The effect of pressure on the rate of the benzidine rearrangement: II. O, o’-hydrazotoluene

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Citation
The Review of Physical Chemistry of Japan (1967), 36(2): 100-110

Issue Date
1967-04-30

URL
http://hdl.handle.net/2433/46887

Type
Departmental Bulletin Paper
THE EFFECT OF PRESSURE ON THE RATE OF
THE BENZIDINE REARRANGEMENT
II. o, o'-Hydrazotoluene

By Jiro Osugi, Muneo Sasaki and Ichiro Onishi

The rates of the acid-catalysed rearrangement and of the oxidation of o, o'-
hydrazotoluene in aqueous ethanol (96 vol. % EtOH) have been measured at pres-
sures up to 3000 kg/cm².

The rates of the rearrangements of one-proton and two-proton mechanisms were
increased by pressure. In the two-proton mechanism, as a small negative volume of
activation and a positive entropy of activation are observed, it seems likely that
the second proton transfer is a pre-equilibrium.

The oxidation accompanied with the rearrangement in acidic solution includes
two concurrent reactions: one is independent of [H⁺] and the other is inversely
proportional to [H⁺], both being strongly accelerated by pressure. Because of the
large negative volumes of activation, it is implied that each reaction goes through
an ionic activated complex.

Introduction

In 1922, Jacobson reviewed the benzidine rearrangement, but kinetic studies were scarcely
carried out.

In 1950, Hammond and Shine found that the rearrangement of hydrazobenzene is of the second
order in acid concentration, but since Carlin and Odioso discovered in 1953 the abnormality that
the rearrangement of o, o'-hydrazotoluene had an order in acid, not of 2 but of 1.6, kinetic studies
have been carried out vigorously, and with the accumulation of new informations for the rearrange-
ment, various reaction mechanisms have been suggested.

Because the plot of logarithm of k, where k represents apparent rate constant of hydrazobenzene
rearrangement, against Hammett's acidity function (−H°), is linear with a slope of 2.1 and k
was 4.8 times larger with D₅O⁺ than with H₃O⁺, Ingold and his co-workers suggested that not only
the first but the second proton transfer is a pre-equilibrium, and further, each reaction went through
a polar-transition-state.

On the contrary, the rate measurement of the rearrangement in weak acid studied by Hammond,

\[ \text{Received January 15, 1967} \]

1) P. Jacobson, Ann., 428, 76 (1922)
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and the π-complex theory postulated by Dewar in 1945, although modified frequently, were opposed to Ingold's scheme in the point that the second proton transfer is a rate-determining step.

But evidently, the order in acid of the rearrangement of o, o'-hydrazotoluene increases with acidity in the wide range as proved by Ingold and present authors. Therefore, Dewar's theory is inconsistent with the kinetic results, with respect to o, o'-hydrazotoluene, at least.

Up to now, benzidine rearrangement has been entirely studied at atmospheric pressure, and the rate study under high pressure could not been found except the previous report showing that the rate of rearrangement of hydrazobenzene is slightly retarded by pressure. In the present experiment, the authors studied the effect of pressure on the rate of rearrangement of o, o'-hydrazotoluene and discussed the reaction scheme from the volumes of activation of the rearrangement.

Although there has already been a study at 1 atm for the oxidation of hydrazobenzene in alkaline solution in the presence of dissolved oxygen, there has not yet been any study of the oxidation of hydrazo-compounds in acidic solution. The authors also studied the pressure effect on the oxidation reaction.

Experimentals

Materials

G. R. grade reagent of 99.5 vol.% EtOH, lithium chloride and hydrochloric acid were used for this work. o, o'-Hydrazotoluene (B) was synthesized by Cohen's method, recrystallized by 95 vol.% EtOH and washed with petroleum ether, to get white crystal, m.p. 165°C. o, o'-Azotoluene (A) was synthesized by melting (B), and washed with hydrochloric acid, recrystallized from EtOH, to get red crystal, m.p. 54.6°C. o, o'-Tolidine (P) was recrystallized from alcohol, and its molecular extinction coefficients agreed with those obtained by Carlin.

Procedure

HCl-LiCl aqueous solution of 0.42 m/ was added to 10 mL of 99.5 vol.% EtOH. In the present experiment, the concentrations of the components in this aqueous solution were controlled so as to give the available concentrations after mixing. i.e. for EtOH, 96 vol.% and for hydrochloric acid and ionic strength, the fixed values considering the compressibility of EtOII. The concentration of dissolved oxygen was estimated to be about 2×10⁻³ mole/l.

Keeping this solution in the thermostat at constant temperature, a scanty amount of (B) was added. In the case of 1 atm runs, the solution was maintained in the thermostat throughout each run, and in the case of high pressure runs, an aliquot of this solution which was poured in a glass syringe was put into the cylindrical pressure vessel. The initial concentration of (B) was estimated to be about

6) M. J. S. Dewar, Nature, 156, 784 (1945)
8) J. Osugi and T. Hitouji, This Journal, 34, 88 (1964)
$5 \times 10^{-5} \sim 10^{-4}$ mole/l and the high pressure equipment employed was the same as that reported previously. As soon as the available pressure was fixed, 1~2 ml of the solution which had been maintained in the thermostat was neutralized by an ethanolic solution of sodium hydroxide, and the initial concentrations of (B), (A) and (P) were determined from the absorbances at 245, 285 and 320 m$\mu$. After an appropriate time interval, pressure was withdrawn and the reaction was pursued by analysing each component in the reaction mixture by the same way.

The values of molecular extinction coefficients used for analysis are shown in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>245 m\r $\mu$</th>
<th>285 m\r $\mu$</th>
<th>320 m\r $\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>o, o'-hydrazotoluene</td>
<td>20.1</td>
<td>4.03</td>
<td>0.123</td>
</tr>
<tr>
<td>o, o'-tolidine</td>
<td>3.94</td>
<td>21.8</td>
<td>5.60</td>
</tr>
<tr>
<td>o, o'-azotoluene</td>
<td>7.18</td>
<td>6.30</td>
<td>12.7</td>
</tr>
</tbody>
</table>

Results

In this work, as the reaction was studied in the presence of dissolved oxygen, the rearrangement and oxidation proceeded concurrently. But the sum of each concentration of (B), (P) and (A) was...

![Plot of logarithms of apparent first order rate constants against those of [H$^+$], 20°C, $\mu=0.1$ in 96 vol.% EtOH](image)
maintained constant within the error of 1%. Therefore, the rearrangement and oxidation products are only (P) and (A), respectively. These results were consistent with Ingold’s and Carlin’s.

As the overall rate of disappearance of (B) was proportional to [B], the apparent rate constant of the rearrangement, \( k_r \), and that of the oxidation, \( k_{ox} \), were obtained by dividing the overall rate constant of the decrease of (B), into the ratio of [P] to [A].

\[
-\frac{d[B]}{dt}_{obs} = (k_r + k_{ox})[B]_{obs}
\]  

\[ \text{Rearrangement} \]

In the case of ionic strength, \( \mu = 0.1 \), the curve of Fig. 1 was obtained by plotting \( \log k_r \) against \( \log [H^+] \), the slope of which increased with acidity. And the plots of \( k_r/[H^+] \) against \( [H^+] \) give straight lines as shown in Fig. 2. The result is indicated by the following relation.

\[
\frac{k_r}{[H^+]} = k_1 - k_2[H^+]
\]

Therefore, it is evident that two reactions occur concurrently; one is of the first order in \([H^+]\) (one-proton mechanism), and the other is of the second order in \([H^+]\) (two-proton mechanism). This event is consistent with the results observed by Ingold. From Fig. 2, the rate constant \( k_1 \) of one-proton mechanism and the rate constant \( k_2 \) of two-proton mechanism can be obtained (Table 2).

Fig. 3 illustrates the plots of \( \log (k^p/k^l) \) against \( P \) for \( k_1 \) and \( k_2 \), where \( k^l \) and \( k^p \) are rate constants at 1 atm and \( P \) kg/cm², respectively. The slopes of these curves were extrapolated to \( P=0 \), and by
Fig. 3 Dependence of the rates of the rearrangement on pressure (24.7°C)

<table>
<thead>
<tr>
<th>Pressure (kg/cm²)</th>
<th>k₁ (l/mole⁻¹min⁻¹)</th>
<th>k₂ (l²mole⁻²min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.37</td>
<td>1.8</td>
</tr>
<tr>
<td>3000</td>
<td>0.396</td>
<td>4.2</td>
</tr>
<tr>
<td>20.0</td>
<td>0.573</td>
<td>3.0</td>
</tr>
<tr>
<td>24.7</td>
<td>0.626</td>
<td>4.4</td>
</tr>
<tr>
<td>24.7</td>
<td>0.669</td>
<td>5.0</td>
</tr>
<tr>
<td>24.7</td>
<td>0.703</td>
<td>6.4</td>
</tr>
<tr>
<td>24.7</td>
<td>0.943</td>
<td>5.4</td>
</tr>
<tr>
<td>24.7</td>
<td>1.17</td>
<td>12.5</td>
</tr>
<tr>
<td>28.5</td>
<td>1.62</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Using equation (3) the volumes of activation of one-proton, \( \Delta V_{1}^{\dagger} \), and of two-proton, \( \Delta V_{2}^{\dagger} \), were calculated. Further, the energies of activation \( E_{1}^{\dagger}, E_{2}^{\dagger} \) and the entropies of activation \( \Delta S_{1}^{\dagger}, \Delta S_{2}^{\dagger} \) were obtained at each pressure (Table 3).

<table>
<thead>
<tr>
<th>Volume of activation (cc mole⁻¹)</th>
<th>Pressure (kg/cm²)</th>
<th>Energy of activation ( E_{1}^{\dagger} ) (kcal mole⁻¹)</th>
<th>Entropy of activation ( \Delta S_{1}^{\dagger} ) (cal mole⁻¹ deg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k₁ ) (one-proton)</td>
<td>( \Delta V_{1}^{\dagger}, -2.5 )</td>
<td>26.9</td>
<td>+0.6</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>21.6</td>
<td>+3.3</td>
</tr>
<tr>
<td>( k₂ ) (two-proton)</td>
<td>( \Delta V_{2}^{\dagger}, -7.2 )</td>
<td>21.0</td>
<td>+4.1</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>21.9</td>
<td>+8.9</td>
</tr>
</tbody>
</table>
The Effect of Pressure on the Rate of the Benzidine Rearrangement II

\[ \frac{\partial \ln k}{\partial P} = -\frac{\Delta V^\dagger}{RT} \]  

(3)

Oxidation

The results shown in Fig. 4 can be interpreted by the next relations, (4) or (4'), and the numerical values of \( k_{o1} \) and \( k_c \) were given (Table 4).

![Graph showing the relationship between the apparent first order rate constant of oxidation and [H⁺] (24.7°C).](image)

\[ k_{ox}[H^+] = k_0 [H^+] + k_{o1} \]  

(4)

\[ k_{ox} = k_0 + k_{o1} \left[ \frac{1}{[H^+]} \right] \]  

(4')

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure (kg/cm²)</th>
<th>( k_{o1} \times 10^6 ) (mole⁻¹ min⁻¹)</th>
<th>( k_0 \times 10^4 ) (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>1</td>
<td>0.25</td>
<td>2.3</td>
</tr>
<tr>
<td>20.0</td>
<td>2000</td>
<td>5.0</td>
<td>26</td>
</tr>
<tr>
<td>20.0</td>
<td>3000</td>
<td>10</td>
<td>63</td>
</tr>
<tr>
<td>24.7</td>
<td>1</td>
<td>0.5</td>
<td>3.0</td>
</tr>
<tr>
<td>24.7</td>
<td>1000</td>
<td>3.0</td>
<td>12</td>
</tr>
<tr>
<td>24.7</td>
<td>2000</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>24.7</td>
<td>3000</td>
<td>23</td>
<td>80</td>
</tr>
<tr>
<td>28.5</td>
<td>1</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td>28.5</td>
<td>3000</td>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>33.0</td>
<td>1</td>
<td>4.0</td>
<td>8.5</td>
</tr>
</tbody>
</table>
Fig. 5 shows the dependence of $k_0$ and $k_{31}$ on pressure, and $\Delta V^0_0$ and $\Delta V^0_{31}$ can be obtained by the way mentioned above, and the energies of activation $E_0^0$, $E_{31}^0$ were also obtained. These results are shown in Table 5.

![Graph of log(\(k_0^*/k_0\)) vs pressure (kg/cm²)](image)

**Table 5** Kinetic data for oxidation (\(24.7°C, \mu = 0.02\))

<table>
<thead>
<tr>
<th></th>
<th>Volume of activation (cc mole(^{-1}))</th>
<th>Pressure (kg/cm²)</th>
<th>Energy of activation (E^0) (kcal mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$ (non-proton)</td>
<td>$\Delta V^0_0$, -40</td>
<td>1 3000</td>
<td>19 14.6</td>
</tr>
<tr>
<td>$k_{31}$</td>
<td>$\Delta V^0_{31}$, -50</td>
<td>1 3000</td>
<td>37 33</td>
</tr>
</tbody>
</table>

**Discussion**

From the events of Figs. 2 and 4, it can be easily understood that not only the rearrangement reaction, but also the oxidation reaction proceeds through two concurrent processes respectively. As the general reaction scheme, the following can be proposed.

\[
\begin{array}{c}
\text{X}^- \rightleftharpoons \text{B} \rightleftharpoons \text{BH}^+ \rightleftharpoons \text{BH}_2^{++} \\
\text{A} \quad \text{A} \quad \text{P} \quad \text{P}
\end{array}
\] (5)
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\[ \text{B} + \text{H}^+ \xrightarrow{K_1} \text{BH}^+ \quad (6) \]
\[ \text{BH}^+ + \text{H}^+ \xrightarrow{K'_{-1}} \text{BH}_2^{++} \quad (7) \]
\[ \text{BH}^+ \xrightarrow{k_{*1}} \text{P} \quad (8) \]
\[ \text{BH}_2^{++} \xrightarrow{k_{*2}} \text{P} \quad (9) \]
\[ \text{B} \xrightarrow{K_2} \text{X}^- + \text{H}^+ \quad (10) \]
\[ \text{B} + \text{O}_2 \xrightarrow{\text{slow}} \text{XO}_2^- + \text{H}^+ \quad (11) \]
\[ \text{XO}_2^- \xrightarrow{\text{fast}} \text{A} + \text{HO}_2^- \quad (12) \]
\[ \text{X}^- + \text{O}_2 \xrightarrow{\text{slow}} \text{YO}_2^- + \text{H}^+ \quad (13) \]
\[ \text{YO}_2^- \xrightarrow{\text{fast}} \text{A} + \text{O}_2^- \quad (14) \]

where \( \text{X}^- \) and \( \text{Y}^- \) are the substances which are produced by the loss of one and two protons from \( \text{B} \).

**Rearrangement**

When the reaction (6) is a pre-equilibrium, assuming the stationary state with respect to \([\text{BH}_2^{++}]\), the rate of rearrangement is given by equation (15),

\[ \frac{d[P]}{dt} = k_{*1}K_1[H^+][\text{B}]_{\text{obs}} + \frac{k_{*2}k'K_1[H^+]^2}{k_{-1} + k_{*2}'}[\text{B}]_{\text{obs}}, \quad (15) \]

where \([\text{B}]_{\text{obs}}\) is the concentration of \([\text{B}]\) observed after the neutralization of reacting solution with sodium hydroxide, that is,

\[ [\text{B}]_{\text{obs}} = [\text{B}] + K_1[H^+][\text{B}] + \frac{k'K_1[H^+]^2}{k_{-1} + k_{*2}'}[\text{B}]. \quad (16) \]

As it is assumed that the second and third terms of the right hand side of equation (16) are both negligible, \([\text{B}]_{\text{obs}}\) is nearly equal to \([\text{B}]\).

From equation (15),

i) if \( k'_{-1} \gg k_{*2} \), i.e., equation (9) is a rate-determining step,

\[ \frac{d[P]}{dt} = k_{*1}K_1[H^+] [\text{B}]_{\text{obs}} + k_{*2}K'K_1[H^+]^2 [\text{B}]_{\text{obs}} \quad (17) \]

where \( K' = k' / k'_{-1} \).

ii) if \( k' < k'_{-1} \ll k_{*2} \), i.e., (7) is a rate-determining step,

\[ \frac{d[P]}{dt} = k_{*1}K_1[H^+] [\text{B}]_{\text{obs}} + k'K_1[H^+]^2 [\text{B}]_{\text{obs}} \quad (18) \]

Each of equations (17) and (18) can explain the kinetic order observed, but neither can demon...
strate which the rate-determining step is.

Considering equations (17) and (18), it is evident that these apparent volumes of activation of one-proton mechanism, $dV_{1t}$, and of two-proton mechanism, $dV_{2t}$, are represented as follows,

$$dV_{1t} = dV_{K1} + d^*V_{1t}$$

(19)

$$dV_{2t} = dV_{K1} + dV_{K1'} + d^*V_{2t}$$

(20)

or

$$dV_{2t} = dV_{K1} + d^*V_{2t}$$

(21)

where $dV_{K1}$ and $dV_{K1'}$ are the changes of the volumes in equilibria (6) and (7), respectively, and $d^*V_{1t}$, for example, represents the volume of activation accompanying the step (8).

Assuming that $dV_{K1}$ is small negative,\(^{10}\) it seems likely that $d^*V_{1t}$ scarcely contributes to the apparent volume of activation $dV_{1t}$, because the observed value is small negative, $-2.5$ cc/mole.

In the two-proton mechanism, it may be assumed that in equation (20) the contribution of $d^*V_{2t}$ to $dV_{2t}$ is as small as that of $d^*V_{1t}$ to $dV_{1t}$, and so, from equations (19), (20) and (21),

$$dV_{2t} - dV_{1t} = dV_{K1}$$

or

$$dV_{2t} = dV_{K1}.\text{ or } dV_{K1}.$$

As this difference can be obtained from the experimental results,

$$dV_{2t} - dV_{1t} = (-7.2) - (-2.5) = -4.7 \text{ cc/mole},$$

it is not unreasonable to regard the value, $-4.7$ cc/mole, as the same as the value of the volume change of protonation of aniline in aqueous acidic solution, as observed by Hamann.\(^ {10} \)

Then, it seems likely that the second proton transfer is a pre-equilibrium. The fact that the observed entropies of activation are not negative shows that perhaps there might not be included a slow proton transfer step, because if $H_3O^+$ and substrate were bound together in the transition state, the entropies of activation would probably be negative.\(^ {10} \)

**Oxidation**

Considering the scheme mentioned above, the following rate equation can be derived for the oxidation reaction,

$$\frac{d[A]}{dt} = k_1[B][O_2][OH^-] + \frac{k_{11} [K_2][O_2]}{[H^+] [OH^-]}$$

(22)

and it can explain the observed kinetic order.

Applying Hinshelwood's postulate\(^ {10} \) for the oxidation reaction of hydrazobenzene in the presence of dissolved oxygen in alkaline solution to the case of hydrazotoluene, the elementary steps could be described as follows,

$$B \xrightleftharpoons[k_{-3}^{}]{k_3} X^- + H^+ \quad K_3 = k_3/k_{-3}$$

(23)

$$X^- \xrightleftharpoons[k_{-4}^{}]{k_4} Y^- + H^+ \quad K_4 = k_4/k_{-4}$$

(24)


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\[ Y^{-} + O_{2} \xrightarrow{k_{b}} A^{-} + O_{2}^{-} \]  \hspace{1cm} (25)

hence,

\[ -\frac{d[B]}{dt} = \frac{k_{b}k_{s}K_{2}[O_{2}][B]}{[H^{+}][k_{-}[H^{+}]+k_{-}[O_{2}]]} \]  \hspace{1cm} (26)

If \( k_{-}[H^{+}] > k_{b}[O_{2}] \),

\[ -\frac{d[B]}{dt} = \frac{k_{b}k_{s}K_{2}[O_{2}]}{k_{-}[H^{+}][B]} \]  \hspace{1cm} (27)

on the other hand, if \( k_{-}[H^{+}] < k_{b}[O_{2}] \),

\[ -\frac{d[B]}{dt} = \frac{k_{b}K_{2}[O_{2}]}{[H^{+}][B]} \]  \hspace{1cm} (28)

But the second term of equation (4') is inversely proportional to \([H^{+}]\) and the rate of decrease of \( o, o'\)-hydrazotoluene was sensitive to the concentration of dissolved oxygen; so, neither (27) nor (28) can interpret the experimental results.

From the comparison of equation (4') with (22), \( k_{0} \) and \( k_{01} \) are represented by the relation (29).

\[ k_{0} = k_{0}*[O_{2}] \hspace{0.5cm} k_{01} = k_{01}*[O_{2}] \]  \hspace{1cm} (29)

Considering the change of concentration of dissolved oxygen due to compression, the apparent volumes of activation shown in Table 5 will be described by the following relationships,

\[ \Delta V_{01} = \Delta V_{01}^{a} + \Delta V_{K_{1}} - RT \frac{\partial}{\partial P} \ln \alpha \]  \hspace{1cm} (30)

\[ \Delta V_{0} = \Delta V_{0}^{a} - RT \frac{\partial}{\partial P} \ln \alpha \]  \hspace{1cm} (31)

where \( \alpha \) is the ratio of volume of the solution at 1 atm to that at \( P \) \( \text{kg/cm}^{2} \), i.e., \( \alpha = v^{1}/v^{0} \).

It being estimated that \( RT \frac{\partial}{\partial P} \ln \alpha \approx 2 \text{cc/mole} \), these reduce to,

\[ \Delta V_{01}^{a} = -48 \text{cc/mole} \]

\[ \Delta V_{0}^{a} = -38 \text{cc/mole} . \]

In the present case, as it is known that \( \Delta V_{K_{2}} = -10 \sim -15 \text{cc/mole} \), \( \Delta V_{01}^{a} \) and \( \Delta V_{0}^{a} \) come to have large negative values.

\[ \Delta V_{01}^{a} = -30 \sim -40 \text{cc/mole} . \]

Thus it seems likely that the oxidation reaction goes through two paths, the transition states of which are both very polar.

The apparent energies of activation for \( k_{0} \) and \( k_{01} \) are described respectively, as follows,

where $\Delta H_K$ is an enthalpy change of the dissociation equilibrium (10).

Assuming that the enthalpies of activation of the steps (11) and (13) are the same order, and that the enthalpy change of the equilibrium (10) is larger than that of the dissociation of o-toluidinium ion in aqueous solution which was estimated to be 8 kcal/mole, the difference between the apparent energy of activation for $k_2$ and that for $k_1$ may be attributed to the enthalpy change of the step (10).

Anyway, the results obtained through this work seems not to be inconsistent with Ingold's "polar-transition-state theory", although the present authors could not give any conclusive evidence. And further studies are in progress.

Acknowledgement

The authors express their deep sense of gratitude to Mr. K. Hamanoue for his helpful advice through this work.

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