_2, which comprises the effects of polarity, of resonance and of steric hindrance, but is proportional to the value obtained by deducting the steric effect which hinders the approach of proton. If the correctional terms for the steric effect of the substituents are expressed by Δ_{s1} and Δ_{s2}, the rate constants of the rate-determining steps are indicated as follows,

$$k_1^*=\alpha K_2\Delta_{s2}, \qquad k_2^*=\alpha K_1\Delta_{s1}. \qquad (3)$$

Therefore, equation (1) becomes as follows,

$$k=\alpha K_1K_2\Delta_{s1}+\alpha K_1K_2\Delta_{s2}, \qquad (4)$$

where the larger the steric effect is, the smaller the values Δ_{s1} and Δ_{s2} are. If the equilibrium constants K_1 and K_2 are presumed to be proportional to the equilibrium constants $\boldsymbol{K}_1$ and $\boldsymbol{K}_2$, of the protonation on free ortho-substituted anilines which are equivalent to the rings (a) and (b) of hydrazo-compound, equation (4) becomes as follows,

$$k=\rho\alpha \boldsymbol{K}_1\boldsymbol{K}_2\Delta_{s1}+\rho\alpha \boldsymbol{K}_1\boldsymbol{K}_2\Delta_{s2}, \qquad (5)$$

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12) J. Clark and D. D. Perrin, *Quart. Rev.*, **18**, 295 (1964)

13) V. Sterba and M. Vecera, *Collect. Czech. Chem. Commun.*, **31**, 3486 (1966)

where ρ is the proportional constant.

Since $\log K_1 = pK_{a1}$, $\log K_2 = pK_{a2}$, equation (5) becomes

$$\log k = \log(\rho\alpha) + pK_{a1} + pK_{a2} + \log(\Delta_{s1} + \Delta_{s2}). \qquad (6)$$

As $\Delta_{s1} = \Delta_{s2} = \Delta_s$ in symmetrical compounds, equation (6) is written by

$$\log k = \log(\rho\alpha) + pK_{a1} + pK_{a2} + \log(2\Delta_s). \qquad (7)$$

As reported previously[1], the logarithm of the rate constant of the rearrangement of symmetrical 2, 2′-dimethoxyhydrazobenzene was expressed as follows,

$$\log k = \log(\rho\alpha) + pK_{a1} + pK_{a2} + \gamma E_s. \qquad (8)$$

From equations (7) and (8), the next equation is obtained.

$$\log(2\Delta_s) = \gamma E_s. \qquad (9)$$

As $\gamma = 1.51$ and E_s (Taft's steric factor)$=0.99$, $\Delta_s = 15.8$ is obtained from equation (9).

Then, in the case of 2-methoxy-2′-methylhydrazobenzene, since the steric factor of 2-methyl-substituent E_s is zero, if the substituent of ring (a) is presumed to be 2-methoxy-, $\Delta_{s1} = \Delta_s = 15.8$ and $\Delta_{s2} = 1$ are obtained. The correctional term of equation (6) then becomes

$$\log(\Delta_{s1} + \Delta_{s2}) = \log(15.8 + 1) = 1.22. \qquad (10)$$

Therefore, if $\log k$ for this compound is plotted against $pK_{a1} + pK_{a2} + 1.22 = 5.44 + 5.30 + 1.22 = 11.96$, a straight line of slope of 1.00 should be obtained.

The rate constants of the rearrangement of various compounds obtained by the author and the

Table 6 The rate constants of the rearrangement in 85 vol% aqueous ethanolic solution at 25°C under atmospheric pressure

Substituents		Ionic strength	One-proton k_1 ($l\cdot$mole$^{-1}\cdot$min^{-1})	Two-proton k_2 ($l^2\cdot$mole$^{-2}\cdot$min^{-1})
2-OCH_3,	2′-OCH_3	0.05	270	
2-OCH_3,	2′-CH_3	0.05	72	
2-CH_3,	2′-CH_3	1.00	3.51	70
2-Cl,	2′-CH_3	1.00	0.0235	0.127
2-Br,	2′-Br	1.78	0.00016	0.00023

Table 7 The scales of abscissas

Substituents		One-proton $pK_{a1}+pK_{a2}+\gamma E_s$	Two-proton $pK_{a1}+pK_{a2}$
2-OCH_3,	2′-OCH_3	12.4	
2-OCH_3,	2′-CH_3	11.96	
2-CH_3,	2′-CH_3	10.60	10.60
2-Cl,	2′-CH_3	8.45	8.45
2-Br,	2′-Br	6.10	6.10

scales of abscissas are summarized in Tables 6 and 7, respectively.

As shown in Fig. 8, in which the logarithm of the rate constants of the rearrangement are plotted against the scales of abscissas, a good linearity of the slope of 1.00 is obtained in one-proton mechanism, and its coefficient of correlation is 0.999. Although the experimental data for the two-proton mechanism are insufficient, if a straight line is presumed to be obtained, the slope of line is somewhat larger than 1.00. Therefore, it is considered that the fission between both the rings depends to some extent on the basicities of the rings in the two-proton mechanism.

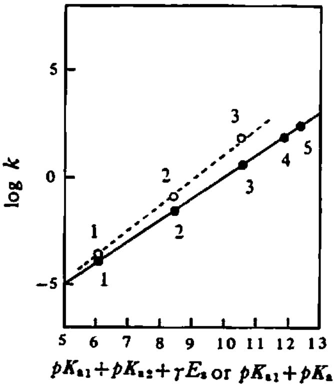

Fig. 8 The linear free energy relationships

●: One-proton,

○: Two-proton

1: 2, 2'-Br_2-, 2: 2-Cl-2'-CH_3-,
3: 2, 2'-$(CH_3)_2$-, 4: 2-OCH_3-2'-CH_3-,
5: 2,2'-$(OCH_3)_2$-

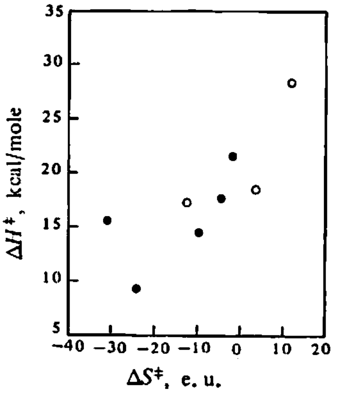

Fig. 9 Relationship between enthalpies of activation and entropies of activation

●: One-proton,

○: Two-proton

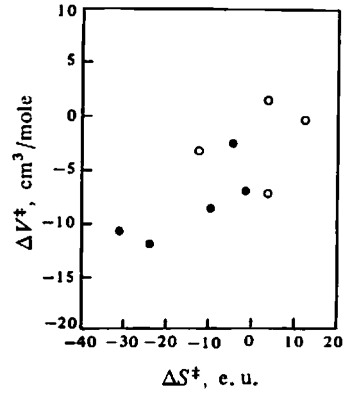

Fig. 10 Relationship between volumes of activation and entropies of activation

●: One-proton,

○: Two-proton

Fig. 9 shows the relationship between the enthalpies of activation and the entropies of activation. Considerable divergences being observed, it is presumed that many characters of the substituents influence each other, and it is considerably difficult to account for the fact.

Fig. 10 illustrates the relationship between the volumes of activation and entropies of activation.

The observed tendency in Fig. 10 is considered to be reasonable on the assumption that the solvation around the transition state influences the volumes of activation.

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