

Study on Kinetics of Reaction of Benzyl Chloride with H₂S-Rich Aqueous Monoethanolamine under Liquid-Liquid-Liquid Phase-Transfer Catalysis

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Abstract— This thesis work engages the study of treatment of hydrogen sulphide gas based on phase transfer catalysis for the production of DiBenzyl Sulphide and other organic sulphides at room temperature and optimizing the conditions for 100% selectivity and maximum conversion. This study focuses on the condition optimization for preparation of Dibenzyl sulphide and also maximum absorption of H₂S on cheaper solvents. Benzyl chloride was used as the reactant and MethylEthylAmine (MEA) for absorption of H₂S gas. Phase transfer catalyst chosen was PEG-400 for its non-pollutant nature and cost of course. Toluene was made the organic Solvent. The amount of catalyst required was around 0.12wt% because of its low reactivity. The optimum time was around 7-8 hrs and the sulphide concentration for DBS formation was 1.646 kmol/m³ at a temperature of 60°C. The experiments were done using one variable at a time approach as it was a simple system.

Keywords: Hydrogen Sulphide; Dibenzyl Sulphide; Monoethanol Amine; Phase Transfer Catalyst; Selectivity; Optimization

I. INTRODUCTION

The removal and recovery of hydrogen sulfide (H₂S) from the gas streams by ammonium hydroxide are well documented (Kohl and Nielsen, 1997). Process was also developed (Hamblin, 1973) for removal of H₂S from gas streams using ammonium hydroxide to produce ammonium hydrosulfide, which was further oxidized by an air stream to get an effluent stream containing ammonium polysulfide and treating the ammonium polysulfide containing stream to recover elemental sulfur. Recently, Asai et al. (1989) studied the rates of simultaneous absorption of H₂S and ammonia into water in an agitated vessel with a flat interface and Rumpf et al. (1999) studied the simultaneous solubility of ammonia and hydrogen sulfide in water at temperatures from 313 to 393 K and total pressures up to 0.7 MPa. On the other hand, aqueous alkanolamines are now-a-days widely used in industry for the removal of H₂S from gas streams as discussed in Chapter 1. Lot of research works are also devoted to the study on the equilibrium solubility of pure H₂S, mixture of acid gases (H₂S and CO₂), and the mathematical representation of the experimental solubility data for H₂S, CO₂ and their mixture using various alkanolamines (Austgen et al., 1989; Weiland et al., 1993; Kaewsichan et al., 2001; Al-Baghli et al., 2001; Sidi Boumedine et al., 2004).

II. PROCESS

A. Preparation of Hydrogen Sulfide rich MEA

Preparation of this solution is done simultaneously with the production of H₂S gas from the kipp's apparatus which is an apparatus for the preparation of the small volume of gases. It consists of 3 stacked cylinders where it is filled with different reactants which is in our case Iron(II) Sulfide and Hydrochloric acid. The middle cylinder has a tube with stopcock ahead from which the gas was collected. For preparation of this solution, first MEA was added to a suitable amount of distilled water and 30-35 wt% of alkanolamine was made ready into which the Hydrogen Sulfide gas from kipp's apparatus was bubbled through a 250 cm³ gas bubbler. Since this reaction is exothermic, the MEA solution was kept in an ice bath for efficient absorption of the acidic gas and to prevent oxidation of sulfide. The unabsorbed gas from the first solution was sent to the second containing 1M NaOH where it would react to form some products without escaping into the atmosphere. The experiments continued till the desired quantity of sulfide is obtained in the solution.

B. Experimental Methodology

The convention one variable at a time approach (OVAT) was followed where other variables were kept constant and only one varied and studied at a time. As in most scientific disciplines, chemists have historically followed the practice of changing one variable at a time (OVAT) during optimization. This method is useful to see the main effect of each variable on conversion and selectivity separately. The data obtained by this method, can be used to get the order of reaction, optimize a simple reaction system, estimate kinetic parameters, to evaluate some thermodynamic parameters.

III. EXPERIMENTAL PROCEDURE

In a typical experimental run, 50 cm³ of aqueous phase containing a known concentration of sulfide was charged into the reactor and kept well agitated until the steady state temperature was reached. Then 50 cm³ of the organic phase containing measured amount of organic reactant (benzyl chloride), catalyst (PEG 400), and solvent (toluene), kept separately at the reaction temperature was charged into the reactor. The reaction mixture was then agitated at a constant speed of stirring. Approximately 0.5 cm³ of the organic layer was withdrawn at a regular time interval (1 hr) after stopping the agitation and allowing the phases to separate.

IV. ANALYSIS

A. Estimation of Sulfide Concentration

Hydrogen sulfide and soluble sulfides can be determined by oxidation with potassium iodate in an alkaline medium. 15 cm³ of standard (0.025M) potassium iodate solution was taken in a conical flask. 10 cm³ of sulfide solution containing about 2.5 mg of sulfide was then added to it followed by the addition 10 cm³ of 10M sodium hydroxide solution. The mixture was boiled gently for about 10 minutes, cooled, and 5 cm³ of KI solution and 20 cm³ of 4M sulphuric acid solution were added to it. The liberated iodine was titrated, which was equivalent to the unused potassium iodate, with a standard 0.1M sodium thiosulfate in the usual manner. The potassium iodate in the alkaline medium oxidizes the sulfide to sulfate as given by the following reaction. For sulfide solution having sufficiently high sulfide concentration, suitable dilution was made before the estimation of sulfide by above mentioned procedure.

B. Analysis of Organic Phase

All the samples from the organic phase were analyzed by gas-liquid chromatography (GLC) using a 2 m × 3 mm stainless steel column packed with 5% SE 30. A gas chromatograph (Chemito Model 8610 GC) interfaced with a data processor (Shimadzu C-R6A Chromatopac) was used for the analysis. The column temperature was programmed with an initial temperature of 150°C for 2 min, increased at a rate of 20 °C/min up to 300°C and maintained at 300°C for 4 min. Nitrogen was used as carrier gas at a pressure of 0.8 bar. An injector temperature of 250°C was used during the analysis. A flame ionization detector was used at a temperature of 300°C. The products were characterized by GLC. The composition of the samples being analyzed was calculated by direct comparison of the peak areas against a calibration curve. The term selectivity of the two products, DBS and BM, used in this study are defined as the fraction of BC converted to a particular product divided by the total conversion of BC. %Selectivity of DBS = (moles of DBS formed/ moles of BC converted)*100%

V. DISCUSSION

The reaction of benzyl chloride with H₂S-rich aqueous monoethanolamine (MEA) in presence of a PTC (PEG 400) and solvent toluene leads to products (DBS and BM). One can selectively prepare either DBS or BM using the same reagents only by selecting proper operating conditions. The high MEA/H₂S mole ratio, high benzyl chloride concentration, and long reaction time lead to selective preparation of DBS. On the other hand, opposite trend was observed for BM. The reaction was found to be kinetically controlled with an apparent activation energy value of 10.2 kJ mol⁻¹. The process was determined to follow a complex mechanism involving the transfer of two active ion pairs (Q+S²⁻Q⁺ and Q⁺SH⁻) from the aqueous phase to the organic phase and react with benzyl chloride to produce DBS and BM, respectively. The DBS is also formed by the reaction of BM and benzyl chloride. The high MEA/H₂S mole ratio, high benzyl chloride concentration, and long reaction time lead to selective preparation of DBS. On the other hand, opposite trend was observed for BM. A maximum BC conversion of

100% and a maximum DBS selectivity of 97% were predicted under certain experimental conditions. Conditions for dual maximization of BC conversion (100%) and DBS selectivity (95.2%) were found as: temperature 333K, catalyst concentration 0.15 kmol/m³, BC/sulfide mole ratio 2.83, MEA/sulfide mole ratio 3.7.

VI. SCOPE OF FURTHER WORK

This chapter shows the scope for works that can be proceeded on the same system for further improvement of the process based on the results of this experiment. And it tells what significant contributions can be made to phase transfer field by scaling up the process for industries.

A. Investigation of Mechanistic Pathways

There have been fewer studies on the mechanism of tri-phase systems. As this system had a good selectivity and conversion percentage, studying the mechanism would open up for new routes to synthesize different products. Aqueous phase can be analyzed to know the presence of several species (Cl⁻, Br⁻, HS⁻, S²⁻, Q⁺ etc.) in it and then to quantify it to get better insight into the mechanistic pathway.

B. Finding out Effect of other Parameters

The effect of pH of H₂S-rich ammonia or alkanolamine solution needs to be explored. S²⁻/HS⁻-ratio plays an important role in selectivity of benzyl mercaptan and benzyl sulfide which in turn depends on the pH of the alkaline solution. Effects of other anions as co-catalyst and addition of alkali (NaOH for example) that can influence the reaction rate and selectivity of desired products can also be tried. In the present study, toluene has been used as a solvent in most of the cases because it is cheap. The physical properties of organic solvent play an important role on the PTC reaction, not only by influencing the intrinsic organic reaction but also by affecting the transport properties of PTC and active catalyst species (QSQ and QSH) (Yang et al., 2003). Other types of solvents like chlorobenzene, n-heptane, dichloromethane can be tried out.

C. Reusability of Catalyst

As one of the main positives of the 3 phase system is reusability, the factor can be studied which was not done in the above study. Studies can also be conducted with other kinds of PTC (solid PTC like 1,3,5-tris (benzyltriethylammonium bromide) benzene (TBTABB) (Balakrishnan et al., 2009a) or Polymer-bound PTC like polymer-anchored-2-benzyl-2-phenyl-1,3-bis (triethylmethylene ammonium chloride) (PABPBAC).

D. Statistical Modelling & single pot synthesis using H₂S

Statistical models can be developed to find out kinetic parameters and the kinetic equation exactly matching our system for further optimization of the conditions. As this is a two-step process which involves the absorption of H₂S and then followed by the synthesis of fine chemicals, it will be tough when done in an industry, so it's very essential to develop a single pot method or continuous process where H₂S can be allowed to react directly with aromatic compounds.

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