The effect of pressure on the rate of the benzidine rearrangement IV: 2,2'-dimethoxyhydrazobenzene

Author(s): Osugi, Jiro; Sasaki, Muneo; Onishi, Ichiro

Citation: The Review of Physical Chemistry of Japan (1970), 40(1): 39-47

Issue Date: 1970-12-20

URL: http://hdl.handle.net/2433/46946

Type: Departmental Bulletin Paper

Textversion: publisher

Kyoto University

Kyotobunsekihokoki 40, 1970, 39-47
THE EFFECT OF PRESSURE ON THE RATE OF
THE BENZIDINE REARRANGEMENT IV
2,2'-Dimethoxyhydrazobenzene

BY JIRO OSUGI, MUNEO SASAKI AND ICHIRO ONISHI

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. $E_t^{*}=10.0$ kcal/mole, $\Delta S_t^{*}= -24$ e.u., $\Delta V_t^{*}=-12$ cc/mole for rearrangement and $E_d^{*}=14.4$ kcal/mole, $\Delta S_d^{*}= -11$ e.u., $\Delta V_d^{*}=5$ 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'-dibromo- hydrazobenzene, 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'-dimethoxy- hydrazobenzene which had electron-releasing substituents in contrast with bromine and had been reported to follow one-proton mechanism\(^2\).

---

(Received June 30, 1970)

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

Materials
2,2'-Dimethoxyhydrazobenzene (B) was synthesized 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 0.665 mol/l (a) and aqueous solution of sodium hydroxide of 0.665 mol/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 = 3.5~5.15. The initial concentration of (B) was around 2 × 10⁻⁴ mol/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 pKₐ of monochloroacetic acid (4.34 at the ordinary atmospheric pressure at 5°C) was almost the same as that of acetic acid.

The reaction products were analyzed by means of thin layer chromatography 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>
<thead>
<tr>
<th></th>
<th>(P)</th>
<th>(A)</th>
<th>(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rₜ</td>
<td>0.16</td>
<td>0.58</td>
<td>0.48</td>
</tr>
<tr>
<td>color</td>
<td>gray-brown</td>
<td>yellow</td>
<td>violet-brown</td>
</tr>
</tbody>
</table>

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

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)
The Effect of Pressure on the Rate of the Benzidine Rearrangement IV

41

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

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>235 m(\mu)</th>
<th>250 m(\mu)</th>
<th>305 m(\mu)</th>
<th>340 m(\mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B)</td>
<td>13.99</td>
<td>19.61</td>
<td>0.855</td>
<td>0.080</td>
</tr>
<tr>
<td>(P)</td>
<td>8.78</td>
<td>6.12</td>
<td>19.27</td>
<td>1.71</td>
</tr>
<tr>
<td>(A)</td>
<td>8.58</td>
<td>6.51</td>
<td>8.67</td>
<td>9.92</td>
</tr>
<tr>
<td>(D)</td>
<td>7.40</td>
<td>2.39</td>
<td>0.40</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Results and Considerations

The oxidation reaction occurred together with the rearrangement because the studies were performed in aerated solutions as reported previously. 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 may be considered to be most appropriate, which the present work supports as discussed in the later section.

\[
\begin{align*}
  \text{OCH}_2\text{CH}_2\text{O} & \quad \text{H}_2\text{N} \quad \text{NH}_2 \quad \text{(P)} \\
  \text{H}_2\text{N} \quad \text{NH}_2 & \quad \text{N} = \text{N} \quad \text{OCH}_2 \text{CH}_2\text{O} \quad \text{(A)} \\
  \text{OCH}_2 & \quad \text{H}_2\text{O} \quad \text{(D)} \\
  \text{+H}_2\text{O} & \quad \text{+B} \quad \text{+O}_2
\end{align*}
\]

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

\(k_{AP}\) and \(k_{AD}\) are calculated from the slopes of the straight lines obtained by plotting \((\Delta[P]/\Sigma) \times \log ([B]/[B])\) and \((\Delta[D]/\Sigma) \times \log ([B]/[B])\) against time, respectively (Figs. 1, 2). And when \(k_{AP}\)'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 \(k_{AP}/k_{AD}\) 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 \(X = \Delta[P]+\Delta[D]+\Delta[A]-(1/2)\Delta[D]\) and \([B]\) were kept constant at any time during the reaction. \([B]\) 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])
- : (d[P]/dΣ) log ([B]₀/[B])
- : (d[D]/dΣ) log ([B]₀/[B])
Initial concentration of B (mole/l):
- : 3.26 x 10⁻⁴
- : 2.56 x 10⁻⁴
- : 28.3 x 10⁻⁴

Fig. 2 First order plot (25°C, 700 kg/cm², [B]₀ = 3 x 10⁻⁴ mole/l, pH = 4.47)
The ordinate represents,
- : log ([B]₀/[B])
- : (d[P]/dΣ) log ([B]₀/[B])
- : (d[D]/dΣ) log ([B]₀/[B])

Fig. 3 Relationship between k_H⁺ and [H⁺] (5°C) pressure (kg/cm²):
- : 1
- : 700
- : 1,400
- : 2,000
The Effect of Pressure on the Rate of the Benzidine Rearrangement IV

Table 3 The ratio of $k_{ap}$ to $k_{ar}$

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>1 kg/cm²</th>
<th>700 kg/cm²</th>
<th>1,400 kg/cm²</th>
<th>2,000 kg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.19</td>
<td>0.12</td>
<td>0.09</td>
<td>0.07</td>
</tr>
<tr>
<td>10</td>
<td>0.23</td>
<td>0.16</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
<td>0.16</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.31</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.32</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

(S-1)

\[ \begin{align*}
B + H^+ & \rightarrow BH^+ \\
& \rightarrow P \text{ (Rearrangement)} \\
& \rightarrow D \text{ (Disproportionation)}
\end{align*} \]

Slow $k_1$ fast $k_2$

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:

\[ \frac{d[P]}{dt} = k_{r}K[H^+][B], \] (1)

\[ \frac{d[D]}{dt} = k_{o}K[H^+][B], \] (2)

\[ \frac{d[D]}{d[P]} = \frac{k_{o}}{k_{r}}. \] (3)

Therefore, the ratio of $d[D]/d[P]$ 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:

\[ \frac{d[P]}{dt} = \frac{k_{o}k_{r}K[H^+][B]}{k_{r} + k_{a}[B]}, \] (4)

\[ \frac{d[D]}{dt} = \frac{k_{o}k_{r}K[H^+][B]}{k_{r} + k_{a}[B]}, \] (5)

\[ \frac{d[D]}{d[P]} = \frac{k_{a}}{k_{r} [B]} \] (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.

![Graph showing the relationship between $(d[D]/dt)/(d[P]/dt)$ and reaction time.](image)

**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] (mole/l):

- •: $28.3 \times 10^{-4}$
- ○: $3.26 \times 10^{-4}$

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 $k_{AP}$ and $k_{AD}$ should be the apparent rate constants of rearrangement and disproportionation, respectively.

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

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>1 kg/cm²</th>
<th>700 kg/cm²</th>
<th>1,400 kg/cm²</th>
<th>2,000 kg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>92</td>
<td>174</td>
<td>150</td>
<td>172</td>
</tr>
<tr>
<td>10</td>
<td>128</td>
<td>171</td>
<td>218</td>
<td>237</td>
</tr>
<tr>
<td>15</td>
<td>172</td>
<td>222</td>
<td>324</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>220</td>
<td>301</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>270</td>
<td>363</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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."
The Effect of Pressure on the Rate of the Benzidine Rearrangement IV

3.0
2.5
2.0
1.5
1.0

Fig. 5 Dependence of the rate constants on temperature
Rearrangement: ●: 1 kg/cm²
O: 2,000 kg/cm²
Disproportionation: ●: 1 kg/cm²

Dependence of the rate constants on pressure
Rearrangement
Disproportionation

Fig. 6

Figs. 5 and 6 show the effect of pressure on the rate constants of rearrangement and disproportionation.

Table 5 Activation parameters for one-proton mechanism of rearrangement

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Pressure P, kg/cm²</th>
<th>Volumes of activation ΔV⁺, cc/mole</th>
<th>Energies of activation E⁺, kcal/mole</th>
<th>Entropies of activation ΔS⁺, e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 CH₃ 2' CH₃</td>
<td>1</td>
<td>-2.5</td>
<td>20.9</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>3,000</td>
<td></td>
<td>21.6</td>
<td>3.3</td>
</tr>
<tr>
<td>2 Br 2' Br</td>
<td>1</td>
<td>-10.7</td>
<td>16.3</td>
<td>-34</td>
</tr>
<tr>
<td></td>
<td>3,000</td>
<td></td>
<td>13.2</td>
<td>-41</td>
</tr>
<tr>
<td>2 CH₃O 2' CH₃O</td>
<td>1</td>
<td>-12</td>
<td>10.0</td>
<td>-23.6</td>
</tr>
<tr>
<td></td>
<td>2,000</td>
<td></td>
<td>8.9</td>
<td>-26.0</td>
</tr>
</tbody>
</table>

† 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

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Reaction medium†</th>
<th>Ionic strength</th>
<th>Temperature °C</th>
<th>k₄ × 10⁵ /mole⁻¹·sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃O 2' CH₃O</td>
<td>85% E</td>
<td>0.05</td>
<td>25</td>
<td>450,000 (present work)</td>
</tr>
<tr>
<td></td>
<td>60% D</td>
<td>0.1</td>
<td>0</td>
<td>154,000 (Banthorpe)⁶⁷</td>
</tr>
<tr>
<td>CH₂ 2' CH₃</td>
<td>96% E</td>
<td>0.07</td>
<td>25</td>
<td>1,000 (authors)³⁰</td>
</tr>
<tr>
<td></td>
<td>60% D</td>
<td>0.5</td>
<td>0</td>
<td>140 (Banthorpe)³⁰</td>
</tr>
<tr>
<td>Br 2' Br</td>
<td>85% E</td>
<td>1.8</td>
<td>25</td>
<td>0.27 (authors)⁰⁷</td>
</tr>
<tr>
<td></td>
<td>60% D</td>
<td>1.0</td>
<td>25</td>
<td>8 (Banthorpe)⁹⁰</td>
</tr>
</tbody>
</table>

† 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., it seems probable that the distance between the adjacent two nitrogen atoms unfolded asymmetrically is not so long (5−7 Å) as presumed by Ingold⁹ 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/or 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 (5-1), equation (3) is valid. And moreover, the kinetically observed rate constants, k₁ (rearrangement) and k₂ (disproportionation) can be defined as

\[ k_1 = k_2^*K, \quad k_2 = k_d^*K, \quad k_2 = k_2(A[D]/A[P]). \]  

(7)

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

Table 7  Rate constants of disproportionation k₂ in l-mole⁻¹·min⁻¹

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>1 kg/cm²</th>
<th>1,000 kg/cm²</th>
<th>1,400 kg/cm²</th>
<th>2,000 kg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>18</td>
<td>15</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>27</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>15</td>
<td>43</td>
<td>36</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>20</td>
<td>68</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>25</td>
<td>86</td>
<td>73</td>
<td>73</td>
<td>73</td>
</tr>
</tbody>
</table>

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

The Effect of Pressure on the Rate of the Benzidine Rearrangement IV

\[ E^* = 14.4 \text{ kcal/mole} \]
\[ \Delta S^* = -10.7 \text{ cal/mole-deg} \]
\[ \Delta V^* = +5 \text{ cc/mole} \]

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 \( \Delta V^* \). 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.

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