SEMI-CONTINUOUS GAS-LIQUID CATALYZED REACTION OF *o*-PHENYLENE DIAMINE AND CARBON DISULFIDE BY TERTIARY AMINES

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ABSTRACT

A semi-continuous reactor is used to carry out the catalyzed reaction of *o*-phenylene diamine and carbon disulfide to synthesize 2-mercaptobenzimidazole (MBI) in a gas phase/alkaline solution two-phase medium. Tertiary amine, which is relatively less expensive, was used as the catalyst to promote the reaction rate. In addition, gas-phase carbon disulfide of higher temperature is introduced to the reactor for reaction. The main advantage of the present system is that the reaction can be carried out at a relatively higher temperature in the semi-continuous reactor. Carbon disulfide, which is first dissolved in the organic phase, reacts with tertiary amine in the organic-phase solution to produce an active intermediate (R_3N-CS_2). Second, this active intermediate (R_3N-CS_2) further reacts with *o*-phenylene diamine to produce the desired product MBI. Based on the experimental observations, a reaction mechanism is proposed, and a kinetic model, which considered the two-step reaction is developed. A pseudo first order rate law is sufficient to describe the reaction. The effect of the reaction conditions, such as: amount of tertiary amines (TEA, TPA and TBA) and ammonia (NH_3), agitation speed, initial concentration of carbon disulfide, flow rate of gas phase, amount of *o*-phenylene diamine and temperature, on the apparent rate constant are investigated in detail.

Keywords: synthesis of 2-mercaptobenzimidazole, gas-liquid reaction, semi-continuous reactor, catalyzed reaction.

INTRODUCTION

Phase-transfer catalysis (PTC) is an effective technique to synthesize products from two or more immiscible reactants which exist in different phases. Typically, quaternary ammonium salts have been used as the phase-transfer catalyst to enhance this reaction. By adding a small catalytic amount of quaternary salt, the reaction rate is dramatically accelerated and the conversion of reactant is increased. The main function of the quaternary salt is to bring nucleophiles (anions) from the aqueous phase to the organic phase for reacting with organic reactants in an organic solution in a normal phase transfer catalytic reaction (NPTC). Recently, this technique has also been successfully extended to the synthesis of specialty chemicals from homogeneous solutions [1,2]. However, the application of phase-transfer technique to gas-liquid systems has received little discussion.

In the past, the procedure for synthesizing 2-mercaptobenzimidazole (MBI) has involved the reaction of *o*-phenylene diamine and reactants in a mixture of methanol-water catalyzed by active carbon [3]. However, this reaction needs to be carried out at a relatively high temperature in order to obtain the desired product over a long time period. In the later, quaternary ammonium salts [4,5,6,] were employed as a catalyst in the reaction of *o*-phenylene diamine and carbon disulfide to synthesizie MBI. However, the kinetics and mechanism of the reaction have not been discussed. In addition, MBI has also been obtained by other techniques in using various reactants [7,8]. Recently, Wang and Liu [9,10,11] synthesizied mercaptobenzimidazole (MBI) from the catalyzed reaction of *o*-phenylene and carbon disulfide in a batch homogeneous solution or two-phase solution by appropriate choice of the organic solvents. The primary advantage of these processes is that the catalyzed reaction is carried out at moderate reaction temperature. However, it is favorable for the reaction to be carried out at a higher temperature to increase the rate and the yield. Nevertheless, the boiling point of carbon disulfide has limited the application of PTC to carry out the reaction in a batch reactor at a higher temperature in the homogeneous solution or liquid-liquid two-phase solution.

In order to increase the reaction rates, a higher temperature is used in this study. The catalyzed reaction of *o*-phenylene diamine and carbon disulfide by tertiary amine to synthesize MBI is carried out in a gas phase/liquid solution two-phase medium in this work. The main advantage of this new process is that a reaction temperature higher than boiling point of carbon disulfide is used to enhance the reaction. In order to fulfill this requirement in this study, a semi-continuous reactor is employed to carry out the reaction in this work. Carbon disulfide (CS_2) mixed with dichloromethane (CH_2Cl_2), which is used as the gas phase, is introduced to the reactor for reaction with *o*-phenylene diamine catalyzed by tertiary amine. Based on the experimental evidence, the reaction mechanism is proposed and the kinetics is developed. A pseudo-first-order rate law is sufficient to describe the kinetic behaviors. Effects of the reaction conditions, including the amount of ammonia and tertiary amines, the concentration of carbon disulfide, the flow rate of gas phase, the amount of *o*-phenylene diamine and temperature, on the conversion are investigated.

EXPERIMENTAL SECTION

Materials: Carbon disulfide (CS_2), *o*-phenylene diamine ($C_6H_4(NH_2)_2$), tertiary amines (R_3N) including triethylamine (TEA), tripropylamine (TPA) and tributylamine (TBA), ammonia (NH_3), organic solvents including ethanol and dichloromethane, and other reagents used were all GR-grade chemicals for synthesis.

Procedures: Kinetics of synthesizing 2-mercaptobenzimidazole (MBI)

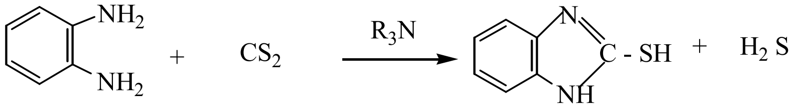
The reactor is a 125-ml four necked Pyrex flask, capable of agitating the solution, inserting the thermometer, taking samples, and feeding the reactants. A reflux condenser is attached to the port of the reactor to recover the species from the gas phase. The reactor is submerged into a constant temperature water batch in which the temperature can be controlled to ±0.1℃. To start an experimental run, known quantities of *o*-phenylene diamine, caffeine (internal standard), and tertiary amine were dissolved in the organic-phase solution (ethanol and water mixture) and introduced into the reactor. The liquid solution was stirred mechanically by a two-blade paddle (5.5 cm) at 700 rpm. Then, a mixture of carbon disulfide and dichloromethane in gas phase is continuously introduced to the liquid solution to initiate the reaction. During the reaction, an aliquot of 0.1 ml was withdrawn from the solution at a chosen time. The sample was immediately poured into methanol at 4℃ for dilution and retardation of the reaction and then analyzed by HPLC.

The product MBI for identification was purified from the reaction without containing tertiary amine by vacuum evaporation to strip off the organic solvent and carbon disulfide. Then, it was recrystallized from ethanol as white crystals.

The product (MBI) and the reactants (carbon disulfide, and *o*-phenylene diamine) were identified by NMR and IR analyses. The results obtained from the instrumental analysis are consistent with those of the literature reports. An HPLC Model (Shimadzu) with an absorbance detector (254 nm, SPD-6A) was employed to measure the amounts of reactants and product. The column used was Shim-Pack CLC-ODS RP-18 (5 μm). The eluent was $CH_3CN/H_2O = 20/80$ (with 5mM KH_2PO_4 + 0.1% H_3PO_4) (volume ratio) with a flow rate of 1.0 ml/min.

REACTION MECHANISM AND KINETIC MODEL

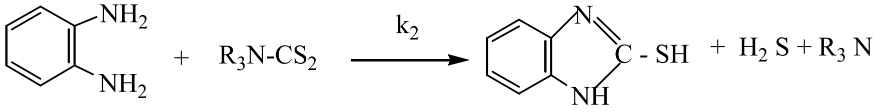
The principle of gas-liquid catalyzed reaction is the same as that of the mass transfer accompanied with the chemical reaction in gas-liquid system [12,13,14] The key point is how to manipulate the equation change of the multi-components in applying to the physical systems, i.e. the reaction system involves the dissolving gas-phase reactant in the liquid-phase, the mass transfer of reactant in gas phase, and the chemical reaction resistance in liquid phase. For the catalyzed two-phase reaction of *o*-phenylene diamine and carbon disulfide to synthesize 2-mercaptobenzimidazole (MBI), the dissolving carbon disulfide in liquid phase and the reaction of carbon disulfide and *o*-phenylene diamine in organic phase are the two important factors in affecting the yield or the conversion. In this work, the overall gas-liquid reaction can be expressed as,



(R1)

Thus, we consider only the homogeneous reaction for synthesizing MBI in the organic-phase solution. It is obvious that carbon disulfide first dissolves in EtOH/H_2O mixture solution and then reacts with tertiary amine to form an active intermediate (R_3N-CS_2). In this work, the dissolving carbon disulfide in organic phase is fast from our previous work [15]. Furthermore, the mass transfer of species in the homogeneous organic-phase solution is also fast when the solution is agitated at moderate speed. This active intermediate (R_3N-CS_2) further reacts with *o*-phenylene diamine to produce the desired product MBI, i.e. the reaction mechanism is proposed as

$$CS_2 \quad + \quad R_3N \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad R_3N\text{-}CS_2 \tag{R2}$$



(R3)

In the alkaline solution, KOH will further react with H_2S, and with CS_2 to produce the inert inorganic substance including K_2S, K_2CO_3 and K_2CS_3.

Reaction (R2) is fast and reaches an equilibrium state within 5 minutes [15]. Normally, it takes about 2 hours to obtain an 80% conversion of *o*-phenylene diamine at moderate reaction condition. Therefore, we conclude that the reaction of *o*-phenylene diamine and tertiary amine is in an equilibrium state relative to reaction (R3).

The reaction rates of (R2) and (R3) are expressed as

$$r_1 = k_1[CS_2][R_3N] - k_{-1}[R_3N\text{-}CS_2] \tag{1}$$

$$r_2 = k_2[R_3N\text{-}CS_2][C_6H_4(NH_2)_2] \tag{2}$$

A pseudo-steady state hypothesis (PSSH) is assumed to apply to the active intermediate (R_3N-CS_2), i.e.

$$\frac{d[R_3N - CS_2]}{dt} = 0 \tag{3}$$

No byproducts were detected during or after the reaction. Thus, it is reasonable to assume that the consumption rate of R_3N-CS_2 in reaction (R3) equals to the production rate of R_3N-CS_2 in reaction (R2). Thus, we obtain the following equation from Equations (1) and (2), i.e.

$$k_1[CS_2][R_3N] - k_{-1}[R_3N\text{-}CS_2] = k_2[R_3N\text{-}CS_2][C_6H_4(NH_2)_2] \tag{4}$$

Rearranging Equation (4), we obtain

$$[R_3N - CS_2] = \frac{[R_3N][CS_2]}{\frac{k_2}{k_1}[C_6H_4(NH_2)_2] + K} \tag{5}$$

where the equilibrium constant K is defined as

$$K = \frac{k_{-1}}{k_1} \tag{6}$$

Substituting Equation (5) into Equation (2), we obtain

$$r_2 = \frac{k_2[C_6H_4(NH_2)_2][CS_2][R_3N]}{(\frac{k_2}{k_1})[C_6H_4(NH_2)_2] + K} \tag{7}$$

As stated, reaction (R2) reaches an equilibrium within a couple of minutes relative to reaction (R3). Thus, it is reasonable to assume that $k_{-1}[R_3N\text{-}CS_2] >> k_2[R_3N\text{-}CS_2][C_6H_4(NH_2)_2]$ at low concentration of *o*-phenylene diamine or low rate of reaction (R1), i.e.

$$K >> (\frac{k_2}{k_1})[C_6H_4(NH_2)_2] \tag{8}$$

Therefore, Equation (7) is reduced to

$$r_2 = (\frac{k_2}{K})[CS_2][R_3N][C_6H_4(NH_2)_2] \tag{9}$$

In this work, carbon disulfide was used in large excess relative to its stoichiometric quantity. Also, the concentration of R_3N remains constant. Thus, Equation (9) is written as

$$r_2 = -\frac{d[C_6H_4(NH_2)_2]}{dt} = k_{app}[C_6H_4(NH_2)_2] \tag{10}$$

where the apparent rate constant k_{app} is defined as,

$$k_{app} = (\frac{k_2}{K})[CS_2][R_3N] \tag{11}$$

As shown in Equation (11), the k_{app}-value is constant for a constant concentration of CS_2 and R_3N,.

Integrating Equation (10), we obtain

$$-\ell n(1-X) = k_{app}\, t \tag{12}$$

where X is the conversion of *o*-phenylene diamine and is defined as

$$X = 1 - \frac{[C_6H_4(NH_2)_2]}{[C_6H_4(NH_2)_2]_0} \tag{13}$$

in which $[C_6H_4(NH_2)_2]_0$ is the initial concentration of *o*-phenylene diamine.

RESULTS AND DISCUSSION

The boiling point of carbon disulfide at atmosphere is 46.2℃. Therefore, it is difficult to carry the liquid-liquid two-phase phase transfer catalytic reaction at temperature higher than 46.2℃ in a batch reactor, since a larger amount of CS_2 will evaporate to the gas phase. In this work, the reaction, which is carried out under a semi-continuous reactor, can be operated at a temperature higher than the boiling point of carbon disulfide. First, a mixture of carbon disulfide (bp 46.2℃) and dichloromethane (bp 39.6℃) in gas phase is prepared and then continuously introduced to the reactor. The concentration of carbon disulfide is first set by mixing the appropriate amount ratio of CS_2 and CH_2Cl_2 of liquid phases. The liquid mixture is then heated to vapor phase via a heater. The flow rate of feeding CS_2/CH_2Cl_2 gas is controlled by the feed pump. Second, carbon disulfide is then dissolved in an EtOH/H_2O solution which contains *o*-phenylene diamine and tertiary amine. Thus, carbon disulfide reacts with tertiary amine to produce an active intermediate ($R_3N\text{-}CS_2$), which can further react with *o*-phenylene diamine to produce the desired product 2-mercaptobenzimidazole (MBI). Effects of the reaction conditions on the conversion of *o*-phenylene diamine and the rate are discussed below.

(a) Effect of tertiary amines and ammonia

Based on the experimental observation, the gas-liquid catalyzed reaction of carbon disulfide and *o*-phenylene diamine by tertiary amine follows a pseudo first order rate law. A rational reaction mechanism is proposed and used along with a pseudo-steady-state-hypothesis (PSSH) are employed to develop the pseudo first order rate law. Effects of the ammonia (NH_3) and tertiary amines (R_3N) including triethylamine (TEA), tripropylamine (TPA) and tributylamine (TBA) on the conversion of *o*-phenylene diamine are shown in Figure 1. The conversion of *o*-phenylene daimine is low in the absence of ammonia or tertiary amines. Ammonia (NH_3) also exhibits catalytic activity for enhancing the reaction of *o*-phenylene diamine and carbon disulfide in the organic-phase solution. The order of the reactivity for these three tertiary amines and ammonia is: TBA > TPA > TEA > NH_3. Both the reactions using these four catalysts obey pseudo first order rate law. For these four catalysts, the conversion is increased with the increase in the hydrophobic property, the steric hindrance and the size of the alkyl group. The influence of these three factors on the conversion is not signification at higher temperature, i.e. a larger conversion is obtained when a more hydrophobic tertiary amine acts as the catalyst and also correspond to the boiling point of tertiary amine.

(b) Effects of the amount of tertiary amines and ammonia

The effects of the amount of tertiary amines including TEA, TPA TBA and NH_3, on the conversion of *o*-phenylene diamine are shown in Figures 2-5. They all follow pseudo first order rate law in using these four catalysts at various amounts. As shown in Figure 2, the conversion of *o*-phenylene diamine is increased with the increase in the amount of TEA. Similar results, as shown in Figures 3-5, were obtained for using TPA, TBA and NH_3, respectively. The dependence of the apparent rate constants (k_{app}) of the reaction on the concentrations of tertiary amine and ammonia are shown in Table 1. In the absence of alkali compounds, the reaction rate is low. However, the reaction is dramatically accelerated by adding a small amount of tertiary amines or ammonia.

(c) Effect of agitation speed

Figure 6 shows the effect of the agitation speed on the conversion of *o*-phenylene diamine. The conversion is increased with the increase in the agitation speed. However, this change in conversion due to the variation of agitation speed is not significant. In general, this small deviation of conversion due to the change of agitation speed can be attributed to the rapid dissolving rate of carbon disulfide and the rapid mass transfer of species in the liquid-phase solution. The liquid solution is homogeneous. Once the compound CS_2 is dissolved in the organic solution, the mass transfer resistance of the species in the homogeneous solution is small. Therefore, the resistance of the dissolving rate of carbon disulfide in the organic solvent relative to the resistance of the reaction rate is small. This confirms the argument for fast dissolving and mass transfer of CS_2 in EtOH/H_2O solution. The dependence of the apparent rate constant (k_{app}) on the agitation speed is also depicted in Table 1. As expected, the deviation in k_{app}-value due to the variation of agitation speed from 0 to 1000 rpm is also small.

(d) Effect of the concentration of carbon disulfide

In this work, CH_2Cl_2 (inert) is used as the carrier to bring the gas-phase carbon disulfide to the liquid-phase reaction solution. It also acts as the diluter for carbon disulfide. In principle, CH_2Cl_2 and CS_2 can be recovered from the semi-continuous reactor. The concentration of carbon disulfide is first set by mixing the appropriate amount ratio of CS_2 and CH_2Cl_2 of liquid phases. The liquid mixture is then heated to vapor phase via a heater. The flow rate of feeding CS_2/CH_2Cl_2 gas is controlled by the feed pump. Figure 7 shows the effect of the concentration of CS_2 on the conversion of *o*-phenylene diamine. As expected, the conversion is increased with the increase in the concentration of CS_2. As stated above, carbon disulfide is first dissolved in EtOH/H_2O solution and then reacts with tertiary amine to produce an active intermediate ($R_3N\text{-}CS_2$) in the homogeneous organic solution. Therefore, high concentration of $R_3N\text{-}CS_2$ is obtained when a higher concentration of CS_2/CH_2Cl_2 is introduced to the reaction solution. This is why the conversion of *o*-phenylene diamine is increased using a larger concentration of CS_2/CH_2Cl_2. The effect of the concentration of CS_2 on the apparent rate constant k_{app} is also shown in Table 1. As expected, the conversion is increased with the increase in the concentration of carbon disulfide.

(e) Effect of the gas flow rate

The gas flow rate of CS_2/CH_2Cl_2 also influences the conversion of *o*-phenylene diamine in the semi-continuous reactor, and as stated, the gas flow rate is controlled by the feed pump. The effect of the gas flow rate on CS_2/CH_2Cl_2 on the conversion of *o*-phenylene diamine is shown in Figure 8 which indicates that the conversion is decreased with the increase in the flow rate. A larger flow rate promotes the amount of carbon disulfide escape to the vapor phase from liquid solution. Thus, the production of active intermediate (CS_2-R_3N) is small Hence, the conversion of *o*-phenylene diamine (or the reaction rate) is enhanced by a higher flow rate of carbon disulfide. The dependence of the apparent rate constant k_{app} on the gas flow rate is shown in Table 1. Naturally, the apparent rate constant k_{app} is decreased with the increase in the flow rate.

(f) Effect of the amount of *o*-phenylene diamine

The effect of the amount of *o*-phenylene diamine on the conversion of *o*-phenylene diamine is shown in Figure 9. The conversion is decreased with the increase in the concentration of *o*-phenylene diamine. This result is the same as that obtained from the liquid-liquid two-phase reaction. This phenomenon is probably due to the fact that the reaction system contains more than one basic reaction. The reason that this occurs is accounted as follows:

$$R_3N + CS_2 \longrightarrow R_3N - CS_2$$

$$C_6H_4(NH_2)_2 + R_3N - CS_2 \longrightarrow C_6H_4(NH_2)_2\,CS_2 - R_3N + 2H^+$$

$$\longrightarrow C_6H_4(NH)_2C^+S^- + H_2S + R_3N$$

$$\longrightarrow C_6H_4(N)(NH)CSH + H_2S + R_3N$$

The effect of the concentration of *o*-phenylene diamine on the apparent rate constant k_{app} is also shown in Table 1, which indicates that the apparent rate constant k_{app} is decreased with the increase in the concentration of *o*-phenylene diamine.

(g) Effect of the temperature

Effect of temperature on the conversion of *o*-phenylene diamine is shown in Figure 10. As expected, the conversion is increased with increased the temperature. The reaction also follows a pseudo first order rate law. The activated energy for the reaction of *o*-phenylene diamine and carbon disulfide catalyzed by tributylamine (TBA) in a gas-liquid two-phase medium is 25.64 Kcal/mol according to Arrhenius plot.

The apparent rate constant k_{app}, which is shown in Table 1, is increased with the increase in temperature..

CONCLUSION

In this work, the reaction of *o*-phenylene diamine and carbon disulfide in synthesis of 2-mercaptobenzimidazole (MBI) is successfully carried out in a semi-continuous reactor. A gas stream of CS_2/CH_2Cl_2 mixture is continuously fed to the reactor to prepare for reaction with *o*-phenylene diamine in the liquid phase solution. By feeding the gas-phase carbon disulfide, the reaction can be carried out at a higher temperature to enhance the reaction. The present process provides the feasible conditions to carry out the reaction at higher temperature. The experimental results show that the reaction follows the pseudo first order rate law from which the apparent rate constants k_{app} at various reaction conditions were obtained. Tributylamine (TBA) exhibits higher reactivity among the tertiary amine and ammonia. The dissolving rate of CS_2 in organic solvent and the mass transfer rate in the organic-phase solution are both larger. Therefore, the effect of agitation speed on the conversion of *o*-phenylene diamine is insignificant. The conversion of *o*-phenylene diamine is increased with the increase in the concentration of tertiary amine, temperature and concentration of carbon disulfide. However, the conversion is decreased with the increase in the flow rate of CS_2/CH_2Cl_2 and the concentration of *o*-phenylene diamine.

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Table 1 Effects of the reaction conditions on the apparent rate constants k_{app} (min^{-1}); 0.01 M, 0.6747 g of $C_6H_4(NH_2)_2$, volume ratio of $EtOH/H_2O=1/1$ (100 ml), 1.43 ml/min of gas flow rate, 15 ml/100 ml of CS_2/CH_2Cl_2

NH_3, M	blank	0.010	0.020	0.030	0.036	----	
k_{app}x10^3	0.63	5.48	10.00	14.64	21.67	----	
TEA, M	blank	0.005	0.010	0.013	0.015	0.020	
k_{app}x10^3	0.63	3.93	9.41	12.97	16.43	24.52	
TPA, M	blank	0.005	0.008	0.010	0.015	0.018	
k_{app}x10^3	0.63	4.13	6.13	10.13	16.50	22.00	
TBA, M	blank	0.005	0.008	0.010	0.015	0.018	
k_{app}x10^3	0.63	5.00	7.98	10.83	19.52	25.83	
Stirring speed, rpm	0	200	400	600	700	800	1000
k_{app}x10^3	9.11	9.56	10.44	10.81	10.83	10.98	10.78
[CS_2], ml	3	6	9	12	15	20	
k_{app}x10^3	6.67	9.05	9.41	9.88	10.83	11.67	
Gas flow rate, ml/min	0.98	1.43	2.27	2.91	3.43	----	
k_{app}x10^3	12.50	10.83	8.69	6.43	5.83	----	
[$C_6H_4(NH_2)_2$], g	0.200	0.400	0.675	0.800	1.000	1.200	
k_{app}x10^3	25.78	15.00	10.83	6.56	5.67	4.22	
Temperature, ℃	50	55	60	65			
k_{app}x10^3	2.56	4.15	10.83	13.30			

CAPTION OF FIGURES

Figure 1 Effect of tertiary amines and ammonia on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 0.010 M of tertiary amines or ammonia, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate=1.43 mL/min, CS_2/CH_2Cl_2=15 mL/100 mL, 700 rpm, 60℃

Figure 2 Effect of the amount of TEA on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate=1.43 mL/min, CS_2/CH_2Cl_2=15 mL/100 mL, 700 rpm, 60℃

Figure 3 Effect of the amount of TPA on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate=1.43 mL/min, CS_2/CH_2Cl_2=15 mL/100 mL, 700 rpm, 60℃

Figure 4 Effect of the amount of TBA on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate=1.43 mL/min, CS_2/CH_2Cl_2=15 mL/100 mL, 700 rpm, 60℃

Figure 5 Effect of the amount of NH_3 on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate=1.43 mL/min, CS_2/CH_2Cl_2=15 mL/100 mL, 700 rpm, 60℃

Figure 6 Effect of the agitation speed on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 0.010 M of TBA, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate=1.43 mL/min, CS_2/CH_2Cl_2=15 mL/100 mL, 60℃

Figure 7 Effect of the amount of the concentration of CS_2 on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 0.010 M of TBA, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate=1.43 mL/min, CS_2/CH_2Cl_2= y mL/100 mL, 700 rpm, 60℃

Figure 8 Effect of the amount of the gas flow rate on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 0.010 M of TBA, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate= y mL/min, CS_2/CH_2Cl_2= 15 mL/100 mL, 700 rpm, 60℃

Figure 9 Effect of the amount of the o-phenylene diamine on the conversion of *o*-phenylene diamine; 0.010 M of TBA, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate= 1.43mL/min, CS_2/CH_2Cl_2= 15 mL/100 mL, 700 rpm, 60℃

Figure 10 Effect of the temperature on the conversion of *o*-phenylene diamine; 0.6747 g of $C_6H_4(NH_2)_2$, 0.010 M of TBA, 100 mL of solution (volume ratio=1/1 of EtOH and water), Flow rate= 1.43 mL/min, CS_2/CH_2Cl_2= 15 mL/100 mL, 700 rpm

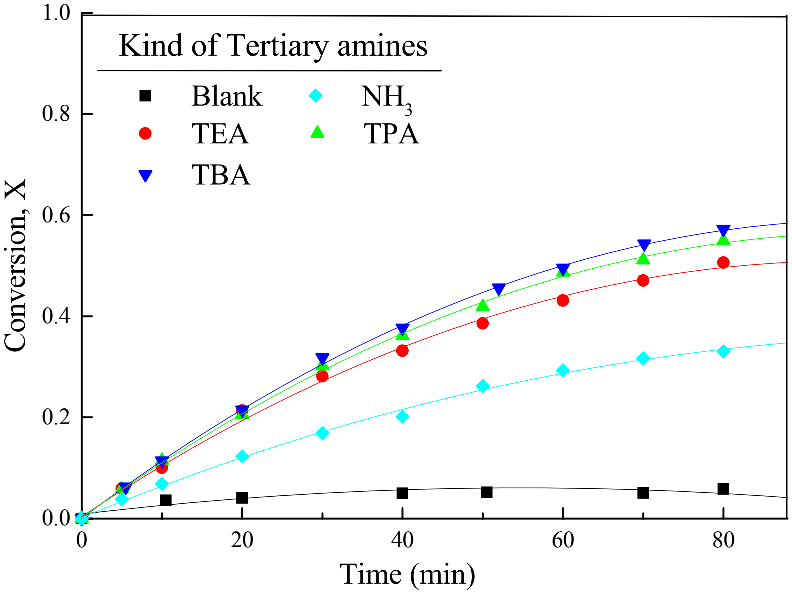
Kind of Tertiary amines
■ Blank
◆ NH_3
● TEA
▲ TPA
▼ TBA
Conversion, X
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Time (min)

Fig 1

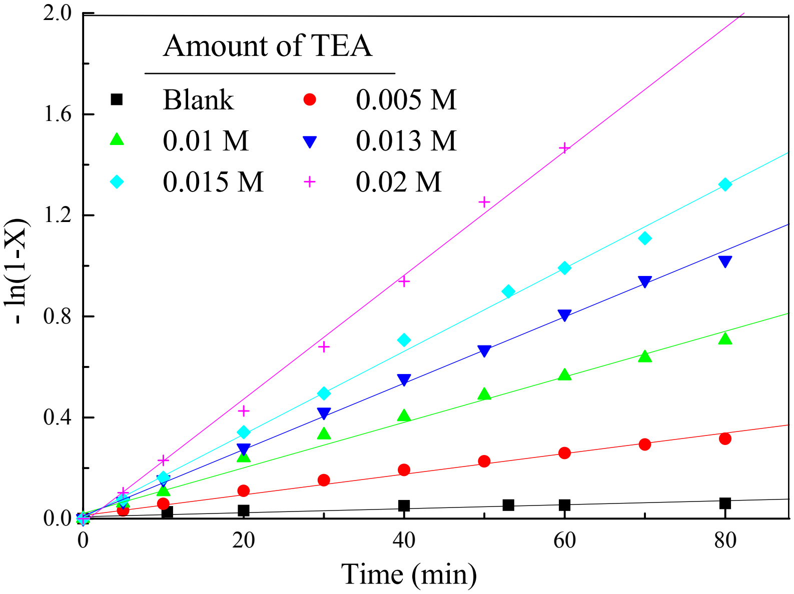
Amount of TEA
■ Blank
● 0.005 M
▲ 0.01 M
▼ 0.013 M
◆ 0.015 M
+ 0.02 M
- ln(1-X)
2.0
1.6
1.2
0.8
0.4
0.0
0
20
40
60
80
Time (min)

Fig 2

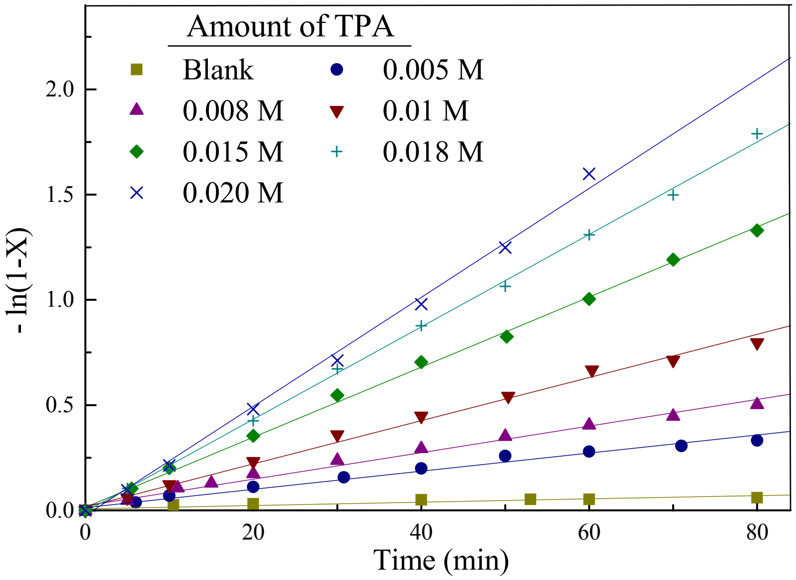
Amount of TPA
■ Blank
● 0.005 M
▲ 0.008 M
▼ 0.01 M
◆ 0.015 M
+ 0.018 M
× 0.020 M
- ln(1-X)
0.0
0.5
1.0
1.5
2.0
0
20
40
60
80
Time (min)

Fig 3

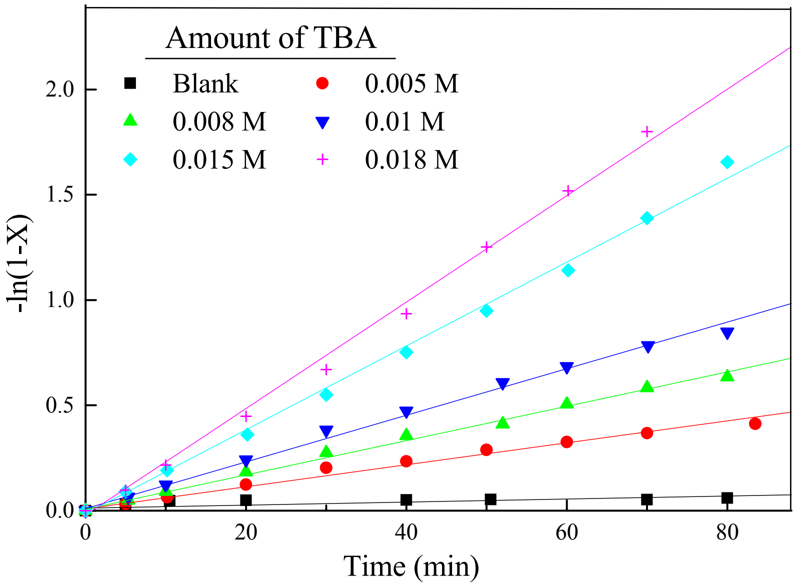
Amount of TBA
■ Blank
● 0.005 M
▲ 0.008 M
▼ 0.01 M
◆ 0.015 M
+ 0.018 M
-ln(1-X)
0.0
0.5
1.0
1.5
2.0
0
20
40
60
80
Time (min)

Fig 4

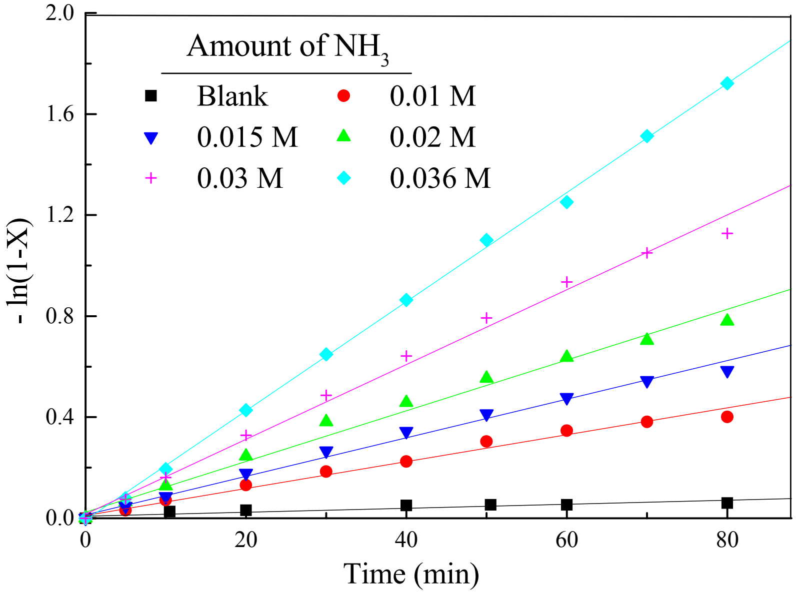
Amount of NH$_3$
Blank
0.01 M
0.015 M
0.02 M
0.03 M
0.036 M
- ln(1-X)
2.0
1.6
1.2
0.8
0.4
0.0
0
20
40
60
80
Time (min)

Fig 5

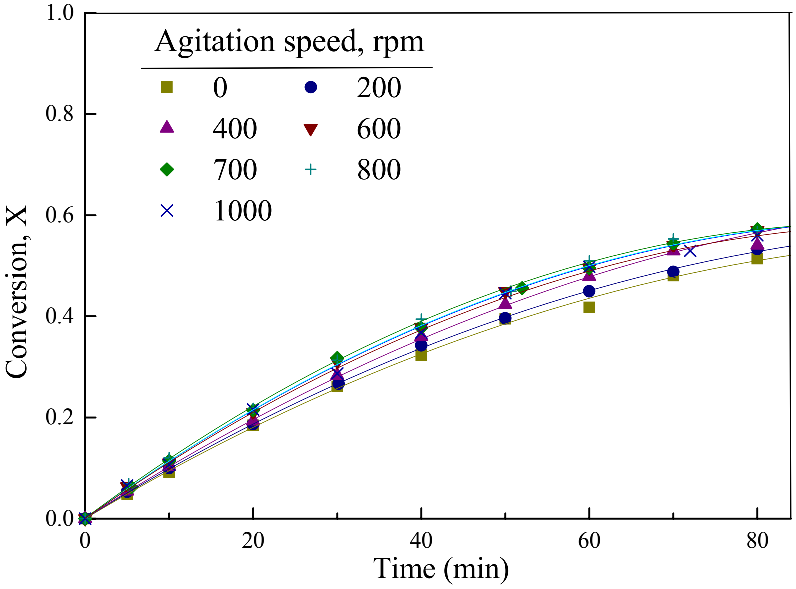
Agitation speed, rpm
0
200
400
600
700
800
1000
Conversion, X
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Time (min)

Fig 6

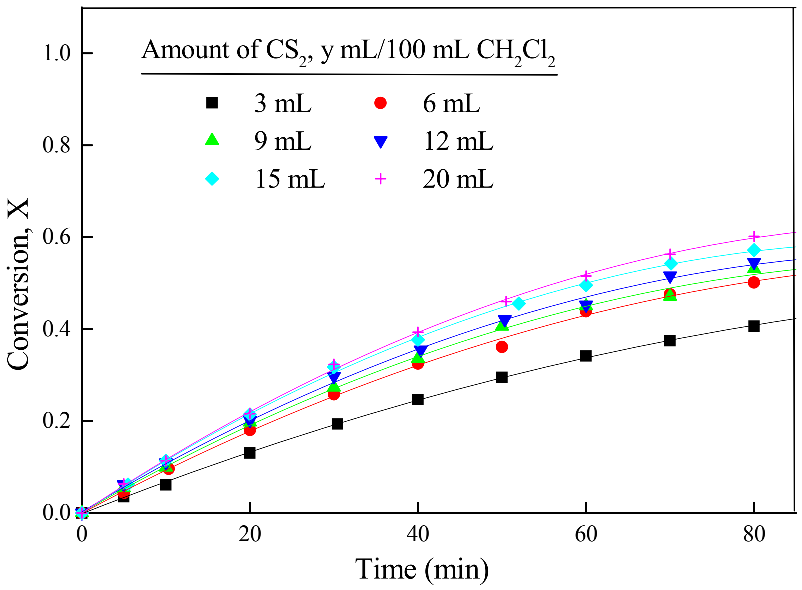
Amount of CS$_2$, y mL/100 mL CH$_2$Cl$_2$
■ 3 mL
● 6 mL
▲ 9 mL
▼ 12 mL
◆ 15 mL
+ 20 mL
Conversion, X
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Time (min)

Fig 7

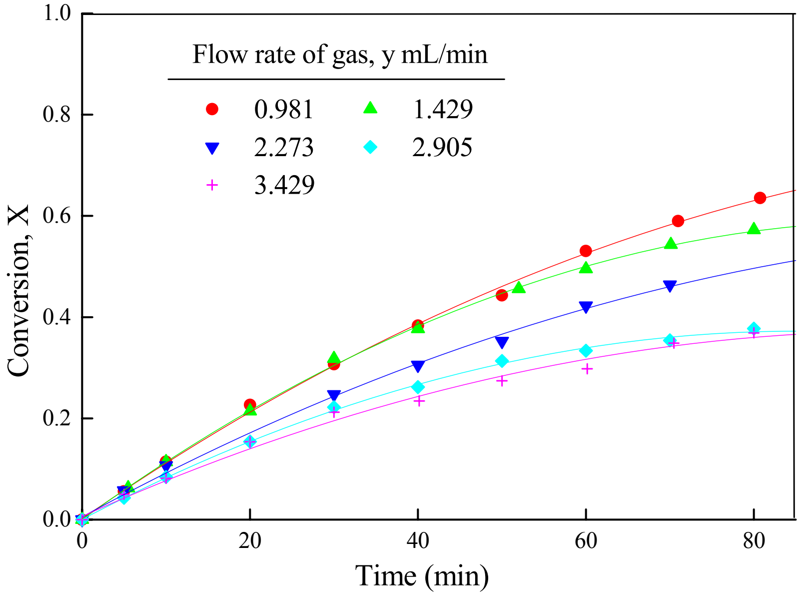
Flow rate of gas, y mL/min
● 0.981
▲ 1.429
▼ 2.273
◆ 2.905
+ 3.429
Conversion, X
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Time (min)

Fig 8

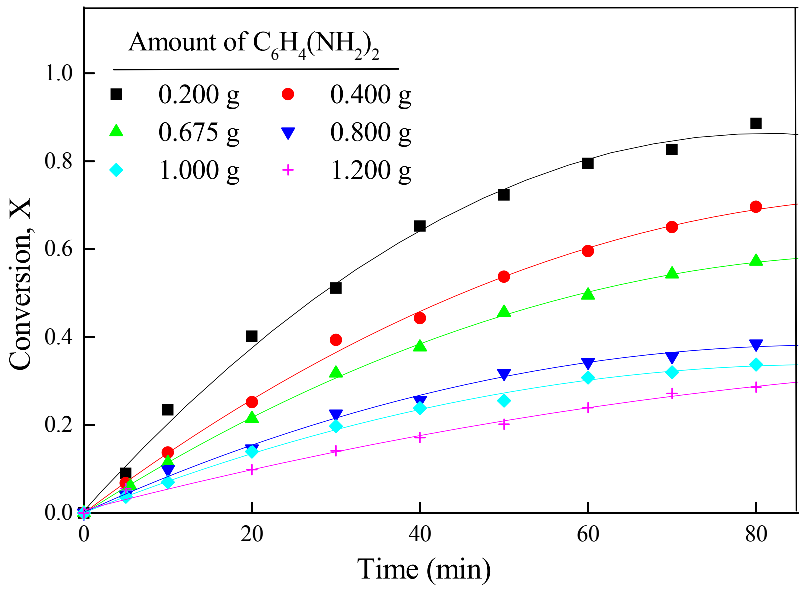
Amount of $C_6H_4(NH_2)_2$
■ 0.200 g
● 0.400 g
▲ 0.675 g
▼ 0.800 g
◆ 1.000 g
+ 1.200 g
Conversion, X
0.0
0.2
0.4
0.6
0.8
1.0
0
20
40
60
80
Time (min)

Fig 9

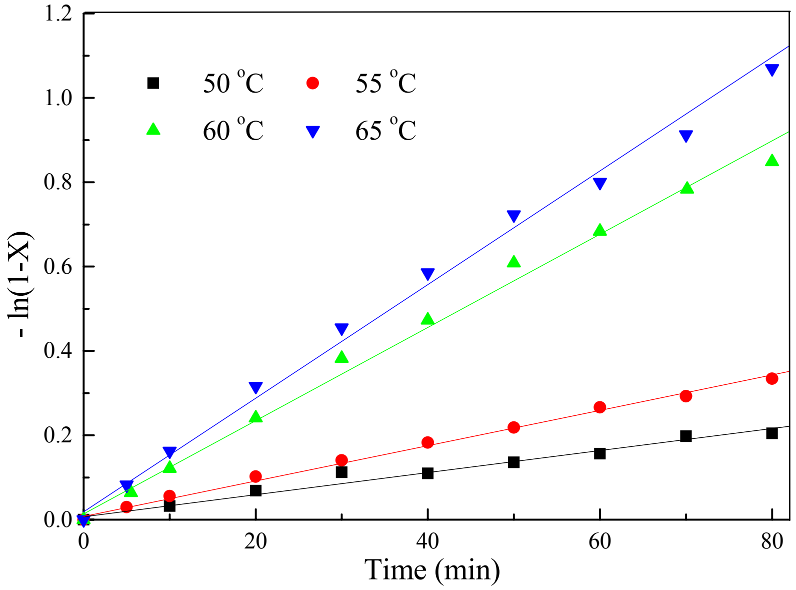
■ 50 °C
● 55 °C
▲ 60 °C
▼ 65 °C
- ln(1-X)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
20
40
60
80
Time (min)

Fig 10