# Preparation of Styrene Derivatives Containing Sulfide Group: Kinetic Studies on The Addition Reaction of Thiophenol to 1,4-Divinylbenzene

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ABSTRACT: The addition reaction of thiophenol to 1,4-divinylbenzene affords mono-adduct, 4-vinyl-1-[(2-phenylthio)ethyl]benzene with about 70%, and di-adduct, 1,4-bis[(2-phenylthio)ethyl]benzene. Reaction rate dependence on the reagent concentration was studied by gas chromatography. The reaction rate depends on the first order of the thiophenol concentration and one half order of AIBN concentration. The addition reaction proceeds by a radical chain mechanism and the rate determining step is thought to be the hydrogen abstraction from thiophenol by the intermediate carbon radical. The ratio of the overall reaction rate constants of the first addition  $(k_1)$  and second addition  $(k_2)$  to the two vinyl groups of 1,4-divinylbenzene,  $k_2/k_1$  was estimated using a computer curve fitting method in comparison with the experimental data. The values of  $k_2/k_1$  are in the range of 0.18 to 0.25 at 60°C and 75°C, respectively. The reaction temperature is a disadvantage to obtain much higher yields of the mono-adduct.

KEY WORDS Addition Reaction / Thiophenol / 1,4-Divinylbenzene / 4-vinyl-1-[(2-phenylthio)ethyl]benzene / Kinetic Studies / Reaction Mechanism / Reaction Rate Constant / Computer Simulation /

In recent years attention has been paid to modification of monomers to improve and develop the characteristic properties of the homo- and copolymers.<sup>1-4</sup> The addition reaction of a thiol group to an unsaturated carbon–carbon bond is well known.<sup>5-7</sup> Screttas *et al.* carried out the addition reaction of thiophenol to olefin and diolefin to synthesize sulfide derivatives.<sup>8</sup> The studies on the addition reaction of thiophenol to styrene showed that the reaction rate depends on the concentration of thiophenol, and the rate determining step is the hydrogen transfer from thiophenol to the intermediate carbon radicals.<sup>9-12</sup>

In the previous paper,<sup>13</sup> the authors discussed the preparation of styrene derivatives containing a sulfide group. The addition reaction of thiophenol to 1,4-divinylbenzene in benzene at 75°C gave about 70% yield of the mono-addition product, 4-vinyl-1-[(2-phenylthio)ethyl]benzene. The addition reaction was significantly affected by the initiation mode and reaction temperature. A small amount of initiator, such as AIBN or BPO, extremely increased the addition reaction compared with the absence of the initiators. The addition reaction of thiophenol (TP) to 1,4-divinylbenzene (DVB) proceeds by a mechanism of the radical chain reaction and the progressive addition reaction of thiophenol to the monoadduct yields the di-adduct, because the mono-adduct has a vinyl group capable to

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participate in the second addition reaction with thiophenol.

In this paper, the authors discuss the kinetic behavior of the addition reaction of thiophenol to 1,4-divinylbenzene and estimated the ratio of the overall reaction rate constants of the second addition over the first addition,  $k_2/k_1$ , by means of a computer simulation.

## RESULTS AND DISCUSSION

## Rate Dependence on Reagent Concentration

The addition reaction of thiophenol to olefin is considered to proceed in a radical chain mechanism in the presence of a radical initiator. In the thiophenol with DVB system, kinetic studies have not yet been done and the authors investigated the reaction rate dependence on the concentration of the reagents to anticipate reaction conditions obtaining much higher yield of 1.

CH₂=CH-
$$\bigcirc$$
-CH=CH₂ + HS- $\bigcirc$   $\xrightarrow{R}$  CH₂=CH- $\bigcirc$ -CH₂-CH₂-S- $\bigcirc$  1

The rate dependence on the concentration of TP was studied at the fixed concentration of DVB (Figure 1). When the concentration of TP increased from an equimolar of  $DVB_{\star}$  to two times as much, the reaction rate also increased.

A logarithmic plot of the TP concentration  $(\log [TP]_0)$  and the reaction rate  $(\log R)$  correlates in a straight line with a slope constant of about 1 as shown in Figure 2, where the *R* means the initial reaction rate. Hence, the reaction rate can be expressed as follows, where k' is a constant.

$$R = k' [TP]^1 \tag{1}$$

The effect of the concentration of DVB on the reaction rate was also examined and the results are shown in Figure 3. Though the ratios of  $[DVB]_0/[TP]_0$  changed from 1 to 2, the reaction rate almost did not change. Therefore,



**Figure 1.** Relationship between the concentration of TP and yield of 1 in benzene at 75°C under nitrogen atmosphere.  $[AIBN]_0 = 6.7 \times 10^{-4} \text{ moll}^{-1}$ ;  $[DVB]_0 = 0.185 \text{ moll}^{-1}$ ;  $[TP]_0/[DVB]_0 = \bigoplus, 1.0; \bigcirc, 1.4; \Box, 1.7; \triangle, 2.0.$ 



Figure 2. Reaction rate dependence on the TP concentration. Reaction conditions are the same as in Figure 1.



Figure 3. Relationship between the concentration of DVB and yield of 1 in benzene at 75°C under nitrogen atmosphere.  $[AIBN]_0 = 6.7 \times 10^{-4} \text{ mol}1^{-1}$ ;  $[TP]_0 = 0.185 \text{ mol}1^{-1}$ ;  $[DVB]_0/[TP]_0 = \bigoplus, 1.0; \bigcirc, 1.4; \Box, 1.7; \triangle, 2.0.$ 

it is concluded that the reaction rate is independent of the concentration of DVB. Thus, eq 1 can be rewritten as follows, where

## Kinetics of Addition of Thiophenol to Divinylbenzene



Figure 4. Reaction rate dependence on the AIBN concentrations in benzene at 75°C under nitrogen atmosphere.  $[TP]_0 = [DVB]_0 = 0.185 \text{ mol}1^{-1}$ .

k" means a constant.

$$R = k'' [TP]^1 [DVB]^0$$
 (2)

This means that DVB does not participate in the rate determining step of the addition reaction of thiophenol to DVB. Hence, the rate determining step is thought to be the hydrogen abstraction step from thiophenol by the intermediate carbon radical.

The results of the reaction rate dependence on the concentration of the initiator, AIBN, are shown in Figure 4. The reaction rate depends on the one half order of AIBN concentration and that the reaction rate can be expressed finally as follows, where k is overall reaction rate constant.

$$R = k[AIBN]^{1/2}[TP]^{1}[DVB]^{0}$$
 (3)

The fact that the reaction rate is directly proportional to the one half order of the radical initiator concentration demonstrates that the reaction of thiophenol to DVB progresses in a radical chain mechanism.

## **Reaction Mechanism**

Based on the results of the rate dependence on the concentrations of the reagents, elementary reactions of the addition reaction of thiophenol to DVB are shown in Scheme 1. A similar reaction scheme has already been discussed by Sievertz<sup>9,10</sup> and the authors.<sup>12,13</sup>

$$I \xrightarrow{k_{d}} 2R \cdot$$
 (4)

$$\mathbf{R} \cdot + \mathbf{T} \mathbf{P} \xrightarrow{\mathbf{K}_{\mathbf{i}}} \phi \mathbf{S} \cdot + \mathbf{R} \mathbf{H}$$
 (5)

$$\phi s \cdot + \text{DVB} \xrightarrow{k_{a1}} \text{CH}_2 = \text{CH}\phi \dot{\text{CH}}_2 - s - \phi \qquad (6)$$

$$A \cdot + TP \xrightarrow{k_{tr1}} CH_2 = CH\phi CH_2 CH_2 S\phi + \phi S \cdot$$
 (7)

$$\phi S' + 1 \xrightarrow{k_{a2}} \phi SCH_2 \dot{C}H\phi CH_2 CH_2 S\phi \qquad (8)$$

1

$$B \cdot + TP \xrightarrow{k_{tr2}} \phi SCH_2CH_2\phi CH_2CH_2S\phi + \phi S \cdot$$
(9)  
2

$$2\phi \mathbf{S} \cdot \xrightarrow{\mathbf{k}_3} \mathbf{P}_3 \tag{10}$$

$$\phi \mathbf{S} \cdot + \mathbf{A} \cdot \xrightarrow{\mathbf{K_4}} \mathbf{P_4} \tag{11}$$

$$\begin{array}{cccc} 2A & \xrightarrow{-3} & P_5 \\ \phi S & & k_6 & p \end{array} \tag{12}$$

$$2B \cdot \xrightarrow{k_7} P_7$$
(13)

Applying the steady state assumption, the condition of  $k_{a1} \gg k_{tr1}$  and  $k_{a2} \gg k_{tr2}$  at the initial state of the reaction, the overall reaction rate (*R*), where *k* is overall reaction rate constant, can be expressed as follows;

# $R = k[AIBN]^{1/2}[TP]^{1}[DVB]^{0}$ (15)

Equation 15 coincides with the experimentally derived eq 3, meaning that the rate determining step is the hydrogen abstraction from thiophenol by the intermediate carbon radical  $(\mathbf{A} \cdot)$ .

If the addition reaction only progresses by recycling the addition reaction of the benzenethiyl radical to DVB as eq 6 and the hydrogen abstraction reaction by the intermediate radical as eq 7, the yield of 1 may increase to about 100%. According to previous studies by the authors,<sup>13</sup> the second addition of benzenethiyl radical to the mono-adduct 1 as the eq 8 and 9 actually occurs and results in a decrease in the yield of 1. The reaction time is also a controlling factor to obtain 1 in a high yield in which the higher the reaction temperature is, the shorter the reaction time to give a maximum yield of 1. Evaluation of  $k_2/k_1$  by a Computer Simulation

The addition reaction of thiophenol to DVB afforded a maximum yield of the mono-adduct 1 with about 70%. The addition reaction of the thiyl radical to the vinyl groups of DVB can take place easily and quantitatively, but the yield of the mono-adduct 1 did not reach 100%, because the second addition of thiophenol to the resulting mono-adduct 1 occurred simultaneously under the reaction conditions as shown in Scheme 1.

To obtain the mono-adduct 1 in a high yield and to restrain the second addition reaction of thiophenol to 1, it is necessary to know the ratio of the overall second addition reaction rate constant to that of the overall first addition reaction rate constant,  $k_2/k_1$ . The authors used a relatively simple computer program, based on the algorithm theory without consideration of the polymerization of DVB and 1, to estimate the ratio of  $k_2/k_1$ , in comparison with the experimental data. Considering a consecutive reaction of DVB  $\xrightarrow{k_1} \mathbf{1} \xrightarrow{k_2} \mathbf{2}$ , the overall reaction rate constant k correlates with two terms of the reaction rate constants of  $k_a$  and  $k_{\rm tr}$ , and the ratio of  $k_2/k_1$  is proportional to the  $k_{tr2}/k_{tr1}$ , because the rate determining step of the reaction is the hydrogen abstraction from thiophenol by the intermediate carbon radical.

Figure 5 shows the experimental results and computer simulation curves. The addition reaction was carried out at  $60^{\circ}$ C in benzene under nitrogen atmosphere using a radical initiator with  $[TP]_0/[DVB]_0$  being 2. The vertical axis indicates the yield of 1 and the yield was calculated based on the initial concentration of DVB.

As shown in Figure 5, the calculated curve with  $k_2/k_1$  of 0.18 almost completely fits with the experimental points. The other curves deviate from the experimental points very much. In other words, under the reaction conditions, the ratio of the reaction rate constants of the second addition to the first addition,  $k_2/k_1$  is 0.18. The error range is considered to be less than 10%.



**Figure 5.** Evaluation of  $k_2/k_1$  by the computer curve fitting.  $\triangle$  are the experimental data in benzene at 60°C under nitrogen atmosphere. [AIBN]<sub>0</sub> = 3.4 × 10<sup>-3</sup> mol1<sup>-1</sup>; [DVB]<sub>0</sub> = 0.30 mol1<sup>-1</sup>; [TP]<sub>0</sub>/[DVB]<sub>0</sub> = 2.0. The curves were drawn by taking  $k_2/k_1 = a$ , 0.10; b, 0.16; c, 0.18; d, 0.20; e, 0.30; f, 0.50.



**Figure 6.** Relationship between the molar ratio of  $[TP]_0/[DVB]_0$  and yield of 1 in benzene at 60°C under nitrogen atmosphere.  $[AIBN]_0 = 3.4 \times 10^{-3} \text{ mol}1^{-1}; [DVB]_0 = 0.3 \text{ mol}1^{-1}; [TP]_0/[DVB]_0 = •, 1.0; \bigcirc, 1.5; \triangle, 2.0$ . The curves were drawn based on the computer simulation with the value of  $k_2/k_1$  of 0.18.

Figure 6 shows the results of the addition reaction of TP to DVB in benzene at 60°C under nitrogen atmosphere with varying reagent feed ratios from 1 to 2. At first, the calculated curves with  $k_2/k_1$  of 0.18 completely fit with the experimental points, when the ratios of the reagents  $[TP]_0/[DVB]_0$  took 1, 1.5, and 2. Another interesting feature is that the reaction time giving a maximum yield becomes shorter with increasing molar ratio of  $[TP]_0/[DVB]_0$  from 1 to 2. For instance, the maximum yield of 1 attained for 90 min, when the molar ratio of  $[TP]_0/[DVB]_0$  is 2. But, the resulting mono-adduct 1 quickly decreased



**Figure 7.** Relationship between the molar ratio of  $[TP]_0/[DVB]_0$  and yield of 1 in benzene at 75°C under nitrogen atmosphere.  $[AIBN]_0 = 6.7 \times 10^{-4} \text{ mol}1^{-1};$   $[DVB]_0 = 0.185 \text{ mol}1^{-1};$   $[TP]_0/[DVB]_0 = •, 1.0; \bigcirc, 1.5;$   $\triangle$ , 2.0. The curves were drawn based on the computer simulation with the value of  $k_2/k_1$  of 0.25.

because of the second addition of TP to form the di-adduct 2. However, at the molar ratio  $[TP]_0/[DVB]_0$  being 1, though the reaction rate of forming 1 is lower than that at the molar ratio  $[TP]_0/[DVB]_0$  being 2, the second addition reaction was much more restricted.

The same behavior also appears in the addition reaction carried out at 75°C under nitrogen atmosphere (Figure 7). At 75°C, the calculated curves fit the experimental points at the ratio  $k_2/k_1$  of 0.25, which is much higher than that (0.18) at  $60^{\circ}$ C. High temperature increases the reaction rate constant of the first addition; at the same time, it also increases the reaction rate constant of the second addition. That is, selectivity toward the mono-adduct production decreases with increasing reaction temperature. The experimental points deviated little from the calculated curves after the yield of 1 reached maximum. The deviations may result from polymerizations of DVB and 1. After reaction for 5 h in benzene at 60°C under nitrogen atmosphere with the molar ratio of  $[TP]_0/[DVB]_0$  being 1, the final yield of the mono-adduct 1 is about 70%; at the same time about 25% of the di-adduct 2 and less than 5% of the oligomers were recovered.

Figure 8 shows the temperature dependence of the addition reaction. The reactions are



**Figure 8.** Temperature dependence of  $k_2/k_1$ . [AIB-N]<sub>0</sub>=3.4×10<sup>-3</sup> mol1<sup>-1</sup>; [DVB]<sub>0</sub>=0.30 mol1<sup>-1</sup>; [TP]<sub>0</sub>/ [DVB]<sub>0</sub>=1.0. •. 60°C;  $\triangle$ , 65°C;  $\bigcirc$ , 75°C. The curves were drawn based on the computer simulation. The values of  $k_2/k_1$  were estimated to be 0.18 at 60°C, 0.20 at 65°C and, 0.25 at 75°C.

carried out at three different temperatures, 60, 65, and 75°C under nitrogen atmosphere at an equimolar ratio of  $[TP]_0/[DVB]_0$ . The calculated curves well agree with the experimental points, when  $k_2/k_1$  take 0.18 at 60°C, 0.20 at 65°C, and 0.25 at 75°C. The higher the reaction temperature is, the bigger is the value of  $k_2/k_1$ . The  $k_2/k_1$  are in the range of 0.18 to 0.25. This means the second addition of TP to 1 is more temperature dependent than the first addition of TP to DVB. The vinyl group of DVB is more active than that of the mono-adduct 1.

## CONCLUSION

Kinetic studies of the addition reaction of thiophenol to 1,4-divinylbenzene were conducted under nitrogen atmosphere with varying molar ratios of  $[TP]_0/[DVB]_0$  from 1 to 2 at various temperatures. The addition reaction rate depends on the first order of thiophenol concentration and the one half order of AIBN concentration. The reaction proceeds in a radical chain mechanism and the rate determining step is hydrogen abstraction from thiophenol by the intermediate carbon radical. Increasing the thiophenol concentration would accelerate the reaction rate; at the same time, the second addition also becomes vigorous to reduce the yield of the monoadduct 1. The estimated values of  $k_2/k_1$  by means of computer simulation are in the range of 0.18 to 0.25, which become greater with increasing reaction temperature. From these results, it is concluded that the most suitable condition for giving the highest yield of 1, is that the reaction should be carried out at below 60°C with an equimolar ratio of thiophenol and 1,4-divinylbenzene. Using the calculated value of  $k_2/k_1$  of 0.18 at 60°C, the optimized reaction condition is elucidated to be that the addition reaction should be carried out with the reagent ratio  $[TP]_0/[DVB]_0$  taking 1/4, the maximum yield of the mono-adduct 1 may reach 95% for 4 h. However, about 75% of the mono-adduct 1 and about 20% of the oligomers calculated based on thiophenol were obtained experimentally. The experimental yield may be improved by adding a suitable inhibitor toward the radical oligomerization.

#### **EXPERIMENTAL**

## Materials

Thiophenol (TP) (Wako Pure Chem. Co.) and 1,4-divinylbenzene (DVB) (Hokkou Chem. Co.) were purified by distillation in a reduced pressure under nitrogen atmosphere. Azobisisobutyronitrile (AIBN) (Wako Pure Chem. Co.) was used after recrystallization in hexane. Solvent benzene was used by distillation under nitrogen atmosphere after degassed with bubbling pure nitrogen for 2 h.

## Addition Reaction of Thiophenol to DVB

In a 50 ml round bottom flask equipped with a three-way stopcock, the benzene solutions of thiophenol, DVB, and AIBN were charged by hypodermic syringe under nitrogen atmosphere. All addition reactions were carried out in benzene at various temperatures under nitrogen atmosphere.

The yield of 1 was determined by a gas chromatography equipped with a Silicon GE SE-30, 2m column and a flame ion detector. Column temperature,  $250^{\circ}$ C; injection temperature,  $300^{\circ}$ C; carrier gas flow, N<sub>2</sub>, 32 ml min<sup>-1</sup>. The retention time was recorded in minute: thiophenol, 0.3; DVB, 0.4; and 1, 6.3, respectively. Diphenyl sulfide was used as an external standard for the quantitative analysis of 1. The di-adduct 2 did not observe by the gas chromatography under this condition. By changing the G.C. conditions: column temperature, 260°C; injection temperature, 330°C; and carrier gas flow, N<sub>2</sub>, 50 ml min<sup>-1</sup>; the di-adduct 2 was detected in the retention time, 56.3 min.

#### Computer Simulation

The computer NEC PC-9801 VM2 was used to estimate the values of  $k_2/k_1$  using the laboratory made program, based on the algorithm theory. The theoretical curve was calculated by the equation of the consecutive reaction with  $A \rightarrow B \rightarrow C$ .

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