

α -Cyano- β -Piperonylacrylic Acid의 가수분해 메카니즘과 그의 반응속도론적 연구

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Kinetics and Mechanism of the Hydrolysis of α -Cyano- β -piperonylacrylic Acid.

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요 약. α -Cyano- β -piperonylacrylic acid의 가수분해 속도상수를 자외선분광기를 사용하여 구하였 으며 아울러 넓은 pH 범위에 잘 맞는 반응속도식도 얻었다. 이 식에 의하면 넓은 pH 범위, 특히 중 전에 잘 규명된 바 없는 산성용매 속에서의 반응 및 hydroxide ion의 촉매역할 등도 정략적으로 잘 설명할 수 있음을 알았다. 즉 pH 4.0 이하에서의 가수분해반응은 α -Cyano- β -piperonylacrylic acid에 물분자가 첨가되므로써 시작되며 pH 5.0~7.5에서는 α -Cyano- β -piperonylacrylic acid와 α -Cyano- β -piperonylacrylate anion에 물 분자가 경쟁적으로 첨가되며 pH 8.0에서는 α -Cyano- β -piperonylacrylate anion에 물분자만이 첨가되며 pH 12.0 이상에서는 hydroxide ion만이 α -Cyano- β -piperonylacrylate anion에 첨가됨을 알았다.

Abstract. The rate constants of the hydrolysis of α -cyano- β -piperonylacrylic acid were determined by Ultraviolet spectrophotometry at various pH and a rate equation which can be applied over wide pH range was obtained. The reaction mechanism of hydrolysis of α -cyano- β -piperonylacrylic acid and especially the catalytic contribution of hydroxide ion which not studied carefully before in acidic media, can be fully explained by the rate equation obtained. The rate equation reveals that; below pH 4.0, the reaction is initiated by the addition of water molecule to α -cyano- β -piperonylacrylic acid.

At pH 5.0-7.5, α -cyano- β -piperonylacrylic acid compete with α -cyano- β -piperonylacrylate ion in adding of water. At pH 8.0, water is the only nucleophile for α -cyano- β -piperonylacrylate ion, however, above pH 12.0, hydroxide ion is an addendum and the acceptor is α -cyano- β -piperonylacrylate ion.

Introduction

Addition reactions to carbon-carbon double bonds are electrophilic, however, the double

bonds having electron attracting group is nucleophilic in which the addition of anion is the rate-determining step¹. In spite of many applications, the number of qualitative observations

and the fact that analogies with more carefully studied reactions suggest quite plausible mechanism for the nucleophilic addition reaction in basic and neutral media, it has been the subject of only a few kinetic studies²⁻⁷. Ogata⁸ have studied the mechanism of the addition of aniline to methylvinylketone to form 1-aniline-*o*-butan-2-one. Davies and others⁹ have investigated the mechanism and solvent effect of the addition of alcohol to vinylsulphones and sulphonamides in the presence of base catalyst.

The mechanism of the nucleophilic addition of methylvinylketone¹⁰, acrylonitrile¹¹, tricyanovinylbenzene¹², 1,1-dicyano-2-*p*-dimethylaminophenyl-2-halogenoethylene¹³ and morpholine or pyrrolidine addition to olefins activated by various electron attracting group in basic media¹⁴ has also been reported. As shown in above references, some kinetic studies for Michael addition and their related reactions in alkali solution has been presented. However, in the intermediate pH range and weak acidic media, only a few carefully studied works have been reported. In acidic media, the cleavage of nitrostyrene was suggested by Crowell and Kim to take place in a slightly different mechanism¹⁵⁻¹⁷. The purpose of this investigation is to determine the rate constants over a wide pH range and to reveal the reaction mechanism of hydrolysis of α -cyano- β -piperonylacrylic acid, especially, in acidic media which is not studied carefully before.

Experimental

α -cyano- β -piperonylacrylic acid (CPA) was prepared by condensation of piperonal and α -cyanoacetate. All buffer solutions were prepared from reagent grade chemicals (E. Merck) and distilled water. The pH of buffer solutions were determined by Zerometric II pH meter (Beckman) and the ionic strength was kept constant at 0.1 by adding sodium chloride solution.

The reaction vessels used were 100 ml. volumetric flasks in the thermostat(25°C). At zero time, 2 ml of a freshly prepared methanol solution of CPA was pipetted into 100 ml. flask containing 98 ml. of buffer solution. The sample were analyzed on a Beckman model DU spectrophotometer at 347 nm As the product of hydrolysis, piperonal was formed and identified by the melting point of *p*-nitrophenylhydrazone (199°C;lit. 200°C)

Results and Discussion

The initial concentration of CPA ($2 \times 10^{-5} M$) was kept constant over wide pH range. Table 1 gives an example of the change of optical

Table 1. The change of optical densities(O.D) of α -cyano- β -piperonyl-acrylic acid with time at pH 3.45 & 25°C.

| time(sec.) | OD | time(sec.) | OD |
|--------------------|-------|--------------------|-------|
| 0 | 0.370 | 17.5×10^4 | 0.353 |
| 2.5×10^4 | 0.367 | 24.1×10^4 | 0.348 |
| 7.1×10^4 | 0.363 | 33.5×10^4 | 0.340 |
| 12.5×10^4 | 0.358 | | |

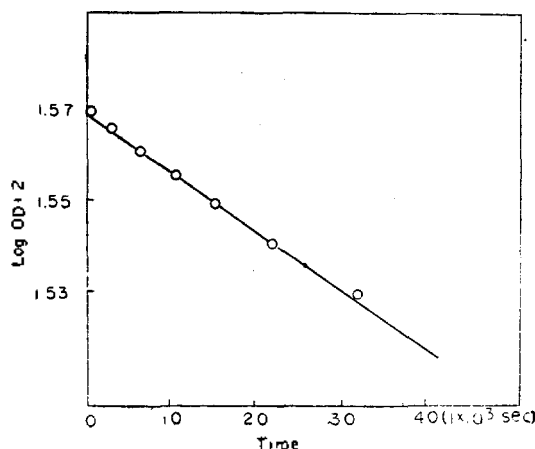


Fig. 1. The plots of Log OD of α -cyano- β -piperonylacrylic acid vs time at pH 3.45, 25°C and 0.1 ionic strength.

Table 2. Rate constants (k_t) for the hydrolysis of α -cyano- β -piperonyl-acrylic acid at various pH and 25°C.

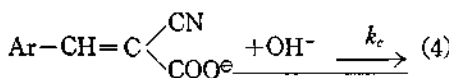
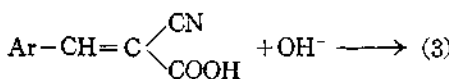
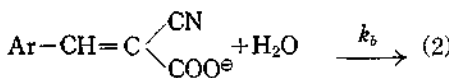
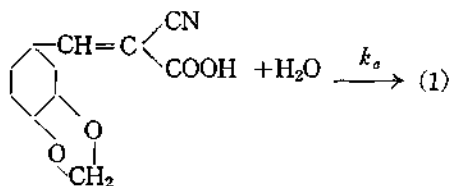
| pH | $k_t(\text{sec}^{-1})$ | | pH | $k_t(\text{sec}^{-1})$ | |
|------|------------------------|-----------------------|-------|------------------------|-----------------------|
| | observed | calculated* | | observed | calculated |
| 0.00 | 1.02×10^{-8} | 1.07×10^{-8} | 7.42 | 3.77×10^{-7} | |
| 0.50 | 1.04×10^{-8} | | 7.45 | 3.45×10^{-7} | 3.93×10^{-7} |
| 1.00 | 1.06×10^{-8} | 1.13×10^{-8} | 7.75 | 5.30×10^{-7} | |
| 1.50 | 2.22×10^{-8} | | 7.70 | 5.07×10^{-7} | |
| 2.00 | 1.69×10^{-8} | 1.76×10^{-8} | 8.04 | 5.42×10^{-7} | 3.71×10^{-7} |
| 2.05 | 5.41×10^{-8} | | 8.45 | 4.38×10^{-7} | 3.81×10^{-7} |
| 2.45 | 2.99×10^{-8} | 6.05×10^{-8} | 8.75 | 4.61×10^{-7} | |
| 3.05 | 8.52×10^{-8} | 7.68×10^{-8} | 9.15 | 3.69×10^{-7} | 3.90×10^{-7} |
| 3.45 | 2.53×10^{-7} | 3.10×10^{-7} | 9.20 | 6.26×10^{-7} | |
| 3.75 | 1.61×10^{-7} | | 9.72 | 3.27×10^{-7} | 4.11×10^{-7} |
| 3.90 | 3.68×10^{-7} | 3.50×10^{-7} | 9.90 | 8.75×10^{-7} | 4.60×10^{-7} |
| 4.25 | 1.61×10^{-7} | | 10.20 | 5.76×10^{-7} | |
| 4.75 | 1.54×10^{-7} | 5.10×10^{-7} | 10.65 | 5.36×10^{-7} | 9.07×10^{-7} |
| 4.75 | 6.45×10^{-7} | | 11.05 | 9.21×10^{-7} | 1.43×10^{-6} |
| 5.15 | 5.53×10^{-7} | 6.0×10^{-7} | 11.50 | 8.96×10^{-6} | |
| 5.70 | 6.91×10^{-7} | | 12.00 | 1.00×10^{-5} | 1.09×10^{-5} |
| 6.25 | 3.92×10^{-7} | 4.31×10^{-7} | 12.50 | 2.79×10^{-5} | |
| 6.55 | 4.15×10^{-7} | 4.10×10^{-7} | 13.00 | 1.05×10^{-4} | 1.05×10^{-4} |
| 6.85 | 3.69×10^{-7} | | 13.50 | 4.26×10^{-4} | |
| 6.90 | 3.13×10^{-7} | 3.87×10^{-7} | 14.00 | 9.21×10^{-4} | 1.05×10^{-3} |
| 7.20 | 5.29×10^{-7} | | | | |

* calculated by the equation(16).

density of CPA with time at pH 3.45 and Fig. 1. shows a logarithmic plots of optical density (OD) vs time at various pH. As shown in Fig. 2, this reaction is typically first-order, giving a straight line. The first-order rate constants (k_t) calculated from the straight line at various pH are given in Table 2 and Fig. 2 shows pH-rate profile of this reaction.

As shown in Fig. 2, the change of $\log k_t$ vs. pH is very complicated; from pH 0 to 5.70, the $\log k_t$ increases gradually and at pH 5.70, the maximum point is obtained and from pH 5.9 to 10.5, the $\log k_t$ remains constant and above pH 11.0, the slope is 1.0, i.e., k_t is directly proportional to the hydroxide ion concentration. One may expect that the follo-

wing four reactions will proceed at various pH range.



The dissociation constant of CPA determined by potentiometric titration is $1.59 \times 10^{-6} (K_{\text{CPA}})$

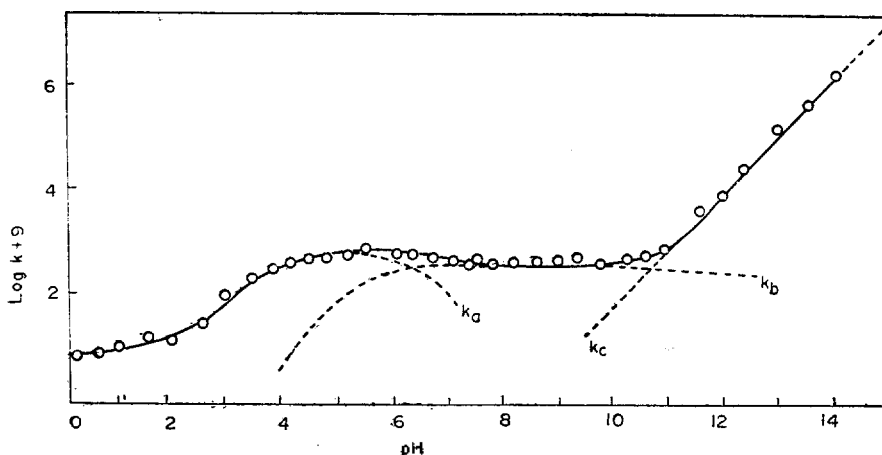


Fig. 2. pH-rate profile for the hydrolysis of α -cyano- β -piperonyl-acrylic acid at 25 °C and ionic strength 0.1. Circles are experimental point and curve is drawn according to equation (16) and the dotted line represents the contribution of each rate constant.

of these reactions, (3) can be ruled out since almost all of CPA is ionized to its conjugate base in media. As a consequence, reaction (1), (2), and (4) are remained and the over all rate equation for this reaction is given by the following,

$$\begin{aligned} \text{Rate} &= -d(\text{CPA})/dt = k_t(\text{CPA})_T \\ &= k_a(\text{CPA}) + k_b(\text{CPA}^\ominus) + k_c(\text{CPA}^\ominus)(\text{OH}^-) \quad (5) \end{aligned}$$

where $(\text{CPA})_T$ is the total concentration of CPA added and (CPA) is the concentration at equilibria, respectively. By definition,

$$\begin{aligned} K_{\text{CPA}} &= (\text{H}^+) (\text{CPA}^\ominus) / (\text{CPA}) \quad \text{or} \\ (\text{CPA}) &= (\text{H}^+) (\text{CPA}) / K_{\text{CPA}} \quad (6) \\ (\text{CPA}) + (\text{CPA}^\ominus) &= (\text{CPA})_T \quad (7) \end{aligned}$$

Substituting equation (6) and $K_{\text{CPA}} = 1.59 \times 10^{-6}$ mole l^{-1} into equation (7),

$$(\text{CPA}^\ominus) = (\text{CPA})_T \left(1 - \frac{(\text{H}^+)}{(\text{H}^+) + K_{\text{CPA}}} \right) \quad (8)$$

From (5) and (8),

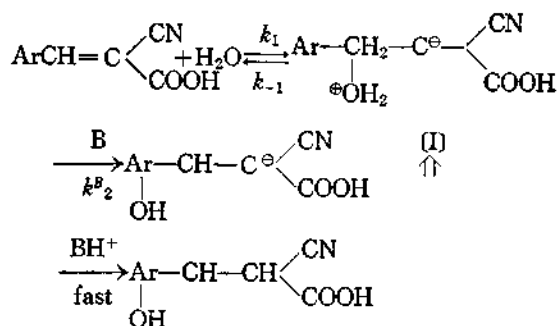
$$\begin{aligned} \text{Rate} &= \left\{ k_a \left(\frac{(\text{H}^+)}{(\text{H}^+) + K_{\text{CPA}}} \right) + k_b \left(1 - \frac{(\text{H}^+)}{(\text{H}^+) + K_{\text{CPA}}} \right) \right. \\ &\quad \left. + k(\text{OH}^-) \right\} (\text{CPA})_T \quad (9) \end{aligned}$$

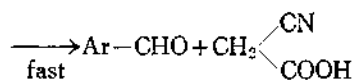
From equation (5) and (9), the apparent rate constant (k_t) is,

$$\begin{aligned} k_t &= k_a \left(\frac{(\text{H}^+)}{(\text{H}^+) + K_{\text{CPA}}} \right) \\ &\quad + k_b \left(1 - \frac{(\text{H}^+)}{(\text{H}^+) + K_{\text{CPA}}} \right) + k_c(\text{OH}^-) \quad (10) \end{aligned}$$

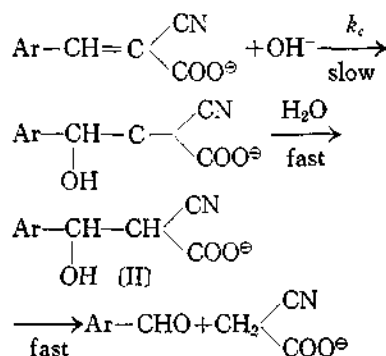
$$\begin{aligned} \text{or, } k_t &= k_a \left(\frac{(\text{H}^+)}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) \\ &\quad + k_b \left(1 - \frac{(\text{H}^+)}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) + k_c(\text{OH}^-) \end{aligned}$$

The last term is proportional to the hydroxide ion concentration and the k_a and k_b terms are very complex and are not simply proportional to the hydroxide ion concentration. To explaining these rate terms, the following mechanisms are proposed as similar to the case of the nitrostyrene and ethylcinnamate.





On the other hand, around neutral pH, water molecule would be added to the CPA or its conjugated base. Therefore, the mechanism of hydrolysis in basic media is,



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

$$\frac{1}{k_a} = \frac{1}{k_1} + \frac{1}{\frac{k_1}{k_{-1}} k_2^B (B)} \quad (11)$$

If only water and hydroxide ion are the general base (B) present, equation (11) becomes,

$$\frac{1}{k_a} = \frac{1}{k_1} + \frac{1}{k_1/k_{-1} \{k_2^{\text{H}_2\text{O}}(\text{H}_2\text{O}) + k_2^{\text{OH}}(\text{OH}^-)\}} \quad (12)$$

It can be seen that if the concentration of general base is high, k_a will take the limiting value, $k_1=6.91 \times 10^{-7}$ which is the maximum point in Fig. 2. At pH 1.0 in which $k_2^{\text{OH}}(\text{OH}^-)$ is negligibly small compared to the $k_2^{\text{H}_2\text{O}}(\text{H}_2\text{O})$, the value of $k_1/k_{-1} k_2^{\text{H}_2\text{O}}(\text{H}_2\text{O})$ is found to be 1.08×10^{-8} . From this data and observed k_i which is obtained at pH in which the concentration of hydroxide ion is not negligibly small the value of $k_1/k_{-1} k_2^{\text{OH}}$ obtained is 7.55×10^8 . Substituting all of this values into the equation (12), k_a becomes

$$k_a = \frac{7.45 \times 10^{-15} + 5.21 \times 10^{-17}/(\text{H}^+)}{7.02 \times 10^{-7} + 7.55 \times 10^{-11}/(\text{H}^+)} \quad (13)$$

Similarly,

$$k_b = \frac{3.98 \times 10^{-15} + 2.78 \times 10^{-17}/(\text{H}^+)}{3.80 \times 10^{-7} + 7.55 \times 10^{-11}/(\text{H}^+)} \quad (14)$$

For the calculation of k_b^B , 3.45×10^{-7} which is obtained at pH 7.45 was taken as the limiting value. The value k_b^B of water or hydroxide ion for CPA will not be equal to that of CPA. However, we took the same value used for CPA as shown in k_a calculation because these values could not be calculated precisely. The value of k_c is obtained from the slope of the straight line in Fig. 2.

$$k_c(\text{OH}^-) = k_c K_w / (\text{H}^+) = 1.05 \times 10^{-17}/(\text{H}^+) \quad (15)$$

Substituting all of the constants obtained into equation (5), the over-all rate constant, k_i becomes

$$\begin{aligned} k_i = & \frac{7.45 \times 10^{-15} + 5.21 \times 10^{-17}/(\text{H}^+)}{7.02 \times 10^{-7} + 7.55 \times 10^{-11}/(\text{H}^+)} \\ & \left(\frac{(\text{H}^+)}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) + \\ & \frac{3.98 \times 10^{-15} + 2.78 \times 10^{-17}/(\text{H}^+)}{3.80 \times 10^{-7} + 7.55 \times 10^{-11}/(\text{H}^+)} \\ & \left(1 - \frac{(\text{H}^+)}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) + 1.05 \times 10^{-17}/(\text{H}^+) \end{aligned} \quad (16)$$

Table. 2 and Fig. 2 show that the value of over-all rate constant k_i calculated by equation (16) are in good agreement with the observed.

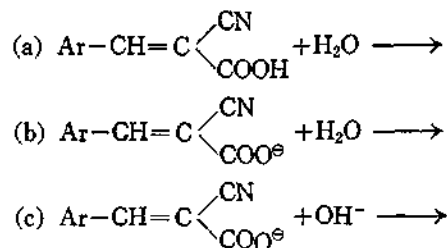
From the rate equation, the mechanism of hydrolysis of CPA over wide pH range is fully explained; at pH 4.0, water is added only to CPA and at pH 5.0, the ratio of addition of water to CPA and CPA^\ominus is 6 to 1. At pH 6.0, the ratio is 2 to 3. While, at pH 9.0, only water is added to CPA^\ominus . However, around pH 10.0, water and hydroxide ion competitively added to CPA^\ominus and as the pH is increased, the portion of the more reactive hydroxide ion addition is increased. Water and hydroxide ion would be added more rapidly to CPA than to CPA^\ominus , and this may be the reason why the rate constant shows a maximum point around pH 5.70.

Conclusion

(1) A following rate equation for the hydrolysis of α -cyano- β -piperonylacrylic-acid which can be applied over wide pH was obtained and analyzed in detail.

$$k_t = \frac{7.45 \times 10^{-15} + 5.21 \times 10^{-17} / \{H^+\}}{7.02 \times 10^{-7} + 7.55 \times 10^{-11} / \{H^+\}} + \left(\frac{\{H^+\}}{\{H^+\} + 1.59 \times 10^{-6}} \right) + \frac{3.98 \times 10^{-15} + 2.78 \times 10^{-17} / \{H^+\}}{3.80 \times 10^{-7} + 7.55 \times 10^{-11} / \{H^+\}} + \left(1 - \frac{\{H^+\}}{\{H^+\} + 1.59 \times 10^{-6}} \right) + 1.05 \times 10^{-17} / \{H^+\}$$

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



Below pH 4.0 or around pH 8.0, only the (a) and (b) reaction proceed, respectively.

However, from pH 5.0 to 7.5, these two reactions occur competitively.

Above pH 12.0, the hydrolysis of α -cyano- β -piperonylacrylic acid is initiated by the addition of hydroxide ion to CPA[⊖]. The mechanism and catalytic contribution of hydroxide ion and water, not studied carefully before can also be fully explained by the above rate equation.

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