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<th>The effect of pressure on the rate of the benzidine rearrangement V: 2-chloro-2'-methylhydrazobenzene</th>
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<tbody>
<tr>
<td>Author(s)</td>
<td>Osugi, Jiro; Onishi, Ichiro</td>
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<tr>
<td>Citation</td>
<td>The Review of Physical Chemistry of Japan (1972), 41(1/2): 32-41</td>
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Kyoto University
THE EFFECT OF PRESSURE ON THE RATE OF
THE BENZIDINE REARRANGEMENT V
2-Chloro-2’-methylhydrazobenzene

BY JIRO OSUGI AND ICHIRO ONISHI

The effect of pressure on the rate of the acid-catalyzed rearrangement of
2-chloro-2’-methylhydrazobenzene in 85 vol% aqueous ethanolic solution was
studied under the conditions of 15–30°C and 1.1–1500 kg/cm². As a result, it
was observed that two different reactions concurred; one was of first order with
respect to [HCl] (one-proton mechanism) and the other was of second order (two-
proton mechanism), and the former was fairly, while the latter was slightly
accelerated by pressure.

Based on the activation parameters obtained, i.e., \( E^* = 22.2 \text{ kcal/mole} \), \( \Delta S^* = -1.6 \text{ e.u.} \), \( \Delta V^* = -6.8 \text{ cm}^3/\text{mole} \) for one-proton mechanism and \( E^* = 18.0 \text{ kcal/mole} \), \( \Delta S^* = -12.4 \text{ e.u.} \), \( \Delta V^* = -5.2 \text{ cm}^3/\text{mole} \) for two-proton mechanism, the reaction mechanisms and the transition states were discussed. The
existence of a linear relationship between the logarithms of the rate constants
of the rearrangement and \( \rho K_a \) values of ortho-substituted anilinium ions was
suggested, by correcting \( \rho K_a \) for the steric effect of ortho-substituents.

Introduction

The so-called benzidine rearrangement is an acid-catalyzed rearrangement and the rate of the
rearrangement of hydrazobenzene is of second order with respect to the acid concentration (two-
proton mechanism). But in the cases of 2, 2’-dimethyl-1a, 2, 2’-dimethoxy-1b and 2, 2’-dibromo-
hydrazobenzene1c, it was observed that the order of reaction in acid fell to one (one-proton mechanism)
or that two reactions of first and of second order concurred, depending on the electrostatic character of
the substituents. The reactions of one-proton mechanism was found to be always accelerated by
pressure irrespective of the substituents.

Considering the negative values of the volume of activation for one-proton mechanism, it was
presumed that the transition state of one-proton mechanism was polar, strongly solvated and compact.
As the compounds treated previously were all symmetrical, in order to obtain further information about
an unsymmetrical compound, the effect of pressure on the rate of the rearrangement of 2-chloro-2’-
The Effect of Pressure on the Rate of the Benzidine Rearrangement V

methyldihydrazobenzene was studied.

Experimental

Materials

G. R. grade reagents of 99.5 vol% ethanol, of hydrochloric acid and of lithium chloride were used. 2-Chloro-2'-methylazobenzene (A) was synthesized by the condensation of 2-methylaniline and 2-chloronitrosobenzene, and a red crystal melting at 84°C was obtained by the recrystallization from ethanol. 2-Chloro-2'-methylhydrazobenzene (B) was prepared by the reduction of (A) with zinc dust and ammonium chloride, and was recrystallized from ethanol, and white crystal melting at 122°C was obtained.

<table>
<thead>
<tr>
<th>Compound</th>
<th>245 mµ</th>
<th>285 mµ</th>
<th>340 mµ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B)</td>
<td>21.17</td>
<td>4.32</td>
<td>0.02</td>
</tr>
<tr>
<td>(P)</td>
<td>4.17</td>
<td>24.60</td>
<td>0.85</td>
</tr>
<tr>
<td>(A)</td>
<td>6.76</td>
<td>5.97</td>
<td>15.70</td>
</tr>
</tbody>
</table>

Table 2 Elementary analysis and molecular weight

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Cl (%)</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B)</td>
<td>Calc.</td>
<td>67.10</td>
<td>5.63</td>
<td>12.04</td>
<td>15.23</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>66.83</td>
<td>5.67</td>
<td>12.09</td>
<td>15.41</td>
</tr>
<tr>
<td>(P)</td>
<td>Calc.</td>
<td>67.10</td>
<td>5.63</td>
<td>12.04</td>
<td>15.23</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>66.99</td>
<td>5.58</td>
<td>12.02</td>
<td>15.35</td>
</tr>
<tr>
<td>(A)</td>
<td>Calc.</td>
<td>67.68</td>
<td>4.81</td>
<td>12.14</td>
<td>15.37</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>67.39</td>
<td>4.94</td>
<td>12.25</td>
<td>15.40</td>
</tr>
</tbody>
</table>

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

obtained. 3-Chloro-3'-methylbenzidine (P) was prepared by the rearrangement of (B), was recrystallized from ethanol, and almost colorless crystal melting at 97°C was obtained. Molecular extinction coefficients of (B), (P) and (A) are shown in Table 1 and Fig. 1*).

The results of elementary analysis of (B), (P) and (A), and molecular weights are listed in Table 2.

Procedure

The reaction medium was prepared by mixing 35 vol.% aqueous ethanolic solutions of hydrochloric acid and lithium chloride so as to get the fixed concentration, i.e. [HCl] = 0.05~0.80 mole/l for hydrochloric acid and \( \mu = 1.00 \) for ionic strength at high pressure, considering the compressibility of the medium, and the reaction was studied under the conditions of 15~30°C and 1~1,500 kg/cm².

The high pressure apparatus used for this work was the same as reported previously, but at this time, instead of using a glass syringe, a flexible teflon tube of 6 mm diameter closed with glass rods was used as the reaction vessel under high pressure. After an appropriate time interval, an aliquot of the reaction solution was diluted with an aqueous ethanolic solution of sodium hydroxide, and each component of (B), (P) and (A) in the reaction solution was determined from the absorbances at three wave lengths, 245, 285 and 340 mμ, since it had been already confirmed by thin layer chromatography that no disproportionation reaction occurred.

Results

As the dissolved oxygen was not removed from the reaction solution, both reactions of

---

Fig. 2 Dependency of the apparent first order rate constants on the acid concentrations

Fig. 3 Dependency of the apparent first order rate constants on the acid concentrations

Pressure (kg/cm²):
- : 1, □: 500, △: 1,000,
○: 1,500

Temperature (°C):
30, 25, 20, 15 from top to bottom

---

4) D. V. Benthorp and A. Cooper, J. Chem. Soc., (B) 1968, 605

* B) (P) and (A) are probably new compounds and there are no literatures for melting points.
The Effect of Pressure on the Rate of the Benzidine Rearrangement V

rearrangement and oxidation concurred. The apparent rate constants of the rearrangement were obtained from the slopes of lines obtained by plotting \( \frac{d[P]}{d(t)} \) versus time, where \( d[P] \) indicates the increases of \( [P] \) and \( d[A] \) indicate the increases of \( [P] \) and \( [A] \) at a fixed reaction time and \( [B]_0 \) indicates the initial concentration of \( [B] \).

Fig. 2 illustrates the relationship between the apparent rate constants and the acid concentrations in which the slope of the curve continuously increases with increasing acidity. Therefore, it is obvious that two reactions occur, i.e. one is of first order with respect to the acid concentration (one-proton mechanism) and the other is of second order (two-proton mechanism).

\[
k_{app} = k_1[HCl] + k_2[HCl]^2,
\]

\[
\frac{k_{app}}{[HCl]} = k_1 + k_2[HCl],
\]

where \( k' \) is the rate constant of the rate-determining step when the second protonation is slow.

The rate constants of one-proton mechanism \( k_1 \) and of two-proton mechanism \( k_2 \) summarized in Table 3 were obtained from Fig. 3 in which \( k_{app}/[HCl] \) is plotted against \( [HCl] \). Figs. 4 and 5 illustrate the dependencies of the rate constants on temperature and pressure. The activation parameters are summarized in Table 4.
J. Osugi and I. Onishi

Table 3 The rate constants of the rearrangement ($\mu=1.00$)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure (kg/cm²)</th>
<th>$k_1 \times 10^2$ (L·mole⁻¹·min⁻¹)</th>
<th>$k_2 \times 10^3$ (L²·mole⁻²·min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1</td>
<td>0.65</td>
<td>4.36</td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>0.95</td>
<td>4.10</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>1.26</td>
<td>7.50</td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>1.64</td>
<td>8.02</td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>1.87</td>
<td>8.80</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>2.35</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>2.71</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>3.10</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>1,500</td>
<td>3.55</td>
<td>15.5</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>4.30</td>
<td>20.4</td>
</tr>
</tbody>
</table>

Table 4 The activation parameters for the rearrangement

<table>
<thead>
<tr>
<th>$\Delta V^#$ (cm³/mole)</th>
<th>Pressure (kg/cm²)</th>
<th>$E^#$ (kcal/mole)</th>
<th>$\Delta S^#$ (e. u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ (one-proton)</td>
<td>-6.8</td>
<td>1</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,500</td>
<td>22.6</td>
</tr>
<tr>
<td>$k_2$ (two-proton)</td>
<td>-3.2</td>
<td>1</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,500</td>
<td>22.4</td>
</tr>
</tbody>
</table>

One-proton mechanism: \( \frac{\Delta V}{\Delta F} = -0.08 \), \( \frac{\Delta S}{\Delta F} = 0.06 \)

Two-proton mechanism: \( \frac{\Delta V}{\Delta F} = -0.42 \), \( \frac{\Delta S}{\Delta F} = -0.42 \)

Discussions

On the one-proton mechanism, the value of $-6.8$ cm³/mole of the apparent volume of activation is similar to the values of other one-proton mechanism, i.e. $-2.5$ cm³/mole for 2, 2'-dimethyl-1°>, $-10.7$ cm³/mole for 2, 2'-dibromo-1°) and $-12$ cm³/mole for 2, 2'-dimethoxyhydrazobenzene. Since the volume changes of pre-equilibrium of the protonation are presumed to be about $-5$ cm³/mole, not only Ingold's postulation, that is the so-called polar transition state theory, is supported, but also it can be assumed that these transition states are so compact and strongly solvated, and that the volume increases due to the fission of NH⁺: NH after the protonation can be sufficiently overcome.

For the two-proton mechanism, the apparent volumes of activation obtained, i.e. $-3.2$ cm³/mole in this study, $-7.2$ cm³/mole for 2, 2'-dimethyl-1°>, $-0.4$ cm³/mole for 2, 2'-dibromohydrazobenzene and $1.5$ cm³/mole for hydrazobenzene, are either slightly negative or slightly positive. Since the

7) J. Osugi and T. Hitouji. This Journal, 34, 88 (1964)
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volume changes of the pre-equilibrium of the first and second protonation are presumed to be both negative, it is reasonable that the apparent volumes of activation of the two-proton mechanism are either slightly negative or slightly positive, because the volume decrease of the protonation ($dV_{K_1} + dV_{K_2}$) is comparable to the volume increase of the fission of $\text{NH}_2^+ : \text{NH}_2^+$ ($dV_{K_3}$). At all events, the transition state of the two-proton mechanism is considered to be somewhat less polar.

As the reactions of ortho-substituted compounds do not obey the Hammett law, the relationship between the rates of the rearrangements and the $pK_a$ values of ortho-substituted anilinium ions which correspond to the conjugate acids of aniline moieties of 2, 2'-disubstituted-hydrazobenzene, is considered.

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

$$k_1 = k_1^* K_1,$$  \hspace{1cm} (1)

$$k_2 = k_2^* K_1 K_2 \text{ or } k_2 = k' K_1,$$  \hspace{1cm} (2)

where $K_1$ and $K_2$ indicate the equilibrium constants of the first protonation on a-ring and of the second protonation on b-ring, respectively.

Although it is presumed that $pK_a$ value of diprotonated cation in which two vicinal nitrogen atoms exist is probably 9 or 10, smaller than that of monoprotonated cation, the relationship between $pK_a$ of monoprotonated hydrazo-compound and that of free anilinium ion is not obvious. Provided that the equilibrium constants of the protonation for 2, 2'-disubstituted-hydrazobenzene, $K_1$ and $K_2$, are proportional to that for ortho-substituted-aniline, $K_1$ and $K_3$, equations (1) and (2) can be expressed as follows.

$$k_1 = k_1^* p K_1,$$  \hspace{1cm} (3)

$$k_2 = k_2^* p' K_1 K_2,$$  \hspace{1cm} (4)

$$\text{or } k_2 = k'^* p^* K_1,$$  \hspace{1cm} (4')

where $p$, $p'$ and $p^*$ are proportional constants.

Then in the case of the one-proton mechanism, after the first protonation on a-ring, the electrons which exist between two nitrogen atoms, $\text{NH}_2^+ : \text{NH}$, move from b- to a-ring and the heterolytic fission is facilitated as postulated by Ingold. The rate constant of the rate-determining step $k_1^*$ is probably proportional to the donative character of electrons from b- to a-ring, or to the electron density of $\text{NH}$.


or to the basicity of b-ring, and it is probably proportional to the basicity of corresponding aniline (b). Therefore, equation (3) becomes as follows.

\[ k_1 = \rho \alpha K_1 K_2 \]  

where \( k_1 = \alpha K_2 \), and \( \alpha \) is a proportional constant.

For the two-proton mechanism, if the second protonation is in pre-equilibrium and the following fission has no correlation with the basicity of the ring, then equation (4) is left as it is. If the second protonation is in the rate-determining step, the ease of the protonation probably depends on the basicity of b-ring and \( k' \) is proportional to \( K_2 \), and equation (4') can be rewritten,

\[ k_2 = \rho' \beta K_1 K_2 \]  

where \( \beta \) is a proportional constant.

Therefore, in either case, the apparent rate constants of the rearrangement, \( k_1 \) and \( k_2 \), are given as follows,

\[ \begin{align*}
    k_1 &= \rho \alpha K_1 K_2, \\
    k_2 &= \rho' \beta K_1 K_2 \\
\end{align*} \]

And further, these rate constants, \( k_1 \) and \( k_2 \), are indicated by \( \rho K_a \) of anilinium ion as follows,

\[ \begin{align*}
    \log k_1 &= \log (\rho \alpha) + \rho K_{a1} + \rho K_{a2}, \\
    \log k_2 &= \log (\rho' \beta) + \rho K_{a1} + \rho K_{a2}, \\
\end{align*} \]

The \( \rho K_a \) values of conjugate anilinium ions of ortho-substituted aniline in 85 vol\% aqueous ethanolic solution were obtained by referring to the deduction by J. Clark and D. D. Perrin\(^{10} \), and to the values obtained by Grunwald\(^{10} \) and Ingold\(^{11} \) as summarized in Table 5. And as a trial, as shown in Fig. 6, the logarithms of the rate constants, \( k_1 \) (l-mole\(^{-1}\)-min\(^{-1}\)) and \( k_2 \) (l-mole\(^{-2}\)-min\(^{-1}\)), of the rearrangement of 2-chloro-2'-methylhydrazobenzene \((k_1 = 2.15 \times 10^{-2}, k_2 = 12.7 \times 10^{-2})\) and that of other hydrazo-compounds reported previously, i.e. 2, 2'-dimethylhydrazobenzene \((k_1 = 0.573, k_2 = 3.0)\)\(^{10} \), 2, 2'-di-


bromohydradobenzene \((k_1 = 1.6 \times 10^{-4}, k_2 = 2.3 \times 10^{-4})^{(10)}\), 2, 2'-dimethoxyhydrazobenzene \((k_1 = 270)^{(10)}\) and hydrazobenzene \((k_2 = 3.57)^{(2)}\), were plotted against the values of \((pK_{a1} + pK_{a2})\). Although the ethanol content of the reaction medium of 2, 2'-dimethoxyhydrazobenzene and hydrazobenzene are different from those cases of other compounds, a straight line of slope of 1.04 and the correlation coefficient of 0.99 were obtained for one-proton mechanism by the least square method. Therefore, it is clear that \(\log k_1\) is closely correlated with \((pK_{a1} + pK_{a2})\).

As shown in Fig. 6, in the case of 2, 2'-dimethoxyhydrazobenzene, a large divergence from a straight line is observed and it is probably due to the steric effect of the substituents which is different from those of the other substituents. The electron donation which causes the fission does not result from the protonated a-ring \(\text{RC}_6\text{H}_4\text{NH}_2^+\), but from the electro-neutral un-protonated b-ring, \(\text{R'C}_6\text{H}_4\text{NH}^-\). The basicity or \(pK_a\) is not reasonable for this point because the effects of substituent \(R'\) on b-ring would appear synthetically including the induced resonance effect and the steric effect for \(H^+\) addition. It is necessary to estimate the electron density of NH of electro-neutral 2'-methoxyaniline ring (b-ring), by reducing the steric effect which hinders the approach of \(H^+\) to b-ring.

Taft's steric factor of the ortho-substituent is indicated by \(E_a\), and if the electron density of NH of electro-neutral 2'-methoxyaniline ring (b-ring) is expressed by the value of \((pK_{a1} + \gamma E_a)\) obtained by deducting the steric effect from \(pK_{a2}\), the rate constant of the rearrangement of one-proton mechanism becomes as follows.

<table>
<thead>
<tr>
<th>Substituents</th>
<th>(pK_a)</th>
<th>(E_a \times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5.55</td>
<td></td>
</tr>
<tr>
<td>2 OCH_3</td>
<td>5.44</td>
<td>+0.99</td>
</tr>
<tr>
<td>2 CH_3</td>
<td>5.35</td>
<td>0.00</td>
</tr>
<tr>
<td>2 F</td>
<td>3.52</td>
<td>+0.49</td>
</tr>
<tr>
<td>2 Cl</td>
<td>3.15</td>
<td>+0.18</td>
</tr>
<tr>
<td>2 Br</td>
<td>3.06</td>
<td>0.00</td>
</tr>
<tr>
<td>2 I</td>
<td>2.62</td>
<td>-0.20</td>
</tr>
</tbody>
</table>
\[ \log k = \log (\rho \alpha) + (\rho K_{a1} + \rho K_{a2} + \gamma E) \]

where \( \gamma \) is a proportional constant.

Table 6 The scales of abscissa when \( \log k \) are plotted

<table>
<thead>
<tr>
<th>Substituents</th>
<th>One-proton ( \rho K_{a1} + \rho K_{a2} + \gamma E )</th>
<th>Two-proton ( \rho K_{a1} + \rho K_{a2} + \gamma E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 OCH₃, 2' OCH₃</td>
<td>12.2</td>
<td>10.9</td>
</tr>
<tr>
<td>2 CH₃, 2' CH₃</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>2 Cl, 2' CH₃</td>
<td>8.5</td>
<td>8.5</td>
</tr>
<tr>
<td>2 Br, 2' Br</td>
<td>6.1</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Using the values, \( \log (\rho \alpha) = -10.0 \) and \( \gamma = 1.51 \), which were obtained from the assumption that a straight line of slope of 1.00 is obtained for the one-proton mechanism of 2, 2'-dibromo- and 2, 2'-dimethoxyhydrazobenzene, the data were plotted again in Fig. 7.

Fig. 7 The linear free energy relationship
- : one-proton
O : two-proton

Not only the data for 2, 2'-dibromo- and 2, 2'-dimethoxyhydrazobenzene, but also the data for 2-chloro-2'-methylhydrazobenzene show the straight line and the good correlation is obtained. In the latter case, it is presumed that the ortho-substituent of b-ring is methyl radical and not chlorine, because otherwise the linearity would be changed to the worse. Therefore, whether the rearrangement reaction is the one-proton mechanism or not, is determined by considering which ring of the two, a or b, is protonated at first step. That is, it is concluded that the reaction is the one-proton mechanism when the first protonation occurs in less basic 2-chloroaniline ring (a-ring).

Considering the difference between \( \rho K_{a} \) of 2-methylanilinium ion (5.35) and that of 2-chloroanilinium ion (3.15), the concentration of mono-protonated cation (II), protonated to methyl-substituted b-ring, is about 100 times as large as that of mono-protonated cation (I), protonated to chlorine-substituted a-ring.

If the \( \rho K_{a} \) value of diprotonated cation (III) in which two vicinal nitrogen atoms (NH₂⁺ and NH₂⁺) exist is presumed to be 9 or 10, smaller than that of mono-protonated cation (I), as described above, the concentration of mono-protonated cation (I) is \( 10^7 \text{ to } 10^8 \) times as large as that of diprotonated cation.
Therefore, it is considered that the rate constant of the rate-determining step of the two-proton mechanism $k_2^*$ is $10^5$--$10^6$ times as large as that of the one-proton mechanism $k_1^*$. Although it is difficult to reach the conclusion on the two-proton mechanism, because of the scantiness of the data, if the linear relationship is assumed to be established between $\log k_2$ and the value of $(pK_{a1} + pK_{a2})$, the slope of the line should be somewhat large. Therefore, if the first and the second protonations are in pre-equilibrium, it is considered that the electron-donative effect of the substituents influences more or less the rate constant of the rate-determining step. These considerations would make further studies of this problem necessary.

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