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Kinetic investigation on Liquid-Liquid-Solid Phase Transfer Catalyzed Synthesis of Dibenzyl Disulfide with H₂S-laden Methyldiethanolamine

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Graphical abstract



Highlights

- In all experimental run, selectivity of the product DBDS was 100%.
- Reaction was kinetically controlled with activation energy 56.03 kJ/mol.
- Anion Exchange resin Amberlite IR-400 showed good reusability.
- Developed kinetic model predicts the results quite well at all temperatures.
- The proposed mechanism can successfully explain the course of the reaction.

ABSTRACT

An investigation has been done on the utilization of H_2S for the synthesis of dibenzyl disulfide (DBDS) using amberlite-400 as a phase transfer catalyst. This involves absorption of H_2S in aqueous monoethanolamine (MEA) followed by reaction of this H_2S laden MEA with organic reactant benzyl chloride (BC) to yield DBDS under liquid-liquid-solid (L-L-S) phase transfer catalysis condition. The effect of various parameters on the conversion of BC was studied and the selectivity of desired product was 100% at some level of process parameters. A suitable reaction mechanism has been proposed and a mathematical model has been developed to explain the kinetics of the reaction. Waste minimization therefore affected with the utilization of H_2S -laden gas for production of a value-added fine chemical.

Keywords: dibenzyl disulfide, Liquid-liquid-solid phase transfer catalyst, Hydrogen sulphide, Kinetics

NOMENCLATURE

MEA	monoethanolamine
BC	benzyl chloride
РТС	phase transfer catalyst
H_2S	hydrogen sulfide
DBS	dibenzyl sulfide
DBDS	dibenzyl disulfide
S ²⁻	sulfide anion

S ₂ ²⁻	disulfide anion
QSQ	catalyst active intermediate
Q_2S_2	catalyst active intermediate
$[S_2^{2-}]$	concentration of disulfide anion (kmol/m ³)
[Cl ⁻]	concentration of chloride anion (kmol/m ³)
[RCl] _{org,0}	initial concentration of organic substrate in organic phase (kmol/m ³)
[RCl] _{org}	concentration of organic substrate in organic phase at any time t (kmol/m ³)
[Q ⁺] _{tot}	total concentration of catalyst per total system volume (kmol/m ³)
k _{app} ``	apparent reaction rate constant [min ⁻¹]
k _{org}	overall reaction rate constant [m ³ /(kmol of catalyst .min)]
K _{Cl}	equilibrium attachment/detachment constant for S_2^{2-} ions [m ³ /(kmol of catalyst .min)]
K _S	equilibrium attachment/detachment constant for Cl^{-} ions [m ³ /(kmol of catalyst .min)]
θ_{S}	fraction of total number of catalyst cation attached to S_2^{2-}
θ_{Cl}	fraction of total number of catalyst cation attached to Cl^-
θ_{CIS}	fraction of total number of catalyst cation attached to both S_2^{2-} and Cl^{-}
X _{RCl}	fractional conversion of reactant
t	time (min)

1. INTRODUCTION

Due to decline in light-to-process crude, refineries around the world are forced to process heavy crude that contains substantial amount of organo-sulfur and organo-nitrogen compounds. Typically hydro-desulfurization process converts those organosulfur compounds to form hydrogen sulfide (H₂S) and ammonia (NH₃). H₂S is a toxic gas, poisonous even in a very small concentration, corrosive in presence of water and classified as a hazardous industrial waste [1, 2]. Lots of work has already been done on removal and recovery of hydrogen sulfide so far. Vilmain removed hydrogen sulfide using aqueous chlorine solution by reactive absorption in a mechanically agitated gas-liquid reactor [3]. Copper-zinc oxide supported on mesoporous silica reported good absorption capacity for hydrogen sulfide [4]. Ferrous and alum water were also used for the removal of hydrogen sulfide [5].

The removal of H_2S from various gas streams using aqueous solution of alkanolamines is a commercialized industrial process since early thirties [6]. In refineries and natural gas processing gas industries removal of NH_3 and H_2S are done by scrubbing with water and amine treating unit respectively. Once H_2S is absorbed, it is converted into element sulfur using Claus process, which is conventional method to produce elemental sulfur from H_2S but it is very energy expensive. Another disadvantage of this method is high production rate of elemental sulfur in comparison to the rate of consumption, so the disposal of elemental sulfur is a severe problem for refineries. Thus, an alternative process to Claus process has been in high demand for better utilization of hydrogen sulfide. The present work was undertaken to develop substitute of Claus process. This work dealt with the synthesis of dibenzyl disulfide from hydrogen sulfide under the presence Amberlyte IR-400 as phase transfer catalyst.

Dibenzyl disulfide is very important compound and having very diversified applications in the field of organic synthesis. Several methods have been described for the preparation of organic disulfides using different reagents and catalysts. Dhar synthesized disulfide by alkylation of alkyl halides with

tetrathiotungstate and tetrathiomolybdates [7]. Benzyltriethylammonium tetracosathioheptamolybdate $[(C_6H_5CH_2N(Et)_3)_6Mo_7S_{24}]$ was found to be a good reagent for the synthesis of disulfide from alkyl halides [8]. Disulfides were synthesized by oxidative coupling of thiols in presence of air using Fe (III)/NaI as a catalyst [9]. Thiols were oxidized into their corresponding disulfides through oxidative coupling in presence of potassium phosphate as a catalyst [10]. Disulfide were also synthesized by oxidative cleavage of aryl or alkyl tert-butyl sulfide [11]. Landini and Rolla synthesized primary and secondary dialkyl and aryl alkyl sulfides by using sodium sulfide in presence of Phase transfer catalyst (PTC) [12]. In the same way Wang and Tsang prepared symmetrical thioethers using sodium sulphide (Na₂S) and n-bromobutane [13]. Sen reported synthesis of dibenzyl sulfide from benzyl chloride using H₂S-rich aqueous monoethanolamine [14]. A few literatures are available on the preparation of symmetrical thioethers from H₂S-laden alkanolamine in presence of PTC. Na₂S was also used for preparation of aliphatic polysulfides in presence of quaternary onium salt and for reduction of nitroarens to anilines under PTC condition [15, 16]. Bandgar reported synthesis of variety of symmetrical disulfides from aryl alkyl halides by reduction of sulfur with borohydride exchange resin in methanol [17].

Phase transfer catalysis is a technique to lead a reaction from the reactants present in two mutually insoluble phases under mild operating conditions. It is now commercially mature discipline having wide range of industrial applications such as intermediates, perfumes, agrochemicals, pharmaceuticals and polymers [18, 19]. Many organic compounds have been synthesized under the presence of different PTC [20-24]. Sonavane also developed a one-pot method for synthesis of disulfides from the reaction of sulfur with sodium sulfide in the presence of didecyldimethylamonium bromide (DDAB) as a PTC [25, 26]. Disulfides were also synthesized from alkyl halides using thiourea and elemental sulfur in presence of polyethylene glycol (PEG 200) [27]. The conventional soluble PTCs are having one disadvantage of separation. Distillation or extraction can be used for the separation of the catalyst but it may increase complexity of the process and may affect purity and cost of the product. These drawbacks can be overcome with the use of solid PTC such as polymeric resins and the phenomena is known as Liquid-

Liquid-Solid (L-L-S) PTC. Tri-phase PTC has several other advantages over soluble PTC in terms of recovery and reusability of the catalyst. Amberlite IR-400 resin has been used for sometimes as a heterogeneous catalyst for the synthesis of organic compounds [28]. The aim of the work is to utilize H_2S to synthesis fine chemical dibenzyl disulfide selectively. This work has a great industrial relevance as it could replace the conventional Claus method followed in most refineries.

2. EXPERIMENTAL SECTION

2.1 Chemicals. Toluene (\geq 99%), Monoethanolamine (MEA) (\geq 99%) and Benzyl Chloride of analytical grade were procured from Rankem (India), New Delhi, India. Amberlite IR-400 (Cl⁻ form) was obtained from Merck (India) Ltd., Mumbai, India.

2.2 Experimental Setup. All the reactions were carried out in a 6.5 cm internal diameter, fully baffled mechanically agitated batch reactor of capacity 250 cm³. 2 cm diameter six-bladed glass disk turbine impeller with digital speed regulation system, kept at a height of 1.5 cm from the bottom of the reactor, was used for stirring the reaction mixture. The reactor was kept in an isothermal water bath (\pm 1°C) having PID controller.

2.3 Preparation of H₂S-laden Aqueous MEA. 30-35 wt. % aqueous MEA solution was prepared by adding adequate quantity of raw MEA in measured amount of distilled water. Then H_2S gas was bubbled through the aqueous MEA solution in gas bubbler, placed in ice bath. This gas bubbling process was continued till desired sulfide concentration was attained. Sulfide concentration was estimated using iodometric titration

2.4 Experimental Procedure. In each experimental run, 50 cm³ of aqueous alkanolamine solution containing a known concentration of sulfide was taken into the 250 cm³ reactor and kept well agitated by

stirrer until the steady state temperature was reached. Then 50 cm³ of the organic phase containing measured quantity of organic reactant (benzyl chloride) dissolved in solvent (toluene) and the catalyst (Amberlite IR-400) was added into the reactor. The reaction mixture was then agitated at a constant speed of stirring. Minimal amount of sample from the organic phase was withdrawn by micropipette at regular time intervals after stopping the agitation and allowing the phases to separate.

2.5 Organic Phase Analysis. In present work, analysis of organic phase were performed on GC (Agilent GC 7890B) by using a capillary column DB-5MS, 2 m x 3 mm, coupled with flame ionization detector. The product was further confirmed by GC-MS (Agilent 5977A).

3. RESULT AND DISCUSSION

3.1 Parametric Study.

3.1.1 Effect of Stirring Speed. The speed of agitation was varied from 1000 to 2500 rpm in both the conditions, with and without catalyst to determine effect of mass transfer resistance of reactants on the reaction rate. Fig. 1 shows that rate of reaction is practically same in all stirring speeds. Therefore, it can be assumed that beyond 1500 rpm, increase in stirring speed has no influence on reaction rate, so reaction can be safely considered as a kinetically controlled reaction. Thus, the further synthesis was carried out at 1500 rpm to remove mass transfer resistance. In absence of catalyst the rate of reaction is very low, therefore, further experiments have been performed in presence of catalyst only.

3.1.2 Effect of Sulfur Loading. Disulfide and polysulfide anions can easily be obtained by dissolving elemental sulfur powder in S^{2-} anion rich aqueous phase [25]. The effect of this elemental sulfur loading on synthesis of DBDS was investigated by adding different concentration of sulfur powder in H₂S-laden

MEA. The colour of aqueous MEA changed from greenish to reddish brown indicating formation of polysulfide anions S_x^{2-} (where x = 1, 2, 3, 4) depending on sulfur loading.

At low sulfur loading, hydrosulfide (HS⁻) and sulfide (S²⁻) ions are the dominating sulfur species giving BM and DBS respectively as the product [29]. So the selectivity of DBDS at 0.25 and 0.49 of sulfur to sulfide mole ratio was found to be low and it was almost negligible in absence of sulfur loading (Fig. 2). Whereas at high sulfur loading, polysulfide anions $S_{3,4,5}^{2-}$ are the dominating sulfur species, giving unwanted products like trisulfidse and polysulfides, which consequently gives again low DBDS selectivity. 100% selectivity of DBDS was observed at 1.875 kmol/m³ of sulfur due to presence of only disulfide anions S_2^{2-} . So 1.875 kmol/m³ of sulfur was considered as an optimum reaction parameter and further experiments were performed at this condition.

3.1.3 Effect of Catalyst Concentration. The influence of catalyst loading on BC conversion was determined both in presence and absence of catalyst keeping other reaction condition constant (Fig. 3). It was noticed that BC conversion was only 61% in absence of catalyst even after 480 min of reaction. A drastic increase in BC conversion was observed with catalyst loading and conversion was observed to increase with increase in catalyst loading.

In the presence of catalyst, Sulfide (S²⁻) and disulfide (S_2^{2-}) anions of aqueous phase react with quaternary ammonium halide (Q⁺) to give catalyst active intermediates QSQ and Q₂S₂ respectively. These catalyst intermediates then migrate from aqueous to organic phase to react with BC to give DBS and DBDS respectively. With increase in catalyst concentration, more catalyst intermediates are formed and travel to organic phase giving increased conversion of BC.

In present work, 100% selectivity of DBDS was observed due to adequate quantity of sulfur powder in aqueous phase giving only disulfide S_2^{2-} anions.

Table 1 shows enhancement of initial reaction rate at different catalyst loading as compared to that in absence of Amberlite catalyst. Enhancement factor indicates the importance of Amberlite IR-400 as a PTC in DBDS synthesis.

In order to calculate order of reaction with respect to Amberlite IR-400 catalyst, natural logarithm of initial reaction rate of different catalyst concentration was plotted against natural logarithm of Amberlite concentration (Fig. 4). The order of reaction, obtained from slope of plot, was 0.55 which is considered as 1st order with respect to catalyst concentration.

3.1.4 Effect of Temperature. The effect of temperature on conversion of BC was studied under otherwise similar conditions. The temperature was varied from 303 to 333K keeping other experimental conditions constant. The effect of temperature on conversion of BC is shown in Fig. 5. The expected nature of increased BC conversion with increase in temperature was noticed according to transition theory.

Initial reaction rate was calculated at different temperature for Arrhenius plot. Natural logarithm of initial reaction rate was plotted against 1/T (K⁻¹) and apparent activation energy was calculated from slope of the plot (Fig. 6). The apparent activation energy of kinetically controlled reaction was obtained as 56.03 kJ/mol.

3.1.5 Effect of Benzyl Chloride Concentration. The effect of reactant concentration was investigated by varying organic reactant concentration (BC) keeping constant sulfide concentration in aqueous phase i.e. different initial BC/ Sulfide mole ratio. Decrease in BC conversion was noticed with increase in ratio due to limitation of sulfide anions present in aqueous phase (Fig. 7). At 1.04 BC/sulfide mole ratio, optimum

conversion was obtained but reduced to 94% for 1.39. So it is concluded that low initial BC/ sulfide mole ratio is preferable for present work to get maximum conversion.

From the plot of ln(initial rate) vs. ln(concentration of BC) (Fig. 8), the order of reaction with respect to BC concentration was obtained as 2.44, which is close to 2. Hence the order of reaction is second order with respect to the concentration of reactant.

3.1.6 Effect of Sulfide Concentration. Sulfide concentration of aqueous phase was varied from 1.75 to 2.5 kmol/m³ keeping constant MEA concentration (35 wt %). There was slight decrease in conversion noticed with decreasing sulfide concentration but almost 98% conversion was achieved at 2.50 kmol/m³ sulfide range at 480 min of reaction time (Fig. 9).

From the plot of ln (initial rate) against ln(initial sulfide concentration) (Fig. 10), the slope of linear fit line was found out to be to be 2.14. Since this value is closer to 2, the reaction was considered second order with respect to the sulfide concentration.

3.2 Catalyst recovery and reuse. After completion of synthesis process, agitation was stopped and aqueous and organic phases were allowed to settle down in a separating funnel. Organic phase, present on top of aqueous phase, containing product was removed and Amberlite catalyst was allowed to settle down in aqueous phase. The catalyst present in aqueous phase was first recovered using filter paper then it was washed with acetone first to remove organic traces, then with water and 50% aqueous sodium chloride (NaCl) solution. After washing, catalyst was dried at 50°C in oven to remove any adsorbed substance present on it. For each run, recovered catalyst was reused in kinetic run four times and data were obtained shown in Fig. 11.

From the Fig. 11, it is seen that reusability of Amberlite is excellent up to four uses. But in every run, decrease in conversion was observed due to loss of catalyst in aqueous and organic phase and during catalyst washing process.

3.3 Proposed mechanism of synthesis of Dibenzyl Disulfide under L-L-S PTC. The mechanism of reaction between BC with H₂S- laden MEA and sulfur powder in aqueous phase using Amberlite IR-400 as a PTC is shown in Scheme 2. Generally aqueous phase reactions are faster as compare to organic phase reactions, so an ionic equilibrium exists in aqueous phase between RNH₂ (MEA)-H₂O-H₂S which results in formation of three active inorganic nucleophiles namely hydroxide (OH)⁻, sulfide (S²-) and disulfide $(S_2^{2^-})$ as represented in aqueous phase. In the present system, hydrosulfide anion (HS⁻) is not expected to stay due to presence of sulfur powder in aqueous phase. Sulfur shifts ionic equilibrium to right giving only sulfide (S²-) and disulfide $(S_2^{2^-})$ anions in aqueous phase. The product was obtained from both catalytic and non-catalytic contribution.

3.3.1 Non- catalytic Contribution. Ethanolamine sulfide ((RNH₃)₂S) and ethanolamine disulfide ((RNH₃)₂S₂), formed in aqueous phase via reaction (2) and (3) respectively in Scheme 2, are insoluble in organic phase. So they are expected to react with BC in aqueous-organic interface to give DBS and DBDS respectively as shown in reaction (7)-(9). Due to 2^{nd} order reaction rate of nucleophilic reaction, DBS is expected to form via formation of intermediate product $C_6H_5CH_2SNH_3R$ which again reacts with BC to give desired DBS. The formed product travels from interface to organic phase from where selective separation of products takes place.

3.3.2 Catalytic Contribution. Mass transfer and surface reaction are two important steps in presence of solid catalyst in L-L-S PTC [30]. Synthesis steps involves:

Step 1: Diffusion of aqueous anions S^{2-} and S^{2-}_{2-} from bulk aqueous phase to PTC.

Step 2: Ion exchange reaction of these nucleophiles with catalyst cation (Q^+) to form catalyst active intermediate QSQ and Q_2S_2 as shown in reaction (4)-(6) and leaving Cl⁻ anion.

Step 3: Diffusion of organic reactant BC from bulk organic phase to PTC.

Step 4: Synthesis reaction of BC at catalyst active site present at aqueous organic interphase to give desired products (reaction 10-12).

Step 5: Diffusion of anion Cl⁻ and product from interface to aqueous and organic phase respectively as shown in scheme 2.

3.4 Kinetic modeling. The GC analysis shows that the formation of DBS is very less as compared to DBDS. This observation can be attributed to less diffusion of aqueous sulfide (S^{2-}) anion in comparison to disulfide (S^{2-}_2) anion in the aqueous phase and the corresponding insignificant formation of catalyst active intermediate QSQ as compare to Q_2S_2 in the ion exchange step. The overall rate of reaction between the organic substrate RCl and a di-ionic inorganic nucleophile S^{2-}_2 to form organic product RS₂R in the presence of PTC, Q⁺Cl⁻ then can be expressed as a function of the concentrations of RCl and Q⁺S^{2-}_2Q^+, i.e.

$$2 \text{ RCl} + Q^+ S_2^{2-} Q^+ \to RS_2 R + 2 Q^+ Cl^-$$
(13)

Rate,
$$-r_{org} = -\frac{d[RCl]_{org}}{dt} = k_{org}[RCl]_{org}^2[Q^+S_2^{2-}Q^+]_s$$
 (14)

In the present work, a rigorous model based on the modification of the Langmuir-Hinshelwood/Eley-Rideal mechanism will be developed and experimental data from the reaction between benzyl chloride in the organic phase and disulfide in the aqueous phase to yield dibenzyl disulfide will be used to verify it. This reaction system belongs to a general class of esterification reactions where the nucleophile is extracted from the aqueous phase using a phase transfer catalyst. The reaction is mediated by polymersupported quaternary ammonium chloride and conducted in the batch slurry mode.

The whole reaction can be compared to the Eley- Rideal reaction mechanism [30], which includes reaction between an adsorbed reactant with an un-adsorbed reactant from the bulk phase. Here, ion-exchange step can be considered as the adsorption of first reactant to convert inactive sites into active sites, and in organic phase reaction step, second reactant reacts with adsorbed reactant to yield desired product RS_2R .

We assume that the reaction mechanism consist of an ion-exchange reaction step between S_2^{2-} and Q^+X^- to form an active site, $Q^+S_2^{2-}Q^+$ followed by reaction of RCl at this site to form a final product, RS₂R, and an inactive site, Q^+Cl^- . These steps may be described as follows:

Ion Exchange step:

$$2 (Q^{+}Cl^{-})_{s} + (S_{2}^{2-})_{aq} \leftrightarrow (Q^{+}S_{2}^{2-}Q^{+})_{s} + 2 (Cl^{-})_{aq}$$
(15)

Organic phase reaction step:

$$(Q^{+}S_{2}^{2}-Q^{+})_{s} + 2 (RCl)_{org} \leftrightarrow 2 (Q^{+}Cl^{-})_{s} + (RS_{2}R)_{org}$$
(16)

The reversible ion-exchange step may be compared to the Langmuir-Hinshelwood adsorption/desorption mechanism. We can express the Equation (15) using traditional notations of heterogeneous catalysis as,

$$(S_2^{2-}) + 2 (Q^+Cl^-) \leftrightarrow 2 (Cl^-) + (Q^+S_2^{2-}Q^+)$$
(17)

Where Q⁺ is catalyst's cation.

Assuming the formation of transitional site $Cl^-Q^+S_2^{2-}Q^+Cl^-$ between the forward and backword reaction steps, the whole reaction can be written as,

$$(S_2^{2-}) + 2(Q^+Cl^-) \leftrightarrow Cl^-Q^+S_2^{2-}Q^+Cl^- \leftrightarrow 2(Cl^-) + (Q^+S_2^{2-}Q^+)$$
(18)

We can split the ion exchange step as two separate equilibrium attachment/detachment steps. The attachment/detachment of S_2^{2-} anion on the inactive site of Q⁺Cl⁻ can be seen in the forward reaction step as,

$$2 (Q^{+}Cl^{-})_{s} + (S_{2}^{2-})_{aq} \leftrightarrow Cl^{-}Q^{+}S_{2}^{2-}Q^{+}Cl^{-}$$
(19)

Similarly, attachment/detachment of Cl^- anion on an active site of $Q^+S_2^{2-}Q^+$ can be seen in the backward reaction step as,

$$(Q^+S_2^{2-}Q^+)_s + 2 (Cl^-)_{aq} \leftrightarrow Cl^-Q^+S_2^{2-}Q^+Cl^-$$
(20)

Assuming the rates of attachment/detachment are in equilibrium, Equation (21) and Equation (22) can be obtained from Equation (19) and (20), respectively as,

$$\theta_{\text{CIS}} = K_{\text{S}}[S_2^{2-}]_{\text{aq}}(1 - \theta_{\text{S}} - \theta_{\text{CIS}})$$
(21)

$$\theta_{\rm CIS} = K_{\rm CI} [\rm CI^{-}]_{aq}^2 (1 - \theta_{\rm CI} - \theta_{\rm CIS})$$
⁽²²⁾

Where, K_S and K_{Cl} are the equilibrium attachment/detachment constants for S_2^{2-} and Cl^- anions, respectively; $[S_2^{2-}]$ and $[Cl^-]$ are the concentrations of S_2^{2-} and Cl^- anions in the aqueous phase, respectively; and θ_S , θ_{Cl} , θ_{ClS} are the fractions of total number of triphase catalyst cations attached to S_2^{2-} , Cl^- and both S_2^{2-} and Cl^- anions, respectively.

Mathematically, this can be written as: $\theta_{Cl} + \theta_{ClS} + \theta_S = 1$, which signifies that the sum total of all the fractions of active and inactive sites of the catalyst equals to unity. It is assumed that once, transition sites $Cl^-Q^+S_2^{2-}Q^+Cl^-$ are formed, they are instantaneously transformed either into active sites $Q^+S_2^{2-}Q^+$ or inactive sites Q^+Cl^- . At any instant of time there is very less fraction of transition site (θ_{ClS}) present in the reaction mixture as compare to active and inactive sites (θ_{Cl} and θ_S) but can't be neglected so, $\theta_{Cl} + \theta_S \approx 1$. Equation (21) and (22) can be re-written as

$$\theta_{\rm S} = K_{\rm S}[S_2^{2-}]_{\rm aq}(1 - \theta_{\rm S} - \theta_{\rm Cl}) \tag{23}$$

$$\theta_{\rm Cl} = K_{\rm Cl} [{\rm Cl}^{-}]_{\rm aq}^2 (1 - \theta_{\rm S} - \theta_{\rm Cl})$$
⁽²⁴⁾

We have obtained a hyperbolic equation for the fraction of active PTC sites by combining the expressions for θ_S and θ_{Cl} as

$$\theta_{\rm S} = \frac{K_{\rm S}[S_2^{2-}]_{\rm aq}}{1 + K_{\rm Cl}[{\rm Cl}^{-}]_{\rm aq}^2 + K_{\rm S}[S_2^{2-}]_{\rm aq}}$$
(25)

We can also write above equation in terms of catalyst concentration,

$$[Q^{+}S_{2}^{2}-Q^{+}] = [Q^{+}]_{tot} \frac{\kappa_{s}[s_{2}^{2}-]_{aq}}{1+\kappa_{cl}[Cl^{-}]_{aq}^{2}+\kappa_{s}[s_{2}^{2}-]_{aq}}$$
(26)

Where, $[Q^+]_{tot}$ and $[Q^+S_2^{2-}Q^+]$ are the total concentrations of catalyst and the concentration of catalyst attached to S_2^{2-} anions, respectively.

We obtain Equation (27) for the rate of the organic reactions by combining Equation (14) and Equation (26) as,

$$-r_{org} = -\frac{d[RCl]_{org}}{dt} = k_{org}[RCl]_{org}^2[Q^+]_{tot} \frac{K_s[S_2^{--}]_{aq}}{1 + K_{cl}[Cl^-]_{aq}^2 + K_s[S_2^{--}]_{aq}}$$
(27)

$$-\frac{d[RCl]_{org}}{dt} = k_{org}[RCl]_{org}^2[Q^+]_{tot} \frac{K_S[S_2^{2-}]_{aq}}{1+K_{cl}[Cl^-]_{aq}^2+K_S[S_2^{2-}]_{aq}}$$
(28)

Let us introduce fractional conversion of reactant (X_{RCl}), which can be calculated as

$$X_{RCl} = \frac{[RCl]_{org,0} - [RCl]_{org}}{[RCl]_{org,0}}$$
(29)

Where, $[RCl]_{org,0}$ and $[RCl]_{org}$ represents initial concentration of benzyl chloride and concentration at any time respectively. Now we can write Equation (28) in the form of fractional conversion as

$$-r_{org} = \frac{dX_{RCl}}{dt} = k_{org} [RCl]_{org,0} [Q^+]_{tot} \frac{K_S [S_2^{-2}]_{aq} (1 - X_{RCl})^2}{1 + K_{Cl} [Cl^-]_{aq}^2 + K_S [S_2^{-2}]_{aq}}$$
(30)

$$= \frac{dX_{RCl}}{(1 - X_{RCl})^2} = k_{org} [RCl]_{org,0} [Q^+]_{tot} \frac{K_S[S_2^{2^-}]_{aq}}{1 + K_{Cl} [Cl^-]_{aq}^2 + K_S[S_2^{2^-}]_{aq}} dt$$
(31)

$$= \frac{dX_{RCl}}{(1 - X_{RCl})^2} = k_{app} dt$$
(32)

Where $k_{app} = k_{org}[RCl]_{org,0}[Q^+]_{tot} \frac{K_S[S_2^{2-}]_{aq}}{1+K_{Cl}[Cl^-]_{aq}^2+K_S[S_2^{2-}]_{aq}}$. The terms in the k_{app} can be calculated

experimentally. Thus, after integration of Equation (32) we get,

(33)

$$\frac{X_{RCL}}{1 - X_{RCL}} = k_{app}t$$

From the Equation (33) it is clear that the reaction follows second order kinetics.

3.5 Validation of kinetic model. The kinetic model was validated by considering Equation (33) was valid at different temperatures by plotting of $X_{RCl}/(1-X_{RCl})$ against time (Fig. 12). The slope of each line gives apparent rate constant k_{app} at different temperatures as shown in Table 2. Fig. 13 shows comparison of calculated conversions of BC based on app. rate constants and experimentally obtained conversions of BC. Good agreement has been observed between calculated and experimental conversions.

4. CONCLUSION

A detailed study has been carried out on the synthesis of DBDS from BC using Amberlite IR-400 as a solid phase transfer catalyst. It is seen that at different speed of agitation there was no significant change on the rate of reaction so the reaction was found to be kinetically controlled and all experiments were done at a speed of 1500 rpm. The reaction was found to be approximately first order with respect the concentration of the catalyst, second order with respect to the reactant concentration and second order with respect to the sulfide concentration. 100% selectivity of DBDS was observed at 1.875 kmol/m³ of sulfur loading. The obtained activation energy, for DBDS synthesis, from Arrhinius plot was 56.03 kJ/mol. Catalyst was recovered and reused four times with successive decrease in the conversion of BC. A mathematical model was developed, based on kinetic study and proposed mechanism, to account for the calculation of the rate constant and it was validated using experimental data.

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ASSOCIATED CONTENT

Supporting information

Gas Chromatographs, NMR and MS spectra.

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Fig. 1. Effect of stirring speed on the rate of reaction. Operating conditions: Volume of aqueous and organic phase = 5.0×10^{-5} m³each; concentration of BC = 2.6 kmol/m³ in org. phase; concentration of toluene = 6.6 kmol/m³ in org. phase; concentration of catalyst = 0.29 kmol/m³ in org. phase; concentration of sulfide = 2.53 kmol/m³, MEA/H₂S mole ratio = 2.28; Temperature = 323 K; Sulfur loading= 1.875 kmol/m³.



Fig. 2. Effect of Sulfur Powder Loading on DBDS Selectivity. Operating conditions: Volume of aqueous and organic phase = 5.0×10^{-5} m³ each; concentration of BC = 2.6 kmol/m³ in org. phase; concentration of toluene = 6.6 kmol/m³ in org. phase; concentration of Catalyst = 0.29 kmol/m³ in org phase; concentration of Sulfide = 2.53 kmol/m³; MEA/H₂S mole ratio = 2.28; Temperature = 323 K; Agitation Speed= 1500 rpm.



Fig. 3. Effect of catalyst loading on BC conversion. Operating conditions: Volume of aqueous and organic phase = 5.0×10^{-5} m³each; concentration of BC = 2.6 kmol/m³ in org. phase; concentration of toluene = 6.6 kmol/m³ in org. phase; concentration of Sulfide = 2.53 kmol/m³; MEA/H₂S mole ratio = 2.28; Temperature = 323 K; Sulfur loading = 1.875 kmol/m³; Agitation Speed= 1500 rpm.



Fig. 4. In (Initial Reaction Rate) Vs In (Catalyst Concentration). All other conditions are same as Fig. 3.



Fig. 5. Effect of Temperature on BC conversion. Operating conditions: Volume of aqueous and organic phase = 5.0×10^{-5} m³ each; concentration of BC = 2.6 kmol/m³ in org. phase; concentration of toluene = 6.6 kmol/m³ in org. phase; concentration of Catalyst = 0.29 kmol/m³ in org phase; concentration of Sulfide = 2.53 kmol/m³; MEA/H₂S mole ratio = 2.28; Sulfur loading = 1.875 kmol/m³; Agitation Speed= 1500 rpm.



Fig. 6. Arrhenius plot of ln (Initial Reaction Rate) vs 1/T. All other conditions are same as Fig. 5.



Fig. 7. Effect of BC concentration on reactant conversion. Operating conditions: Volume of aqueous and organic phase = 5.0×10^{-5} m³ each; concentration of Catalyst = 0.29 kmol/m³ in org phase; concentration of Sulfide = 2.53 kmol/m³; MEA/H₂S mole ratio = 2.28; Sulfur loading= 1.875 kmol/m³; Agitation Speed= 1500 rpm.



Fig. 8. Plot of ln(initial rate) vs. ln(reactant concentration). All other conditions are same as Fig. 7.



Fig. 9. Effect of sulfide concentration on BC conversion. Operating conditions: Volume of aqueous and organic phase = 5.0×10^{-5} m³ each; concentration of BC = 2.6 kmol/m³ in org. phase; concentration of toluene = 6.6 kmol/m³ in org. phase; concentration of Catalyst = 0.29 kmol/m³ in org phase; Temperature = 323 K; MEA concentration = 5.77 kmol/m³; Sulfur loading= 1.875 kmol/m³; Agitation Speed= 1500 rpm.



Fig. 10. Plot of vs. ln(initial rate) vs. ln(conc. of sulfide). All other conditions are same as Fig. 9.



Fig. 11. Conversion of BC with the cycle number. Volume of aqueous and organic phase = 5.0×10^{-5} m³ each; concentration of BC = 2.61 kmol/m³; concentration of Catalyst = 0.29 kmol/m³ org phase; MEA/H₂S mole ratio = 2.28; Temperature = 323 K; Sulfur loading= 1.875 kmol/m³, Agitation Speed= 1500 rpm



Fig. 12. Validation of the kinetic model with experimental data at different temperature. Volume of organic phase = $5.0 \times 10^{-5} \text{ m}^3$, Volume of Aqueous Phase = $5.0 \times 10^{-5} \text{ m}^3$, concentration of toluene= 6.6 kmol/m^3 in org. phase, concentration of BC = 2.6 kmol/m^3 in org. phase, concentration of Catalyst = 0.29 kmol/m^3 org. phase; Sulfide Conc. = 2.53 kmol/m^3 , MEA/H₂S mole ratio = 2.28, Sulfur loading = 1.875 kmol/m^3 , Stirring Speed= 1500 rpm.



Fig. 13. Comparison of calculated and experimental BC conversions at 480 min different temperatures and all conditions are as same as Fig. 12.



Scheme 1. Overall reaction system



Scheme 2. Proposed mechanism of synthesis of DBDS by H2S-laden MEA under L-L-S PTC

Concentration of Amberlite IR-	Initial reaction rate (kmol/m ³ s)	Enhancement	
400 (kmol/m ³ org phase)	at 5% Conversion	factor	
0.00	0.00222	1.0	
0.15	0.00350	1.6	
0.29	0.00485	2.2	
0.44	0.00617	2.8	
0.58	0.00755	3.4	

Table 1: Effect of catalyst loading on Initial reaction rate^a

^aAll other conditions are same as Fig. 3.

Table 2. Apparent rate constants (k_{app}) at different temperatures^b

Temperature (°C)	30	40	50	60
$k_{app}(\min^{-1})$	0.01673	0.03276	0.05033	0.10171

^b All the considerations are same as mentioned in Fig. 12.