

α -Cyano- β -piperonylacrylic Acid 에 대한 *n*-Propylmercaptan 의 친핵성 첨가반응에 관한 연구

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The Kinetics and Mechanism of Nucleophilic Addition of *n*-Propylmercaptan to α -Cyano- β -piperonylacrylic Acid.

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요 약. α -Cyano- β -piperonylacrylic acid 에 대한 *n*-Propylmercaptan 의 친핵성 첨가반응 속도 상수를 측정하여 넓은 pH 범위에서 잘 맞는 반응속도식을 구하였다. 이 식에 의하면 넓은 pH 범위에서 일어나는 복잡한 반응메카니즘을 정량적으로 잘 설명 할 수 있었다.

즉 pH 4.5 이하에서는 α -Cyano- β -piperonyl acrylic acid 에 mercaptan 이 직접 첨가되며 pH 4.5~6.5 사이에서는 주로 α -Cyano- β -piperonyl acrylate ion 에 mercaptan 분자가 첨가되고 pH 7.5 부터는 α -Cyano- β -piperonylacrylate ion 에 mercaptan 분자와 mercaptide ion 의 첨가가 경쟁적으로 일어나며 pH 10 이상에서는 α -Cyano- β -piperonylacrylate anion 에 mercaptide ion 의 첨가만이 일어남을 알수 있었다.

Abstract. The rate constants of the nucleophilic addition of *n*-propyl-mercaptan to α -cyano- β -piperonylacrylic acid were determined at various pH and a rate equation which can be applied over wide pH range is obtained. The rate equation reveals that below pH 4.5 the reaction is initiated by the attack of *n*-propylmercaptan to α -cyano- β -piperonylacrylic acid. At pH 4.5~6.5, however, *n*-propylmercaptan is added to α -cyano- β -piperonylacrylate ion; at pH 7.04~9.5 the competitive reaction between *n*-propylmercaptan and *n*-propylmercaptide ion is anticipated to occur. Above pH 10 the addendum is *n*-propylmercaptide ion and the acceptor is α -cyano- β -piperonylacrylate ion.

Introduction

A carbon-carbon double bond does not generally act as an acidic site. However, the double bonds having electron attracting group, unlike ordinary carbon double bonds, are electrophilic.

During the past decade a great deal of information has appeared in the literature^{1,2} concerning the mechanism of nucleophilic addition and qualitative observation to explain a plausible mechanism³⁻⁷ in basic solution. However, only a few kinetic studies have been reported.

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Kharash⁸ and Hurd⁹ have suggested a mechanism of the addition of mercaptan to carbonyl

compounds in basic media. Stewart¹⁰ pointed out the alkaline scission of 4-hydroxy-3-methoxy- β -nitrostyrene. Walker and Young¹¹ also determined the rate constants and activation energies for the hydrolytic decomposition of chalcone.

Noyce and others¹² not only synthesized a ketal, 1,3-diphenyl-3-hydroxy-1-propanone by an indirect route, but also provided kinetic evidence for the occurrence of the ketal in the acid catalyzed condensation of benzaldehyde and acetophenone. Patai and others¹³⁻¹⁵ have studied the elimination of malonitrile from 4,4-dicyano-3-nitrochalcone and malonitrile in methanol. The kinetics of the reaction of barbituric acid with β -nitrostyrene derivatives in non-alkaline media has been reported.¹⁶ In acidic media, the cleavage of nitrostyrene, according to Crowell and Kim takes place in a slightly different mechanism^{17,18}. Truce and others¹⁹ have studied the stereochemistry of the mercaptan addition reaction. The mechanisms of the reaction of mercaptan with maleic anhydride²⁰, methylacrylate²¹, β -nitrostyrene²², ethylcinnamate²³, has been reported. The purpose of this investigation is to determine each rate constant over a wide pH range and to reveal the reaction mechanism of the addition of *n*-propylmercaptan to α -cyano- β -piperonylacrylic acid.

Experimental

α -Cyano- β -piperonylacrylic acid (CPA) was prepared by condensation of piperonal and α -cyanoacetate²⁴. Reagent grade (Tokyo-kasei) *n*-propylmercaptan was used. All buffer solutions were prepared from reagent grade chemicals (E. Merk) 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 rate vessels used were 100 ml. volumetric

flasks in the thermostat (25°C). At zero time, 1 ml. of a freshly prepared methanol solution ($1 \times 10^{-3} M$) of CPA was pipetted into the 100 ml. flask containing 95~98 ml. of buffer solution and 1~4 ml. methanol solution of *n*-propylmercaptan (0.1 M). The sample were analyzed on a Beckman model DU quartz spectrophotometer at 347 mu.

Result

The concentration of *n*-propylmercaptan was always in a larger excess (20~100 times) than the concentration of CPA. Table 1 gives an example and Fig. 1 shows a logarithmic plots of concentration vs. time at various concentration of *n*-propylmercaptan. This reaction is typically pseudo-first-order, giving a straight line. As shown in Fig. 2, the pseudo-first-order rate constant (k_i) vs. various mercaptan concentration was used to calculate the second-order rate constant for this reaction. The second-order rate constants (k_i) at various pH 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 (23) and the dashed lines show the contribution of individual rate terms.

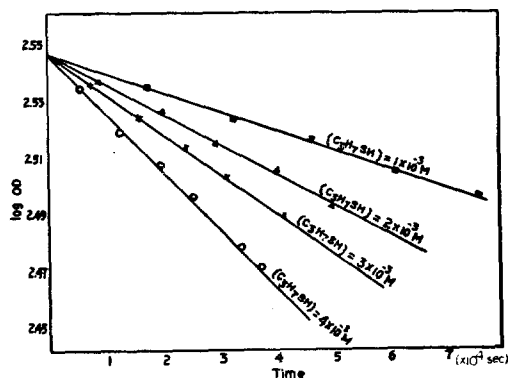


Fig. 1. The plots of log OD of α -cyano- β -piperonylacrylic acid vs. time at pH 4.00, 25°C and 0.10 ionic strength.

Table 1. The changes of optical density of α -cyano- β -piperonylacrylic acid vs. time at pH 4.00 and 25°C.

Concentration of <i>n</i> -propylmercaptan							
$4.0 \times 10^{-3} M$		$3.0 \times 10^{-3} M$		$2.0 \times 10^{-3} M$		$1.0 \times 10^{-3} M$	
Time $\times 10^{-4}$ (sec.)	O. D.	Time $\times 10^{-4}$ (sec.)	O. D.	Time $\times 10^{-4}$ (sec.)	O. D.	Time $\times 10^{-4}$ (sec.)	O. D.
0	0.355	0	0.352	0	0.351	0	0.343
0.610	0.345	0.810	0.342	1.050	0.342	1.680	0.336
1.200	0.336	1.605	0.333	2.100	0.334	3.190	0.329
1.825	0.326	2.400	0.325	3.050	0.326	4.650	0.323
2.410	0.318	3.110	0.318	4.100	0.318	6.110	0.314
3.250	0.304	4.105	0.308	5.050	0.310	7.600	0.306
3.610	0.300						

Table 2. Pseudo-first-order (k_1) and second-order rate constants (k_2) for the reaction of α -cyano- β -piperonylacrylic acid with *n*-propylmercaptan and various pH and 25°C.

pH	[<i>n</i> -C ₃ H ₇ SH]	k_1 (sec. ⁻¹)	pH	[<i>n</i> -C ₃ H ₇ SH]	k_2 (sec. ⁻¹)
0.00	1×10^{-3}	2.80×10^{-7}	0.50	1×10^{-3}	3.00×10^{-7}
	2×10^{-3}	4.50×10^{-7}		2×10^{-3}	4.40×10^{-7}
	3×10^{-3}	6.25×10^{-7}		3×10^{-3}	5.79×10^{-7}
	4×10^{-3}	8.00×10^{-7}		4×10^{-3}	7.19×10^{-7}
	$k_1 (M^{-1} \text{ sec.}^{-1}) = 1.75 \times 10^{-4}$			$k_2 (M^{-1} \text{ sec.}^{-1}) = 1.40 \times 10^{-4}$	
1.00	1×10^{-3}	4.14×10^{-7}	1.50	1×10^{-3}	2.65×10^{-7}
	2×10^{-3}	5.94×10^{-7}		2×10^{-3}	4.54×10^{-7}
	3×10^{-3}	7.74×10^{-7}		3×10^{-3}	6.44×10^{-7}
	4×10^{-3}	9.53×10^{-7}		4×10^{-3}	8.35×10^{-7}
	$k_1 (M^{-1} \text{ sec.}^{-1}) = 1.80 \times 10^{-4}$			$k_2 (M^{-1} \text{ sec.}^{-1}) = 1.90 \times 10^{-4}$	
2.00	1×10^{-3}	0.22×10^{-6}	2.50	1×10^{-3}	0.27×10^{-6}
	2×10^{-3}	0.50×10^{-6}		2×10^{-3}	0.62×10^{-6}
	3×10^{-3}	0.77×10^{-6}		3×10^{-3}	0.91×10^{-6}
	4×10^{-3}	1.07×10^{-6}		4×10^{-3}	1.22×10^{-6}
	$k_1 (M^{-1} \text{ sec.}^{-1}) = 3.00 \times 10^{-4}$			$k_2 (M^{-1} \text{ sec.}^{-1}) = 3.20 \times 10^{-4}$	
3.00	1×10^{-3}	0.67×10^{-6}	3.50	1×10^{-3}	0.98×10^{-6}
	2×10^{-3}	1.29×10^{-6}		2×10^{-3}	2.18×10^{-6}
	3×10^{-3}	1.96×10^{-6}		3×10^{-3}	3.22×10^{-6}
	4×10^{-3}	2.59×10^{-6}		4×10^{-3}	4.48×10^{-6}
	$k_1 (M^{-1} \text{ sec.}^{-1}) = 6.70 \times 10^{-4}$			$k_2 (M^{-1} \text{ sec.}^{-1}) = 1.20 \times 10^{-3}$	
4.00	1×10^{-3}	1.20×10^{-6}	4.50	1×10^{-3}	1.63×10^{-6}
	2×10^{-3}	2.75×10^{-6}		2×10^{-3}	3.50×10^{-6}
	3×10^{-3}	4.32×10^{-6}		3×10^{-3}	5.42×10^{-6}
	4×10^{-3}	5.85×10^{-6}		4×10^{-3}	7.30×10^{-6}
	$k_1 (M^{-1} \text{ sec.}^{-1}) = 1.55 \times 10^{-3}$			$k_2 (M^{-1} \text{ sec.}^{-1}) = 1.90 \times 10^{-3}$	

5.00	1×10^{-3}	3.68×10^{-6}	5.50	1×10^{-3}	2.00×10^{-6}
	2×10^{-3}	4.85×10^{-6}		2×10^{-3}	3.18×10^{-6}
	3×10^{-3}	6.05×10^{-6}		3×10^{-3}	4.40×10^{-6}
	4×10^{-3}	7.25×10^{-6}		4×10^{-3}	5.58×10^{-6}
	$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 1.20 \times 10^{-3}$			$k' (\text{M}^{-1}\text{sec.}^{-1}) = 1.20 \times 10^{-3}$	
6.00	1×10^{-3}	3.25×10^{-6}	6.50	1×10^{-3}	3.45×10^{-6}
	2×10^{-3}	4.50×10^{-6}		2×10^{-3}	4.81×10^{-6}
	3×10^{-3}	5.85×10^{-6}		3×10^{-3}	6.15×10^{-6}
	4×10^{-3}	7.52×10^{-6}		4×10^{-3}	7.52×10^{-6}
	$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 1.30 \times 10^{-3}$			$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 1.35 \times 10^{-3}$	
7.00	1×10^{-3}	1.00×10^{-5}	7.50	1×10^{-3}	3.45×10^{-5}
	2×10^{-3}	1.28×10^{-5}		2×10^{-3}	4.32×10^{-5}
	3×10^{-3}	1.56×10^{-5}		3×10^{-3}	5.16×10^{-5}
	4×10^{-3}	1.85×10^{-5}		4×10^{-3}	6.06×10^{-5}
	$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 2.80 \times 10^{-3}$			$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 9.00 \times 10^{-3}$	
8.00	1×10^{-3}	1.15×10^{-5}	8.50	1×10^{-3}	6.05×10^{-5}
	2×10^{-3}	2.35×10^{-5}		2×10^{-3}	9.70×10^{-5}
	3×10^{-3}	3.55×10^{-5}		3×10^{-3}	1.33×10^{-4}
	4×10^{-3}	4.75×10^{-5}		4×10^{-3}	1.71×10^{-4}
	$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 1.20 \times 10^{-2}$			$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 3.70 \times 10^{-2}$	
9.00	1×10^{-3}	0.32×10^{-4}	9.50	1×10^{-3}	1.22×10^{-4}
	2×10^{-3}	2.50×10^{-4}		2×10^{-3}	3.92×10^{-4}
	3×10^{-3}	4.65×10^{-4}		3×10^{-3}	6.70×10^{-4}
	4×10^{-3}	6.80×10^{-4}		4×10^{-3}	9.45×10^{-4}
	$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 2.20 \times 10^{-1}$			$k_2 (\text{M}^{-1}\text{sec.}^{-1}) = 2.75 \times 10^{-1}$	

Table 3. Second-order rate constants (k_2) for the addition reaction of *n*-propylmercaptan to α -cyano- β -piperonylacrylic acid at 25 °C.

pH	Buffer solution	$k_2 (\text{M}^{-1}, \text{Sec.}^{-1})$	
		Observed	Calculated
0.00	HCl	1.75×10^{-4}	1.70×10^{-4}
0.50	"	1.40×10^{-4}	1.74×10^{-4}
1.00	"	1.80×10^{-4}	1.80×10^{-4}
1.50	"	1.90×10^{-4}	2.00×10^{-4}
2.00	"	3.00×10^{-4}	2.40×10^{-4}
2.50	"	3.20×10^{-4}	3.70×10^{-4}
3.00	"	6.70×10^{-4}	6.70×10^{-4}
3.50	HAc+NaAc	1.20×10^{-3}	1.13×10^{-3}
4.00	"	1.55×10^{-3}	1.55×10^{-3}
4.50	"	1.90×10^{-3}	1.76×10^{-3}
5.00	"	1.20×10^{-3}	1.75×10^{-3}
5.50	"	1.20×10^{-3}	1.60×10^{-3}
6.00	"	1.30×10^{-3}	1.58×10^{-3}

6.50	NaH ₂ PO ₄ +Na ₂ HPO ₄	1.35×10 ⁻³	1.58×10 ⁻³
7.00	"	2.80×10 ⁻³	2.44×10 ⁻³
7.50	"	9.00×10 ⁻³	4.98×10 ⁻³
8.00	"	1.26×10 ⁻²	1.33×10 ⁻²
8.50	NaOH+Boric acid	3.70×10 ⁻²	3.90×10 ⁻²
9.00	"	2.20×10 ⁻¹	1.20×10 ⁻¹
9.50	"	2.75×10 ⁻¹	3.78×10 ⁻¹
10.00	"	1.20	1.20

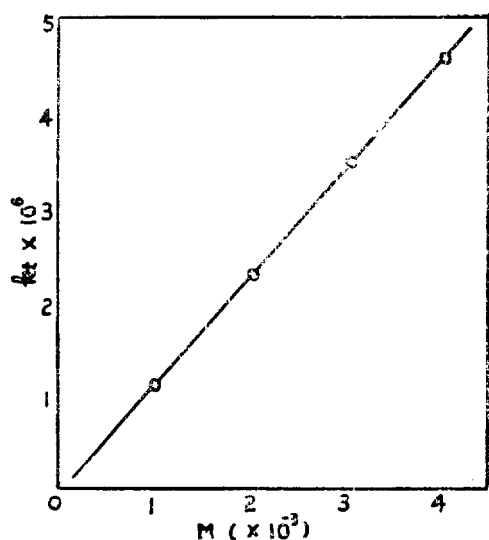


Fig. 2 The plots of k_t vs. (*n*-propylmercaptan) at pH 4.00.

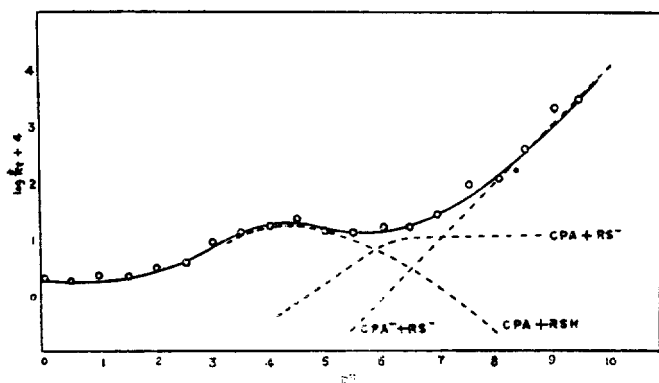
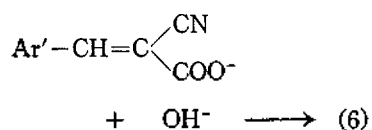
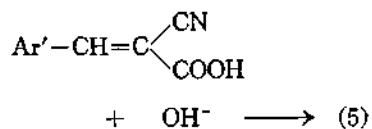
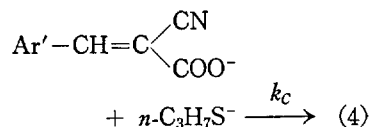
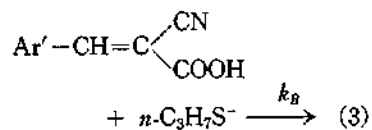
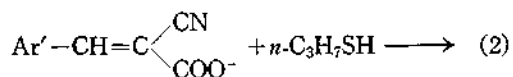
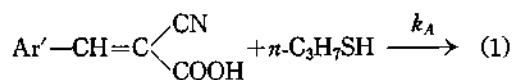


Fig. 3. pH-Rate profile for the addition reaction of *n*-propylmercaptan to α -cyano- β -piperonylacrylic acid at 25°C. Circles are experimental points. Curve is theoretical and the dashed lines show the contribution of each component in equation (23).

Discussion

As shown in Fig. 3, the change of $\log k_t$ vs. pH is very complicated; up to pH 4.5, the $\log k_t$ increased gradually and at pH 4.5 the maximum point is obtained; from pH 4.5 to pH 6.5 the $\log k_t$ remained constant; and above pH 7.5 the slope is 1.0, i. e., k_t is proportional to the hydroxide ion concentration.

It is to be expected that the following six reactions should proceed at various pH ranges:



where Ar' is 3,4-methylenedioxyphenyl radical. Of these reactions, the reaction (2), can be ruled out since the dissociation constant of CPA ($K_{CPA}=1.59 \times 10^{-6}$) determined by potentiometric titration is much larger than that of *n*-propylmercaptan ($K_{RSH}=2.19 \times 10^{-11}$)²⁵. Reaction (5) and (6) are also negligible since almost all of the CPA is ionized to its anion in basic media, and the rate constant of the addition of hydroxide ion to a carboxylate anion (unpublished value: $8.77 \times 10^{-8} M^{-1} \text{sec}^{-1}$) is much smaller than that of mercaptide ion.

Consequently, only (1), (3) and (4) remain, therefore, the overall rate equation for this addition reaction is given by the following:

$$\begin{aligned} \text{Rate} &= -d(\text{CPA})/dt = k_i(\text{CPA})_T(\text{RSH})_T \\ &= k_A(\text{CPA})(\text{RSH}) + k_B(\text{CPA})(\text{RS}^-) \\ &\quad + k_C(\text{CPA}^-)(\text{RS}^-) \end{aligned} \quad (8)$$

Where $(\text{CPA})_T$ is the total concentration of CPA added, and (CPA) is the concentration of equilibria, respectively:

$$\begin{aligned} K_{CPA} &= (\text{H}^+)(\text{CPA}^-)/(\text{CPA}) \\ \therefore (\text{CPA}) &= (\text{H}^+)(\text{CPA}^-)/K_{CPA} \end{aligned} \quad (9)$$

$$(\text{CPA}) + (\text{CPA}^-) = (\text{CPA})_T \quad (10)$$

Substituting equation (9) and $K_{CPA}=1.59 \times 10^{-6}$ mole l^{-1} into equation (10).

$$\begin{aligned} (\text{CPA}^-) &= (\text{CPA})_T / (1 + (\text{H}^+)/K_{CPA}) \\ &= \left(\frac{1.59 \times 10^{-6}}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) (\text{CPA})_T \end{aligned} \quad (11)$$

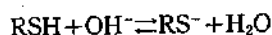
and

$$\begin{aligned} (\text{CPA}) &= (\text{CPA})_T \left(1 - \frac{1}{1 + (\text{H}^+)/K_{CPA}} \right) \\ &= \left(\frac{(\text{H}^+)}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) (\text{CPA})_T \end{aligned} \quad (12)$$

Similarly,

$$(\text{RSH}) = \left(\frac{(\text{H}^+)}{(\text{H}^+) + 2.19 \times 10^{-11}} \right) (\text{RSH})_T \quad (13)$$

For the reaction,



$$(\text{RS}^-) = (K_{RSH}/K_w)(\text{RSH})(\text{OH}^-) \quad (14)$$

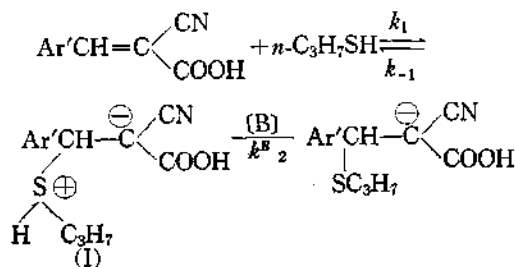
Substituting (11), (12), (13), (14), $K_{RSH}=2.19 \times 10^{-11}$ and $K_w=1.00 \times 10^{-14}$ into the equation (9),

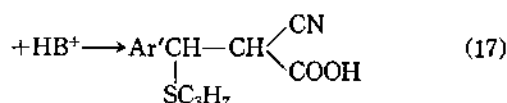
$$\begin{aligned} \text{Rate} &= \left\{ k_A \left(\frac{(\text{H}^+)}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) \right. \\ &\quad \left(\frac{(\text{H}^+)}{(\text{H}^+) + 2.19 \times 10^{-11}} \right) \\ &\quad + k_B \left(\frac{1.59 \times 10^{-6}}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) \\ &\quad + k_C \left(\frac{(\text{H}^+)}{(\text{H}^+) + 2.19 \times 10^{-11}} \right) \\ &\quad \left. \left(\frac{2.19 \times 10^{-12}}{1.00 \times 10^{-14}} \right) (\text{OH}^-) \right\} (\text{CPA})_T (\text{RSH})_T \end{aligned} \quad (15)$$

From equation (8) and (15) the apparent rate constant (k_i) is:

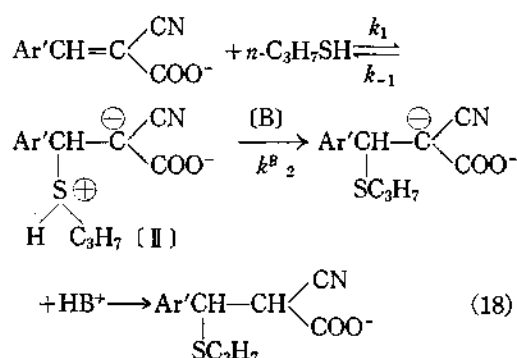
$$\begin{aligned} k_i &= k_A \left(\frac{(\text{H}^+)}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) \left(\frac{(\text{H}^+)}{(\text{H}^+) + 2.19 \times 10^{-11}} \right) \\ &\quad + k_B \left(\frac{1.59 \times 10^{-6}}{(\text{H}^+) + 1.59 \times 10^{-6}} \right) \left(\frac{(\text{H}^+)}{(\text{H}^+) + 2.19 \times 10^{-11}} \right) \\ &\quad + 2.19 \times 10^2 k_C (\text{OH}^-) \left(\frac{(\text{H}^+)}{(\text{H}^+) + 2.19 \times 10^{-11}} \right) \end{aligned} \quad (16)$$

The last term is a rate equation for the Michael type reaction in which mercaptide anion is added to the double bond in basic media. Kharash and Hurd^{8,9} has already explained this reaction mechanism. The k_A and k_B terms are not simply proportional to the hydroxide ion concentration. To explain these rate terms, the following addition mechanisms are proposed as similar to the case of the nitrostyrene and ethylcinnamate^{17,18,23}.





and



In the above equations B is general base. At low pH, neutral mercaptan molecule would be added to the CPA or its conjugate base.

When steady-state approximation is applied with respect to the (I) or (II), k_A is given by the following equation:

$$\frac{1}{k_A} = \frac{k^{\beta_2} \sum (\text{B}) + k_{-1}}{k_1 k^{\beta_2} \sum (\text{B})} = \frac{1}{k_1} + \frac{1}{(k_1/k_{-1})(k^{\beta_2} \sum (\text{B}))} \quad (19)$$

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

$$\frac{1}{k_A} = \frac{1}{k_1} + \frac{1}{(k_1/k_{-1})(k_2^{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_2^{\text{OH}}[\text{OH}^-])} \quad (20)$$

It can be seen that if the concentration of general bases were high, k_A will take the limiting value $k_1 = 1.93 \times 10^{-3}$ which is the maximum point in Fig. 3.

At low pH in which $k_2^{\text{OH}}[\text{OH}^-]$ is negligibly small to the $k_2^{\text{H}_2\text{O}}[\text{H}_2\text{O}]$, the value of $k_1 k_2^{\text{H}_2\text{O}} / k_{-1}[\text{H}_2\text{O}]$ can be determined by the k_1 and observed rate constant k_t and is found to be 2.01×10^{-4} . The data at pH 3.0 gave the value 8.60×10^{-7} for $k_1 k_2^{\text{OH}} / k_{-1}$. This measures the efficiency of hydroxide ion as the base catalyst, B, in our mechanism. As a result, if only water and hydroxide ion are present, k_A becomes

$$\frac{1}{k_A} = \frac{1}{1.90 \times 10^{-3}} + \frac{1}{2.01 \times 10^{-4} + 8.60 \times 10^{-7}[\text{OH}^-]}$$

$$\text{or } k_A = \frac{3.80 \times 10^{-7} + 1.63 \times 10^{-9}/[\text{H}^+]}{2.20 \times 10^{-3} + 8.60 \times 10^{-7}/[\text{H}^+]} \quad (21)$$

Similarly,

$$k_B = \frac{2.28 \times 10^{-7} + 1.03 \times 10^{-9}/[\text{H}^+]}{1.40 \times 10^{-3} + 8.60 \times 10^{-7}/[\text{H}^+]} \quad (22)$$

For the calculation of k_B , the value of $k_1 k^{\beta_2} / k_{-1}$ used for hydroxide ion and water are the same as the above equation (20) since these values cannot be calculated precisely. Nucleophilic addition constant of *n*-propylmercaptide ion, $k_C = 5.4 \times 10^{-8} \text{ M}^{-2} \text{ sec}^{-1}$ is determined by the values $k_t = 1.20 \times 10^{-2}$ at pH 8 and $k_t = 1.20$ at pH 10.

As a result, overall rate constant becomes

$$k_t = \left(\frac{3.60 \times 10^{-7} + 1.63 \times 10^{-9}/[\text{H}^+]}{2.20 \times 10^{-3} + 8.60 \times 10^{-7}/[\text{H}^+]} \right) \left(\frac{[\text{H}^+]}{[\text{H}^+] + 1.59 \times 10^{-6}} \right) + \left(\frac{2.28 \times 10^{-7} + 1.03 \times 10^{-9}/[\text{H}^+]}{1.40 \times 10^{-3} + 8.60 \times 10^{-7}/[\text{H}^+]} \right) \left(\frac{1.59 \times 10^{-6}}{[\text{H}^+] + 1.59 \times 10^{-6}} \right) + 1.20 \times 10^{-10}/[\text{H}^+] \quad (23)$$

Table 3 and Fig. 3 show that the values of overall rate constant k_t calculated by equation (23) are in good agreement with the observed value. From the rate equation the mechanism of nucleophilic addition reaction of *n* propylmercaptan to CPA over wide pH range is fully explained; below pH 4.5 mercaptan molecule is directly added to CPA molecule, but from pH 4.5 to pH 6.5 it is added to conjugate base of CPA; around pH 7.5 *n*-propylmercaptan and *n*-propylmercaptide ion are competitively added to carboxylate anion of CPA; and as the pH is increased, more reactive mercaptide anion is added to CPA⁻.

Moreover, equation (14) shows that at pH

8.0 the ratio of mercaptide ion to mercaptan molecule is 1 to 4, while at pH 10 only the mercaptide 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 4.5.

Conclusion

1) The kinetics of addition of *n*-propylmercaptan to-cyanopiperonylacrylic acid over a wide pH range was presented and analyzed in detail. A following rate equation which can be applied over wide pH range obtained:

$$k_t = \left(\frac{3.60 \times 10^{-7} + 1.63 \times 10^{-9} / (H^+)}{2.10 \times 10^{-3} + 8.60 \times 10^{-7} / (H^+)} \right) \left(\frac{(H^+)}{(H^+) + 1.59 \times 10^{-6}} \right) + \left(\frac{2.28 \times 10^{-7} + 1.03 \times 10^{-9} / (H^+)}{1.40 \times 10^{-3} + 8.60 \times 10^{-7} / (H^+)} \right) \left(\frac{1.59 \times 10^{-6}}{(H^+) + 1.59 \times 10^{-6}} \right) + 1.20 \times 10^{-10} / (H^+)$$

2) From this rate equation, the mechanism of nucleophilic addition reaction over wide pH range can be fully explained; below pH 4.5 mercaptan molecule is directly added to CPA molecule, but from pH 4.5 to pH 6.5 mercaptide ion is added to CPA; around pH 7.5 *n*-propylmercaptan and *n*-propylmercaptide ion are competitively added to the conjugate base of CPA; and as the pH is increased, more reactive mercaptide anion is added to CPA⁻.

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