

## Some Aspects of Pressure Effects in Solution\*

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Received June 28, 1969

One aspect of pressure effects is the solvent effect of alcoholic solutions of anhydrous cobaltous chloride. In alcohols higher than ethanol, it shows the same color and has absorption peak at the same wave length (660 m $\mu$ ) as in ethanol.

We measured the visible absorption spectra at normal pressure and at higher pressure (up to 10,000 kg/cm<sup>2</sup>) and the conductivity at normal pressure, and found very remarkable distinction between the properties of those solutions depending on the molecular structure of the alcohols used as solvent.

The other aspect is the effect of pressure on the reaction rates of benzidine rearrangements which has been investigated in the last few years. The importance of rate data under high pressure is evident in interpreting the reaction mechanisms, which have been proposed by Ingold, Dewar, Wittig and Shine. The rate of rearrangement of 2, 2'-dibromohydrazobenzene followed by the spectroscopic method is expressed by the following equation.

$$k_{obs} = k_1[\text{HCl}] + k_2[\text{HCl}]^2$$

From the temperature and pressure dependence of  $k_1$  and  $k_2$ , the reaction mechanisms are discussed, comparing the results reported previously.

One aspect of the pressure effect is the solvent effect in equilibrium. In solution, the pressure effect appears through solvent and has two significances. One is through the change of macroscopic properties with pressure (this effect can be understood by the meaning of  $\Delta V$  of the change.). The other is through the change of specific molecular interaction by the contraction of the distance between solute and solvent molecules.

The former of the pressure effects has been well discussed. In the following investigation I will show a case of pressure effect on the rather strong specific interaction which may be considered as co-ordination of solvent molecules to a solute molecule.

The well known high pressure optical vessel used up to 10,000 atm is shown in Fig. 1. The thickness of sapphire window is 10 mm, diameter 10 mm and the path length 2 or 3 mm. The measurements are performed at room temperature. The pressure of the vessel is determined by the pressure at the first stage of the intensifier which is corrected by free piston gauge, and the piston ratio of the intensifier.

The absorption spectra of cobaltous chloride in various solvents is shown in Fig. 2. It is well known that cobaltous chloride shows a pink color in water, a magenta color in methanol, and a blue color in ethanol.

\* Lecture invited in the Second International High Pressure Conference, Germany, 1968.

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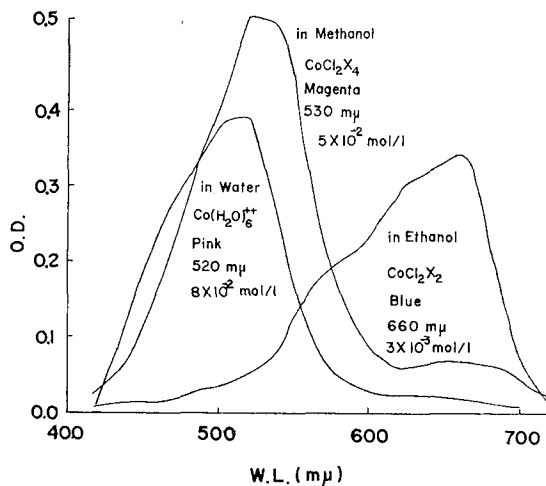
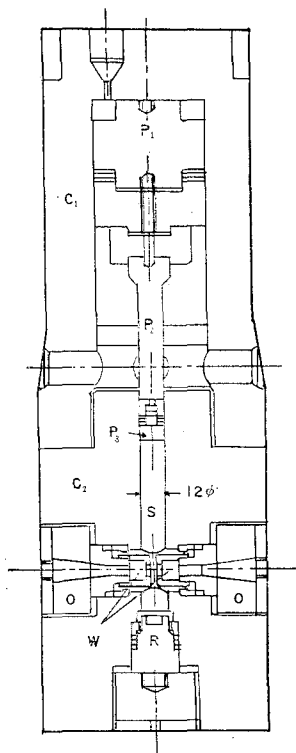


Fig. 1. High pressure optical cell. Fig. 2. Absorption spectra of cobaltous chloride solution.

These difference is considered to be due to the different molecular species existing in the solution as indicated in Fig. 2, that is,  $\text{Co}(\text{H}_2\text{O})_6^{++}$  as chromophore in water,  $\text{CoX}_4\text{Cl}_2$  (or  $\text{CoX}_2\text{Cl}_2$ ) in methanol, and  $\text{CoX}_2\text{Cl}_2$  in ethanol where X represents a solvent molecule.<sup>1)</sup>

In alcohols higher than ethanol, it shows the same blue color and has absorption band at the same wave length as in ethanol. However, there have been few investigations on these solutions. We measured the visible absorption spectra of  $\text{CoCl}_2$  in various alcohols at high pressure up to 10,000 atm and found a very remarkable pressure effect.<sup>2)</sup>

The absorption spectra in ethanol solution at high pressure is shown in Fig. 3. These measurements are reversible and reproducible. In the figure, optical density is shown against wave length. The numbers in the figure indicate the pressure in  $\text{kg}/\text{cm}^2$  unit. The intensity of the absorption band near  $660\text{m}\mu$  corresponding to the blue color decreases with the increase of pressure, and at  $2,000\text{ kg}/\text{cm}^2$  it is nearly two-tenth of that at normal pressure.

The absorption spectra in *iso*-butanol solution at high pressure is shown in Fig. 4. The same tendency as in ethanol solution is shown, but in this case, the rate of decrease of the intensity is rather small. At about  $6,000\text{ kg}/\text{cm}^2$ , the intensity becomes to one-tenth of that at normal pressure.

Thus, the rate of decrease of intensity may have much difference in various alcohols used as solvents.

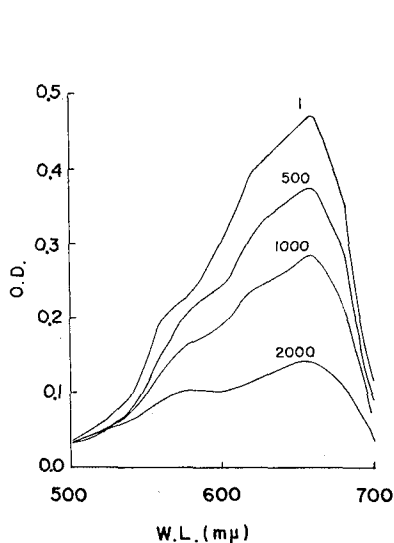


Fig. 3. Absorption spectra of  $\text{CoCl}_2$  in ethanol.

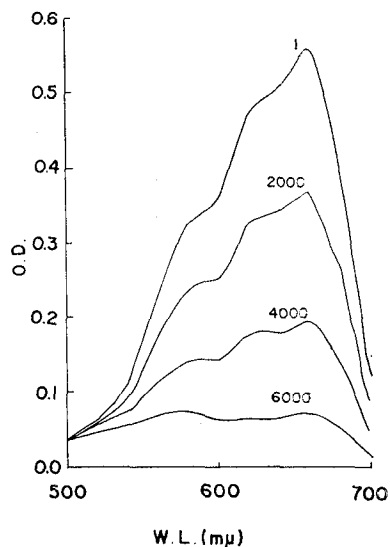


Fig. 4. Absorption spectra of  $\text{CoCl}_2$  in *iso*-butanol.

The ratio of optical density at  $660\text{ m}\mu$  at high pressure to that at normal pressure is shown in Fig. 5. In normal alcohols such as ethanol or *n*-butanol, the rate of decrease is very large, in alcohols with a side chain rather apart from OH group as in *iso*-butanol, the rate is moderate, and in alcohols with side chain close to OH group as in *sec*-butanol, the rate is very small.

In case of other alcohols than cited here, the result is shown in the Table 1. The ratio of optical density at high pressure to that at normal pressure at  $660\text{ m}\mu$  is found. In normal alcohols shown in the first rank, it becomes below one-half at  $2,000\text{ kg/cm}^2$  and to almost zero at  $6,000\text{ kg/cm}^2$ . The side chain alcohols such shown in the second rank as *iso*-butanol and *iso*-pentanol, the ratio is above one half at  $2,000\text{ kg/cm}^2$  and is about one tenth at  $6,000\text{ kg/cm}^2$ . In alcohols in the third rank, the decrease is almost negligible at  $2,000\text{ kg/cm}^2$  and it is nine-

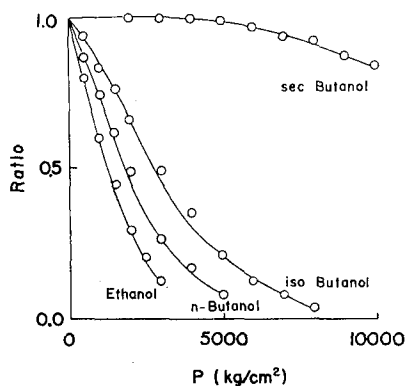


Fig. 5. Ratio of optical density at  $660\text{ m}\mu$  under high pressure.

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Table 1. Ratio of O. D. at 660 m $\mu$ .

Solvent		2000 kg/cm <sup>2</sup>	6000 kg/cm <sup>2</sup>
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	0.30	nil
<i>n</i> -Propanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	0.38	nil
<i>n</i> -Butanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	0.49	nil
<i>n</i> -Pentanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH	0.42	nil
<i>n</i> -Hexanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> OH	0.30	nil
<i>n</i> -Octanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> OH	0.40	nil
<i>iso</i> -Pentanol	(CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> OH	0.52	0.06
<i>iso</i> -Butanol	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH	0.66	0.13
<i>iso</i> -Propanol	CH <sub>3</sub> CH(OH)CH <sub>3</sub>	1.00	0.89
<i>sec</i> -Hexanol	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(OH)CH <sub>3</sub>	0.98	0.93
<i>sec</i> -Butanol	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	1.01	0.97
<i>t</i> -Butanol	CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> OH	1.00(240)	

tenth or above at 6,000 kg/cm<sup>2</sup>.

Comparing the solvent effect of twelve alcohols, the structural effect of solvent molecules is remarkable as shown on the rate of decrease of optical density.

It is well known that the pressure favors ionic dissociation. Considering the molecular species corresponding to blue color to be CoCl<sub>2</sub>X<sub>2</sub> as proposed by Gebert and others,<sup>1)</sup> it may be probable that the phenomena are related with the shift of chemical equilibrium between blue CoCl<sub>2</sub>X<sub>2</sub> and some colorless ionic species.

In ethanol, the existence of ionic equilibrium is mentioned already by some investigators. To make it clear whether there is such equilibrium in other alcohols, we measured the concentration dependences of the absorption intensity and the electrolytic conductance both at normal pressure.

The concentration dependences of effective extinction coefficient of ethanol solution are shown in Fig. 6. The numbers show the concentration in 10<sup>-4</sup> mole/l unit, that is from 1 to 11 in this unit.

Effective extinction coefficient is defined as the optical density divided by the total concentration of CoCl<sub>2</sub> (in mole/l) and the path length (10 cm).

The figure shows Beer's law does not hold in this solution. It is certain that some chemical equilibrium between the chromophore CoCl<sub>2</sub>X<sub>2</sub> and other species is present.

The analogous result on *n*-propanol solution is shown in Fig. 7. Effective extinction coefficient increases with increase of concentration as in ethanol. Similar result is obtained for *n*-butanol and to less extent for *iso*-butanol solution. In alcohols showing large pressure effect, there is some chemical equilibrium.

The result for *iso*-propanol solution is shown in Fig. 8. The concentration of the solution shown by the circle (○) is ten times as large as that of the solution shown by dark point (•). We can see Beer's law hold completely.

The result for *sec*-butanol solution is found in Fig. 9. The obedience to Beer's law is shown also in this case. Thus it may be considered that the equilibrium

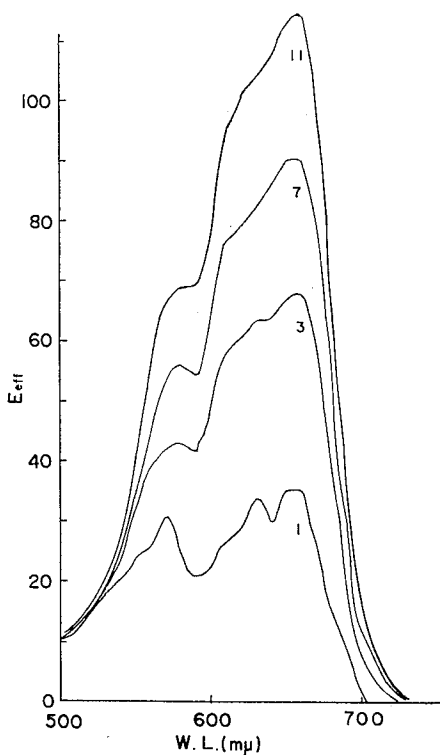


Fig. 6. Absorption spectra of  $\text{CoCl}_2$  in ethanol.

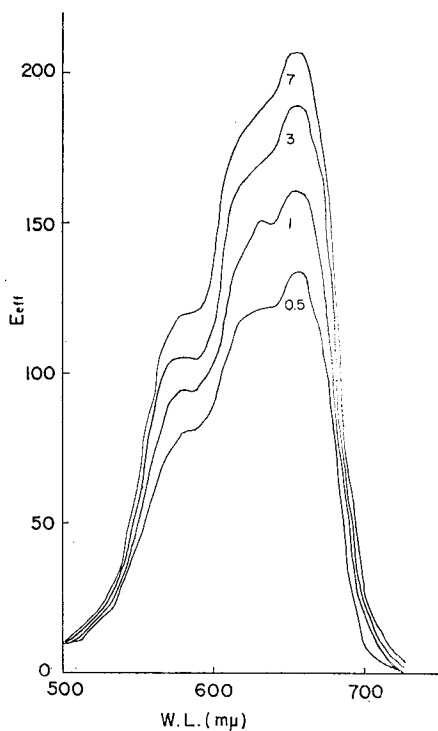


Fig. 7. Absorption spectra of  $\text{CoCl}_2$  in propanol.

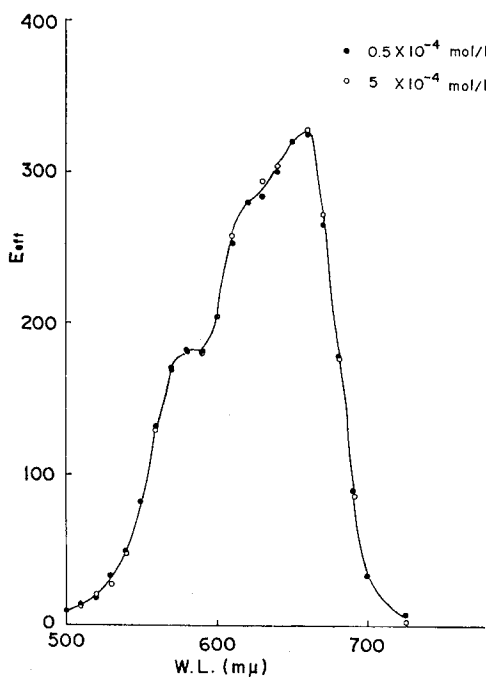


Fig. 8. Absorption spectra of  $\text{CoCl}_2$  in *iso*-propanol.

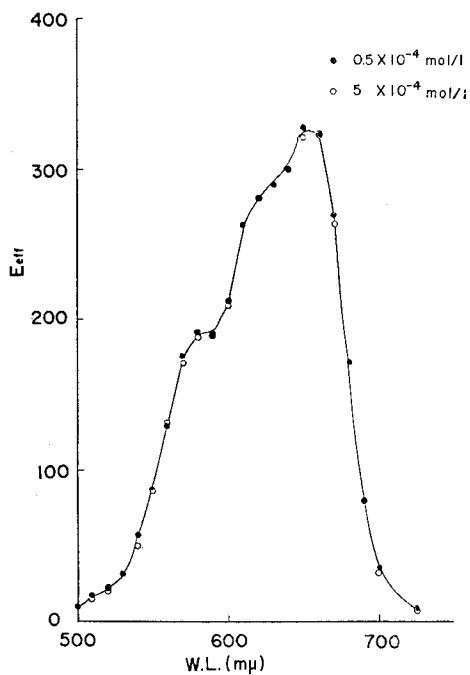


Fig. 9. Absorption spectra of  $\text{CoCl}_2$  in *sec*-butanol.

existing in normal alcohols does not exist in branched alcohols as *iso*-propanol and *sec*-butanol, which show almost no pressure effect.

The conductivity of normal alcohol solution at fairly low concentration is shown in Fig. 10. Normal alcohol solutions have fairly high conductivity. However, in branched alcohols, such as *iso*-propanol, and *sec*-butanol, the conductivity is none or very small and is difficult to measure. Thus the species in equilibrium with chromophore may be considered to be ionic. Equivalent conductance  $\Lambda$  increases with decrease of concentration as in usual electrolytic solution. And the extrapolation of the result of ethanol solution to infinite dilution gives the equivalent conductance at infinite dilution to be  $\Lambda_0 = 41.8 \text{ ohm}^{-1}\text{cm}^2\text{eq.}^{-1}$ . The equivalent conductance thus obtained is reasonably explained as the sum of those of  $\text{Co}^{++}$  ion and  $\text{Cl}^-$  ion which were measured and estimated. Therefore, the ionic species concerning in the equilibrium are  $\text{Co}^{++}$  and  $\text{Cl}^-$  ions. Further, as shown in Fig. 11, the effect of addition of LiCl shows the equilibrium shifts to the constant concentration of chromophore. The numbers in Fig. 11 indicate mole ratio of LiCl to that of  $\text{CoCl}_2$ . The nonlinear relation between  $\Lambda$  and  $\sqrt{C}$  indicates some ion pair formation even at fairly dilute range, and the ion pair may be  $\text{CoCl}^+$ ,  $\text{CoCl}_2$ , or  $\text{CoCl}_3^-$ . Now, it is clear that there exist, in normal alcohols, an equilibrium between chromophore, some ion pairs, and ions  $\text{Co}^{++} + \text{Cl}^-$  and not exist in branched alcohols which shows almost no pressure effect.

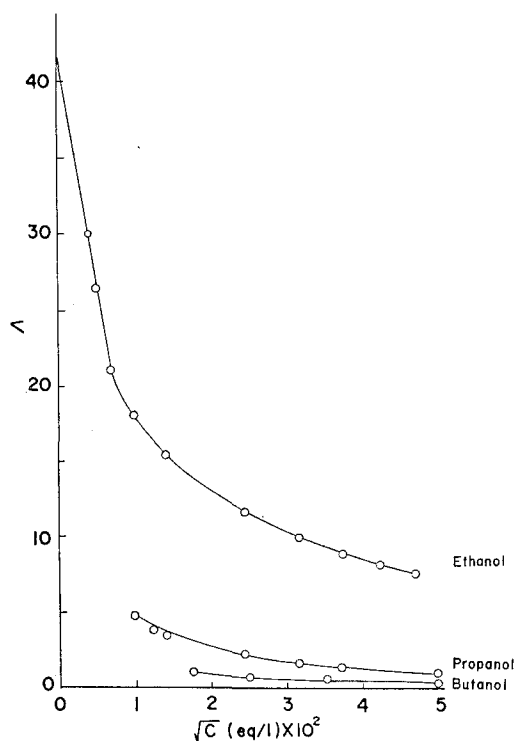


Fig. 10. Conductivity of  $\text{CoCl}_2$  in Alcohols  $\Lambda_0$  ( $\text{CoCl}_2$  in Ethanol) = 41.8.

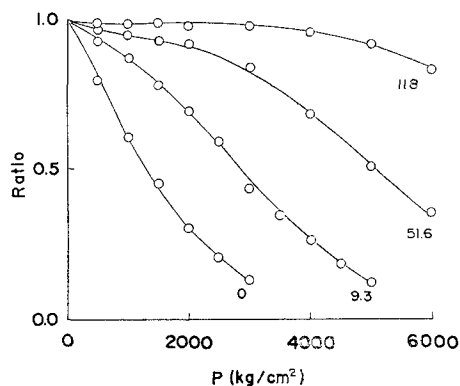


Fig. 11. Ratio of optical density at 660  $m\mu$  under high pressure  $\text{CoCl}_2$  in Ethanol with LiCl.

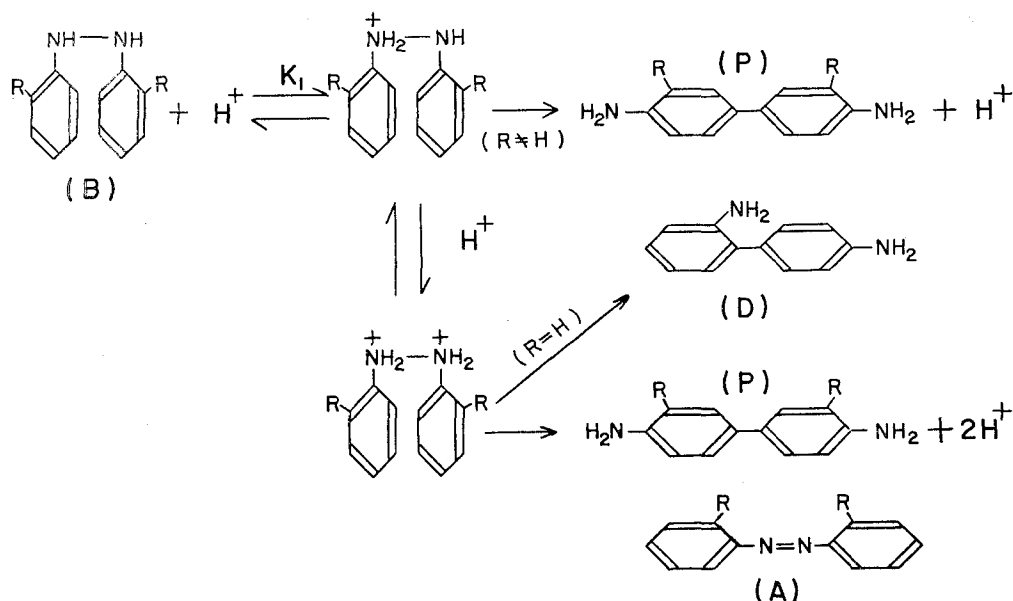


Fig. 12. Scheme of Benzidine rearrangements.

This will be the cause of the very marked distinction in the pressure effect observed in this experiment.

Thus, the extent of ionic equilibrium will be through the difference of the steric interaction of coordinating solvent molecules in the complex  $\text{CoCl}_2\text{X}_2$ .

Almost all pressure effects discussed is due to the macroscopic property of volume change. Steric or structural effect has been considered to be important, but available data are few. This experiment shows remarkable difference of structural effect in coordination of solvents.

The other aspect of pressure effect to discuss is that on reaction rate. On the rearrangement of benzidine, the scheme of reactions is shown in Fig. 12 and many informations were accumulated. Polar transition state by Ingold<sup>31</sup>,  $\pi$ -complex by Dewar<sup>41</sup>, and caged dissociation mechanism<sup>51</sup> and so on have been proposed. Anyway the problem becomes more complex with accumulation of the informations.

We already studied this rearrangement on hydrazobenzene<sup>61</sup> and 2,2'-dimethylhydrazobenzene.<sup>71</sup> In relation to these studies, the rearrangement of 2,2'-dibromohydrazobenzene is studied from the stand point of high pressure kinetics which give us the information of transition parameters.

The experimentals is the same as already published. High pressure apparatus used is a simple piston-cylinder type which can be used conveniently up to 10,000 kg/cm<sup>2</sup>, as shown in Fig. 13. Spectro-photomeric method is used to the determination of concentration of reactant B (2,2'-dibromohydrazobenzene), product P (3,3'-dibromobenzidine) and oxidation product A (2,2'-dibromoazobenzene). Stoichiometrical balance in this reaction is kept within  $\pm 1$  per cent.

Figure 13 shows the plot of the fraction for the rearrangement obeys strictly

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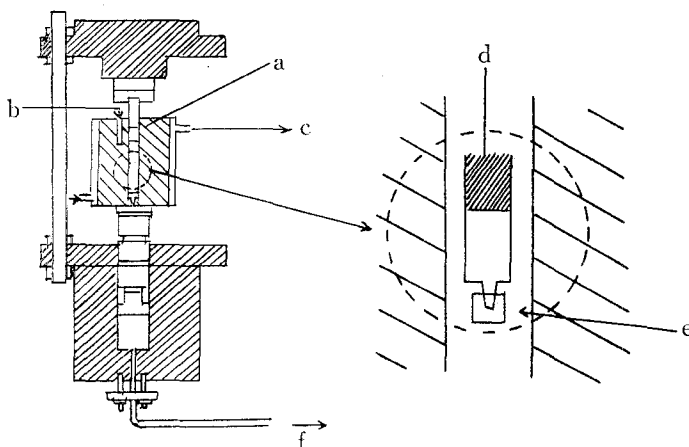


Fig. 13. The high pressure equipment.  
 a, pressure vessel; b, thermocouple; c, thermostatted water;  
 d, glass syringe; e, Teflon; f, to plunger pump.

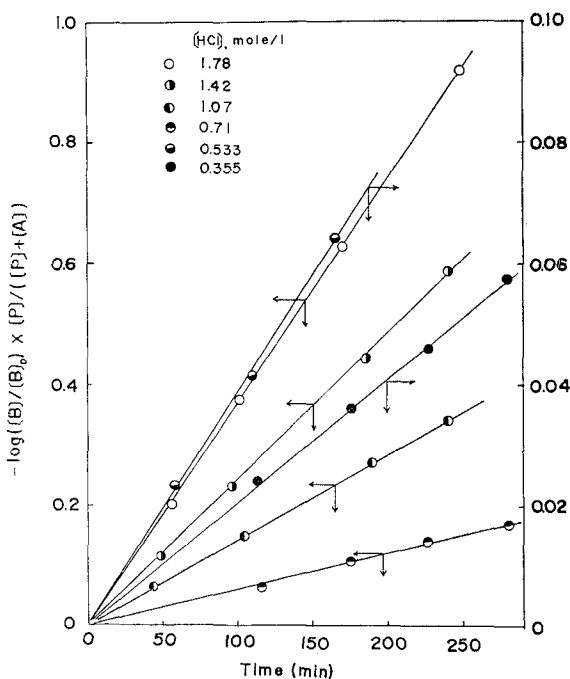


Fig. 14. Plots for following reaction rate.

the first order rate equation with respect to reactant (2, 2'-dibromohydrazobenzene). The left side scale in the Fig. 14 is for the high concentration and the right side scale for the low concentration. Acid dependence of the rate constant  $k_r$  at constant ionic strength, is not integral order, but between 1 and 2. This means the existence of two independent catalytic mechanisms as shown in the following equation.

$$k_r = k_1[\text{H}^+] + k_2[\text{H}^+]^2$$



To obtain the values of  $k_1$  and  $k_2$ ,  $k_r/[H^+]$  is plotted against acid concentration  $[H^+]$ . The results are shown in Fig. 15 at 1 atm and various temperatures and Fig. 16 at 40°C and various pressures. The values of  $k_1$  and  $k_2$  thus obtained are shown in Table 2. Dependences of  $k_1$  and  $k_2$  on temperature are plotted after Arrhenius in Fig. 17 and pressure dependence of  $k_1$  is shown in Fig. 18.  $k_2$  is almost independent of pressure. From these lines, activation parameters, those are activation energy  $E$ , activation entropy  $\Delta S^\ddagger$  and activation volume  $\Delta V^\ddagger$  are obtained.

By considering the activation parameters, we can elucidate the mechanism of the reaction. This is one of the important contribution of pressure effects.

Table 3 shows these activation parameters together with those of hydrazobenzene and 2, 2'-dimethyl hydrazobenzene which were measured in our laboratory.

As mentioned previously, mechanism of benzidine rearrangement is not

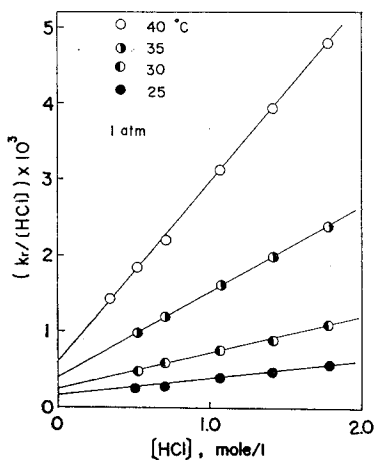


Fig. 15. Dependence of rate constants on  $[HCl]$ .  $k_r/[HCl] = k_1 + k_2[HCl]$

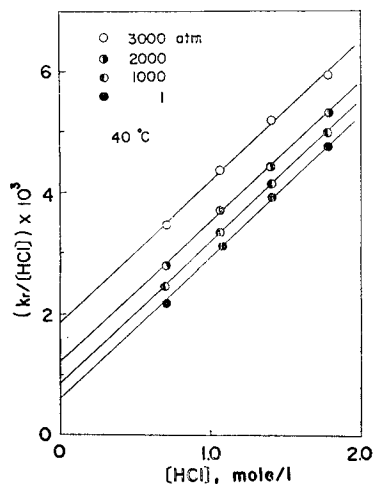


Fig. 16. Dependence of rate constants on  $[HCl]$ .  $k_r/[HCl] = k_1 + k_2[HCl]$

Table 2. Rate constants.

°C	P atm	$k_1 \times 10^3, l \text{ mol}^{-1} \text{ min}^{-1}$	$k_2 \times 10^3, l^2 \text{ mol}^{-2} \text{ min}^{-1}$
40	1	0.60	2.36
	1000	0.84	2.36
	2000	1.19	2.30
	3000	1.83	2.33
35	1	0.40	1.12
30	1	0.25	0.48
	2000	0.54	0.49
	3000	0.84	0.51
25	1	0.16	0.23
	3000	0.60	0.24

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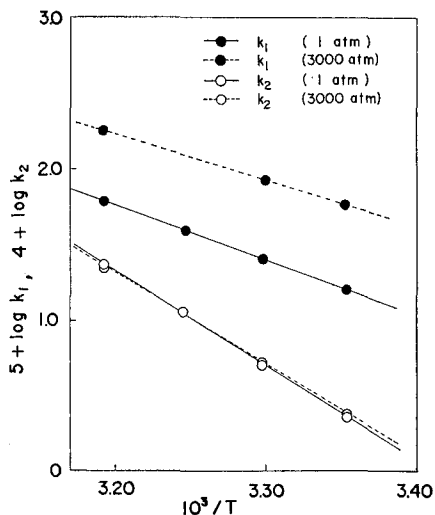


Fig. 17. Dependence of rate constant on temperature.

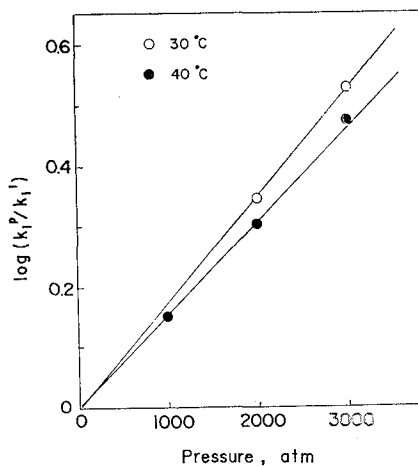
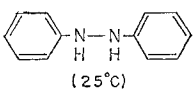
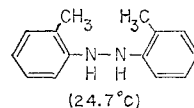
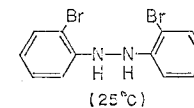
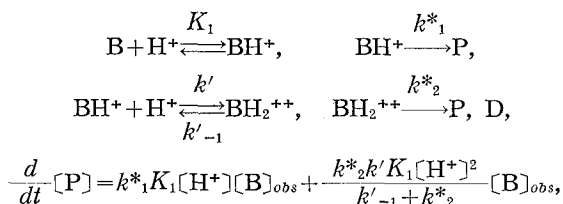


Fig. 18. Dependence of rate constant on pressure.

Table 3

	 (25°C)		 (24.7°C)		 (25°C)	
pressure (atm)	1	3000	1	3000	1	3000
$k_1$ (l mole <sup>-1</sup> min <sup>-1</sup> )	—	—	0.573	0.703	$0.16 \times 10^{-8}$	$0.60 \times 10^{-8}$
E (kcal mole <sup>-1</sup> )	—	—	20.9	21.6	16.3	13.2
$\Delta S^\ddagger$ (cal mole <sup>-1</sup> deg <sup>-1</sup> )	—	—	0.6	3.3	-31.5	-39.0
$\Delta V^\ddagger$ (cc mole <sup>-1</sup> )	—	—	-2.5		-10.7	
$k_2$ (l <sup>2</sup> mole <sup>-2</sup> min <sup>-1</sup> )	3.65	3.49	3.0	6.4	$0.23 \times 10^{-3}$	$0.24 \times 10^{-3}$
E (kcal mole <sup>-1</sup> )	20.8	19.1	21.0	21.9	29.0	28.0
$\Delta S^\ddagger$ (cal mole <sup>-1</sup> deg <sup>-1</sup> )	3.6	-2.4	4.1	8.9	11.8	9.12
$\Delta V^\ddagger$ (cc mole <sup>-1</sup> )	1.5		-7.2		0	

established. We may safely say that this is no mechanism reaction. The proposed mechanism, however, may be interesting from the stand point of organic chemistry. Discussions from the stand point of kinetics are rare, but this reaction consists of the following steps. In these cases, the rate constant of the methyl substituted is biggest and that of the bromo-substituted smallest.



$$\frac{d}{dt}[\text{P}] = k^*_1 K_1 [\text{H}^+] [\text{B}]_{obs} + k^*_2 K' K_1 [\text{H}^+]^2 [\text{B}]_{obs},$$

$$\frac{d}{dt}[\text{P}] = k^*_1 K_1 [\text{H}^+] [\text{B}]_{obs} + k' K_1 [\text{H}^+]^2 [\text{B}]_{obs},$$

$$\Delta V_1^{\ddagger} = \Delta V_{K_1} + \Delta^* V_1^{\ddagger},$$

$$\Delta V_2^{\ddagger} = \Delta V_{K_1} + \Delta V_{K'} + \Delta^* V_2^{\ddagger} \text{ or } \Delta V_2^{\ddagger} = \Delta V_{K_1} + V_{K'}^{\ddagger}.$$

This is due to the electron repelling and the electron attracting nature of substituents.

The changes of activation parameters in these cases can not be understood uniquely by the proposed mechanism, so I will mention the vision of the mechanism by considering the activation parameters.

In the case of hydrazobenzene, considering that the products are benzidine and diphenylene and that the activation volume  $\Delta V^{\ddagger}$  is slightly positive, it is likely that the two aryl fragments are bonded rather loosely in the transition state, although the observed activation volume are composite. This is supported by the results of the entropy change from positive to negative with pressure and by the change of the ratio of the products, that is ratio of benzidine to diphenylene increase with pressure.

In the case of 2, 2'-dimethyl hydrazobenzene, the product is only benzidine, and activation volumes for one-proton and two-proton steps are both negative. These values are able to be explained reasonably by assuming that single and double protonations are both in equilibrium. The activation volumes are represented by the composite terms, as shown in the following.

$$\Delta V_1^{\ddagger} = \Delta V_{K_1} + \Delta^* V_1^{\ddagger}$$

$$\Delta V_2^{\ddagger} = \Delta V_{K_1} + \Delta V_{K'_2} + \Delta^* V_2^{\ddagger}$$

Estimating each term, the observed values are reasonably understood.

On the other hand, the feature is drastic in the case of 2, 2'-dibromohydrazobenzene. The entropy of activation of one proton step is very large negative and that of two proton step is fairly large. And the volume of activation of the former is large negative and that of the latter is nearly zero. These figures are difficult to understand, but it may be sure that the transition state of one proton step is very rigid one which may be analogous to  $\pi$ -complex, and that of two proton step is rather loose. This drastic changes of activation parameters are due to the change of rate controlling step, that is, the protonation of the former two cases is in equilibrium, but in the case of the bromo-substituted, the second protonation is considered to be rate determining.

Anyway, the further accumulation of data, especially on the effect of pressure on the distribution of products and much more data of transition parameters will be required to the elucidation of the benzidine rearrangement.

#### ACKNOWLEDGMENT

The author wishes to express his thanks to Mr. I. Onishi, Mr. M. Sasaki and Mr. Y. Kitamura for their collaboration.

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