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THE BENZIDINE REARRANGEMENT AT HIGH PRESSURE AND HIGH TEMPERATURE

BY JIRO OSUGI, MASARU NAKAHARA and MAKOTO HORIGUCHI

The benzidine rearrangement of hydrazobenzene catalyzed by the zeolite of Y-type was studied at the pressure up to 30 kb. The lowest temperature at which the benzidine rearrangement occurred was measured as a function of pressure. The efficiency of the zeolites (NaY and HY) as catalysts on the benzidine rearrangement in the solid state were confirmed. The kinetic information of the intramolecular rearrangement at 210°C was given. The mean values of the activation volumes of the ortho- and para-rearrangents in the pressure range of 20 to 30 kb are +4.0 and 4.1 cm^3/mole, respectively. The structure of the transition state and the reaction mechanism of the benzidine rearrangement have been discussed.

Introduction

The benzidine rearrangement was first observed in solution by Hofmann[1] in 1863. Three kinds of views were developed about the mechanism of this reaction. The first was suggested by Hughes and Ingold[2] in 1941. They proposed a polar transition state on the basis of the strong solvent effect; the new C–C bond to combine the two benzene rings is mainly electrovalent. The second was suggested by Dewar[3] in 1946. He assumed that the rearrangement goes through a protonated intermediate; the original N–N bond is replaced by a delocalized "π-bond" between the two benzene rings, the "π-bond" holding the rings in parallel, and the rearrangement finishes when the delocalized "π-bond" is transformed to the localized intramolecular C–C bond. The third was suggested by Vecera *et al.*[4] in 1960. They assumed that the protonated hydrazo compound splits homolytically into the radical intermediates in a solvent cage.

The benzidine rearrangement has been studied mostly in solutions and at atmospheric pressure, except for a few high pressure works done in our laboratory. In 1964, Osugi and Hitouji[5] first examined the pressure effect on this rearrangement in ethanol solution, and concluded that this reaction was slightly retarded by pressure. Recently, Osugi, Sasaki and Onishi[6~11] made more precise kinetic

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[1] A. W. von Hofmann, *Proc. Roy. Soc.*, **12**, 576 (1863)
[2] T. R. Hughes and C. K. Ingold, *J. Chem. Soc.*, **1946**, 220
[3] M. J. S. Dewar, *ibid.*, **1946A**, 406; **1946B**, 777
[4] M. Vecera, L. Synek and V. Sterba, *Coll. Czech. Chem. Comm.*, **25**, 1992 (1960)
[5] J. Osugi and T. Hitouji, *This Journal*, **34**, 88 (1964)
[6] J. Osugi, M. Sasaki and I. Onishi, *ibid.*, **36**, 100 (1966)
[7] J. Osugi, M. Sasaki and I. Onishi, *ibid.*, **39**, 57 (1969)

investigation on the benzidine rearrangement of substituted hydrazo compounds in the mixed solvents at high pressure. Most of these works have been done in solutions. It is a new and interesting problem to study the benzidine rearrangement in the solid state. Since there is no solvation effect in the solid state reaction and the displacement of the atoms involved in this intramolecular rearrangement is not so much complicated, the reaction mechanism would be much easier to be analysed.

Experiment

Materials

Hydrazobenzene from Nakarai Chemicals Co. was used after being recrystallized from ethanol solution. Benzidine was supplied by Merck Co., and synthetic zeolite of NaY type, Linde SK 40 (Si/Al=2.5) by Nikka Seiko Co. The zeolite, NaY was dried in vacuum at 120~130°C for about 10 hr. prior to use. A most active zeolite as a solid acid, HY was obtained from the NH_4^+-substituted zeolite, NH_4Y in the usual way.

Apparatus

The cubic anvil apparatus12) was used in the present work, and the design of the reaction cell was described elsewhere13). The low pressure experiment was carried out in the sealed glass tube after degassing for 2 hr. The temperature was measured directly by the chromel-alumel thermocouple.

Pressure-temperature region where the benzidine rearragement occurs

Hydrazobenzene and zeolite, NaY or HY, were mixed in the ratios that are shown in Table 1. It was checked by the thin layer chromatography whether benzidine was formed or not after 30 min. These examinations were repeated till the difference between the highest temperature at which the benzidine rearrangement could not occur and the lowest one where it could occur became about 2°C. In this way, the boundary between the two phases was determined as a function of pressure.

Products anaysis

The concentrations of the products were analyzed by the spectrophotometric method which was employed first by Carlin14). In high pressure runs, the mixture of the reactant and zeolite was not completely free from oxygen on account of the experimental difficulty, and then azobenzene was formed as a byproduct. In view of the simplicity of the reaction mechanism, the products analysis was attempted in the case of the reaction of hydrazobenzene without zeolite, but it was not reproducible. Probably due to the variety of the products which was really recognized in the thin layer chromatograph.

According to Beer's law,

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8) J. Osugi, M. Sasaki and I. Onishi, *This Journal.*, **40**, 39 (1970)
9) J. Osugi and I. Onishi, *ibid.*, **41**, 32 (1972)
10) I. Onishi, *ibid.*, **41**, 42 (1972)
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12) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *ibid.*, **34**, 1 (1964)
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14) R. B. Carlin, R. G. Nelb and R. C. Odioso, *J. Am. Chem. Soc.*, **73**, 1002 (1951)

Table 1 Ratio of the zeolite to the reactant

system / substance	(weight ratio)		(mole ratio)	
	hy+NaY	hy+HY	hy+NaY	hy+HY
hy	1.00	1.00	1.00	1.00
NaY	1.19	—	0.472	—
YH	—	1.00	—	0.438

*hy denotes hydrazobenzene

Table 2 Specific extinction coefficietns

substance	wave length (nm) 245	270	285	320
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

$$D(\lambda)=\varepsilon_{Hy}(\lambda)[Hy]+\varepsilon_{Be}(\lambda)[Be]+\varepsilon_{Di}(\lambda)[Di]+\varepsilon_{Az}(\lambda)[Az]. \quad (1)$$

where $\varepsilon_C(\lambda)$ is the specific extinction coefficent of the component C at the wave length λ. The concentrations of these four components were calculated from the four simultaneous equations given by Eq. (1). The optical densities of the reaction mixtures were measured at 245, 270, 295 and 320 nm by a Shimadzu UV-200S. The values of the specific extinction coefficients used for the analysis are shown in Table 2.

Results and Discussions

Pressure-temperature region where the benzidine rearrangement occurs

The pressure dependence of the reaction temperature, T_r of hydrazobenzene is shown in Figs. 1~4. In Fig.1 the reactant is only hydrazobenzene, in Fig. 2 it is mixed with the catalyst NaY, and in Fig. 3 with HY. The ratio of each mixture is shown in Table 1. These results are compared in Fig. 4.

The benzidine rearrangement which is catalyzed by the proton-type zeolite HY can occur below the melting point of pure hydrazobenzene (~108°C) at low pressure. In other words, the benzidine rearrangement seems to occur in the solid phase. The observation of the state of the surface of the reaction mixture through the glass tube supported the idea that this rearrangement process would not involve any liquid phase. In high pressure runs, however, we are not sufficently sure that the rearrangement occurs in the solid phase because we could not measure the melting point of hydrazobenzene at high pressure. By the analogy to the low pressure reaction and besides by observing the surface condition of the reaction mixture after depressurizing we suppose that the rearrangement goes in the solid state especially in the case of the mixture of hydrazobenzene and zeolite HY, to which a

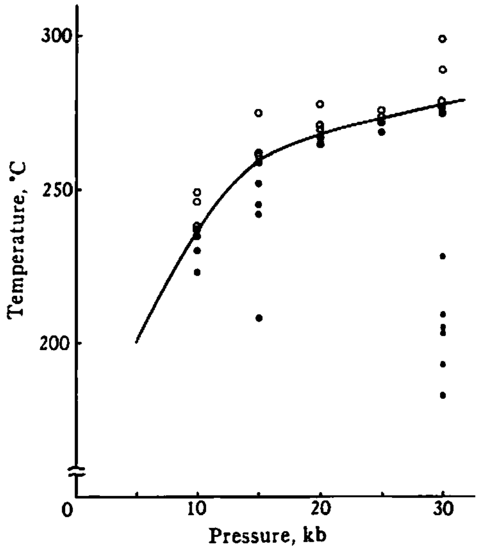

Fig. 1 Pressure-temperature region where the benzidine rearrangement occurs without catalyst
○: reacted, ●: non-reacted

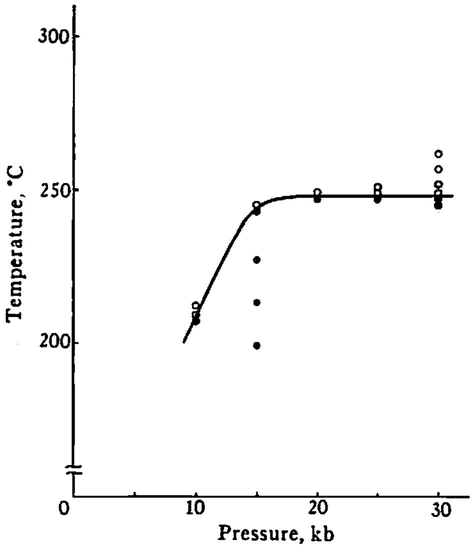

Fig. 2 Pressure-temperature region where the benzidine rearrangement occurs with NaY
○: reacted, ●: non-reacted

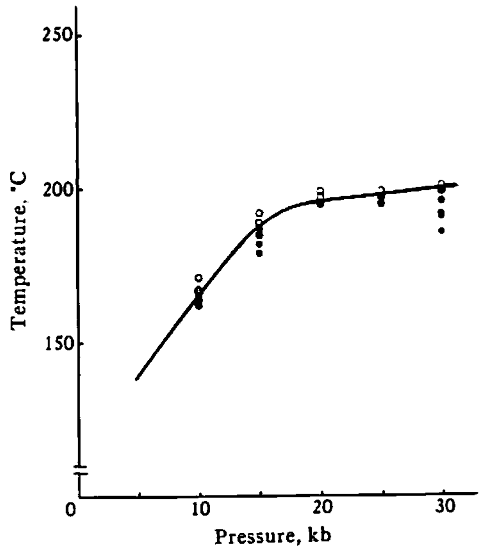

Fig. 3 Pressure-temperature region where the benzidine rearrangement occurs with HY
○: reacted, ●: non-reacted

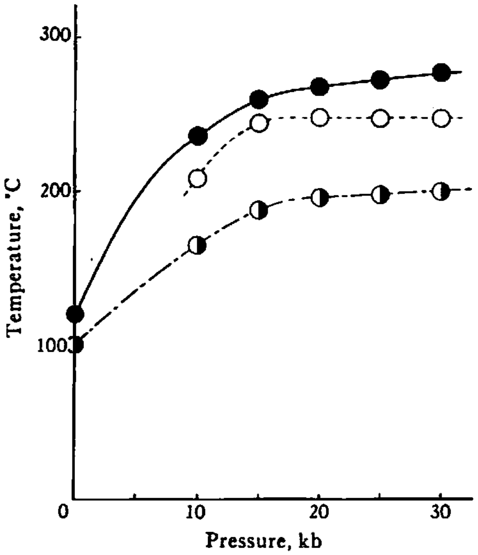

Fig. 4 Pressure-temperature region where the benzidine rearrangement occurs
●: without catalyst, ○: with NaY, ◑: with HY

kinetic consideration is given in the present paper.

As shown in Fig. 4 the reaction temperature T_r, is much higher than the ordinary temperature of the benzidine rearrangement in organic solvents. This would mean that the thermal excitation of the vibrational state of the N-N bond in the initial state is a very important factor of this reaction in the solid state. Over the whole pressure range, the curves of T_r without catalyst, with NaY and with Hy do not cross each other. Thus the sequence of the efficiency of the catalysts does not vary in this pressure range. Moreover, we can see that some Lewis acid sites in NaY are effective to the benzidine rearrangement, while most of the acids employed in this rearrangement in solution are Brönsted acids.

Between 20 and 30 kb, the increasing rate of T_r (0), T_r(NaY) and T_r (HY) with increasing pressure slows down. In particular, in the case of hydrazobenzene and NaY, the reaction temperature T_r (Na Y) is equally 248°C at 20, 25 and 30 kb. This feature would mean that the thermal energy required for the excitation of the N-N vibration for its bond cleavage and that of the C-H vibrations for their new C-C bond formation reach a constant value, either because the increase in the depth of the Morse function of the N-N bond with increasing pressure becomes cancelled by the decrease in the transition state energy, or because the increase in the depth of the potential well of the N-N bond comes to slow in the range of pressure.

Kinetic consideration

As mentioned above, the reaction mixtures were analyzed spectrophotometrically. Then, it was assumed that the products were only benzidine, diphenyline and azobenzene as in the case of the reaction in solution at high pressures. In order to check the validity of the assumption, the self-consistency of the obtained results was examined at 260 and 300 nm. The maximum difference between the value 260 and 300 nm. The maximum difference between the value calculated at 260 and 300 nm and that obtained from the simultaneous equations corresponding to Eq. (1) was 3%.

The time-yield relation of the reaction which is catalyzed by the zeolite HY is shown in Figs. 5

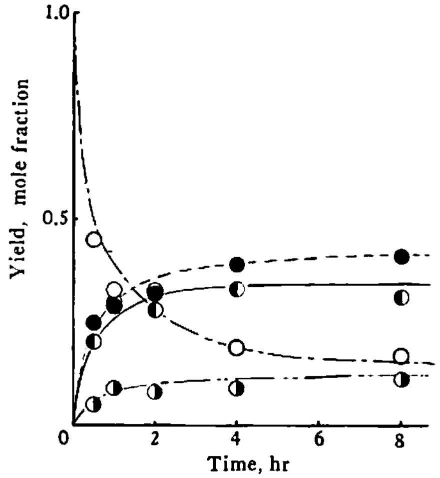

Fig. 5 Time-yield relation of the rearrangement at 20 kb and at 210°C
○: hydrazobenzene, ●: benzidine,
◗: diphenyline, ◑: azobenzene

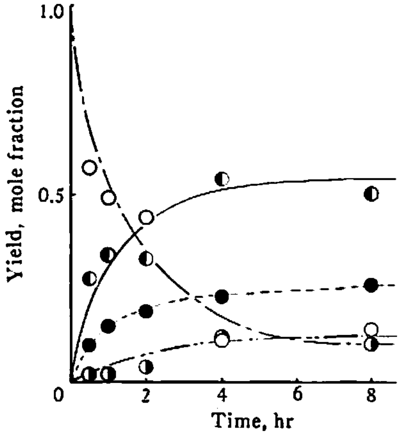

Fig. 6 Time-yield relation of the rearrangement at 30 kb and at 21 0°C
○: hydrazobenzene, ●: benzidine,
◑: diphenyline, ◗: azobenzene

and 6. Some discrepancies in the plots would be ascribed to the fact that the sizes of the particles distributed in the reaction mixture and are not the same in all runs.

Now, we try to set up the following rate equations for the benzidine rearrangement catalysed by HY;

$$d[\mathrm{Be}]/dt=k_{\mathrm{Be}}\alpha[\mathrm{Hy}]=k'_{\mathrm{Be}}[\mathrm{Hy}], \qquad (2)$$

$$d[\mathrm{Di}]/dt=k_{\mathrm{Di}}\alpha[\mathrm{Hy}]=k'_{\mathrm{Di}}[\mathrm{Dy}], \qquad (3)$$

$$d[\mathrm{Az}]/dt=k_{\mathrm{Az}}[\mathrm{O}][\mathrm{Hy}]=k'_{\mathrm{Az}}[\mathrm{Hy}], \qquad (4)$$

and

$$-d[\mathrm{Hy}]/dt=(k'_{\mathrm{Be}}+k'_{\mathrm{Di}}+k'_{\mathrm{Az}})[\mathrm{Hy}], \qquad (5)$$

where each k is the true time independent rate constant, each k' is the pseudo-first order rate constant of the respective reaction, and α is the fraction of the hydrazobenzene molecules which are in favorable contact with the active sites in the zeolite. When we assume k''s are time-independent, we can integrate Eq. (5) with respect to time to obtain the value of $k'_{\mathrm{Be}}+k'_{\mathrm{Di}}+k'_{\mathrm{Az}}$, and each k' in the sum can be obtained as a function of time by the products distribution determined spectrophotometically. The obtained values of k'_{Be}, k'_{Di} and k'_{Az} are shown in Figs. 7~9. The values of k'_{Be} and k'_{Di} at 0.5 hr are larger than those at later time because of the decrease of α with time, and the value of k'_{Az} at 0.5 hr is also larger than that at later time because of the consumption of the oxygen first contained to some extent in the reaction cell. The decrease in α with time seems to indicate that the rearrangement occurs in the solid state, because α would not be time-dependent if the hydrazobenzene molecules have mobility sufficient for their reorientation to favorable sites in the zeolite. These time-dependent k'_{Be} and k'_{Di} were extrapolated to zero time to obtain the activation volumes of each rearrangent. In the calculation it was assumed that α is independent of pressure ;

$$\begin{aligned}\Delta V^{\ast}&=-RT(\partial \ln k/\partial P)_T\\&=RT(\partial \ln \alpha/\partial P)_T-RT(\partial \ln k'/\partial P)_T\\&\fallingdotseq -RT(\Delta \ln k'/\Delta P)_T \qquad (6)\end{aligned}$$

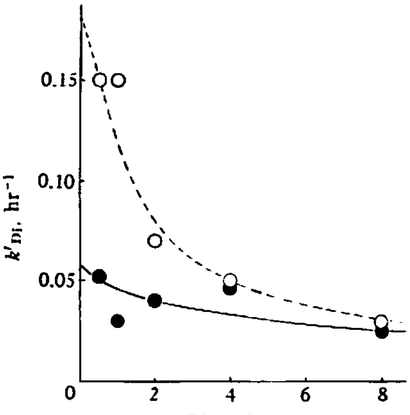

Fig. 7 The plot of k'_{Be} at 20 and 30 kb against time
○: 20 kb, ●: 30 kb

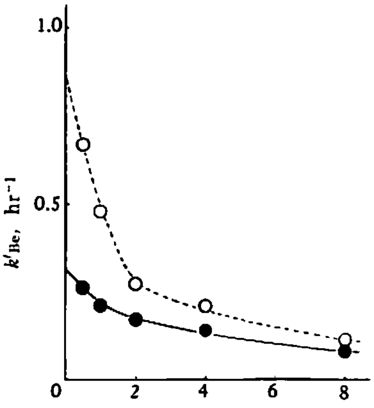

Fig. 8 The plot of k'_{Di} at 20 and 30 kb against time
○: 20 kb, ●: 30 kb

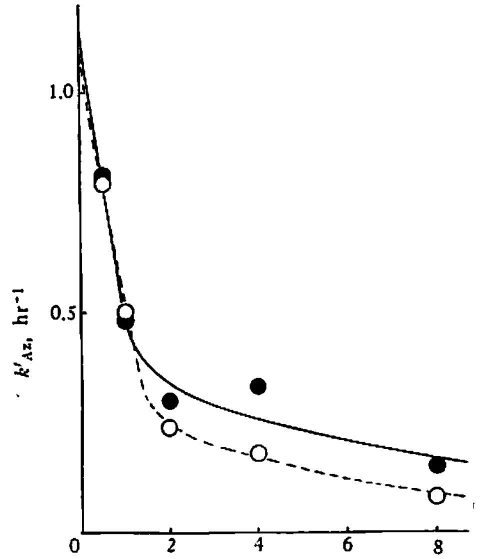

Fig. 9 The plot of k'_{Az} at 20 and 30 kb against time
○: 20 kb, ●: 30 kb

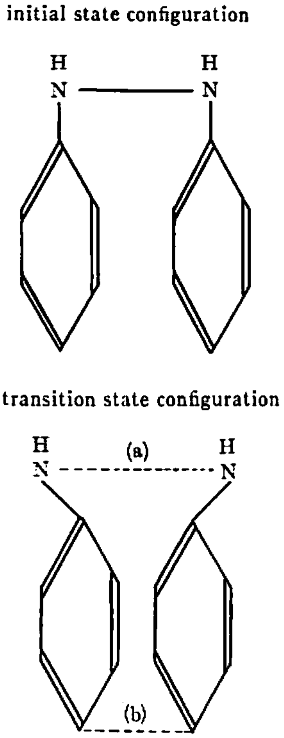

Fig. 10 A molecular model for the rearrangement
factor (a): expansion of the N-N bond
factor (b): approach of the two carbon atoms

Between 20 and 30 kb and at 210°C, we got $\Delta V^{\neq} = +4.0 \mathrm{cm}^3/\mathrm{mole}$ for *p*-benzidine rearrangement and $+4.1 \mathrm{cm}^3/\mathrm{mole}$ for *o*-benzidine rearrangement. As schemed in Fig. 10, there are two factors which are important in the benzidine rearrangement; one is the stretching of the N-N bond, and the other is the approach of the two carbon atoms which will make a new C-C bond between the rings Hence. the positive values of $\Delta V^{\neq}$ would indicate that the stretching of the N-Nbond is not compensated by the partial bond formation between the two carbon atoms. Furthermore, as can be seen in Fig. 4, the kinetically determined phase boundary (not equilibrium boundary in a rigorous sense) means as well as the sign of $\Delta V^{\neq}$ that pressure does not enhance the rearrangement even in the case of the absence of the catalyst. However, for the bimolecular reaction in solution as

$$A + BC \longrightarrow AB + C,$$

or

$$A^- + BC \longrightarrow AB + C^-,$$

where the activation step requires the simultaneous formation of one bond and the breaking of another, it was reviewed by Hamann[15] that the activation volume would be negative, because the solvation

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[15] S. D. Hamann, "Physico-Chemical Effects of Pressure", Chap. 9, Butterworths, London (1957)

effect is negligible in the above reactions. In other words, Hamann postulated that the transition state wold be more similar to the final state than to the initial state, not energetically but volumetrically. Unless the potential energy surface of the reaction is calculated theoretically, it is generally very difficult to khow where the transition state lies in the reaction coordinate. Then the present case is possible. As reviewed by Whalley[16], the kinetic data for the two-proton mechanism of the benzidine rearrangement in solution by Osugi and Hitouji[5] give a large positive activation volume ($\sim 15 \mathrm{cm}^3$/mole) at 20°C. Though there are many differences between both cases, the signs of the activation volumes coincide. Simple unimolecular rearrangents in the solid state like the present one would give an experimental way to obtain the volume change of the molecules themselves, $\Delta V_1^{\ne}$.

Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto 606
Japan

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[16] E. Whalley, *Ann. Rev. Phys. Chem.*, **18**, 205 (1967)