Journal of Molecular Catalysis A: Chemical 411 (2016) 78–86

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Kinetic investigation on liquid–liquid–solid phase transfer catalyzed synthesis of dibenzyl disulfide with H_2S-laden monoethanolamine

Gaurav Singh, Priya G. Nakade, Pratik Mishra, Preeti Jha, Sujit Sen*, Ujjal Mondal

Catalysis Research Laboratory, Department of Chemical Engineering, National Institute of Technology, Rourkela 769008, India

ARTICLE INFO

Article history:
Received 6 September 2015
Received in revised form 11 October 2015
Accepted 12 October 2015
Available online 17 October 2015

Keywords:
Dibenzyl disulfide
Liquid–liquid–solid phase transfer catalyst
Hydrogen sulphide
Kinetics

ABSTRACT

An investigation has been done on the utilization of H_2S for the synthesis of dibenzyl disulfide (DBDS) using Amberlite IR-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 was therefore affected with the utilization of H_2S-laden gas for production of a value-added fine chemical.

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 (H_2S) and ammonia (NH_3). H_2S 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 industries, removal of NH_3 and H_2S are done by scrubbing with water and amine respectively. Once H_2S is absorbed, it is converted into element sulfur using Claus process, which is a 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 in the presence Amberlite 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]. Disulfides 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 (Na_2S) and *n*-bromobutane [13]. Sen reported synthesis of dibenzyl sulfide from benzyl chloride using H_2S-rich aqueous monoethanolamine [14] . A few literatures are available on the preparation of symmetrical thioethers from H_2S-laden alkanolamine in presence of PTC. Na_2S was also used for preparation of aliphatic polysulfides in presence of quaternary onium salt and for reduction of nitroarenes

---

* Corresponding author. Fax: +91 661 2462999.
E-mail addresses: sensujit@nitrkl.ac.in, sensujit@gmail.com (S. Sen).

http://dx.doi.org/10.1016/j.molcata.2015.10.013
1381-1169/

Nomenclature

MEA	Monoethanolamine
BC	Benzyl chloride
PTC	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
$\left[S_2^{2-}\right]$	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)
$\left[Q^+\right]_{tot}$	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_{ClS}	fraction of total number of catalyst cation attached to both S_2^{2-} and Cl^-
X_{RCl}	fractional conversion of reactant
t	time (min)

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 phenomenon is known as liquid–liquid–solid (L–L–S) Tri-phase catalysis. 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 synthesize 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

2.1. Chemicals

Toluene (≥99%), Monoethanolamine (MEA) (≥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 cm^3. 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 (±1 °C) having PID controller.

2.3. Preparation of H_2S-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 a gas bubbler, placed in an 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 cm^3 of aqueous alkanolamine solution containing a known concentration of sulfide was taken into the 250 cm^3 reactor and kept well agitated by stirrer until the steady state temperature was reached. Then 50 cm^3 of the organic phase containing measured quantity of organic reactant (benzyl chloride) was dissolved in the 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 (Scheme 1).

2.5. Organic phase analysis

In the present work, analysis of organic phase was performed on GC (Agilent GC 7890B) by using a capillary column DB-5MS, 2 m × 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