

# Kinetic Studies on the Nucleophilic Addition of Thiophenol Derivatives to 4'-[ *N*-(9-Acridinyl)]-1'-( *N*-methanesulfonyl)-3'-methoxyquinonediimide

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The rate constants for the nucleophilic addition of thiophenol derivatives (*p*-OCH<sub>3</sub>, *H*, *p*-CH<sub>3</sub>, *m*-CH<sub>3</sub>, *p*-Br and *p*-NO<sub>2</sub>) to 4'-[ *N*-(9-acridinyl)]-1'-( *N*-methanesulfonyl)-3'-methoxyquinonediimide (AMQD) were determined by ultraviolet spectrophotometer in water at 5 °C, and rate equations which can be applied over a wide pH range were obtained. On the basis of pH-rate profile, Brønsted plot, adduct analysis, general base catalysis and substituent effect, a plausible mechanism of this addition reaction was proposed: Below pH 2.5, the reaction proceeded by the addition of thiophenol molecule to 6'-position of quinonoid after protonation at the acridinyl nitrogen. Above pH 6.2, the addition of sulfide anion to 6'-position of quinonoid was rate controlling. However, in the range of pH 3.0-6.0, these two reactions occurred competitively.

## Introduction

The nucleophilic addition of activated carbon-carbon double bonds and carbon-nitrogen double bonds has been the subject of extensive mechanistic and synthetic studies.<sup>1-4</sup> Quinonediimides, having two carbon-carbon double bonds and two carbon-nitrogen double bonds, have been especially interested in medicinal science.<sup>5</sup> Moreover, the adducts of thiols to quinonediimide have attracted considerable attention because of the anticancer activity.<sup>6</sup> Many researchers have designed, synthesized, and studied the physical properties of the adducts as well as their medical applications.

Finely and coworkers<sup>6</sup> studied the addition reaction of morpholine to *N,N*-dibenzoquinonesulphonediimide. Jones<sup>7</sup> also prepared adducts by the addition of 1-phenyl-5-mercaptotetrazole to 1,4-benzoquinone. They found that the structures of the adducts obtained from this reaction vary with the reaction conditions and the structure of the substituted benzoquinone.

The most characteristic reaction of the quinonediimide having electron-deficient nonbenzoid structure is the nucleophilic attack at one of the carbon-carbon double bonds. However, the structures of the adducts varies depending upon the reaction conditions and the substrates.<sup>5</sup>

Although synthetic studies for nucleophilic addition of quinonediimide derivatives have been extensively conducted, much less is known about the mechanism of these reactions.<sup>8a-8d</sup> We were particularly interested in the reaction of 4'-[ *N*-(9-acridinyl)]-1'-( *N*-methanesulfonyl)-3'-methoxyquinonediimide (AMQD) (commonly known as acridine derivatives) because the reaction is sensitive to the change of nucleophilicities from amines to thiols.<sup>9</sup> In the previous report,<sup>10</sup> we described the hydrolysis mechanism of AMQD over a wide pH range. However, the kinetic studies for the nucleophilic addition to AMQD have not been reported yet. Therefore, we have investigated mechanism of the addition reaction of thiophenol derivatives to AMQD.

## Experimental

**General procedure.** All chemicals were reagent grade unless otherwise specified. UV spectra were obtained by a Hitachi Recording Spectrophotometer 200-20. IR spectra were taken with a Perkin-Elmer Infrared 710B. NMR spectra were obtained with a Varian 90 MHz spectrometer, using tetramethylsilane as an internal standard. Elemental analysis was performed by Perkin-Elmer 240 CHN Analyzer and melting points were measured with a Haake Buchler apparatus. Mass spectra were determined with a Kratos 25-RFA mass spectrometer.

**Synthesis of AMQD.** AMQD was prepared by known methods.<sup>11-15</sup>

**Product Analysis.** AMQD (1.02 mmol) and *p*-nitrothiophenol (1.03 mmol) were dissolved in 30 mL of a buffer solution (pH=9.0) of boric acid and sodium hydroxide containing 20% methanol. The reaction mixture was stirred for 24h at RT under nitrogen atmosphere. The mixture was extracted with CHCl<sub>3</sub>, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated. The product was recrystallized from ethanol to give 4'-[ *N*-(9-Acridinyl)amino]-6'-*p*-nitrothiophenoxy-1'-( *N*-methanesulfonyl)-*m*-anisidine as a yellow solid (90% yield): mp 164-165 °C; TLC analysis (ethyl acetate) R=0.65; IR (KBr pellet, cm<sup>-1</sup>): 3150-3300 (amine), 1600-1625 (C=C, C=N), 1150, 1350 (SO<sub>2</sub>), 1310, 1500 (NO<sub>2</sub>); <sup>1</sup>H NMR (DMSO-*d*<sup>6</sup>) δ 7.20-8.20 (m, 8H, acridinyl), 7.01 (m, 2H, phenyl), 7.40 (d, 2H, *J*=9.0, *m*-phenyl H), 8.21 (d, 2H, *J*=9.0, *o*-phenyl H), 3.85 (s, 3H, OCH<sub>3</sub>), 3.01 (s, 3H, SO<sub>2</sub>CH<sub>3</sub>); MS: *m/z* (relative intensity) 546 (M<sup>+</sup>, 10), 470 (25), 314 (100), 270 (11), 79 (8), 28 (100). Anal. Calcd for C<sub>27</sub>H<sub>22</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 59.32; H, 4.05; N, 10.24. Found: C, 59.56; H, 4.09; N, 10.23.

**Kinetic studies.** A buffer solution (98 mL) with known concentration in a 100 mL volumetric flask was immersed into the thermostat at 5 °C and allowed to equilibrate for 20 min. Then 1 mL of 2.0 × 10<sup>-3</sup> M AMQD dioxane solution and 1 mL of 2.0 × 10<sup>-3</sup> M thiophenol solu-

tion were added. The flask was quickly shaken and returned to the thermostat. In order to prevent the oxidation of thiophenol by oxygen in the solution, the rate of reaction was measured under nitrogen atmosphere. Aliquot portion (3.0 mL) of the solution was removed from the volumetric flask with a time interval and place in a quartz cuvette. The decrease of absorption at the wavelength of maximum absorption (AMQD:  $\lambda_{\max} = 300$  nm, AMQD<sup>+</sup>:  $\lambda_{\max} = 282$  nm) for the AMQD and AMQDH<sup>+</sup> with time was monitored.

## Results and Discussion

**Determination of Rate constants.** The observed rates of reaction with excess thiophenol concentration were always pseudo-first order. Plots of the first-order rate constants against various thiophenol concentrations were also in all cases linear, showing the reactions are first order to AMQD and thiophenol, respectively. Thus, the second-order rate constants could be calculated from the slope of the plot of  $1/A$  against time for the reaction between equal initial concentration ( $2.0 \times 10^{-5}$  M) of AMQD (Figure 1). The second-order rate constants ( $k_t$ ) determined at various pHs are given Table 1 and Figure 2.

**General base catalysis.** 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 3, this reaction is catalyzed by general base at low acetate ion concentration. However, as the amount of base becomes larger, the rate of addition reaction approaches the limiting values. Figure 3 shows that  $k$  values calculated by equation (9-2) are in good agreement with observed values. Also, to examine the effect of base strength for the rate of this reaction, the rates constants were obtained from equal initial concentration ( $1.25 \times 10^{-4}$  M) of AMQD, thiophenol, and bases at pH 6.0. As shown in Figure 4, the rate constants increase systematically as the base strength increases.

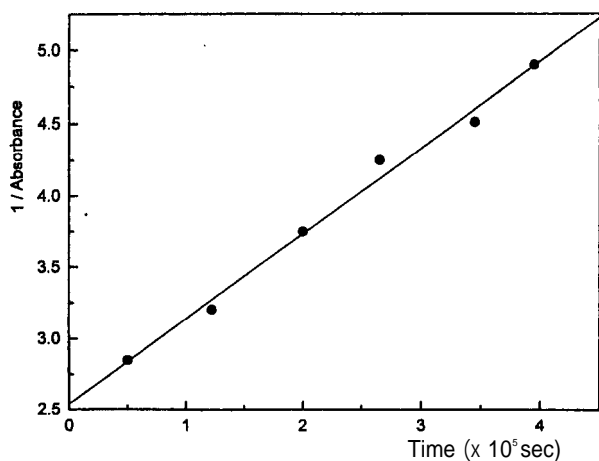
**Substituent effect.** The influence of thiophenol substituents upon the rates of addition correlated satisfactorily with the Hammett equation, using values (Figure 5). Hammett values were -0.71 ( $r=0.998$ ), -0.31 ( $r=0.890$ ) and -0.62

( $r=0.995$ ) for pH=0.0, 6.5 and 9.0, respectively. This result indicates that the rate of addition is accelerated by electron donating groups at all pH ranges, and that the addition reaction proceeds through similar substituent effect in acidic, neutral, and basic media.

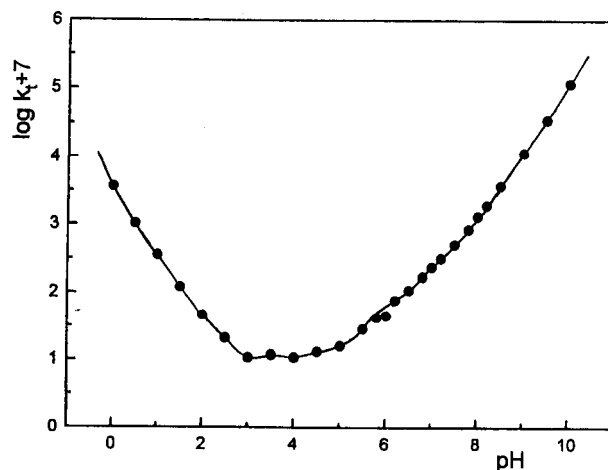
**Rate equation and mechanism.** As shown in Figure 2, the change of  $\log k$  vs. pH is complicated; The rate

**Table 1.** Rate constants for the addition reaction of thiophenol to AMQD at various pH and 5 °C

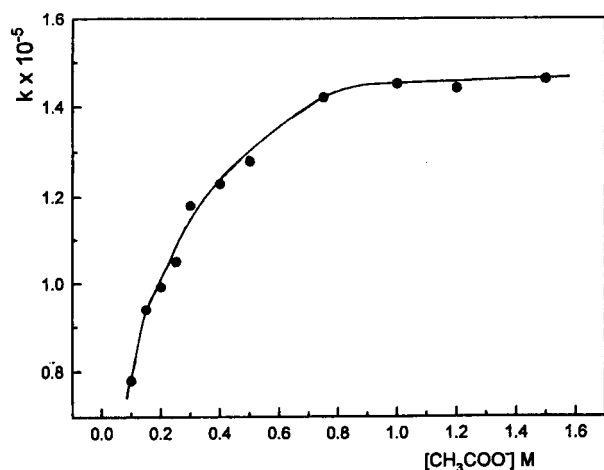
| pH   | Buffer Solution  | $k_t (\text{M}^{-1}\text{sec}^{-1}) \times 10^6$ |       |
|------|--|--|-------|
|      |  | obsd   | calcd |
| 0.0  | HCl  | 366  | 354   |
| 0.5  | HCl  | 103  | 112   |
| 1.0  | HCl  | 35.7   | 36.0  |
| 1.5  | HCl  | 11.9   | 11.8  |
| 2.0  | HCl  | 4.55   | 4.25  |
| 2.5  | HCl  | 2.09   | 1.83  |
| 3.0  | HCl  | 1.07   | 1.07  |
| 3.5  | HOAc+NaOAc   | 1.18   | 0.85  |
| 4.0  | HOAc+NaOAc   | 1.09   | 0.80  |
| 4.5  | HOAc+NaOAc   | 1.33   | 0.90  |
| 5.0  | HOAc+NaOAc   | 1.59   | 1.29  |
| 5.5  | HOAc+NaOAc   | 2.84   | 2.24  |
| 5.8  | HOAc+NaOAc   | 4.18   | 3.60  |
| 6.0  | HOAc+NaOAc   | 4.50   | 5.00  |
| 6.2  | HOAc+NaOAc   | 7.52   | 6.94  |
| 6.5  | KH <sub>2</sub> PO <sub>4</sub> +K <sub>2</sub> HPO <sub>4</sub> | 10.7   | 11.0  |
| 6.8  | KH <sub>2</sub> PO <sub>4</sub> +K <sub>2</sub> HPO <sub>4</sub> | 17.1   | 17.1  |
| 7.0  | KH <sub>2</sub> PO <sub>4</sub> +K <sub>2</sub> HPO <sub>4</sub> | 23.6   | 22.7  |
| 7.2  | KH <sub>2</sub> PO <sub>4</sub> +K <sub>2</sub> HPO <sub>4</sub> | 31.7   | 30.4  |
| 7.5  | KH <sub>2</sub> PO <sub>4</sub> +K <sub>2</sub> HPO <sub>4</sub> | 50.1   | 49.3  |
| 7.8  | KH <sub>2</sub> PO <sub>4</sub> +K <sub>2</sub> HPO <sub>4</sub> | 83.9   | 85.2  |
| 8.0  | H <sub>3</sub> BO <sub>3</sub> +NaOH                             | 128  | 127   |
| 8.2  | H <sub>3</sub> BO <sub>3</sub> +NaOH                             | 187  | 192   |
| 8.5  | H <sub>3</sub> BO <sub>3</sub> +NaOH                             | 359  | 369   |
| 9.0  | H <sub>3</sub> BO <sub>3</sub> +NaOH                             | 1130   | 1130  |
| 9.5  | H <sub>3</sub> BO <sub>3</sub> +NaOH                             | 3450   | 3550  |
| 10.0 | H <sub>3</sub> BO <sub>3</sub> +NaOH                             | 11600  | 11200 |



**Figure 1.** Plot of  $1/\text{Absorbance}$  of AMQD vs. time at pH 6.0 and 5 °C.



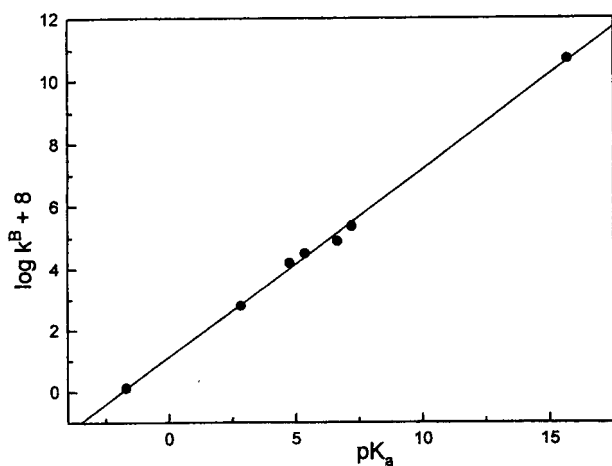
**Figure 2.** A pH-rate profile for the addition reaction of thiophenol to AMQD at 5 °C. Circles are experimental points and solid line is drawn according to equation (8).



**Figure 3.** General base catalyzed addition reaction of thiophenol to AMQD at pH 4.78 and 5 °C. Circles are experimental points and the curve is drawn according to equation (9-2).

**Table 2.**  $pK_a$  and catalytic constants of bases for the addition reaction of thiophenol to AMQD at 25 °C

| Base  | $pK_a$ | $(k_1^{SH}/k_{-1}^{SH}) k_2^B (M^{-1}sec^{-1})$ |
|---|--------|---|
| H <sub>2</sub> O                            | -1.70  | $1.34 \times 10^{-8}$                           |
| ClCH <sub>2</sub> COO <sup>-</sup>          | 2.82   | $6.42 \times 10^{-6}$                           |
| CH <sub>3</sub> COO <sup>-</sup>            | 4.75   | $1.53 \times 10^{-4}$                           |
| Pyridine                                    | 5.36   | $3.17 \times 10^{-4}$                           |
| Lutidine                                    | 6.64   | $6.60 \times 10^{-4}$                           |
| H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> | 7.21   | $2.35 \times 10^{-3}$                           |
| OH <sup>-</sup>                             | 15.7   | $5.23 \times 10^2$                              |



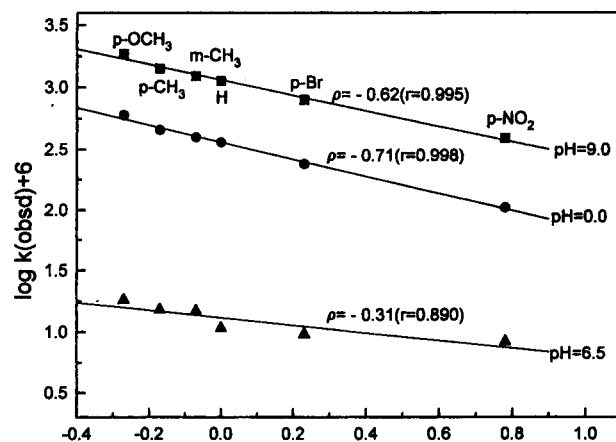
**Figure 4.** Brønsted plot for the addition reaction of thiophenol to AMQD at 5 °C.

constants are proportional to the concentrations of hydronium ion at pH < 2.5 and hydroxide ion at pH > 6.2, respectively. But remains nearly constant at pH 3.0-6.0.

The overall rate constants ( $k_i$ ) can be divided into three parts, each representing a different mechanism.

$$k_i = k_0 + k^H [H_3O^+] + k^{OH} [OH^-] \quad (1)$$

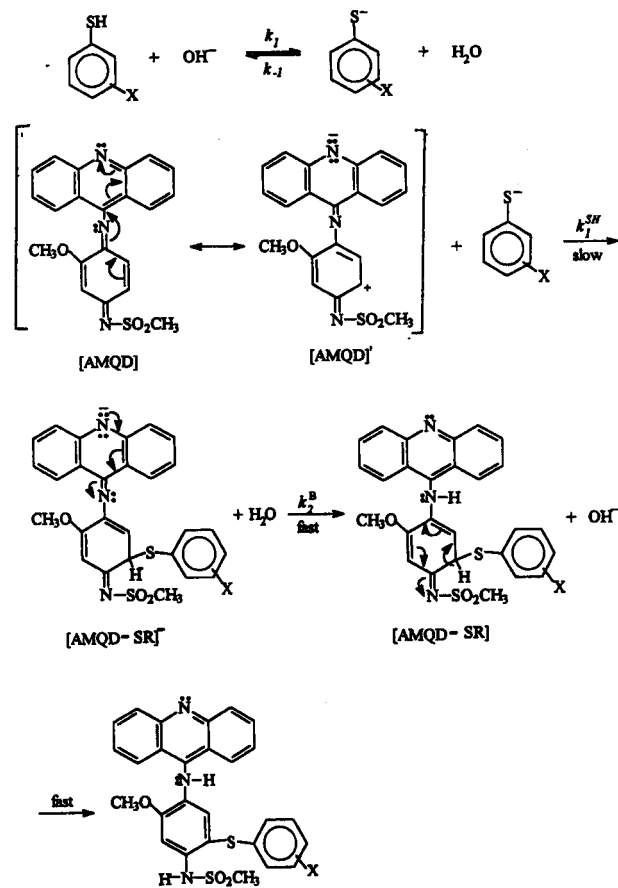
where  $k_0$ ,  $k^H$ ,  $k^{OH}$  are the rate constant for the addition reaction which is insensitive to pH i.e., the rate constant for the



**Figure 5.** Hammett plots for the addition reaction of thiophenol derivatives to AMQD at pH 0.0, 6.5 and 9.0.

solvent catalyzed reaction and hydronium ion and hydroxide ion catalyzed addition reactions, respectively.

At high pH, it is expected that the thiophenoxide and hydroxide anions could be added to AMQD. However, the spectral and analytical data indicated that the product obtained under basic condition (pH=9.0) was the thiophenol adduct. Moreover, the kinetic data showed that the rate for the thiophenoxide anion addition was approximately 15 times faster than that of hydrolysis of AMQD at basic pH.<sup>10</sup> Therefore, the addition mechanism in basic media is,

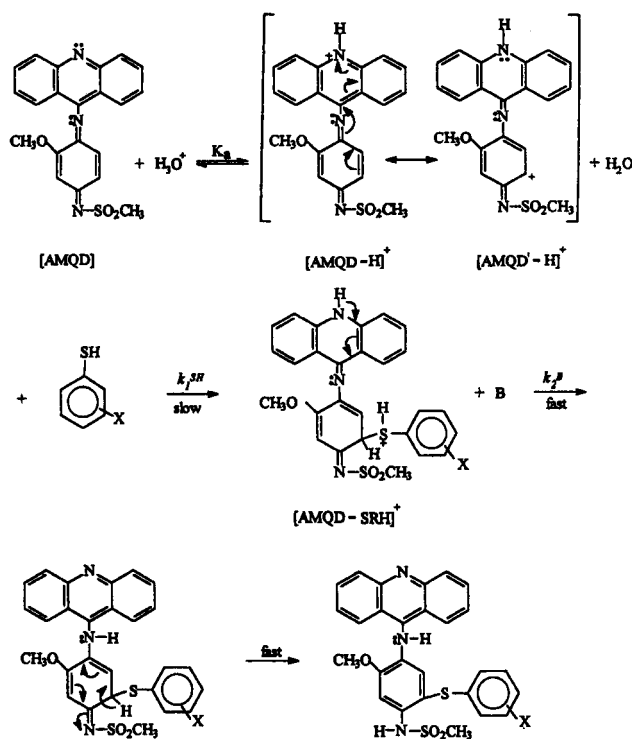


**Scheme 1.**

Kharash<sup>16a</sup> and Hurd<sup>16b</sup> have already proposed a similar mechanism for the nucleophilic addition of mercaptan to carbonyl compounds in basic media. Since the rate of addition reaction is accelerated by the electron donating group with  $\rho = -0.62$  at pH 9.0, the attack of thiophenol anion is the rate determining step in alkaline pHs.

Albert<sup>17</sup> reported that the electron density of the acridinyl group increases due to its resonance stabilization. This was ascertained by the absorption spectrum.<sup>9</sup>

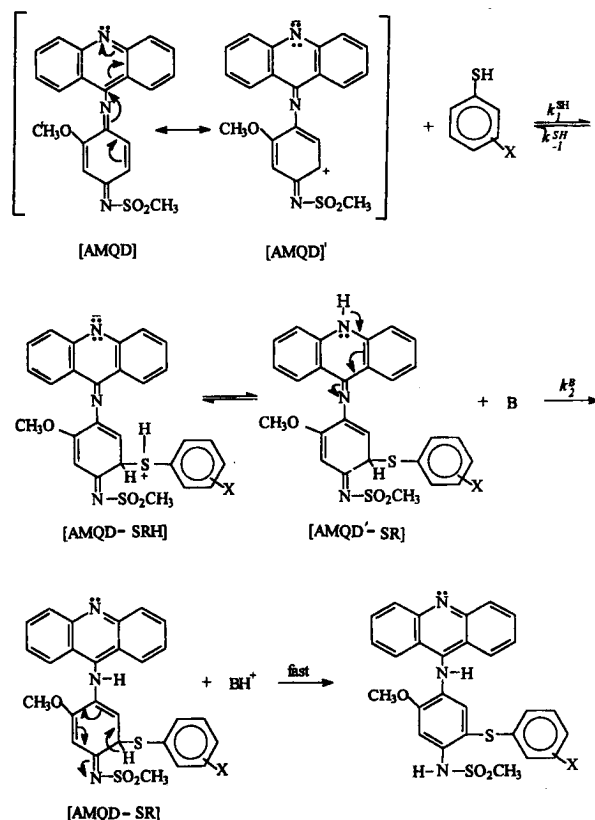
At low pH, the thiophenol and water may in principle added to [AMQD]. However, the second possibility has been ruled out by the much slower rate of the addition of water than that of thiophenol.<sup>18</sup> We propose that the reaction proceeds by the attack of thiophenol to quinonoid after protonation at nitrogen of acridinyl group.



Scheme 2.

First step of the above mechanism is rapid acid-base equilibrium. Since the addition of thiophenol and deprotonation from the intermediate occur in the second and third steps, respectively, the  $k_1^{\text{SH}}$  is expected to decrease but  $k_2^{\text{B}}$  to increase by the electron withdrawing substituent at the thiophenyl ring. Therefore, the observed  $\rho = -0.71$  at pH 0.0 in acidic solution, indicate that the second step must be the rate determining step in this reaction. However, as the amount of general base becomes larger, the addition of thiophenol becomes the rate controlling step and  $k_1^{\text{SH}}$  is limiting values. This is in good agreement with the observed results (Figure 3). But, if the concentration of general base is low, the rate determining step may be changed to the third step. Consequently, the rate constants depend upon  $pK_a$  of the bases as shown in Figure 4.

At pH 3.0-6.0, the rate constants are independent of the



Scheme 3.

pH. Hence the following mechanism is proposed.

As would be expected from acidic mechanism, the rate determining step will be the first step and second steps. If the concentration of general base is high, the first step will be the rate determining step. On the other hand, if the concentration of general base is low, the overall-rate of the reaction will depend on the rate of the second step. These mechanisms are similar to that suggested by Kim *et al.*<sup>19</sup> in the case of nucleophilic addition to the double bonds of olefins at acidic and neutral pH. As shown in above mechanism, if the first step is reversible, the second step is irreversible, and [AMQD'-SR] is very unstable, [AMQD'-SR] concentration will always be very small amount and its changed concentration will never be very large. Therefore, when the steady-state approximation is applied with respect to the [AMQD'-SR],<sup>19</sup> the rate is given by the following equation (2).

$$\text{Rate} = -\frac{d[\text{AMQD}]}{dt} = k_0[\text{AMQD}][\text{RSH}] = k_2^{\text{B}}[\text{AMQD}'\text{-SR}]\sum[\text{B}] \quad (2)$$

$$= \frac{k_1^{\text{SH}}k_2^{\text{B}}\sum[\text{B}]}{k_{-1}^{\text{SH}} + k_2^{\text{B}}\sum[\text{B}]}[\text{AMQD}][\text{RSH}] \quad (3)$$

or

$$\frac{1}{k_0} = \frac{k_{-1}^{\text{SH}} + k_2^{\text{B}}\sum[\text{B}]}{k_1^{\text{SH}}k_2^{\text{B}}\sum[\text{B}]} \quad (4)$$

$$= \frac{1}{k_1^{\text{SH}}} + \frac{1}{\left(\frac{k_1^{\text{SH}}}{k_{-1}^{\text{SH}}}\right)k_2^{\text{B}}\sum[\text{B}]} \quad (5)$$

If water and hydroxide ion are the only general bases present, equation (5) becomes

$$\frac{1}{k_0} = \frac{1}{k_1^{\text{SH}}} + \frac{1}{\left(\frac{k_1^{\text{SH}}}{k_{-1}^{\text{SH}}}\right) \left\{ k_2^{\text{H}_2\text{O}} [\text{H}_2\text{O}] + k_2^{\text{OH}} [\text{OH}^-] \right\}} \quad (6)$$

It can be seen that if the concentration of general base is high,  $k_0$  will take the limiting value  $k_1^{\text{SH}} = 1.46 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  which is the maximum point in Figure 3.

At low pH, since  $k_2^{\text{OH}} [\text{OH}^-]$  is negligible compared to the  $k_2^{\text{H}_2\text{O}} [\text{H}_2\text{O}]$ , the  $(k_1^{\text{SH}}/k_{-1}^{\text{SH}}) k_2^{\text{H}_2\text{O}} [\text{H}_2\text{O}]$  can be determined from the  $k_1^{\text{SH}}$  and observed rate constant ( $k_0$ ) and is found to  $7.48 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ . The data at pH 6.0 gave the value  $4.43 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  for  $(k_1^{\text{SH}}/k_{-1}^{\text{SH}}) k_2^{\text{OH}}$ . This measures the efficiency of hydroxide ion as the base catalyst, B in our mechanism.

As the result, if water and hydroxide ion are the only bases present,  $k_0$  becomes

$$\frac{1}{k_0} = \frac{1.61 \times 10^{-5} + 4.43 \times 10^2 [\text{OH}^-]}{1.15 \times 10^{-11} + 6.82 \times 10^3 [\text{OH}^-]}$$

$$k_0 = \frac{1.15 \times 10^{-11} + 6.82 \times 10^3 [\text{OH}^-]}{1.61 \times 10^{-5} + 4.43 \times 10^2 [\text{OH}^-]} \quad (7)$$

The nucleophilic addition constant for the hydronium  $k^{\text{H}} = 3.53 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  is determined from the value of  $k_1 = 6.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  at pH 0.0 and  $k_1 = 7.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at pH 1.0. Similarly,  $k^{\text{OH}} = 1.12 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  is obtained from the values of the rate constants at pH 9.0 and pH 10.0.

As a result, over all rate equation;

$$k_1 = 3.53 \times 10^{-4} [\text{H}_3\text{O}^+] + \frac{1.15 \times 10^{-11} + 6.82 \times 10^3 [\text{OH}^-]}{1.16 \times 10^5 + 4.43 \times 10^2 [\text{OH}^-]} + 1.12 \times 10^2 [\text{OH}^-] \quad (8)$$

Table 1 and Figure 2 show that the values of over-all rate constant,  $k$ , calculated by equation (8) are in good agreement with observed values.

Similarly, the rate equation obtained for the addition of thiophenol derivatives to AMQD;

p-Methoxythiophenol:

$$k_1 = 6.21 \times 10^{-4} [\text{H}_3\text{O}^+] + \frac{6.77 \times 10^{-11} + 1.26 \times 10^2 [\text{OH}^-]}{3.60 \times 10^5 + 3.71 \times 10^2 [\text{OH}^-]} + 1.91 \times 10^2 [\text{OH}^-]$$

p-Methylthiophenol:

$$k_1 = 4.22 \times 10^{-4} [\text{H}_3\text{O}^+] + \frac{1.20 \times 10^{-11} + 1.02 \times 10^2 [\text{OH}^-]}{2.35 \times 10^5 + 6.35 \times 10^2 [\text{OH}^-]} + 1.40 \times 10^2 [\text{OH}^-]$$

m-Methylthiophenol:

$$k_1 = 3.70 \times 10^{-4} [\text{H}_3\text{O}^+] + \frac{2.69 \times 10^{-11} + 1.12 \times 10^2 [\text{OH}^-]}{3.32 \times 10^5 + 3.47 \times 10^2 [\text{OH}^-]} + 1.21 \times 10^2 [\text{OH}^-]$$

p-Bromothiophenol:

$$k_1 = 1.12 \times 10^{-4} [\text{H}_3\text{O}^+] + \frac{2.73 \times 10^{-11} + 6.22 \times 10^2 [\text{OH}^-]}{2.55 \times 10^5 + 2.55 \times 10^2 [\text{OH}^-]} + 77.1 [\text{OH}^-]$$

p-Nitrothiophenol:

$$k_1 = 9.60 \times 10^{-5} [\text{H}_3\text{O}^+] + \frac{4.41 \times 10^{-11} + 2.00 \times 10^2 [\text{OH}^-]}{1.49 \times 10^5 + 1.85 \times 10^2 [\text{OH}^-]} + 37.3 [\text{OH}^-]$$

If acetate ion is present as a general base catalyst,<sup>20</sup> equation (5) becomes

$$\frac{1}{k_0} = \frac{1}{k_1^{\text{SH}}} + \frac{1}{\left(\frac{k_1^{\text{SH}}}{k_{-1}^{\text{SH}}}\right) \{ k_2^{\text{H}_2\text{O}} [\text{H}_2\text{O}] + k_2^{\text{OH}} [\text{OH}^-] + k_2^{\text{OAc}} [\text{OAc}^-] \}} \quad (9)$$

At low general base concentration, proton removal is rate controlling and the rate is linear in base concentration. As the amount of base becomes larger, the addition of thiophenol becomes the rate determining step and  $k_1^{\text{SH}}$  approaches the limiting values.

The values of the ratio  $(k_1^{\text{SH}}/k_{-1}^{\text{SH}}) k_2^{\text{B}}$  calculated by equation (10)<sup>21</sup> and the  $pK_a$  of the bases are given in Table 2 and Figure 4 shows the Brønsted plot.

From the rate equation and the mechanism for the addition of thiophenol to AMQD over a wide pH range is fully explained; Below pH 2.5, the addition reaction was proceeded by the attack of water to 6' position of quinonoid after protonation at nitrogen of acridinyl and between pH 3.0 and 6.0, the addition of the neutral molecules and sulfide anion occurred competitively. However, above pH 6.2, sulfide anion added to the 6'-position of quinonoid.

As shown above, the rate equations which can be applied over a wide pH range were obtained. On the basis of various kinetic results, a reaction mechanism was proposed. However, to better understand the theory for the exact transition state and intermediate, the detailed mechanism of the nucleophilic addition will be the subject of our future investigation.

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20. From the value of  $k_1^{SH} = 1.46 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $(k_1^{SH}/k_{-1}^{SH}) k_2^{H_2O} [\text{H}_2\text{O}] = 7.48 \times 10^{-7} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $(k_1^{SH}/k_{-1}^{SH}) k_2^{OH}$

$= 4.43 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $[\text{CH}_3\text{COO}^-] = 0.4 \text{ M}$ ,  $[\text{OH}^-] = 6.03 \times 10^{-10} \text{ M}$  and observed rate constant  $k_p$ , the value of catalytic constant of acetate ion  $(k_1^{SH}/k_{-1}^{SH}) k_2^{OAc}$  can be determined and is found to be  $1.50 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ . By substituting above data into equation (9),  $k_0$  is given by the following equation (9-1).

$$\frac{1}{k_0} = \frac{1.65 \times 10^{-5} + 1.53 \times 10^{-4} [\text{OAc}^-]}{1.66 \times 10^{-11} + 2.37 \times 10^{-9} [\text{OAc}^-]} \quad (9-1)$$

As a result, over-all rate constant becomes;

$$k_i = 3.53 \times 10^{-4} [\text{H}_3\text{O}^+] + \frac{1.66 \times 10^{-11} + 2.37 \times 10^{-9} [\text{OAc}^-]}{1.65 \times 10^{-5} + 1.53 \times 10^{-4} [\text{OAc}^-]} + 1.12 \times 10^{-2} [\text{OH}^-] \quad (9-2)$$

Figure 3 shows that the values of over-all rate constant,  $k_p$ , calculated by equation (9-2) are in good agreement with observed values.

$$21. \frac{1}{k_0} = \frac{1}{k_1^{SH}} + \frac{1}{\left( \frac{k_1^{SH}}{k_{-1}^{SH}} \right) \{ k_1^{H_2O} [\text{H}_2\text{O}] + k_2^{OH} [\text{OH}^-] + k_2^B [\text{B}] \}} \quad (10)$$

From the value of  $k_1^{SH} = 1.46 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $(k_1^{SH}/k_{-1}^{SH}) k_2^{H_2O} [\text{H}_2\text{O}] = 7.48 \times 10^{-7} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $(k_1^{SH}/k_{-1}^{SH}) k_2^{OH} = 4.43 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $[\text{B}] = 1.25 \times 10^{-4} \text{ M}$ ,  $[\text{OH}^-] = 10^{-8} \text{ M}$  and observed rate constant  $k_p$ , the value of catalytic constant of various general bases  $(k_1^{SH}/k_{-1}^{SH}) k_2^B$  can be determined.

## Optimization of Synthetic Parameters for Mesoporous Molecular Sieve MCM-41 Using Surfactant CTACl

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High quality MCM-41 is prepared from a gel of molar composition  $\text{SiO}_2$ : 0.20 CTACl: 0.18 TMAOH: 25  $\text{H}_2\text{O}$  aged at 20 °C for 24 hours before crystallization lasting for 48 hours. The (110) and (200) peaks of XRD pattern of high quality MCM-41 are unusually well resolved and the FWHM (full-width-at-half-maximum) of the (100) peak is 0.13° for as-prepared MCM-41 and 0.21° for calcined one, which indicate well-developed crystals. The properties of the crystal depend on the source and concentration of the reactants and the gel aging time. There is no induction period in the course of the synthesis, which is conveniently monitored by pH measurement. Gel aging, during which a spatial distribution of silicate polyanions and micellar cations is established, is essential for preparing high quality MCM-41. Surfactants with the same cationic organic group but different counteranions change the crystallization behavior. Highly basic gel (pH=12.6) favours the lamellar product; the quality of MCM-41 is lower as insufficient TMAOH is available to dissolve the silica.

### Introduction

Zeolite-based molecular sieves have a limited pore diameter and the known mesoporous materials such as silica gel, activated carbon and pillard clay have irregularly spac-

ed pore with broad pore size distribution. There has been increasing demand for crystalline mesoporous molecular sieves with pores of uniform diameter. The synthesis of the mesoporous molecular sieve MCM-41 with one-dimensional channels 16-100 Å in diameter which allow fast diffusion