after elution with acetone. These reaction intermediates, **(8)** and **(20)** were trapped using nucleophiles, *e. g.* methanol, acetone, and ethanol. Isolation of **(6)** in three nucleophilic reactions indicates that addition reaction of **(1)** to **(6)** is reversible. Furthermore, formation of **(15)** implies that a hydride transfer from 9–benzylthioxanthene is followed by ready deprotonation to give **(15)**.

In order to see if **(2)** could be formed from **(17)**, **(1)** and **(17)** were synthesized according to the modified Price's method.[9] Reaction between two different ions gave compound **(2)** in addition to compounds, **(6)**, **(12)**, and **(18)**, *etc.*[14]

In conclusion, the formation of **(2)** in the reaction of **(1)** with dimethylmercury can be explained by the addition reaction of **(1)** to **(6)** which is formed by deprotonation of **(17)**. The compound **(17)** is believed to be formed from a hydride transfer of 9–methylthioxanthene, which is a radical combination product of thioxanthene and methyl radicals.

However, at this moment, we can not rule out the possible involvement of a radical addition reaction (aq. 6, 7). A study on this unsettled question is in progress.

Acknowledgement. The authros are grateful to the Korean Traders Scholarship Foundation for support of this work.

References

(1) K. Kim, *J. Korean Chem. Soc.*, **24**, 34 (1980).

(2) D. M. Shin and K. Kim, *Bull. Korean Chem. Soc.*, **2**, 114 (1981).

(3) J. Y. Chen, H. C. Gardner, and J. K. Kochi, *J. Amer. Chem. Soc.*, **98**, 6150 (1976).

(4) J. K. Kochi, Organometallic Mechanisms and Catalysis, Cha pters 15, 16,18. Academic Press, New York, N.Y. 1978.

(5) W. Rundell and K. Scheffer, Tetrahedron Lett., 993 (1963).

(6) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).

(7) E. D. Bergmann and M. Rabinovitz, *J. Org. Chem.*, **25**, 828 (1960).

(8) E. D. Bergmann, E. Fisher, Y. Hirshberg, D. Lavie, B. Pullman, and D. Shapiro, *Bull. Soc. Chim. Fr.* **19**, 262 (1952).

(9) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

(10) M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.*, **21**, 1692 (1973).

(11) John Wiley and Sons, Inc. Analogous reactions: S. Wawzonck in Heterocyclic Compounds, Vol. 2, Chapter 12. R. C. Elderfield, Ed., 1951.

(12) Karl Ziegler and Curt Ochs, *Ber.*, **55**, 2257 (1922).

(13) K. H. Ahn and K. Kim's unpublished work.

(14) One of referees suggested that perhaps**(17)**could be in an equilibrium with**(6)**, which would then undergo the same type of reaction with 1 as shown below:

$$(17) \rightleftharpoons 6 +_1 H^+$$
$$8$$
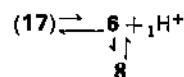
The Kinetics and Mechansm of Nucleophilic Addition of Thioglycolic Acid to β-Nitrostyrene Derivatives

Tae-Rin Kim[†], Tae-Sung Huh* and In-Sup Han**

Department of Chemistry, College of Natural Science, Korea Universitry, Seoul 151, Koera (Received Aug. 6, 1982)

The rate constants of the nucleophilic addition of thioglycolic acid to the derivatives (H, p–CH$_3$, p–CH$_3$O, p–Cl, p–NO$_2$) of β–nitrostyrene were determined by ultraviolet spectrophotometry. The rate equations which can be applied ovre a wide pH range were obtained. Therefrom a reaction mechanism was propsed. Above pH 8.5. sulfide anion adds to the double bond (Michael type addtion). However, below pH 8.5. the neutral molecule and HSCH$_2$COO$^\ominus$ add to the double bond.

Introduction

When the electron density of a carbon–carbon doule bond is reduced by electron–withdrawing substituents, nucleophilic attack at one of the vinylic carbons may occur. In general, the mechanisms of nucleophilic additions to double bonds have not been as much studied or systematized as those of electrophilic addition.[1-7]

In order to verify the mechanism of this type of reaction, we have investigated the addition of n–propylmercaptan and hydrogen cyanide to α–cyano–β–piperonylacrylic acid.[8-9]

The present investigation is a study of kinetics of the addition of thioglycolic acid to β–nitrostyrene derivatives. An attempt has been made to interpret findings in these reactions.

Experimental

β–Nitrostyrene derivatives were prepared by condensation of corresponding benzaldehyde derivatives and nitromethane.[10] Thioglycolic acid (E. Merck) was used without further purification. All buffer solutions were prepared from reagent

*Department of Chemistry, Song Sim Women College, Bucheon 150–71, Korea.

**Department of Chemistry, Kangwon National University, Choonchun 200, Korea.

grade chemicals. The pH of buffer solution were determined by Zerometric II pH meter (Beckman) and ionic strength was kept constant at 0.1 by adding sodium chloride solution.

Kinetics were studied in buffer solutions at $25.0\pm0.1°C$. One ml of aqueous solution $(1.0\times10^{-3}M)$ of thioglycolic acid was added to the 100 ml reaction flask immersed in a thermostatted bath. One ml of freshly prepared methanol solution $(1.0\times10^{-3}M)$ of β-introstyrene was then added and the timing commenced on half-addition. Aliquot portions were sampled at regular intervals into 1 cm silica cells and the reactions were followed spectrophotometrically at the λ_{max} of the starting materials (Table 1).

Results

The reaction of five β-nitrostyrenes with thioglycolic acid was followed by measuring the decrease in the absorption (A) of β-nitrostyrenes at λ_{max}, where the products have negligible absorption.

Figure 1 shows logarithmic plots of concentration of β-nitrostyrene vs. time at various concentrations of thioglycolic acid. As shown in Figure 1, this reaction is typical pseudo-first-order reaction. As shown in Figure 2, the pseudo-first-order rate constants vs. various thioglycolic acid was used to caclulate the second-order rate constant for this reaction. From the slope of the straight line, the rate constant was found to be $10.2M^{-1}$. sec^{-1}.

Figure 3 shows plots of $1/A$ of β-nitrostyrene vs. time. From this figure, the second-order rate constant was found to be 14.1 M^{-1} sec^{-1}. Since the two rate constants agree well with each other, it is clear that this reaction is second-order.

TABLE 1: Wvaelenghths of Absorption Maxima and Molar Extinction Coefficients of β-Nitrostyrene Derivatives

	λ_{max} (nm)	ε	
		β-Nitrostyrene derivatives	Adducts
H	311	1.45×10^4	6.0×10^2
p-CH$_3$	325	1.36×10^4	1.3×10^3
p-CH$_3$O	351	1.85×10^4	1.0×10^3
p-Cl	315	1.65×10^4	8.5×10^2
p-NO$_2$	303	1.94×10^4	9.0×10^3

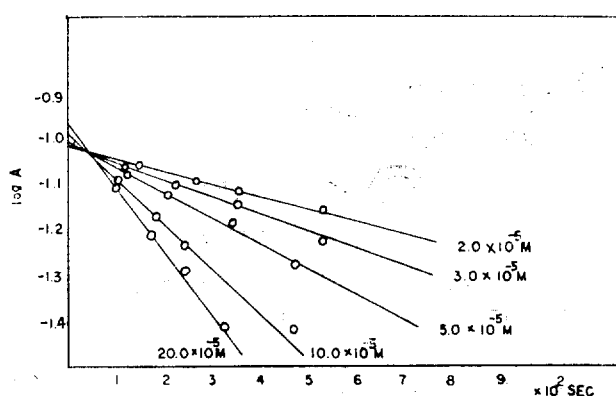**Figure 1.** The change of log A of β-nitrostyrene vs. time with various concentration of thioglycolicacid at pH 3.5, 25°C and 0.1 ionic strenght

TABLE 2: Rate Constants for the Addition Reaction of Thioglycolic Acid to β-nitrostyrene at Various pH and 25°C.

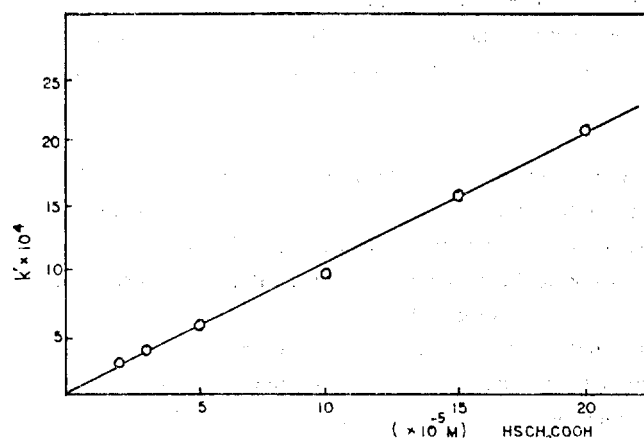| pH	Buffer solution	$k_t(M^{-1}$ sec$^{-1})$	
		Obs.	Calc.
0.0	HCl	10.5	10.5
0.5	HCl	10.3	10.5
1.0	HCl	10.2	10.5
1.5	HCl	10.3	10.5
2.0	HCl	10.4	10.5
2.5	HCl	12.2	10.6
3.0	HCl	13.2	10.9
3.5	HAc + NaAc	14.1	11.8
4.0	HAc + NaAc	20.0	13.9
4.5	HAc + NaAc	32.3	20.2
5.0	HAc + NaAc	34.2	34.1
5.5	HAc + NaAc	41.8	53.8
6.0	HAc + NaAc	51.3	68.6
6.5	HAc + NaAc	72.6	76.2
7.0	KH$_2$PO$_4$ + K$_2$HPO$_4$	80.0	79.6
7.5	KH$_2$PO$_4$ + K$_2$PHO$_4$	83.2	83.0
8.0	H$_s$BO$_s$ + NaOH	87.7	91.0
8.5	H$_s$BO$_s$ + NaOH	115	115
9.0	H$_s$BO$_s$ + NaOH	182	192
9.5	H$_s$BO$_s$ + NaOH	340	362
10.0	H$_s$BO$_s$ + NaOH	1196	1200
10.5	H$_s$BO$_s$ + NaOH	3422	3549
11.0	NaOH	10019	11280

Figure 2. The plot of pseudo first–order rate constant of β-nitrostyrene vs. concentration of thioglycolic acid.
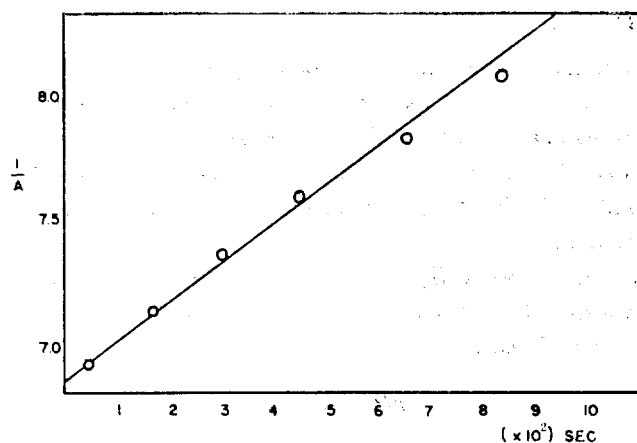
Figure 3. The plot of 1/A of β-nitrostyrene vs. time at pH 3.5 and 25°C.
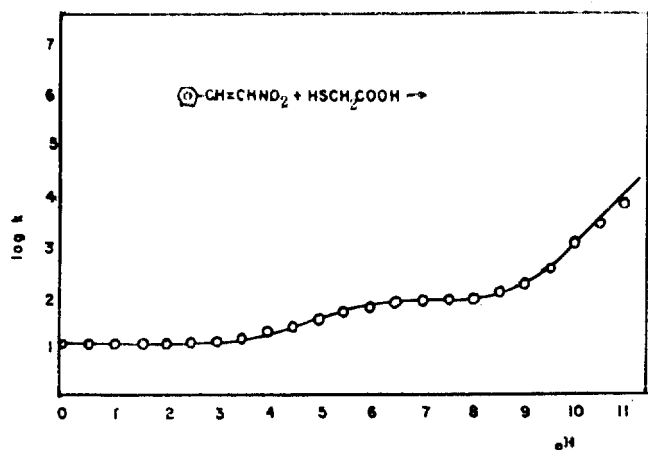
Figure 4. pH–rate profile for the addition reaction of thioglycolic acid to β–nitrostyrene at 25°C. Circles are experimental points and curve is drawn according to equation (8).
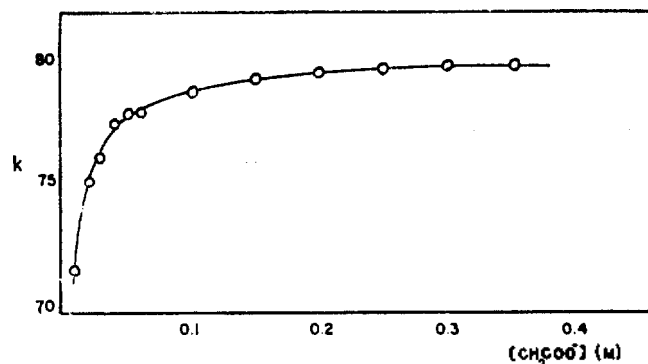

Figure 5. General base catalyzed addition reaction of thioglycolic acid to β–nitrostyrene at pH 4.78 and 25°C. Circles are experimental points and curve is drawn according to equation (5).

For convenience' sake, the rate constants were calculated by the latter method. The second-order rate constants (k_t) at various pH are given in Table 2 and Figure 4. The solid line in Figure 4 represents theoretical values calculated according to the equation (7).

To make sure that this reaction is catalyzed by general base, the rate constants were determined at various acetate ion concentrations at pH 4.78. As shown in Figure 5, this reaction is catalysed by general base at low acetate ion concentration.

Discussion

As shown in Figure 4, the change of log k_t vs. pH is complicated; from pH 0 to 3.0, the log k_t remains constant. However, from pH 3.0 to 6.5, log k_t increases gradually and from pH 6.5 to 8.5 log k_t remains constant. In the range of pH from 8.5 to 11.0, k_t is directly proportional to the hydroxide ion concentration.

The rate constant (k_t) can be divided into two parts; one part is directly proportional to hydroxide ion concentration. The other is not.
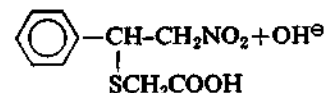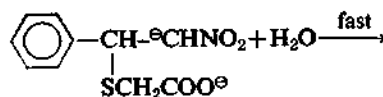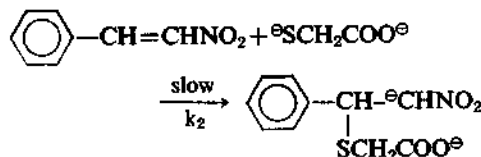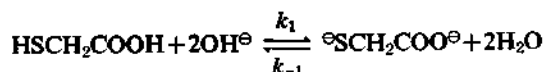
$$k_t = k_{10} + k_1^{OH^-}[OH^-] \tag{1}$$

As thioglycolic acid dissociates according to pH as the following, $HSCH_2COOH$, $HSCH_2COO^\ominus$ and $^\ominus SCH_2COO^\ominus$

are presumed to act as addends.

$$HSCH_2COOH \rightleftharpoons H^\oplus + HSCH_2COO^\ominus$$
$$HSCH_2COO^\ominus \rightleftharpoons H^\oplus + {}^\ominus SCH_2COO^\ominus$$
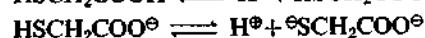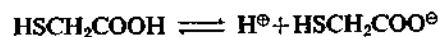
At high pH where $^\ominus SCH_2COO^\ominus$ would be a possible addend the following mechanism is proposed.

$$HSCH_2COOH + 2OH^\ominus \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^\ominus SCH_2COO^\ominus + 2H_2O$$

The rate for the above mechanism is directly proportional to hydroxide ion concentration as in equation (2).

$$\begin{aligned}
Rate &= k_2[NS][RS^\ominus] \\
&= k_1/k_{-1} \cdot k_2[NS][RSH][OH^\ominus] \\
&= k'[NS][RSH][OH^\ominus] \\
k_{obs} &= k_1'[OH^\ominus]
\end{aligned} \tag{2}$$

At low pH where rate is not directly proportional to hydroxide ion concentration, reaction would proceed via different reaction path.

$HSCH_2COOH$ or $HSCH_2COO^\ominus$ would be added to β–nitrostyrenes.
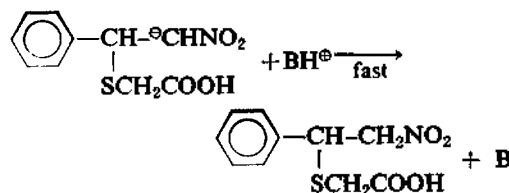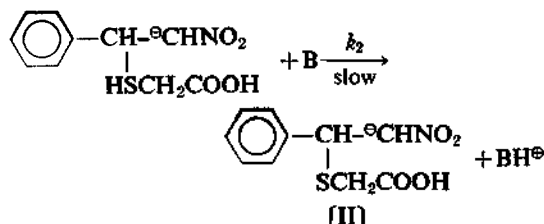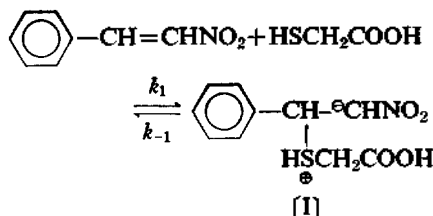
Applying steady–state approximation with respect to the intermediate [I], k_{10} is given by the following equation.

$$\frac{1}{k_{10}} = \frac{1}{k_1} + \frac{1}{k_1/k_{-1} \cdot k_2 \sum[B]} \tag{3}$$

If water and hydroxide ion are the only general bases, B, present, equation (3) becomes,

$$\frac{1}{k_{10}}=\frac{1}{k_1}+\frac{1}{(k_1/k_{-1})\{k_2^{H_2O}[H_2O]+k_2^{OH^-}[OH^-]\}} \quad (4)$$

As shown in Figure 5, the second step shows general base catalysis: k_{10} depends only on the concentration of acetate ion at constant pH, however, the reaction velocity is not a linear function of catalyst concentration. If the concentration of general base is high, k_{10} will take the limiting value, $k_1=80.0\ M^{-1}sec^{-1}$, which is the maximum point. The acetate ion acts as a general base catalyst, equation (4) becomes,

$$\frac{1}{k_{10}}=\frac{1}{k_1}$$
$$+\frac{1}{(k_1/k_{-1})\{k_2^{H_2O}[H_2O]+k_2^{OH^-}[OH^-]+k_3^{OAc^-}[OAc^-]\}} \quad (5)$$

Below pH 3.0, the concentration of hydroxide ion and acetate ion are neglibible, equation (5) becomes,

$$\frac{1}{k_{10}}=\frac{1}{k_1}+\frac{1}{(k_1/k_{-1})\{k_2^{H_2O}[H_2O]\}} \quad (6)$$

The value of $k_1/k_{-1}\ k_2H_2O[H_2O]$ can be determined from $\frac{1}{k_1}=80.0\ M^{-1}sec^{-1}$ and observed rate constant, $k_t=10.5$ at pH $=0.$and is found to be 12.1.

By substituting $k_t=34.2$ at pH 5.0 into equation (4), k_1/k_{-1} $\cdot k_2^{OH^-}=4.76\times10^{10}$ can be obtained.

As a result k_{10} becomes,

$$\frac{1}{k_{10}}=\frac{1}{80.0}+\frac{1}{1.21\times10^1+4.76\times10^{10}[OH^-]}$$
$$=\frac{9.21\times10^1+4.76\times10^{10}[OH^-]}{9.68\times10^2+3.80\times10^{12}[OH^-]}$$
$$\text{or}\ k_{10}=\frac{9.68\times10^2+3.80\times10^{12}[OH^-]}{9.21\times10^1+4.76\times10^{10}[OH^-]} \quad (7)$$

At pH 10.0, where rate is directly proportional to hydroxide ion concentration, k_t was found to be 1196. By substituting above data into equation (1), $k_1^{OH^-}=1.12\times10^7\ M^{-1}sec^{-1}$ can be obtained.

As a result, over-all rate constant becomes;

$$k_t=\frac{9.68\times10^2+3.80\times10^{12}[OH^-]}{9.21\times10^1+4.76\times10^{10}[OH^-]}+1.12\times10^7[OH^-] \quad (8)$$

Figure 4 shows that the values of over-all rate constant, k_t, calculated by equation (8) are in good agreement with observed values.On the basis of the rate equation (8),the mechanism of nucleophilic addition of thioglycolic acid to β-nitrostyrene over wide pH range is fully explained; the ratio of contribution
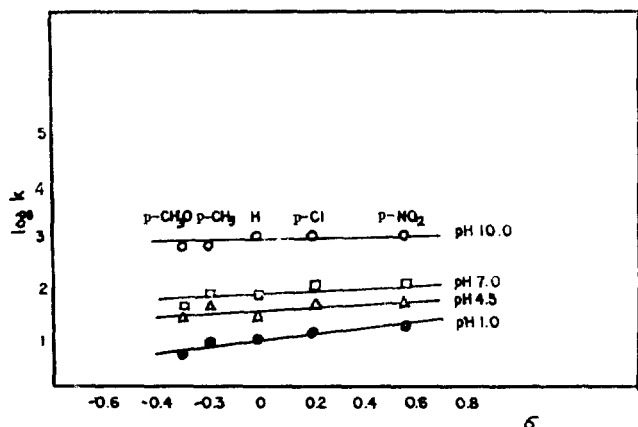

Figure 6. Hammett plots of addition reaction of thioglycolic acid to β-nitrostyrene at various pH.

of $HSCH_2COO^\ominus$ and $^\ominus SCH_2COO^\ominus$ to over-all rate constant at pH 8.0 is 7:1, while at pH 10.0 the ratio is 1:14 and below pH 7.0, $HsCH_2COO^\ominus$ or $HSCH_2COOH$ is added. In the range of pH from 7.0 to 10.0, $HSCH_2COO^\ominus$ and $^\ominus SCH_2COO^\ominus$ are competitively added, however, above pH10.0,$^\ominus SCH_2COO^\ominus$ is added exclusively.

Substituents Effects. Substituents effects have been measured and are shown in Figure 6. As expected from the reaction mechanism, the electron-withdrawing substituents ($\rho=0.56$) accelerate the rate of reaction at pH 1.0. However, since the $^\ominus SCH_2COO^\ominus$ is a good nucleophile, the effect of subs ituents might be negligible at higher pH.

References

(1) S. Patai and Z Rapport, "The Chemistry of Alkenes," p. 464. WileyInterscience. New York, 1964.

(2) E. Winterfeldt, *Angew. Chem. Int. Ed.,* **6,** 423 (1976).

(3) L. A. Kaplan and H. B. Pikard, *J. Amer. Chem. Soc.,* **93,** 3447 (1971).

(4) B. C. Pal, *J. Amer. Chem. Soc.,* **100,** 5170 (1978).

(5) H. Esterbauer, H. Zollner and N. Scholz, *Z. Naturforsch,* **30c,** 466 (1975).

(6) H. Esterbauer, A. Ertl and N. Scholz, *Tetrahedron,* **32,** 285 (1976).

(7) G. Jung, M. Fouad and G. Hensel, *Angew. Chem.,* **24,** 876 (1975).

(8) Y. R. Kim and T. S. Huh, *J. Kor. Chem. Soc.,* **17,** 363 (1973).

(9) K. S. Kwon and T. R. Kim, *J. Kor. Chem. Soc.,* **18,** 423 (1974).

(10) D. E. Worral, "Organic Synthesis," Coll. Vol. I. p. 413. John–Wiley and Sons, Inc., 1958.