Catalyzed reaction of carbon disulfide and *o*-phenylene diamine by tertiary amine

Maw-Ling Wang [*], Biing-Lang Liu

Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 30043, Taiwan, ROC

Abstract

The reaction of carbon disulfide and *o*-phenylene diamine in a two-phase solution to synthesize 2-mercaptobenzimidazole (MBI) catalyzed by the inexpensive tertiary amine was carried out. The reaction, which is accelerated by adding a small amount of tertiary amine, occurs in the organic phase. The mechanism was identified by two steps. First, the reaction of carbon disulfide and tertiary amine takes place to produce an active intermediate (R_3N-CS_2) within a short time of reaction. Then, this active intermediate further reacts with *o*-phenylene diamine to produce MBI. A kinetic model based on the proposed mechanism was built up. The advantage of using two-phase reaction is that the product precipitates from the reaction solution. Only mechanical separation processes, such as: filtration and centrifugation, are required to remove the product from the solution. A pseudo-first-order rate law is sufficiently to describe the reaction. Factors, which affect the conversion of *o*-phenylene diamine and the reaction rate, were investigated in detail.

Keywords: 2-Mercaptobenzimidazole (MBI); Tertiary amine; Kinetics; Mechanism

1. Introduction

The fundamental requirement for a reaction of two molecules to occur is collision. Conversion is low from two immiscible reactants due to their low solubilities and limited contact surface area. The conventional methods to overcome such problems is to carry out the reaction in a high agitation speed, at a high temperature, or utilizing a solvent or cosolvent which exhibited both lipophilic and hydrophilic properties. However, more energy is consumed at high temperature. In addition, byproducts were frequently produced from side reactions at high temperature. In using cosolvent to dissolve both reactants, the reactivity of the nucleophilic reagent is decreased for the solvation and hydrogen bonding with the protic solvent. Hence, the reaction rate is low. The solvation of aprotic solvent and nucleophilic reagent is minimized when the reactions were carried out in an anhydrous condition using expensive aprotic solvent. Nevertheless, the high boiling-point aprotic solvent is difficult to recover. Therefore, this improvement in the reaction of two immiscible reactants is still limited [1].

The problems of the reactions of two immiscible reactants were not solved until the development of phase transfer catalysis [2–7]. It has been considered to be one of the most effective

[*] Corresponding author.

tools in synthesizing organic chemicals through alkylation, arylation, condensation, elimination, reduction and oxidation, and polymerization as well as the simple displacement.

2-Mercaptobenzimidazole (MBI) is an important specialty chemical and is extensively used as inhibitor, antioxidant, antiseptic and adsorbent [8–11] in industries. It was synthesized from the reaction of *o*-phenylene diamine and reactants in a homogeneous solution using the expensive quaternary ammonium hydroxide as the catalyst [12–15]. The removal of catalyst and reactants from MBI product in the homogeneous solution required chemical equilibrium separation processes. The primary objective of this work is to improve the synthetic process for producing MBI by carrying out the reaction of *o*-phenylene diamine and carbon disulfide in a two-phase medium by appropriating choice of organic solvent. The inexpensive tertiary amine was used as the catalyst. The key point to be studied lies in investigating the reaction mechanism and kinetics of the reaction. Dichloromethane, benzene, n-hexane, chlorobenzene and decane were employed as the organic solvents. The most advantage of this process is that the MBI product precipitates from the two-phase solution. The product is purified and removed from the solution only by simple mechanical separation processes, such as: centrifugation and filtration. The effects of the operating conditions on the rate of reaction and conversion were examined.

2. Experimental section

2.1. Materials

Carbon disulfide (CS_2), *o*-phenylene diamine $(C_6H_4(NH_2)_2)$, tertiary amines including TEA (or Et_3N, $(C_2H_5)_3N$), TPA (or Pr_3N, $(C_3H_7)_3N$) and TBA (or Bu_3N, $(C_4H_9)_3N$), DMAP(dimethylaminopyridine), and other reagents are all G.R. grade chemicals for synthesis.

2.2. Procedures

2.2.1. Kinetics of the reaction of carbon disulfide and tributylamine

Tributylamine (Bu_3N) (3.5 ml, 0.1 M in CH_2Cl_2) was put in a UV cell which was submerged into a constant temperature water bath to reach a thermo-equilibrium state. Next, carbon disulfide (1 μl, 4.7×10^{-3} M in CH_2Cl_2) was injected to the UV cell to start the reaction. The absorbance (A_t) vs. time for a UV 364 nm wavelength was then detected. Also, the absorbance (A_∞) for ten half-life periods was also determined. A plot of $\ln[A_\infty/(A_\infty - A_t)]$ vs. time leads to a straight line with slope k_{app}.

2.2.2. Kinetics of synthesizing 2-mercapto-benzimidazole (MBI)

The reactor is a 125-ml four-necked Pyrex flask able to serve the purposes 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 carbon disulfide. The reactor is submerged into a constant temperature water bath in which the temperature can be controlled to ±0.1°C. To start an experimental run, known quantities of *o*-phenylene diamine, carbon disulfide, (caffeine, external standard), and tertiary amine were dissolved in a mixture of organic solvent/water and introduced into the reactor. The mixture was stirred mechanically by a two-blade paddle (5.5 cm) at 1,000 rpm. During the reaction, an aliquot sample of 0.2 ml was withdrawn from the solution at a chosen time. The sample was immediately introduced into the same organic solvent at 4°C for dilution and retarding the reaction, and then analyzed by HPLC.

The product 2-mercaptobenzimidazole (MBI) for identification was purified from the solution of reaction of *o*-phenylene diamine and carbon disulfide without containing tertiary amine by vacuum evaporation to strip off organic solvent and carbon disulfide. Then, it was dissolved into ethanol prepared for recrystallization. A white

crystal form of MBI, which was insoluble in EtOH, was obtained by cooling the solution.

The product (MBI) and the reactants (carbon disulfide and o-phenylene diamine) were identified by NMR and IR. The content of MBI and reactants were analyzed by HPLC instrument. The results obtained from NMR and IR are very consistent with the published data. An HPLC model LC9A (Shimadzu) with an absorbance detector (254 nm, SPD-6A) was employed to measure the contents 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 5 mM $KH_2PO_4 + 0.1\%$ H_3PO_4) (volume ratio) with a flow rate 1.0 ml/min.

3. Kinetic model of the reaction

3.1. Kinetics of the reaction of CS_2 and Bu_3N

In this work, carbon disulfide is a limited reactant. Tributylamine was used in a large excess amount. The reason is that the absorbance of CS_2 is much greater than that of Bu_3N. The reaction of CS_2 and Bu_3N (R_3N) reaches an equilibrium state after 10 minutes or more, i.e.,

$$R_3N + CS_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3N\text{--}CS_2 \tag{R1}$$
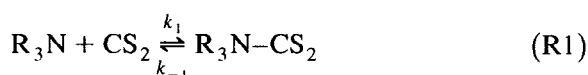
where k_1 and k_{-1} are the intrinsic rate constants of the forward and backward reactions (R1), respectively. The reaction was considered as a simple forward reaction at early time (e.g. four minutes), i.e.,
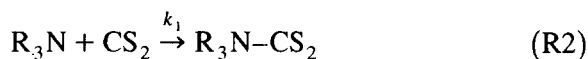
$$R_3N + CS_2 \overset{k_1}{\rightarrow} R_3N\text{--}CS_2 \tag{R2}$$

The rate of reaction (R2) was expressed as

$$\frac{-d[CS_2]}{dt} = k_1[R_3N][CS_2] \tag{1}$$

For a constant concentration of R_3N, the above equation is integrated,

$$\ln\left(\frac{[CS_2]}{[CS_2]_i}\right) = -k_{app}t \tag{2}$$

where

$$k_{app} = k_1[R_3N] \tag{3}$$

The subscript 'i' represents the species at initial condition. Since no other byproducts were produced, Eq. 2 was rewritten as

$$\ln\left(\frac{[CS_2]_i}{[CS_2]_i - [R_3N\text{--}CS_2]}\right) = k_{app}t \tag{4}$$

Applying Beer's law, the concentration of $R_3N\text{--}CS_2$ was expressed by UV absorbance A_t, i.e.,

$$\ln\left(\frac{A_\infty}{A_\infty - A_t}\right) = k_{app}t \tag{5}$$

A plot of $\ln[A_\infty/(A_\infty - A_t)]$ vs. time gives a straight line with slope k_{app}.

3.2. Kinetics of synthesizing 2-mercaptobenzimidazole (MBI)

The overall reaction in the two-phase medium is expressed as depicted in Scheme 1.

From the experimental observation, carbon disulfide does not dissolve in aqueous phase even in the presence of tertiary amine. The reaction of CS_2 and C_6H_4 $(NH_2)_2$ to produce MBI takes place only in the organic phase. However, o-phenylene diamine dissolves both in aqueous and organic phases. o-Phenylene diamine, which reacts with CS_2 in the organic phase, is supplied from the aqueous phase. One of the advantages in using two-phase medium is that the conversion in the organic phase is increased at a low concentration of o-phenylene diamine. The concentration of o-phenylene diamine in the organic phase is adjusted by the distribution of o-phenylene diamine between two phases.

In the organic-phase reaction of synthesizing MBI, it is believed that CS_2 first reacts with tertiary amine (R_3N) to form an active intermediate ($R_3N\text{--}CS_2$). This active intermediate fur-

$$C_6H_4(NH_2)_2 + CS_2 \xrightarrow{R_3N} \text{[structure]} C\text{-SH} + H_2S \qquad (R3)$$
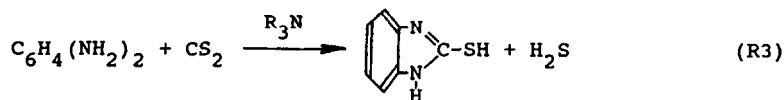
Scheme 1.

ther reacts with o-phenylene diamine to produce the desired product in the organic phase, as depicted in Scheme 2. Reaction (R4) is very fast and reaches an equilibrium state within 10 min. Reaction (R5) is slow relative to reaction (R4) and is obviously a rate-determining step.

The rates of reactions (R4) and (R5) are expressed as

$$r_1 = k_1[CS_2][R_3N] - k_{-1}[R_3N\text{-}CS_2] \qquad (6)$$

$$r_2 = k_2[R_3N\text{-}CS_2][C_6H_4(NH_2)_2] \qquad (7)$$

Assuming that a pseudo-steady-state hypothesis is applied for the intermediate $R_3N\text{-}CS_2$, i.e.,

$$\frac{d[R_3N\text{-}CS_2]}{dt} = 0 \qquad (8)$$

No byproducts were obtained during or after reaction. Therefore, the consumption rate of $R_3N\text{-}CS_2$ in (R5) equals to the production rate of $R_3N\text{-}CS_2$ in (R4), i.e.,

$$k_1[CS_2][R_3N] - k_{-1}[R_3N\text{-}CS_2]$$
$$= k_2[R_3N\text{-}CS_2][C_6H_4(NH_2)_2] \qquad (9)$$

Rearranging Eq. 9, we obtain

$$[R_3N\text{-}CS_2] = \frac{[R_3N][CS_2]}{(k_2/k_1)[C_6H_4(NH_2)_2] + K} \qquad (10)$$

in which K is the equilibrium constant,

$$K = k_{-1}/k_1 \qquad (11)$$

Substituting Eq. 10 into Eq. 7, we have

$$r_2 = \frac{k_2[C_6H_4(NH_2)_2][CS_2][R_3N]}{(k_2/k_1)[C_6H_4(NH_2)_2] + K} \qquad (12)$$

For the case of $k_{-1}[R_3N\text{-}CS_2] \gg k_2[R_3N\text{-}CS_2][C_6H_4(NH_2)_2]$ or

$$(k_{-1}/k_1) = K \gg (k_2/k_1)[C_6H_4(NH_2)_2] \qquad (13)$$

Eq. 12 is rewritten as

$$r_2 = (k_2/K)[CS_2][R_3N][C_6H_4(NH_2)_2] \qquad (14)$$

In this work, carbon disulfide was usually used in a large excess amount relative to its stoichiometric quantity. Also, the concentration of R_3N remains constant. Therefore, Eq. 14 is written as

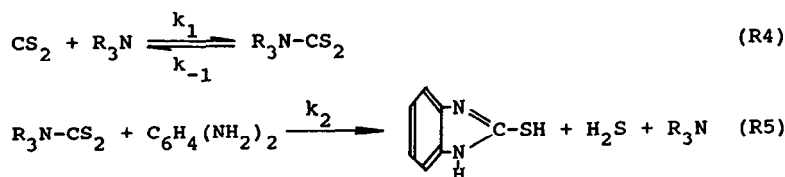$$r_2 = -\frac{d[C_6H_4(NH_2)_2]}{dt} = k'_{app}[C_6H_4(NH_2)_2] \qquad (15)$$

in which

$$k'_{app} = (k_2/K)[CS_2][R_3N] \qquad (16)$$

As indicated by Eq. 15, the reaction can be expressed by a pseudo-first-order rate law,

$$-\ln(1 - X) = k'_{app}t \qquad (17)$$

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

$$X = 1 - ([C_6H_4(NH_2)_2]/[C_6H_4(NH_2)_2]_i) \qquad (18)$$

$$CS_2 + R_3N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3N\text{-}CS_2 \qquad (R4)$$

$$R_3N\text{-}CS_2 + C_6H_4(NH_2)_2 \xrightarrow{k_2} \text{[structure]} C\text{-SH} + H_2S + R_3N \qquad (R5)$$

Scheme 2.

A plot of $-\ln(1-X)$ vs. time gives a straight line with slope k'_{app}. We confirmed that no byproducts were produced during or after reaction.

At a higher $[C_6H_4(NH_2)_2]$, $k_2[C_6H_4(NH_2)_2][R_3N-CS_2]$ plays an important role in the expression of kinetics. Its value is probably higher than that of $k_{-1}[R_3N-CS_2]$. Thus, Eq. 12 attains zeroth order kinetics with respect to $[C_6H_4(NH_2)_2]$, i.e.,

$$r_2 = k_1[CS_2][R_3N] \qquad (19)$$

For a constant concentration of CS_2 and R_3N, Eq. 19 is written as

$$r_2 = -\frac{d[C_6H_4(NH_2)_2]}{dt} = k''_{app} \qquad (20)$$

where

$$k''_{app} = k_1[CS_2][R_3N]/[C_6H_4(NH_2)_2]_i \qquad (21)$$

The reaction is expressed by a zeroth-order rate law,

$$X = k''_{app}t \qquad (22)$$

where X is given in Eq. 18.

In general, Eq. 12 can be integrated to obtain the conversion X of o-phenylene diamine, i.e.,

$$\frac{-d[C_6H_4(NH_2)_2]}{dt}$$
$$= \frac{k_2[C_6H_4(NH_2)_2][CS_2][R_3N]}{(k_2/k_1)[C_6H_4(NH_2)_2] + K} \qquad (23)$$

Integration of Eq. 23 and then appropriate rearrangement, gives the expression in terms of the conversion of o-phenylene diamine X,

$$-(k_2/k_1)X + \frac{K}{[C_6H_4(NH_2)_2]_i}\ln(1-X)$$
$$= -\frac{k_2[R_3N][CS_2]}{[C_6H_4(NH_2)_2]_i}t \qquad (24)$$

The two terms in the left hand side of Eq. 24 represent the characteristics of zeroth-order and first-order rates kinetics, respectively.

Since k_1 is obtained from the reaction of CS_2 and R_3N, Eq. 24 can be rewritten in terms of one parameter (k_{-1}/k_2), i.e.,

$$\frac{[C_6H_4(NH_2)_2]_i}{k_1[R_3N][CS_2]}X - \frac{(k_{-1}/k_2)}{k_1[R_3N][CS_2]}\ln(1-X)$$
$$= t \qquad (25)$$

The value of (k_{-1}/k_2) is then calculated based on the experimental data in conjunction with the technique of parameter estimation.

4. Results and discussion

4.1. Kinetics of the reaction of carbon disulfide and tertiary amines

Jensen and Nielsen [16] carried out the reaction of carbon disulfide and tertiary phosphine to produce a complex intermediate (R_3P-CS_2) in a reddish color. In the later, Fernando and Santos [17] studied the effects of the organic solvents on the reaction of R_3P and CS_2. The rate constants of the reaction of $(C_2H_5)_3P$ and CS_2 were measured by UV [18]. For obtained, because the product R_3P-CS_2 possesses a strong bond between these two reactant molecules. Thus, carrying out the backward reaction in reaction (R4) is relatively easy.

In this work, the active intermediate R_3N-CS_2 can not be isolated and purified from solution because of weak bond between these two reactant molecules. The intrinsic rate constant of reaction (R5) was not determined from the conventional way in this work. The reaction of CS_2 and $C_6H_4(NH_2)_2$ is very slow without adding tertiary amine and would be dramatically enhanced by adding a small amount of tertiary amine. The UV absorbance of CS_2 and R_3N solution is increased during the reaction when the mixed solution was scanned by a UV instrument. Also, an orange color, which indicates the product obtained from the reaction of CS_2 and R_3N, appeared in the solution.
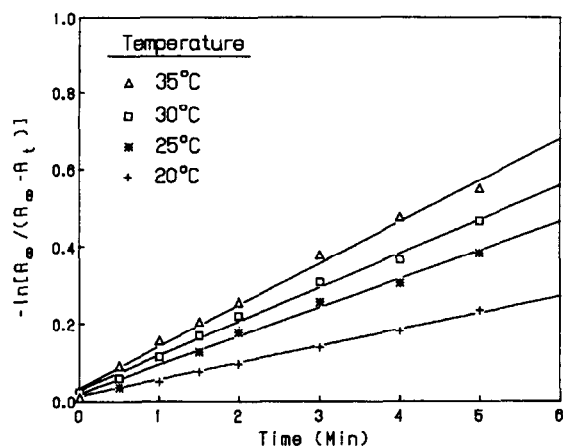
Fig. 1. Reaction of carbon disulfide and tributylamine in a CH_2Cl_2 solvent at various temperatures; $[(C_4H_9)_3N]_i = 0.1$ M, $[CS_2]_i = 4.74 \times 10^{-3}$ M, $\lambda = 364$ nm.

An independent experiment was carried out to examine the reaction of R_3N and CS_2 in a dichloromethane solution. We believe that the forward reaction dominates the whole reaction in the initial four minutes. Therefore, the intrinsic rate constant (k_1) of the forward reaction can be obtained from the kinetic data early in the reaction. The measured absorbance through UV as time is shown in Fig. 1. A straight line with slope (k_{app}) is obtained. Using Eq. 3, the intrinsic rate constants (k_1) are 4.333×10^{-1}, 7.333×10^{-1}, 8.833×10^{-1}, 1.067 min^{-1} M^{-1} at 20, 25, 30 and 35°C, respectively. The activation energy was expressed in terms of Arrhenius equation, i.e.,

$$k_{app} = 2.631 \times 10^3 \exp(1.048 \times 10^4 / T);$$
$$\text{in } CH_2Cl_2 \text{ solvent} \tag{26}$$

4.2. Identification of the reaction mechanism

As stated, o-phenylene diamine $(C_6H_4(NH_2)_2)$ dissolves both in aqueous and organic phases. However, carbon disulfide is insoluble in the aqueous phase. Therefore, the reaction occurs only in the organic phase. 2-Mercaptobenzimidazole (MBI), which was produced from the reaction of o-phenylene diamine

and carbon disulfide, precipitated from the two-phase solution by appropriate choice of the organic solvent. Two fundamental reactions of synthesizing MBI are given by reactions (R4) and (R5). Two experimental runs in different sequential orders of reaction procedures were tested to examine the equilibrium reaction (R4). The first procedure is to conduct the reaction of CS_2 and Bu_3N in a mixture of organic solvent/water for 2 h in advance, and $C_6H_4(NH_2)_2$ was then added to the solution for reaction. The second one is the introduction of CS_2, Bu_3N and $C_6H_4(NH_2)_2$ dissolving in a mixture of organic solvent/water simultaneously to start the reaction. No much difference for the conversion from these two experiments was obtained. The reaction of CS_2 and Bu_3N to produce the active intermediate (R_3N-CS_2) is obviously fast. The reaction of o-phenylene diamine $(C_6H_4(NH_2)_2)$ and the active intermediate (R_3N-CS_2) is obvious a rate-determining step.

Another experiment was carried out to identify the reaction of CS_2 and R_3N in this study. First, TEA dissolves into CH_2Cl_2 and water solution. After reaching an equilibrium state, CS_2 was then added to the solution. No TEA in the aqueous phase was detected. The reason is that TEA reacts with the water-insoluble CS_2 in the organic phase quickly. The content of TEA in the aqueous phase transfers to the organic phase completely.

An experiment for the equilibrium of $C_6H_4(NH_2)_2$ between CH_2Cl_2 and H_2O was also carried out in this work. It takes only 30 s for $C_6H_4(NH_2)_2$ reaching an equilibrium state between two phases. The resistance of mass transfer of o-phenylene diamine between two phases is negligible. Usually, the reaction of synthesizing MBI required more than 7 h to obtain a 80% conversion. Therefore, the reaction of Bu_3N-CS_2 and $C_6H_4(NH_2)_2$ is a rate-determining step for the reaction in synthesizing MBI. For this, $C_6H_4(NH_2)_2$, which dissolved in the aqueous phase, is counted as a source in providing the reactant in the organic phase.

The dissolution of o-phenylene diamine in CH_2Cl_2 and H_2O with the presence of tertiary amine was investigated based on the distribution coefficient (K_d), which is defined as the ratio of the concentration of $C_6H_4(NH_2)_2$ in the organic phase to the concentration of $C_6H_4(NH_2)_2$ in the aqueous phase. Tertiary amines, including TEA, TPA, TBA and DMAP, both dissolved in CH_2Cl_2 and H_2O. Nevertheless, the value of K_d is about 2.10–2.60 and is insensitive to the tertiary amines, and the volume ratio of organic phase to aqueous phase. The effects of organic solvents on the value of K_d of o-phenylene diamine in various concentrations of Bu_3N were also investigated. The order of the K_d value for these organic solvents and H_2O is: CH_2Cl_2 (2.10–2.60) > $CHCl_3$ (1.70–2.00) > C_6H_6 (0.60) > $C_6H_5CH_3$ (0.40).

The equilibrium concentrations of o-phenylene diamine in organic and aqueous phases at various temperatures were also examined. A larger value of the concentration of o-phenylene diamine in the organic phase was obtained at a higher temperature. However, this effect of temperature on the concentration of o-phenylene diamine is insignificantly.

4.3. Factors affecting the kinetics of reaction

4.3.1. Effects of the agitation speed

The effects of the agitation rate on the conversion of $C_6H_4(NH_2)_2$ were investigated for 3.70×10^{-3} moles of $C_6H_4(NH_2)_2$, 5.27×10^{-2} moles of CS_2, 1.679×10^{-3} moles (0.4 ml) of Bu_3N, $CH_2Cl_2/H_2O = 50$ ml/20 ml at 30°C. As stated previously, it takes only 30 s for o-phenylene diamine to reach an equilibrium state between two phases. No improvement in the reaction rate is observed with the agitation rate from 0–1,000 rpm. Therefore, the agitation speed was set at 1,000 rpm for studying the reaction phenomena from which the resistance of mass transfer is kept at a constant value.

4.3.2. Effect of the volume of water

o-Phenylene diamine both dissolves in water and dichloromethane. For using a fixed amount
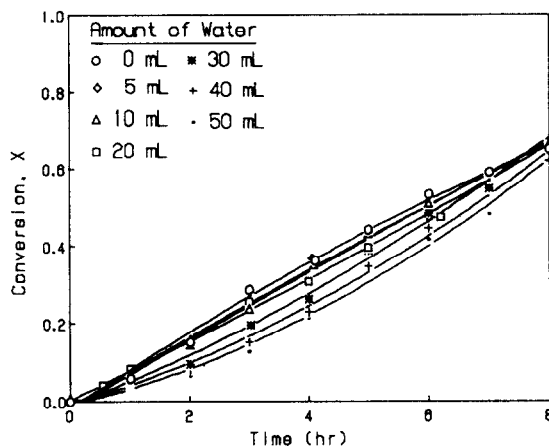

Fig. 2. Effect of the amount of water on the conversion of o-phenylene diamine in the two-phase catalyzed reaction; 3.70×10^{-3} moles of $C_6H_4(NH_2)_2$, 5.27×10^{-2} moles of CS_2, 1.679×10^{-3} moles of TBA, 50 ml of CH_2Cl_2, 1000 rpm, 30°C.

of o-phenylene diamine, the volume of water directly reflects the concentration of o-phenylene diamine in the organic phase to affect the conversion. The effect of the volume of water on the conversion is shown in Fig. 2. When the reaction was carried out in a homogeneous phase without adding water (0 ml of water), a larger conversion of o-phenylene diamine was obtained. However, the conversion is decreased when more water is added. A plot of the k'_{app} value vs. volume of water is depicted in Fig. 3. The value of k'_{app} is decreased with increase of the volume of water.
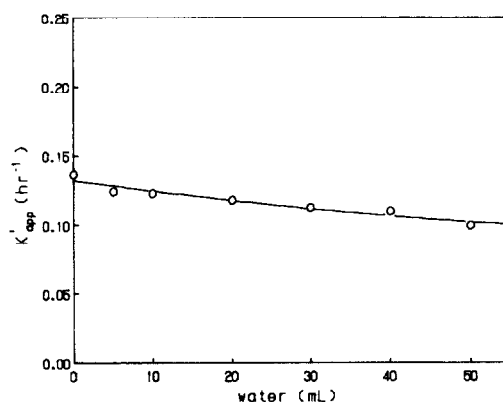

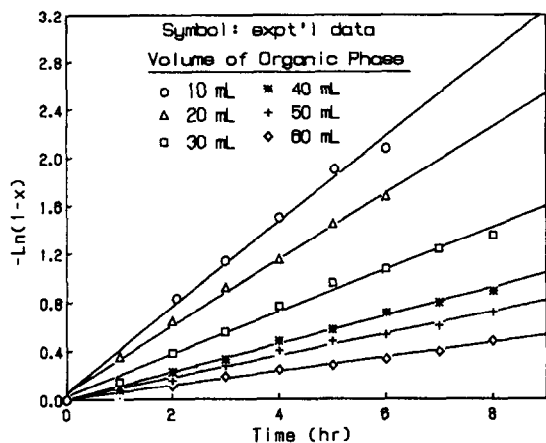Fig. 3. Effect of the amount of water on the k'_{app} value; same reaction conditions as given in Fig. 2.

Fig. 4. Effect of the volume of organic phase on the conversion of o-phenylene diamine in the two-phase catalyzed reaction; 3.17×10^{-3} moles of $C_6H_4(NH_2)_2$, 2.50×10^{-2} moles of CS_2, 1.679×10^{-3} moles of TBA, $H_2O = 50$ ml, 1000 rpm, 30°C.

Fig. 5. Effect of the volume of organic phase on the k'_{app} value; same reaction conditions as given in Fig. 4.

4.3.3. Effect of the volume of organic phase

The effects of the volume of organic phase on the conversion of o-phenylene diamine is shown in Fig. 4. In these experiments, only the volume of organic solvent was altered. The other conditions, such as, the amount of TBA and the amount of CS_2, were fixed. Therefore, the concentration of TBA and CS_2 both changed by changing the volume of organic solvent. From Fig. 4, the conversion of o-phenylene diamine is decreased with the increase of the volume of organic solvent, i.e., the conversion is increased by increasing the concentrations of TBA, CS_2 and $C_6H_4(NH_2)_2$. The results are consistent with the kinetic law. The dependence of k'_{app} on the volume of dichloromethane are shown in Fig. 5. As expected, the value of k'_{app} is decreased with increasing the volume of organic solvent.

4.3.4. Effect of the concentration of R_3N

In general, the reaction rate is low when no catalyst is added. The consumption of C_6H_4 $(NH_2)_2$ is less than 1% after 4 h of reaction time without adding TBA. In Fig. 6, the conversion of $C_6H_4(NH_2)_2$ is highly dependent on the amount of TBA added. The reaction is enhanced by adding more TBA catalyst. Several
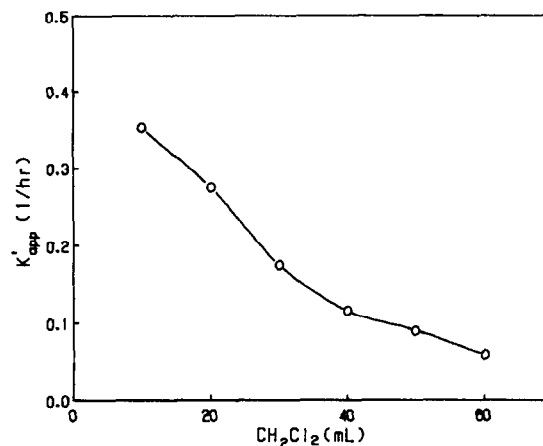
tertiary amines, such as TEA, TPA, TBA and DMAP were employed as the catalysts in the two-phase reactions. The effects of these tertiary amines on the conversion of o-phenylene diamine are shown in Fig. 7. The order of the reactivity for these catalysts is DMAP > TEA > TBA > TPA.

4.3.5. Effect of the organic solvent

Several organic compounds, such as: n-decane, n-hexane, benzene, chlorobenzene and dichloromethane, which are immiscible in wa-
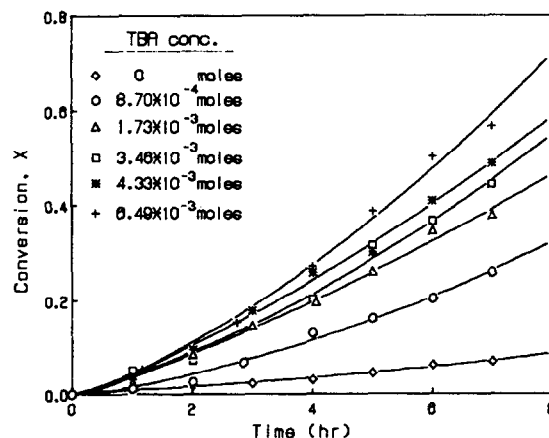

Fig. 6. Effect of the concentration of TBA on the conversion of o-phenylene diamine in the two-phase catalyzed reaction; 4.624×10^{-3} moles of $C_6H_4(NH_2)_2$, 4.16×10^{-2} moles of CS_2, $CH_2Cl_2 / H_2O = 80$ ml/20 ml, 1000 rpm, 30°C.
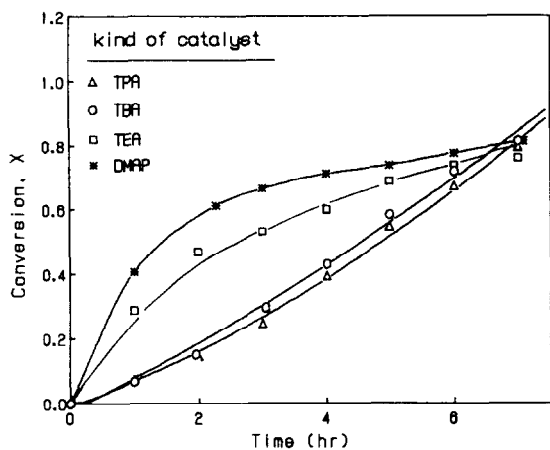
Fig. 7. Effect of catalysts on the conversion of o-phenylene diamine in the two-phase catalyzed reaction; 3.70×10^{-3} moles of o-phenylene diamine, 2.70×10^{-2} moles of CS_2, 25 ml of CH_2Cl_2, 25 ml of H_2O, 1000 rpm, 2.93×10^{-3} moles of catalyst, 30°C.

Fig. 9. Effect of the concentration of CS_2 on the conversion of o-phenylene diamine in the two-phase catalyzed reaction; 3.17×10^{-3} moles of o-phenylene diamine, 1.679×10^{-3} moles of TBA, 50 ml of CH_2Cl_2, 20 ml of H_2O, 1000 rpm, 30°C.

ter, served as the organic solvents in the two-phase reaction. The effects of organic solvents on the conversion are shown in Fig. 8. The order of the conversion of $C_6H_4(NH_2)_2$ in various organic solvents is: dichloromethane > chlorobenzene > benzene > n-hexane > n-decane, which is consistent with the order of the polarity of the organic solvents, i.e., a greater polarity of organic solvent leads to a higher conversion of o-phenylene diamine.
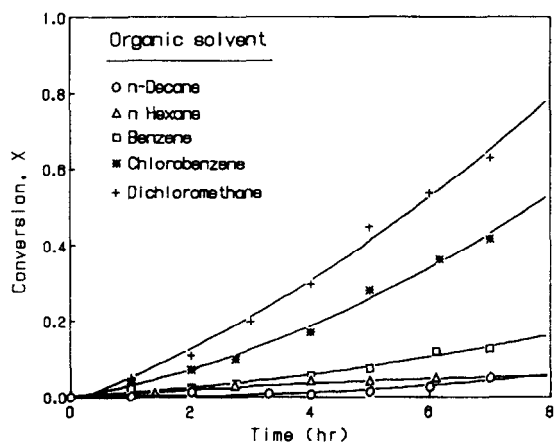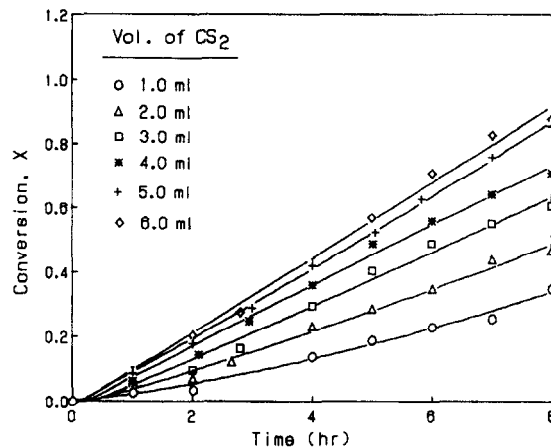

Fig. 8. Effect of the organic solvents on the conversion of o-phenylene diamine in the two-phase catalyzed reaction; 3.17×10^{-3} moles of $C_6H_4(NH_2)_2$, 2.50×10^{-2} moles of CS_2, 1.679×10^{-3} moles of TBA, 1000 rpm, 30°C.

4.3.6. Effect of the concentration of carbon disulfide

Carbon disulfide is insoluble in water and is only soluble in organic solvent. As expected, the concentration of CS_2 directly influences the conversion of C_6H_4 $(NH_2)_2$ and the reaction rate. The conversion is increased with the increase of the concentration of CS_2. The result, which is shown in Fig. 9, is consistent with the model equation shown in Eq. 12. It is obvious that the conversion is increased by increasing the concentration of CS_2 in the organic solution.

4.3.7. Effect of the amount of o-phenylene diamine

The effect of the amount of $C_6H_4(NH_2)_2$ on the conversion is shown in Fig. 10. For this study, the volume of organic solvent and the volume of water are fixed. Therefore, except $C_6H_4(NH_2)_2$, the concentrations of TBA and CS_2 kept constant. As shown in Fig. 10, the conversion is decreased with the increase of the amount of $C_6H_4(NH_2)_2$. Therefore, the use of a high concentration of $C_6H_4(NH_2)_2$ in the organic phase is avoided by carrying out the reaction in a two-phase solution. Parts of $C_6H_4(NH_2)_2$, which dissolve in water, act as
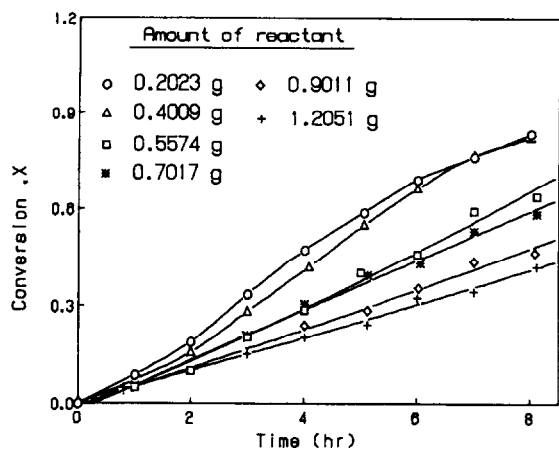
Fig. 10. Effect of the concentration of *o*-phenylene diamine on the conversion of *o*-phenylene diamine in the two-phase catalyzed reaction; 8.31×10^{-2} moles of CS_2, 1.679×10^{-3} moles of TBA, 50 ml of CH_2Cl_2, 20 ml of H_2O, 1000 rpm, 30°C.

the source in providing the reactant in the organic phase.

4.3.8. Effect of temperature

The effect of temperature on the conversion of *o*-phenylene diamine is shown in Fig. 11. The increase of temperature enhances the reaction rate and the conversion of *o*-phenylene diamine. An Arrhenius plot of $-\ln(k'_{app})$ vs. $1/T$ yields the activation energy of the two-phase reaction 51.10 kJ/mol.
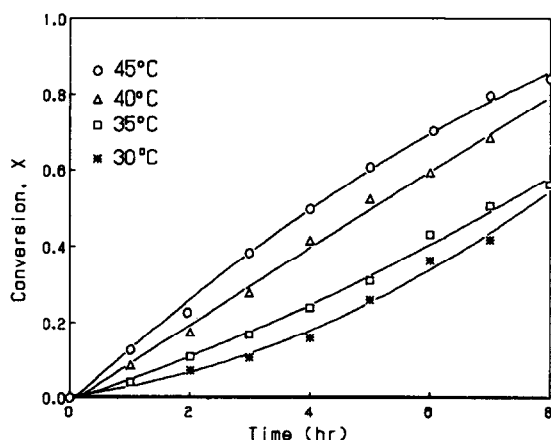

Fig. 11. Effect of temperature on the conversion of *o*-phenylene diamine in the two-phase catalyzed reaction; 0.3431 g of *o*-phenylene diamine, 2.50×10^{-2} moles of CS_2, 1.679×10^{-3} moles of TBA, 25 ml of chlorobenzene, 25 ml of H_2O, 1000 rpm.

4.3.9. Identification of the reaction order in synthesizing MBI

From Eq. 12, the reaction is reduced to zeroth order or first order rate of kinetics, depending on the values of k_1 and k_{-1} and k_2, and the concentration of $C_6H_4(NH_2)_2$. The conventional experiments to determine k_{-1} and k_2 are not available, because R_3N-CS_2 is not isolated and purified. In this work, the method of initial rate is provided to determine the rate constant (k_1) of the forward reaction (R1). In the reaction of synthesizing MBI, the ratio of the intrinsic rate constant (k_{-1}) of the backward reaction (R1) to the intrinsic rate constant (k_2) were determined from Eq. 25 by utilizing the technique of parameter estimation. For example, the reaction of synthesizing MBI was carried out at 30°C with 2.50×10^{-2} moles of CS_2, 3.17×10^{-3} moles of $C_6H_4(NH_2)_2$, 1.679×10^{-3} moles of Bu_3N in CH_2Cl_2. The rate constant (k_1) of the forward reaction (R1) is 8.833×10^{-1} min^{-1} M^{-1} as determined from the independent reactions of CS_2 and Bu_3N. Using the technique of parameter estimation, the value of (k_{-1}/k_2) is 15.65 based on the experimental data. Then, Eq. 25 becomes,

$$2.367X - 500.7\ln(1 - X) = t \qquad (27)$$

The value of the term $[-500.7 \ln(1 - X)]$ from the contribution of first order rate kinetics is much greater than that of the term $(2.367X)$ from the contribution of zeroth order rate kinetics at low concentration of $C_6H_4(NH_2)_2$. This result indicates that the reaction follows a pseudo-first order rate law. Therefore, a pseudo-first order rate law is sufficient to describe the reaction.

5. Conclusion

The synthesis of mercaptobenzimidazole (MBI) from the reaction of carbon disulfide and *o*-phenylene diamine catalyzed by tertiary amine was carried out in a two-phase medium. The advantage of this process is that MBI product

precipitates from the solution by using an appropriate organic solvent, and the inexpensive tertiary amine rather than the quaternary ammonium salt is used as the catalyst. A simple kinetic model, which was based on the reaction of CS_2 and R_3N to produce R_3N-CS_2, and the reaction of R_3N-CS_2 and $C_6H_4(NH_2)_2$, was built up. This model was used to explain the effect of the concentration of *o*-phenylene diamine on the conversion satisfactorily. Based on the experimental data, the reaction of *o*-phenylene diamine and carbon disulfide catalyzed by tertiary amine in a two-phase medium was described by a pseudo-first-order rate law. The conversion of *o*-phenylene diamine is decreased with the increase of the concentration of *o*-phenylene diamine in the organic phase.

Acknowledgements

References

[1] C.M. Starks, Phase Transfer Catalysis. An Overview, Am. Chem. Soc., Symp. Series, *326* (1985) 1.

[2] E.V. Dehmlow and S.S. Dehmlow, Phase Transfer Catalysis, 3rd Ed., VCH, New York, 1993.

[3] C.M. Starks, C. Liotta and M. Halpern, Phase Transfer Catalysis, Fundamentals, Applications, and Industrial Perspectives, Academic Press, New York, 1994.

[4] W.P. Weber and G.W. Gokel, Phase Transfer Catalysis in Organic Synthesis, Springer-Verlag, New York, 1977.

[5] H.H. Freedman, Pure Appl. Chem., *58* (1986) 857.

[6] W.E. Keller, Phase-Transfer Reactions, Fluka-Compendium, *1* (1986).

[7] W.E. Keller, Phase-Transfer Reactions, Fluka-Compendium, *2* (1987).

[8] D.B. Saxena, R.K. Khajuria and O.P. Suri, J. Heterocyclic Chem., *19* (1982) 681.

[9] G. Xue, X.Y. Huang, J. Dong and T. Zhang, J. Electroanal. Chem., *310* (1991) 139.

[10] C. Thomas, Hydrocarbon Oil Containing 2-Mercaptobenzimidazole, US Pat. 2,642,396 (1953).

[11] J.C. Moreira, C.P. Luiz and G. Yoshitaka, Mirkrochim. Acta II, (1990) 107.

[12] J.A. Van Allan and B.D. Deacon, Org. Synth., (1963) 569.

[13] S.H. Blocher, A. Schultze and H.W. Leverkusen, Process for the Production of 2-Mercaptobenzimidazole, US Pat. 3,235,559 (1966).

[14] A.L. Goodman, 2-Mercaptobenzimidazole Preparation, US Pat. 3,895,025 (1975).

[15] B. Scherhag, E. Kopplemann and H. Wolz, Production of 2-Mercaptobenzimidazole by Reacting *o*-Phenylene Diamine and Carbon Disulfide, US Pat. 3,842,098 (1974).

[16] K.A. Jensen and P.H. Nielson, Acta Chem. Scand., *17* (1963) 547.

[17] L.W. Fernando and J.G. Santos, J. Chem. Soc., Perkin Trans. II, (1980) 1323.

[18] C. Trinidad, J.G. Santos and L. Fernando, J. Chem. Soc., Perkin Trans. II, (1986) 1021.