# α-Cyano-β-Piperonylacrylic Acid에 대한 Hydrogen Cyanide 의 친핵성 첨가반응에 관한 연구

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# The Kinetics and Mechanism of Nucleophilic Addition of Hydrogen Cyanide to α-Cyano-β-piperonylacrylic Acid

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요 약. α-Cyano-β-piperonylacrylic acid(CPA)에 대한 hydorogen cyanide 의 친핵성 첨가 반응속도 상수를 측정하여 넓은 pH 범위에서 잘 맞는 반응 속도식을 구하였다. 이 식에 의하면 pH 3 이하에서는 CPA 에 대해 hydrogen cyanide 분자의 첨가 반응이 일어나지만 pH 6 에서 8 사이는 hydrogen cyanide 가 α-cyano-β-piperonyl acrylate ion 에 첨가함을 알수 있고, 또 pH 3 과 6 사이에서 는 이들 두 반응이 경쟁적으로 일어난다. 그리고 pH 9 이상에서는 α-cyano-β-piperonyl acrylate ion 에 cyanide ion 이 첨가하는 반응이 일어나며 pH 3 에서 9 까지의 모든 복잡한 반응 메카니즘도 이 식으로 충분히 설명할 수 있음을 알았다.

**Abstract.** The rate constant of the addition of hydrogen cyanide to α-cyano-β-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 α-cyano-β-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 α-cyano-β-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] In previous papers,[3,4] we investigated the rate and mechanism of hydrolysis of CPA and the addition of n-propyl-mercaptan,

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*Table* 1. The changes of opticaal deosity (OD) of CPA with time at pH 4.10 & 25°C.

| [HCN] $=1\times10^{-3}$ M | | [HCN] $=2\times10^{-3}$ M | | [HCN] $=3\times10^{-3}$ M | | [HCN] $=4\times10^{-3}$ M | |
|---|---|---|---|---|---|---|---|
| time$\times10^3$ (sec) | OD | time$\times10^3$ (sec) | OD | time$\times10^3$ (sec) | OD | time$\times10^3$ (sec) | OD |
| 0 | 0.305 | 0 | 0.307 | 0 | 0.306 | 0 | 0 306 |
| 1.26 | 0.304 | 0.72 | 0.305 | 1.25 | 0.034 | 1.26 | 0.303 |
| 3.72 | 0.300 | 3.75 | 0.299 | 3.75 | 0.296 | 3.72 | 0.298 |
| 8.52 | 0.296 | 8.56 | 0.292 | 8.56 | 0.292 | 8.52 | 0.289 |
| 13.7 | 0.290 | 13.76 | 0.285 | 13.75 | 0.283 | 13.72 | 0.280 |
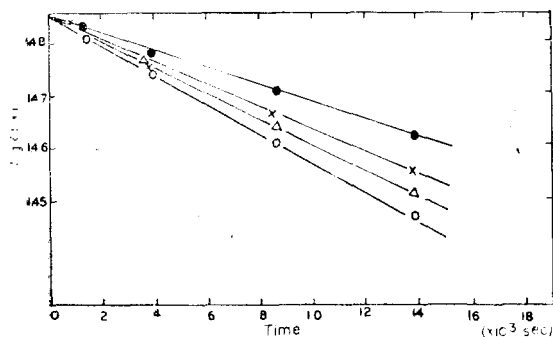


*Fig.* 1 The plots of log(CPA) *vs.* time at pH=4.10 25 °C and 0.10 ionic strength.

over wide pH range. In present studies it is attempted to determine each rate constant over wide pH range and to reveal the reaction mechanism of the addition of hydrogen cyanide to CPA.

## Experimental

CPA was prepared by condensation of piperonal and α-cyanoacetic acid.[5] Reagent grade (kanto) potasium cyanide was used. All buffer solution were prepared from reagent grade chemicals(E. Mark) and distilled water. The pH of buffer solutions were determined by Zeromatic II pH meter(Beckman) and the ionic strength was kept constant 0.1 by adding sodium chloride solution.

The reaction vessels used were 100 m*l* volu-

metric flask in the thermostat(25°C). At zero time, 2 m*l* of a freshly prepared methanol solution $(1\times10^{-3}M)$ of CPA was pipetted into 100 m*l* flask containing 94~97 m*l* of buffer solution and 1~3 m*l* solution of potasium 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 $(2\times10^{-5}M)$ Kas kept constant over wide pH range. The rates of the reaction of CPA with hydrogen cyanide were followed by recording the decrease in optical density of CPA at 347 nm. *Table* 1 gives an example of the change 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 concentration of hydrogen cyanide. As shown in *Fig.* 1, this reaction is typically first-order, giving a straight line. *Fig.* 2 shows a plots of $k_1$ *vs.* various concentration of hydrogen cyanide at pH 4.10. The second-order rate constants $(k_t)$ 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 acocrding 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.

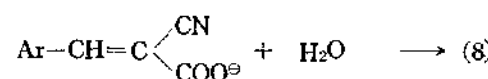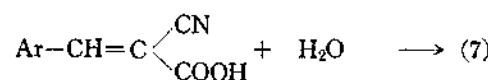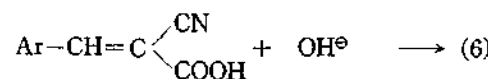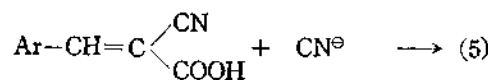One may expect that the following eight reactions will proceed at various pH range.

$$\text{CH}=\text{C}\begin{smallmatrix}\diagup\text{CN}\\\diagdown\text{COOH}\end{smallmatrix}$$

$$+ \quad \text{HCN} \xrightarrow{k_A} \quad (1)$$

$$\text{Ar}-\text{CH}=\text{C}\begin{smallmatrix}\diagup\text{CN}\\\diagdown\text{COO}^{\ominus}\end{smallmatrix} + \text{HCN} \xrightarrow{K_B} (2)$$

$$\text{Ar}-\text{CH}=\text{C}\begin{smallmatrix}\diagup\text{CN}\\\diagdown\text{COO}^{\ominus}\end{smallmatrix} + \text{CN}^{\ominus} \xrightarrow{K_C} (3)$$

$$\text{Ar}-\text{CH}=\text{C}\begin{smallmatrix}\diagup\text{CN}\\\diagdown\text{COO}^{\ominus}\end{smallmatrix} + \text{OH}^{\ominus} \longrightarrow (4)$$

$$\text{Ar}-\text{CH}=\text{C}\begin{smallmatrix}\diagup\text{CN}\\\diagdown\text{COOH}\end{smallmatrix} + \text{CN}^{\ominus} \longrightarrow (5)$$

$$\text{Ar}-\text{CH}=\text{C}\begin{smallmatrix}\diagup\text{CN}\\\diagdown\text{COOH}\end{smallmatrix} + \text{OH}^{\ominus} \longrightarrow (6)$$

$$\text{Ar}-\text{CH}=\text{C}\begin{smallmatrix}\diagup\text{CN}\\\diagdown\text{COOH}\end{smallmatrix} + \text{H}_2\text{O} \longrightarrow (7)$$

$$\text{Ar}-\text{CH}=\text{C}\begin{smallmatrix}\diagup\text{CN}\\\diagdown\text{COO}^{\ominus}\end{smallmatrix} + \text{H}_2\text{O} \longrightarrow (8)$$
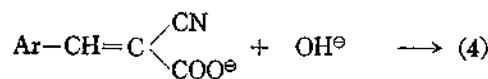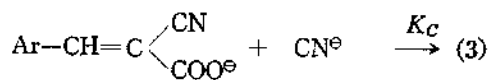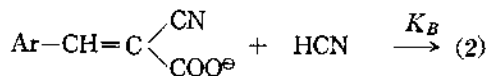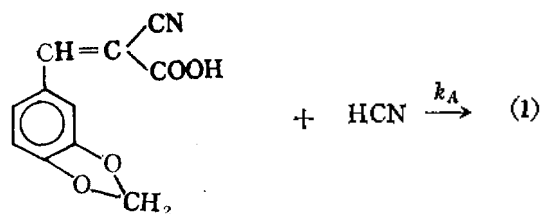
*Table* 2. Second-order rate-constant($k_t$) for the reaction of CPA with hydrogen cyanide at 25 °C.

| Buffer solution | pH | $k_t$ ($M^{-1} \cdot \text{sec.}^{-1}$) | | | |
|---|---|---|---|---|---|
| | | Observed | | Calculated | |
| HCl | 0 | $2.50 \times 10^{-5}$ | pH=0 | $5.20 \times 10^{-5}$ | |
| | 0.55 | $6.0 \times 10^{-5}$ | 1.10 | $1.84 \times 10^{-4}$ | |
| | 1.10 | $1.74 \times 10^{-4}$ | 1.50 | $5.82 \times 10^{-4}$ | |
| | 1.90 | $5.50 \times 10^{-4}$ | 2.00 | $6.10 \times 10^{-4}$ | |
| | 2.20 | $4.57 \times 10^{-4}$ | 2.50 | $8.00 \times 10^{-4}$ | |
| | 2.70 | $6.66 \times 10^{-4}$ | 3.00 | $8.00 \times 10^{-4}$ | |
| NaAc+HAc | 3.00 | $8.42 \times 10^{-4}$ | 3.50 | $7.92 \times 10^{-4}$ | |
| | 3.50 | $8.00 \times 10^{-4}$ | 4.00 | $7.84 \times 10^{-4}$ | |
| | 4.10 | $7.50 \times 10^{-4}$ | 4.50 | $7.50 \times 10^{-4}$ | |
| | 4.50 | $7.50 \times 10^{-4}$ | 5.00 | $6.21 \times 10^{-4}$ | |
| | 5.00 | $6.21 \times 10^{-4}$ | 5.50 | $7.50 \times 10^{-4}$ | |
| | 5.50 | $7.50 \times 10^{-4}$ | 6.00 | $6.20 \times 10^{-4}$ | |
| KH$_2$PO$_4$×K$_2$HPO$_4$ | 6.10 | $5.00 \times 10^{-4}$ | 6.50 | $7.12 \times 10^{-4}$ | |
| | 6.90 | $5.55 \times 10^{-4}$ | 7.00 | $9.40 \times 10^{-4}$ | |
| | 7.25 | $7.50 \times 10^{-4}$ | 7.50 | $9.90 \times 10^{-4}$ | |
| | 7.90 | $1.02 \times 10^{-3}$ | 8.00 | $1.00 \times 10^{-3}$ | |
| | 8.30 | $2.80 \times 10^{-3}$ | 8.50 | $2.12 \times 10^{-3}$ | |
| NaOH+H$_3$BO$_3$ | 8.75 | $4.48 \times 10^{-3}$ | 9.00 | $6.30 \times 10^{-3}$ | |
| | 9.05 | $1.55 \times 10^{-2}$ | 9.50 | $1.10 \times 10^{-2}$ | |
| | 9.20 | $9.00 \times 10^{-3}$ | 10.00 | $1.32 \times 10^{-}$ | |
| | 9.50 | $1.00 \times 10^{-2}$ | 10.50 | $1.06 \times 10^{-2}$ | |
| | 10.00 | $1.20 \times 10^{-2}$ | 11.00 | $1.06 \times 10^{-2}$ | |
| | 10.70 | $1.06 \times 10^{-2}$ | 11.50 | $1.06 \times 10^{-2}$ | |
| | 11.50 | $1.14 \times 10^{-2}$ | 12.00 | $1.06 \times 10^{-2}$ | |
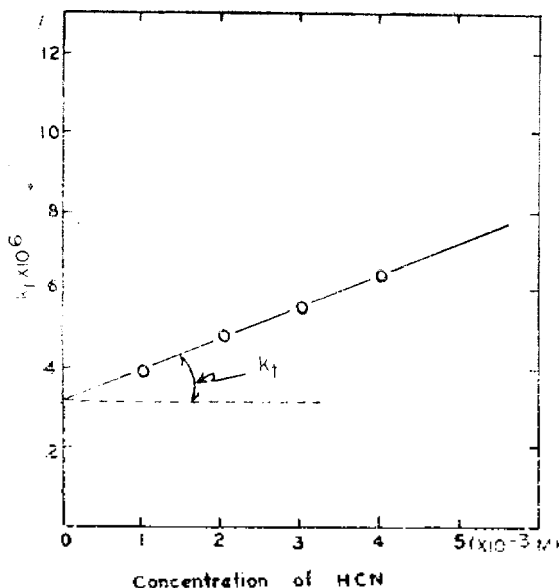
*Fig.* 2. The plots of $k_1$ *vs.* (HCN) at pH=4.10
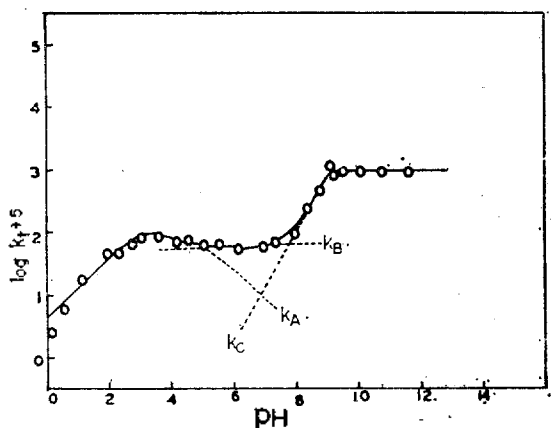


*Fig.* 3. pH-rate profile for the reaction of hydrogen cyanide with CPA at 25 °C and ionic strength.

Among these above reactions, (5) and (6) can be ruled out, since the dissociation constant of CPA($K_{CPA}=1.59\times10^{-6}$) determined by potentiometric titration is much larger than that of hydrogen cyanide ($K_{HCN}=7.2\times10^{-10}$). The reaction (7) and (8) are also neglected, since the rate constant[3] ($k=6.91 \times 10^{-7} sec^{-1}$) of the addition of water to CPA and a carboxylate anion is much smaller than that of hydrogen

cyanide. The reaction (4) is also neglected, since the rate constant[3] ($k=1.05\times10^{-4} M^{-1}\cdot sec^{-1}$) 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;

$$Rate=-\frac{d[CPA]}{dt}=k_t[CPA]_T [HCN]_T$$
$$=k_A[CPA] [HCN]+k_B[CPA]^\ominus[HCN]+$$
$$k_C[CPA^\ominus] [CN^\ominus] \qquad (9)$$

Where $[CPA]_T$ is the total concentration of CPA added and [CPA] is the concentration at equilibria, respectively. since the CPA is dissociated partially in the solution.

$$K_{CPA}=\frac{[H^+] [CPA^-]}{[CPA]} \qquad (10)$$

$$[CPA]_T=[CPA] + [CPA]^\ominus \qquad (11)$$

from equation (10) and (11)

$$[CPA]=\frac{[CPA]_T[H^+]}{[H^+]+k_{CPA}} \qquad (12)$$

$$[CPA^-]=[CPA]_T\left\{1-\frac{[H^+]}{K_{CPA}+[H^+]}\right\} \qquad (13)$$

Similarly,

$$[HCN]=\frac{[H^+] [HCN]_T}{[H^+]K_{HCN}} \qquad (14)$$

$$[CN^-]=[HCN]_T\left\{1-\frac{[H^+]}{K_{HCN}+[H^+]}\right\}. \qquad (15)$$

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

$$Rate=K_A\left\{\left[\frac{[H^+]}{[H^+]+K_{CPA}}\right][CPA]_T\right\}$$
$$\left\{[\frac{[H^+]}{[H^+]+K_{HCN}}] [HCN]_T\right\}$$
$$+ K_B\left\{(1-\frac{[H^+]}{[H^+]+K_{CPA}}) [CPA]_T\right\}$$
$$\left\{[\frac{[H^+]}{[H^+]+K_{HCH}}) [HCN]_T\right\}$$

$$+ k_C \left\{ (1 - \frac{[H^+]}{[H^+] + K_{CPA}}) [CPA]_T \right\}$$

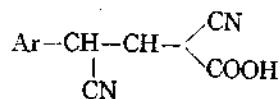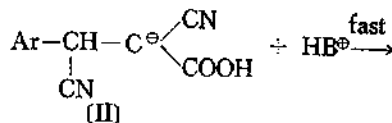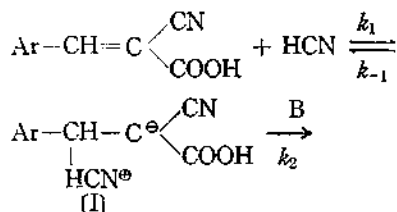$$\left\{ (1 - \frac{[H^+]}{[H^+] + K_{HCN}}) [HCN]_T \right\} \quad (16)$$

Substituting $K_{CPA} = 1.59 \times 10^{-6}$ and $K_{HCN} = 7.2 \times 10^{-10}$ into equation (16)

$$Rate = \left\{ k_A \left( \frac{[H^+]}{[H^+] + 1.59 \times 10^{-6}} \right) \right.$$
$$\left( \frac{[H^+]}{[H^+] + 7.2 \times 10^{-10}} \right)$$
$$+ k_B \left( \frac{1.59 \times 10^{-6}}{[H^+] + 1.59 \times 10^{-6}} \right)$$
$$\left( \frac{7.2 \times 10^{-10}}{[H^+] + 7.2 \times 10^{-10}} \right)$$
$$+ k_C \left( \frac{1.59 \times 10^{-6}}{[H^+] + 1.59 \times 10^{-6}} \right)$$
$$\left. \left( \frac{7.2 \times 10^{-10}}{[H^+] + 7.2 \times 10^{-10}} \right) \right\} [CPA]_T [HCN]_T$$
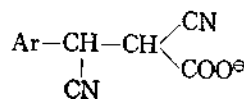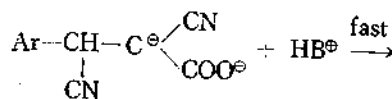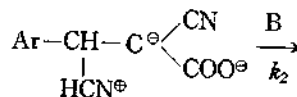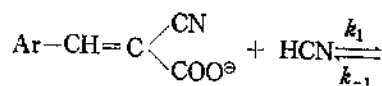$$(17)$$

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

$$k_t = k_A \left( \frac{[H^+]}{[H^+] + 1.59 \times 10^{-6}} \right)$$
$$\left( \frac{[H^+]}{[H^+] + 7.2 \times 10^{-10}} \right)$$
$$+ k_B \left( \frac{1.59 \times 10^{-6}}{[H^+] + 1.59 \times 10^{-6}} \right)$$
$$\left( \frac{7.2 \times 10^{-10}}{[H^+] + 7.2 \times 10^{-10}} \right)$$
$$+ k_C \left( \frac{1.59 \times 10^{-6}}{[H^+] + 1.59 \times 10^{-6}} \right)$$
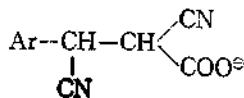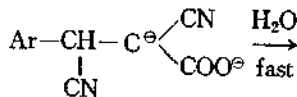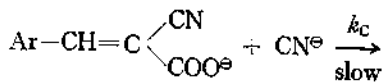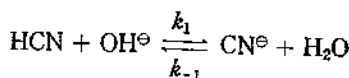$$\left( \frac{7.2 \times 10^{-10}}{[H^+] + 7.2 \times 10^{-10}} \right) \quad (18)$$

To explain these rate terms, the following addition mechanisms are proposed as similar to the case of the nitrostyrene[6] and ethylcinnamate[7]

$$Ar-CH=C\begin{array}{c} CN \\ COOH \end{array} + HCN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$Ar-CH-C^{\ominus}\begin{array}{c} CN \\ COOH \end{array} \overset{B}{\underset{k_2}{\longrightarrow}}$$
$$\overset{|}{HCN^{\oplus}}$$
$$(I)$$

$$Ar-CH-C^{\ominus}\begin{array}{c} CN \\ COOH \end{array} + HB^{\oplus} \overset{fast}{\longrightarrow}$$
$$\overset{|}{CN}$$
$$(II)$$

$$Ar-CH-CH-\begin{array}{c} CN \\ COOH \end{array}$$
$$\overset{|}{CN}$$

and

$$Ar-CH=C\begin{array}{c} CN \\ COO^{\ominus} \end{array} + HCN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$Ar-CH-C^{\ominus}\begin{array}{c} CN \\ COO^{\ominus} \end{array} \overset{B}{\underset{k_2}{\longrightarrow}}$$
$$\overset{|}{HCN^{\oplus}}$$

$$Ar-CH-C^{\ominus}\begin{array}{c} CN \\ COO^{\ominus} \end{array} + HB^{\oplus} \overset{fast}{\longrightarrow}$$
$$\overset{|}{CN}$$

$$Ar-CH-CH\begin{array}{c} CN \\ COO^{\ominus} \end{array}$$
$$\overset{|}{CN}$$

At low pH, neutral hydrogen cyanide would be added to the CPA or it's 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,

$$HCN + OH^{\ominus} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CN^{\ominus} + H_2O$$

$$Ar-CH=C\begin{array}{c} CN \\ COO^{\ominus} \end{array} + CN^{\ominus} \overset{k_C}{\underset{slow}{\longrightarrow}}$$

$$Ar-CH-C^{\ominus}\begin{array}{c} CN \\ COO^{\ominus} \end{array} \overset{H_2O}{\underset{fast}{\longrightarrow}}$$
$$\overset{|}{CN}$$

$$Ar-CH-CH\begin{array}{c} CN \\ COO^{\ominus} \end{array}$$
$$\overset{|}{CN}$$

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

$$\frac{1}{k_A} = \frac{1}{k_1} + \frac{1}{\frac{k_1}{k_{-1}}(k_2 \sum (B))} \quad (19)$$

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

$$\frac{1}{k_A} = \frac{1}{k_1} + \frac{1}{(k_1/k_{-1})\,[k_2^{H_2O}(H_2O) + k_2^{OH}]} \quad (20)$$

It can be seen that if the concentration of general base is high, $k_A$ will take the limiting value $k_1 = 8.00 \times 10^{-4}$ which is the maximum point in *Fig.* 3 at low pH, equation (20) becomes,

$$\frac{1}{k_t} = \frac{1}{k_A} = \frac{1}{k_1} + \frac{1}{\dfrac{k_1}{k_{-1}}(k_2^{H_2O}(H_2O))} \quad (21)$$

The value of $k_1 k_2^{H_2O}(H_2O)/k_{-1}$ can be determined from the $k_1$ and observed rate constant ($k_t$) 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 $k_1 k_2^{OH} [OH^-]/k_{-1}$, substituting the $k_t$ at pH=6.0, $k_1 = 8.00 \times 10^{-4}$, $k_1 k_2^{H_2O}(H_2O)/k_{-1} = 3.25 \times 10^{-5}$ and the concentration of hydroxide into equation (20), $k_1 k_2^{OH}/k_{-1} = 2.30 \times 10^9$ can be obtained. As the result, $k_A$ becomes,

$$\frac{1}{k_A} = \frac{1}{8.00 \times 10^{-4}}$$
$$+ \frac{1}{3.25 \times 10^{-5} + 2.30 \times 10^{-9}[OH^-]}$$
$$= \frac{8.30 \times 10^{-4} + 2.30 \times 10^9 [OH^-]}{2.60 \times 10^{-8} + 1.84 \times 10^6 [OH^-]}$$

$$k_A = \frac{2.60 \times 10^{-8} + 1.84 \times 10^6 [OH^-]}{8.30 \times 10^{-4} + 2.30 \times 10^{-9} [OH^-]}$$

or

$$k_A = \frac{2.60 \times 10^{-8} + 1.84 \times 10^{-8}/[H^+]}{8.30 \times 10^{-4} + 2.30 \times 10^{-5}/[H^+]} \quad (22)$$

Similarly,

$$k_B = \frac{3.25 \times 10^{-6} + 2.30 \times 10^{-8}/[H^+]}{1.00 \times 10^{-3} + 2.30 \times 10^{-5}/[H^+]} \quad (23)$$

$$k_C = \frac{4.87 \times 10^{-7} + 3.45 \times 10^{-7}/[H^+]}{1.50 \times 10^{-2} + 2.30 \times 10^{-5}/[H^+]} \quad (24)$$

For the calculation of $k_B$ or $k_C$, the value of $k_1 k_2/k_{-1}$ 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,

$$k_t = \frac{2.60 \times 10^{-8} + 1.84 \times 10^{-8}/[H^+]}{8.30 \times 10^{-4} + 2.30 \times 10^{-5}/[H^+]}$$
$$\left(\frac{[H^+]}{[H^+] + 1.59 \times 10^{-6}}\right)\left(\frac{[H^+]}{[H^+] + 7.20 \times 10^{-10}}\right)$$
$$+ \frac{3.25 \times 10^{-8} + 2.30 \times 10^{-8}/[H^+]}{1.00 \times 10^{-3} + 2.30 \times 10^{-5}/[H^+]}$$
$$\left(\frac{1.59 \times 10^{-6}}{[H^+] + 1.59 \times 10^{-6}}\right)\left(\frac{7.2 \times 10^{-10}}{[H^+] + 7.2 \times 10^{-10}}\right)$$
$$+ \frac{4.87 \times 10^{-7} + 3.45 \times 10^{-7}/[H^+]}{1.50 \times 10^{-2} + 2.30 \times 10^{-5}/[H^+]}$$
$$\left(\frac{1.59 \times 10^{-6}}{[H^+] + 1.59 \times 10^{-6}}\right)\left(\frac{7.20 \times 10^{-10}}{[H^+] + 7.20 \times 10^{-10}}\right) \quad (25)$$

*Table.* 3 and *Fig.* 3 show that the valus of over-all rate constant $k_t$ calculated by equation (25) are in good agreement with the observed value. From the rate equation (25), 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 molcule, 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 anion 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

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

$$k_t = \frac{2.60 \times 10^{-8} + 1.84 \times 10^{-8}/[H^+]}{8.30 \times 10^{-4} + 2.30 \times 10^{-5}/[H^+]}$$

$$\left(\frac{[H^+]}{[H^+] + 1.59 \times 10^{-6}}\right)\left(\frac{[H^+]}{[H^+] + 7.20 \times 10^{-10}}\right)$$

$$+ \frac{3.25 \times 10^{-8} + 2.30 \times 10^{-8}/[H^+]}{1.00 \times 10^{-3} + 2.30 \times 10^{-5}/[H^+]}$$

$$\left(\frac{1.59 \times 10^{-6}}{[H^+] + 1.59 \times 10^{-6}}\right)\left(\frac{7.20 \times 10^{-10}}{[H^+] + 7.20 \times 10^{-10}}\right)$$

$$+ \frac{4.87 \times 10^{-7} + 3.45 \times 10^{-7}/[H^+]}{1.50 \times 10^{-2} + 2.30 \times 10^{-5} [H^+]}$$

$$\left(\frac{1.59 \times 10^{-6}}{[H^+] + 1.59 \times 10^{-6}}\right)\left(\frac{7.20 \times 10^{-10}}{[H^+] + 7.20 \times 10^{-10}}\right)$$

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

a) Ar—CH=C(CN)(COOH) + HCN ⇌ ——→

b) Ar—CH=C(CN)(COO⁻) + HCN ——→

c) Ar—CH=C(CN)(COO⁻) + CN⁻ ——→
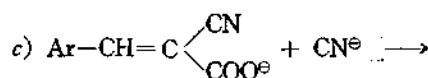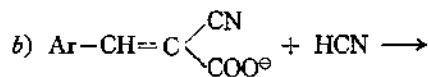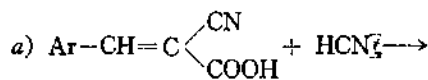
Below pH 3, the reaction is started by addition of hydrogen cyanide molecule to CPA, but, from pH 6 to pH 8 hydrogen cyanide is added to CPA from pH 3 to 6, these two reactions occur competitively. Above pH 9, the reaction is proceeded by addition of cyanide ion to CPA.

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