Kinetic investigations of styrene carbonate synthesis from styrene oxide and CO₂ using a continuous flow tube-in-tube gas-liquid reactor

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ABSTRACT

A continuous method of styrene carbonate (SC) synthesis from styrene oxide (SO) and carbon dioxide (CO₂) is reported, using a semipermeable Teflon® AF-2400-based tube-in-tube gas-liquid reactor. The reaction was performed in the presence of tetrabutylammonium bromide (TBAB) and zinc bromide (ZnBr₂), acting as a highly efficient and economical homogeneous binary catalyst system. The exceptionally high permeation of CO₂ through the membrane, combined with the high surface area to volume ratio in such continuous flow reactors resulted in complete SO conversion (100%) in a significantly reduced reaction time (t₉₅) of 45 min at 120 °C and 6 bar of CO₂ pressure. The effect of various operating conditions such as reaction temperature, CO₂ pressure, residence time and catalyst molar ratio (ZnBr₂/TBAB) was determined. Moreover, a detailed kinetic study of SC synthesis was carried out to determine the corresponding kinetic values (k and Eₐ) and activation parameters (ΔH‡, ΔS‡ and ΔG‡). Based on the experimental data, the reaction was found to be first-order in SO, TBAB and CO₂ concentrations. The activation energy of SC synthesis in the presence of TBAB catalyst alone was calculated to be 55 kJ mol⁻¹ over a temperature range of (90–120 °C), which was reduced to 32 kJ mol⁻¹ as a result of using ZnBr₂ as a co-catalyst.

1. Introduction

The continuously increasing concentration of atmospheric CO₂ is one of the major reasons for global warming. Over the last two decades, much attention has been paid to CO₂ capture and utilization into value-added products. The formation of cyclic carbonates by cycloaddition of CO₂ to epoxide is one of the most favourable reactions for effective CO₂ utilization, as it can be 100% atom economical [1,2]. Cyclic carbonates have several applications, as they can be used as high boiling point polar aprotic solvents e.g. ethylene carbonate and propylene carbonate [3,4], electrolytes in Li-ion batteries [5,6], precursors for the production of polymers such as polycarbonates and polyurethanes [7–11] and also intermediates for the production of pharmaceuticals and many other fine chemicals [12,13]. As CO₂ is available in excess, economical and non-toxic, it can be used in a potential replacement of conventionally undesired phosgene (COCl₂) route for cyclic carbonate synthesis [14–16]. Among methods for CO₂ utilization, synthesis of cyclic carbonates from epoxides and CO₂ is a reaction that has been already commercialized [17–20]. However, because of the thermodynamic and kinetic stability of CO₂ (ΔH˚ = −394 kJ mol⁻¹) [21,22], a highly efficient catalyst system is needed, which can substantially decrease the activation energy, and in so doing allow reactions that require mild conditions.

In recent years, various homogeneous and heterogeneous catalyst systems have been established for the cyclic carbonates formation from terminal epoxides, such as transition metal complexes [23,24], alkyl ammonium and phosphonium halides [25,26], alkaline metal salts [27,28], metal oxides [29,30] and supported catalyst [31–35]. However, most of these catalyst systems are not commercially viable due to low conversion [36–38], high temperature and pressure requirements [39–41], poor reusability [42,43] and less economical downstream separation steps. Among these catalysts, ionic liquids (ILs) or their combination with metallic salts have received considerable attention as homogeneous binary catalyst system because of their high efficiency, ease of catalyst recovery and product purification [44–47]. Previous literature also reported that zinc halides in conjunction with ionic liquids as catalysts could coordinate with the oxygen atom to activate the epoxide by forming the zinc-epoxide adducts [39,48,49]. Moreover, cyclic carbonate synthesis from epoxides and CO₂ is a typical gas-liquid multiphase catalytic process involving a gas-liquid mass transfer in a reactor and the catalytic cycloaddition reaction in the liquid phase. Thus, it was anticipated that an efficient reactor design in terms of high...
rate of heat/mass transfer and continuous flow approach could mitigate many of the limitations observed in above catalyst systems. In this study, a continuous method for SC synthesis has been described in the presence of commercially available, inexpensive ZnBr₂ and TBAB as a highly active combined catalyst system.

Flow chemistry has many advantages over conventional batch reactors, typically including enhanced rates of heat and mass transfer (due to higher surface area to volume ratios and efficient mixing), improved safety (lower inventories), easy and highly reproducible screening of reaction parameters, which may improve the reliability of scale-up and process optimisation [50–53]. Microreactor technology is being increasingly used in flow chemistry due to its wide range of applications in chemical synthesis [54–58]. Among the various reactions studied at the microscale, the gas/liquid biphasic reaction is an important category [59,60]. Generally, gas-liquid flow in a microchannel results in different flow patterns such as slug flow, annular flow, bubble flow and churn flow, depending on the operating conditions and reactor geometry [61]. The method of interfacial contact between liquid and gas phases is an important consideration in biphasic reactions. The majority of biphasic flow chemistry studies are based on segmented (or plug) flow in which mass transfer from gas to liquid phase largely is a function of the degree of interfacial contact [62–65]. This approach results in limited control over the gas dissolution into the liquid phase, leading to decrease in reaction rate because of the decreased concentration of gas in liquid phase [66]. In order to increase the effective (interfacial) surface area, and thus to increase the gas availability in the solution, reactions have been performed in ‘tube-in-tube’ gas-liquid reactors. In these reactors, the inner tube is made of a semi-permeable membrane through which gas can permeate during the reaction leading to a higher throughput. This concentric tubes reactor design has the ability to form microbubbles of gas on the outer walls of amorphous fluoropolymer membrane, which are rapidly dissolved into the countercurrenting liquid. Diffusion-controlled formation of homogeneous saturated gas solutions is thus obtained under flow-through conditions [67]. These reactors have a higher surface area to volume ratios than conventional batch reactors and very high permeation of CO₂ across the Teflon® AF-2400 membrane i.e. (280,000 cB) [54]. This can lead to, significantly improved reaction efficiency in terms of increased mass transfer from gas to the liquid phase. Over the last decade, this novel concept of reactor design has found a wide range of applications in organic chemical synthesis [57,60,66–71].

2. Experimental

2.1. Material and methods

All chemicals required were purchased from Sigma Aldrich. The reagents used were styrene oxide (98%), tetrabutylammonium bromide (99%), tetrabutylammonium chloride (99%), tetrabutylammonium iodide (99%), tetrabutylammonium fluoride (99%), zinc bromide (98%), zinc chloride (98%) and propylene carbonate (99%). The CO₂ gas (99.8%) was supplied by BOC Gases. Batch experiments of SC synthesis were carried out in a stainless steel Parr reactor equipped with a heating controller. The schematic of the batch reactor for styrene carbonate synthesis from styrene oxide and CO₂ is shown in Fig. 3. For continuous flow synthesis and to study the reaction kinetics, the experiments were performed in a gas-liquid (GAM II) tube-in-tube coil reactor (UQ1095) fits over a Uniqsis FlowSyn operating system as shown in Supporting information Figs. S6 and S7 [72]. The qualitative and quantitative analysis of the product samples were carried out by using FTIR and GC. To study the reaction kinetics, the decrease in the concentration of epoxy (SO) was monitored by attenuated total reflection infrared (ATR-IR) spectroscopy. The conversion of epoxy to cyclic carbonate can also be determined by GC analysis using naphthalene as an internal standard. The detailed procedure to determine conversion using FTIR and GC was described in the Supporting information.

2.2. Tube-in-tube gas/liquid reactor

The continuous flow reactor used in this study is a tube-in-tube liquid/gas reactor reported by Ley group [68,70,73]. The inner tube of the reactor is made of an amorphous polymer Teflon® AF-2400 based gas-permeable membrane having dimensions (4 m × 1.0 mm od × 0.8 mm id) containing 2 ml of the reaction volume. Teflon® AF-2400 is a commercially available amorphous glassy fluoropolymer prepared by copolymerization of perfluoroxydiane (m = 87 mol %) and tetrafluoroethylene (n = 13 mol %) as shown in Fig. 1 [74]. It has a unique structure characterized by microvoids having high fractional free volume (FFV %) compared to other polymers [75]. The origin of these microvoids is the loose chain packing caused by the high energy rotation and reorientation of rigid dioxolane rings in an amorphous structure of the polymer. The size distribution of fractional free volume was determined by various techniques assuming cylindrical and spherical pore geometry and was in the range of 3–8 Å [75–78]. These structural properties of AF-2400 along with week van der Walls forces between fluorocarbon chains makes it useful for its application as an excellent semi-permeable membrane for a wide range of gases.

The tube-in-tube reactor consists of a pair of concentric tubes with inner tube surrounded by a pressurised jacket of CO₂ gas. The CO₂ gas was charged into the shell side of the reactor by connecting the outer tube with the CO₂ gas cylinder through a pressure regulator. The shell side of the reactor is held at a constant value of pressure during a typical reaction. The CO₂ gas first dissolves into the surface of inner Teflon® AF-2400 membrane contacting feed flow and then diffuses across the membrane, and finally permeates into the bulk of the reaction mixture. The mass transfer of the gases through membrane depends on diffusion and partition coefficient of gases in the membrane [54,79,80]. To keep the pressure constant on the shell side and to prevent outgassing of the dissolved CO₂, a back pressure regulator (6.9 bar) was installed at the end of the flow stream. This helps to enable the controlled generation of a homogeneous solution of CO₂ in a continuous flow, avoiding segmented flow.

The inner tube was charged with the liquid (styrene oxide), Fig. 2. This inner tube was surrounded by an outer stainless steel tubing (4 m × 3.23 cm OD × 2.61 mm ID). The stainless steel outer tubing has an advantage over thick walled PTFE tubing to ensure better heat transfer between reactor coil and heated reactor station. The CO₂ gas permeates through the inner wall and dissolves into the bulk of the reaction mixture along with the tube, and diffusion-controlled formation of the saturated gas solution is obtained under flow-through conditions. The independent control of liquid and gas phases has the advantage that gas may then be drawn through the membrane on demand within the reactor zone leading to a higher throughput. The reactor coil was fitted over a Uniqsis Flowsyn operating unit as shown in Supporting information Fig. S5. The Flowsyn unit contains a heated reactor station to provide heat (ambient to 260 °C) and high-pressure pumps which can pump liquid from 0.01 to 10 ml/min at pressures up to 200 bar. A schematic of continuous flow tube-in-tube gas-liquid coil reactor is shown in Fig. 3.