

Abstract. The rate constant of the addition of hydrogen cyanide to \(\alpha\)-cyano-\(\beta\)-piperonylacrylic acid (CPA) were determined by UV spectrophotometry at various pH and a rate equation which can be applied over wide pH range was obtained.

From this equation, one may conclude that below pH 3 the reaction is started by the addition of hydrogen cyanide molecule to CPA, however, at pH 6～8, hydrogen cyanide is added to \(\alpha\)-cyano-\(\beta\)-piperonyl acrylate anion. From pH 3 to 6, these two reaction are competitive. Above pH 9, the reaction is proceeded by the addition of cyanide ion to \(\alpha\)-cyano-\(\beta\)-piperonyl acrylate ion. From pH 3 to 9, the complex reaction mechanism can also be fully explained by the rate equation obtained.

Introduction

Unlike the electrophilic addition to carbon

olefinic double bond, nucleophilic addition reactions have been the subject of only a few kinetic studies.\(^1\)\(^-\)\(^2\)\(^-\)\(^3\)\(^4\) We in investigated the rate and mechanism of hydrolysis of CPA and the addition of \(\alpha\)-propyl-mercaptan.

\(^*\) Department of Chemistry, College of Science and Engineering Korea University, Seoul, Korea
Table 1. The changes of optical density (OD) of CPA with time at pH 4.10 & 25°C.

<table>
<thead>
<tr>
<th>[HCN] = 1 × 10⁻³ M</th>
<th>[HCN] = 2 × 10⁻³ M</th>
<th>[HCN] = 3 × 10⁻³ M</th>
<th>[HCN] = 4 × 10⁻³ M</th>
</tr>
</thead>
<tbody>
<tr>
<td>time × 10⁻⁶ OD</td>
<td>time × 10⁻⁶ OD</td>
<td>time × 10⁻⁶ OD</td>
<td>time × 10⁻⁶ OD</td>
</tr>
<tr>
<td>(sec)</td>
<td>(sec)</td>
<td>(sec)</td>
<td>(sec)</td>
</tr>
<tr>
<td>0</td>
<td>0.305</td>
<td>0</td>
<td>0.305</td>
</tr>
<tr>
<td>1.25</td>
<td>0.304</td>
<td>0.75</td>
<td>0.305</td>
</tr>
<tr>
<td>3.72</td>
<td>0.300</td>
<td>3.75</td>
<td>0.299</td>
</tr>
<tr>
<td>6.52</td>
<td>0.296</td>
<td>8.56</td>
<td>0.292</td>
</tr>
<tr>
<td>13.7</td>
<td>0.290</td>
<td>13.76</td>
<td>0.286</td>
</tr>
</tbody>
</table>

Fig. 1. The plots of log(CPA) vs. time at pH = 4.10
25°C and 0.10 ionic strength.

over wide pH range. In present studies it is
tried to determine each rate constant over
wide pH range to reveal the reaction mecha-
nism of the addition of hydrogen cyanide to
CPA.

Experimental

CPA was prepared by condensation of piper-
ronal and α-cyanoacetic acid. Reagent grade
(kanto) potassium cyanide was used. All buffer
solution were prepared from reagent grade che-
amicals(E.Merk) and distilled water. The pH
of buffer solutions were determined by Zeromatic
II pH meter(Beanek) and the ionic strength
was kept constant 0.1 by adding sodium chlor-
side solution.

The reaction vessels used were 100 ml vol-
metric flask in the thermostat(25°C). At zero
time. 2 ml of a freshly prepared methanol solu-
tion (1 × 10⁻³ M) of CPA was pipetted into 100
ml flask containing 94~97 ml of buffer solution
and 1~3 ml solution of potassium cyanide (0.1
M). The sample were analyzed on a Beckman
model DU spectrophotometer at 347 nm.

Results and Discussion

The initial concentration of hydrogen cyanide
was always in a large excess to the concentration
of CPA, while the initial concentration of CPA
(2 × 10⁻³ M) was kept constant over wide pH
range. The rates of the reaction of CPA
with hydrogen cyanide were followed by record-
ing the decrease in optical density of CPA at
347 nm. Table 1 gives an example of the chal-
age of optical density of CPA with time at pH
4.10 and Fig. 1 shows a logarithmic plots of
optical density(OD) vs. time at various concen-
tration of hydrogen cyanide. As shown in
Fig. 1, this reaction is typically first-order, 1

giving a straight line. Fig. 2 shows a plots of 1
vs. various concentration of hydrogen cyanide
at pH 4.10. The second-order rate constants
(k₂) calculated from the slope of the straight
line are given in Table 2 and Fig. 3 shows pH
-rate profile of this reaction.

The solid line in Fig. 3 is a theoretical value
calculated according to the equation(25) and the
dashed lines show the contribution of individual
rate terms. As shown in Fig. 3, the change of log \( k_t \) vs. pH is very complicated; from pH 0 to 3.90, the log \( k_t \) increases gradually and at pH 3.90, the maximum point is obtained and from pH 3.90 to 8.0, the log \( k_t \) remains constant and from pH 8 to 10, \( k_t \) is directly proportional to the hydroxide ion concentration and above pH 10, the log \( k_t \) remains again constant.

One may expect that the following eight reactions will proceed at various pH range.

\[
\begin{align*}
\text{Ar-CH=CCCN} & \xrightarrow{k_A} \text{HCN} \quad (1) \\
\text{Ar-CH=CCCOO} & \xrightarrow{K_B} \text{HCN} \quad (2) \\
\text{Ar-CH=CCCN} & \xrightarrow{K_C} \text{CN} \quad (3) \\
\text{Ar-CH=CCCOO} & \xrightarrow{K_D} \text{OH} \quad (4) \\
\text{Ar-CH=CCCOOH} & \xrightarrow{K_E} \text{CN} \quad (5) \\
\text{Ar-CH=CCCOOH} & \xrightarrow{K_F} \text{H}_2\text{O} \quad (6) \\
\text{Ar-CH=CCCOOH} & \xrightarrow{K_G} \text{H}_2\text{O} \quad (7) \\
\text{Ar-CH=CCCOO} & \xrightarrow{K_H} \text{H}_2\text{O} \quad (8)
\end{align*}
\]

_Table 2_. Second-order rate-constant \((k_t)\) for the reaction of CPA with hydrogen cyanide at 25°C.

<table>
<thead>
<tr>
<th>Buffer solution</th>
<th>pH</th>
<th>( k_t ) (M(^{-1})·sec(^{-1}))</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.55</td>
<td>2.50 × 10(^{-4})</td>
<td>pH=0</td>
<td>5.20 × 10(^{-4})</td>
</tr>
<tr>
<td>NaAc+HAc</td>
<td>3.00</td>
<td>3.50 × 10(^{-4})</td>
<td></td>
<td>3.50 × 10(^{-4})</td>
</tr>
<tr>
<td>KH(_2)PO(_4)</td>
<td>6.10</td>
<td>6.00 × 10(^{-4})</td>
<td></td>
<td>6.00 × 10(^{-4})</td>
</tr>
<tr>
<td>KH(_2)PO(_4)</td>
<td>8.30</td>
<td>2.80 × 10(^{-3})</td>
<td></td>
<td>2.80 × 10(^{-3})</td>
</tr>
<tr>
<td>NaOH+H(_2)BO(_3)</td>
<td>8.75</td>
<td>4.48 × 10(^{-3})</td>
<td></td>
<td>4.48 × 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>9.05</td>
<td>1.55 × 10(^{-3})</td>
<td></td>
<td>1.55 × 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>9.20</td>
<td>9.00 × 10(^{-3})</td>
<td></td>
<td>9.00 × 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>9.50</td>
<td>1.00 × 10(^{-3})</td>
<td></td>
<td>1.00 × 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.20 × 10(^{-3})</td>
<td></td>
<td>1.20 × 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>10.70</td>
<td>1.00 × 10(^{-3})</td>
<td></td>
<td>1.00 × 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>11.50</td>
<td>1.14 × 10(^{-3})</td>
<td></td>
<td>1.14 × 10(^{-3})</td>
</tr>
</tbody>
</table>

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cyanide. The reaction (4) is also neglected, since the rate constant \(k=1.05 \times 10^{-4} \text{ M}^{-1} \cdot \text{sec}^{-1}\) of the addition of hydroxide ion to a carboxylate anion is smaller than that of cyanide ion. Consequently, reaction (1), (2) and (3) are remained and the over-all rate equation for this addition reaction is given by the following:

\[
\text{Rate} = -\frac{d[\text{CPA}]}{dt} = k_1 [\text{CPA}]_T [\text{HCN}]_T
\]

\[
= k_A [\text{CPA}] [\text{HCN}] + k_b [\text{CPA}]^0 [\text{HCN}]^0 + k_c [\text{CPA}]^0 [\text{CN}^0]
\]

Where \([\text{CPA}]_T\) is the total concentration of CPA added and \([\text{CPA}]\) is the concentration at equilibria, respectively, since the CPA is dissociated partially in the solution.

\[
K_{\text{CPA}} = \frac{[\text{H}^+] [\text{CPA}^\cdot]}{[\text{CPA}]}
\]

\[
[\text{CPA}]_T = [\text{CPA}] + [\text{CPA}]^0
\]

from equation (10) and (11)

\[
[\text{CPA}] = [\text{CPA}]_T [\text{H}^+] + k_{\text{CPA}}
\]

\[
[\text{CPA}^\cdot] = [\text{CPA}]_T \left(1 - \frac{[\text{H}^+]}{K_{\text{CPA}} + [\text{H}^+]} \right)
\]

Similarly,

\[
[\text{HCN}] = \frac{[\text{H}^+] [\text{HCN}]_T}{[\text{H}^+] K_{\text{HCN}}}
\]

\[
[\text{CN}^\cdot] = [\text{HCN}]_T \left(1 - \frac{[\text{H}^+]}{K_{\text{HCN}} + [\text{H}^+]} \right)
\]

Substituting equation (12), (13), (14), and (15) in to equation (9)

\[
\text{Rate} = K_A \left[\frac{[\text{H}^+]}{[\text{H}^+] + K_{\text{CPA}}} [\text{CPA}]_T \right] \left[\frac{[\text{H}^+] + K_{\text{HCN}}}{[\text{H}^+] + K_{\text{HCN}}} [\text{HCN}]_T \right]
\]

\[
+ K_B \left[\frac{1}{[\text{H}^+] + K_{\text{CPA}}} [\text{CPA}]_T \right] \left[\frac{[\text{H}^+] + K_{\text{HCN}}}{[\text{H}^+] + K_{\text{HCN}}} [\text{HCN}]_T \right]
\]
Substituting $K_{CPA}=1.59\times10^{-6}$ and $K_{HCN}=7.2\times10^{-10}$ into equation (16)

\[
\text{Rate} = k_A \left( \frac{(H^+)}{(H^+)+1.59\times10^{-6}} \right) \left( \frac{(H^+)}{(H^+)+7.2\times10^{-10}} \right) + k_B \left( \frac{1.59\times10^{-6}}{(H^+)+1.59\times10^{-6}} \right) \left( \frac{7.2\times10^{-10}}{(H^+)+7.2\times10^{-10}} \right) + k_C \left( \frac{1.59\times10^{-6}}{(H^+)+7.2\times10^{-10}} \right) \left( \frac{7.2\times10^{-10}}{(H^+)+7.2\times10^{-10}} \right)
\]

from equation (9) and (17), the apparent rate constant ($k_r$) is,

\[
k_r = k_A \left( \frac{(H^+)}{(H^+)+1.59\times10^{-6}} \right) \left( \frac{(H^+)}{(H^+)+7.2\times10^{-10}} \right) + k_B \left( \frac{1.59\times10^{-6}}{(H^+)+1.59\times10^{-6}} \right) \left( \frac{7.2\times10^{-10}}{(H^+)+7.2\times10^{-10}} \right) + k_C \left( \frac{1.59\times10^{-6}}{(H^+)+7.2\times10^{-10}} \right) \left( \frac{7.2\times10^{-10}}{(H^+)+7.2\times10^{-10}} \right)
\]

At low pH, neutral hydrogen cyanide would be added to the CPA or its conjugate base. On the other hand, at high pH, cyanide ion would be added to the CPA\(^\ominus\). Therefore, the mechanism in basic media is,

\[
\text{HCN} + \text{OH}^\ominus \xrightleftharpoons[\ \kappa_8]{k_1} \text{CN}^\ominus + \text{H}_2\text{O}
\]

\[
\text{Ar-CH=C}^\ominus\text{COOH} + \text{CN}^\ominus \xrightarrow[\ \kappa_8]{k_1} \text{Ar-CH-CH-CN}^\ominus \xrightarrow[\ \kappa_2]{\text{fast}} \text{COO}^\ominus
\]

To explain these rate terms, the following addition mechanisms are proposed as similar to the case of the nitrostyrene\(^\ominus\) and ethylcinnamate\(^\ominus\).

\[
\text{Ar-CH=CH-CN}^\ominus + \text{HCN} \xrightarrow[\ \kappa_1]{\ \kappa_1} \text{Ar-CH-CH-CN}^\ominus \xrightarrow[\ \kappa_2]{\text{fast}} \text{COO}^\ominus
\]

Applying steady-state approximation with respect to the intermediate (I), $k_A$ is given by the following equation.

\[
\frac{1}{k_A} = \frac{1}{k_1} + \frac{1}{\kappa_1} \left( k_2 \Sigma (B) \right)
\]

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If only water and hydroxide ion are the general base (B) present, equation (19) becomes,

\[
\frac{1}{k_A} = \frac{1}{k_i} + \frac{1}{(k_i/k_A)(k_2^{H_2O}(H_2O) + k_2^{OH^-})}
\] (20)

It can be seen that if the concentration of general base is high, \( k_A \) will take the limiting value \( k_i = 8.00 \times 10^{-4} \) which is the maximum point in Fig. 3 at low pH, equation (20) becomes,

\[
\frac{1}{k_i} = \frac{1}{k_A} + \frac{1}{(k_i/k_A)(k_2^{H_2O}(H_2O))}
\] (21)

The value of \( k_i k_2^{H_2O}(H_2O) / k_A \) can be determined from the \( k_i \) and observed rate constant \( (k_i) \) and is found to be 3.25 \times 10^{-5}. The data at pH 6.0 gave the value 2.30 \times 10^{9} for \( k_i k_2^{OH^-} \) \((OH^-)/k_A\), substituting the \( k_i \) at pH=6.0, \( k_i = 8.00 \times 10^{-4} \), \( k_i k_2^{H_2O}(H_2O)/k_A = 3.25 \times 10^{-5} \) and the concentration of hydroxide into equation (20), \( k_i k_2^{OH^-}/k_A = 2.30 \times 10^{9} \) can be obtained. As the result, \( k_A \) becomes,

\[
\frac{1}{k_A} = \frac{1}{8.00 \times 10^{-4}}
+ \frac{1}{3.25 \times 10^{-5} + 2.30 \times 10^{-9}(OH^-)}
+ \frac{1}{8.30 \times 10^{-4} + 2.30 \times 10^{-9}(OH^-)}
+ \frac{1}{2.60 \times 10^{-8} + 1.84 \times 10^{4}(OH^-)}
\]

\[
k_A = \frac{2.60 \times 10^{-8} + 1.84 \times 10^{4}(OH^-)}{8.30 \times 10^{-4} + 2.30 \times 10^{-9}(OH^-)}
\] (22)

or

\[
k_A = \frac{2.60 \times 10^{-8} + 1.84 \times 10^{4}(OH^-)}{8.30 \times 10^{-4} + 2.30 \times 10^{-9}(OH^-)}
\] (22)

Similarly,

\[
k_B = \frac{3.25 \times 10^{-8} + 3.30 \times 10^{-9}/(H^+)}{1.00 \times 10^{-3} + 2.30 \times 10^{-5}/(H^+)}
\] (23)

\[
k_C = 4.87 \times 10^{-7} + 3.45 \times 10^{-7}/(H^+)
\]

For the calculation of \( k_B \) or \( k_C \), the value of \( k_B / k_A \) for hydroxide ion and water are the same as above equation (20), since these value cannot be calculated exactly. As a result, over-all rate constant becomes,

\[
k_3 = \frac{2.60 \times 10^{-6} + 1.84 \times 10^{9}}{8.30 \times 10^{-4} + 2.30 \times 10^{-9} / (H^+)}
\]

\[
\left( (H^+) - 1.50 \times 10^{-6} \right) \left( (H^+) + 7.2 \times 10^{-10} / (H^+) \right)
+ \left( 7.2 \times 10^{-10} / (H^+) \right)
\]

\[
= \frac{4.87 \times 10^{-7} + 3.45 \times 10^{-7} / (H^+)}{1.59 \times 10^{-6} + 1.59 \times 10^{-6} / (H^+)}
\]

\[
\left( 7.2 \times 10^{-10} / (H^+) \right)
\] (25)

Table 3 and Fig. 3 show that the value of over-all rate constant \( k_3 \) calculated by equation (25) are in good agreement with the observed value. From the rate equation (26), the mechanism of nucleophilic addition reaction of hydrogen cyanide to CPA over wide pH range is fully explained; below pH 3, hydrogen cyanide molecule is directly added to CPA molecule, however, from pH 6.0 to pH 8.0 it is added to conjugate base of CPA; from pH 3.0 to 6.0 hydrogen cyanide and cyanide ion are competitively added to carboxylate anion of CPA, above pH 9, more reactive cyanide ion is added to CPA. At pH 8.0, the ratio of hydrogen cyanide to cyanide ion is 1 to 9, while at pH 10 only the cyanide ion is added to the CPA. A nucleophile would be added more rapidly to CPA than to CPA. This may be the reason why the rate constant shows a maximum point around pH 4.0.

Conclusion

A general rate equation which can be applied over wide pH range was obtained;

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$$k_1 = \frac{2.60 \times 10^{-3} + 1.84 \times 10^{-5}}{8.30 \times 10^{-5} + 2.30 \times 10^{-5}} \left( \frac{[\text{H}^+]}{[\text{H}^+] + 1.59 \times 10^{-6}} \right) \left( \frac{[\text{H}^+]}{[\text{H}^+] + 7.20 \times 10^{-10}} \right) + \frac{3.25 \times 10^{-8} + 2.30 \times 10^{-8}}{1.00 \times 10^{-3} + 2.30 \times 10^{-5}} \left( \frac{[\text{H}^+]}{[\text{H}^+] + 1.59 \times 10^{-6}} \right) \left( \frac{[\text{H}^+]}{[\text{H}^+] + 7.20 \times 10^{-10}} \right) + \frac{4.87 \times 10^{-8} + 3.45 \times 10^{-8}}{1.50 \times 10^{-8} + 2.30 \times 10^{-8}} \left( \frac{[\text{H}^+]}{[\text{H}^+] + 1.59 \times 10^{-6}} \right) \left( \frac{[\text{H}^+]}{[\text{H}^+] + 7.20 \times 10^{-10}} \right)$$

(2) From the rate equation, one may conclude that the following three reactions occur.

a) \( \text{Ar} - \text{CH} = \text{C} \equiv \text{CN} + \text{HCN} \rightarrow \)

b) \( \text{Ar} - \text{CH} = \text{C} \equiv \text{COOH} + \text{HCN} \rightarrow \)

c) \( \text{Ar} - \text{CH} = \text{C} \equiv \text{COOH} + \text{CN}^- \rightarrow \)

Below pH 3, the reaction is started by addition of hydrogen cyanide molecule to CPA, but, from pH 6 to pH 8 hydrogen cyanide is added to CPA from pH 3 to 6, these two reactions occur competitively. Above pH 9, the reaction is proceeded by addition of cyanide ion to CPA.

References
2. (a) T. L. Crowell and A. W. Francis Jr., J. Amer. Chem. Soc., 83, 591(1961);