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IONIC LIQUIDS AS CATALYSTS IN THE CYCLOADDITION OF CO₂ TO
STYRENE OXIDE IN SUPERCRITICAL AND SUBCRITICAL STATES

By

Joy Mwalimu

A Thesis
Submitted to the
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Joy Mwalimu

IONIC LIQUIDS AS CATALYSTS IN THE CYCLOADDITION OF CO₂ TO STYRENE OXIDE IN SUPERCRITICAL AND SUBCRITICAL STATES

Joy Mwalimu, M.S.

Western Michigan University, 2005

Supercritical fluids (SCFs) have fascinated researchers ever since the discovery of a critical temperature more than a century ago.¹ Initial studies focused mainly on the physical properties of supercritical phases.² However, their use as reaction media has sparked mainly during the last five to ten years.²

The coupling of CO₂ and Ionic Liquids (ILs) in the synthesis of cyclic carbonates comes from an increasing need for environmentally and toxicologically benign processes for the production of high-value compounds. In my research, CO₂ was utilized as both a replacement solvent and a C₁ feedstock in its fixation to styrene oxide to yield styrene carbonate. Alkali metal salts, quaternary ammonium salts and 1-alkyl-3-methylimidazolium based ILs have been examined as possible catalysts for the reaction under various temperature and pressure conditions. Phase behavior studies by UV-vis have helped us understand the effect of CO₂ pressure on the % conversion. NMR, IR and GC-MS have been used to monitor and identify reaction products.

Results strongly indicate a highly efficient, more environmentally friendly synthetic process.

INTRODUCTION

Chemistry has played a vital role in the advancement of life. The development of drugs and antibiotics resulted in the average life expectancy rising from 47 years in 1900 to 75 years in 1990.³ Use of insecticides, herbicides and fertilizers led to the increase of the world food supply while the development of dyes, plastics, cosmetics and other materials led to an increased quality of life. However, the negative effects of chemistry soon became apparent in the form of pollution of land, water and the atmosphere. This was caused mainly by the use of toxic reactants and reagents, and by-products, emitted in the atmosphere, released into aqueous effluents or merely disposed of on land.

Attempts have been made to design environmentally benign chemical syntheses, which have come to be defined as Green Chemistry. The starting materials, solvents and catalysts are chosen carefully and the synthetic schemes are designed in such a way that they are cost effective, the waste products are minimal and they have minimal effects on the environment.

In recent years the choice of a given solvent for performing a reaction has become increasingly important since they top the list of damaging chemicals. This is because they are used in large quantities and are usually volatile making them difficult to contain.⁴ The choice of the solvent or the solvent system is essential for realizing many chemical transformations that are environmentally benign and highly efficient. Emission of Volatile Organic Compounds (VOCs) facilitate the production of ground level ozone; short-term exposure contributes to eye, nose, and throat irritation while long-term

exposure has been linked to emphysema, fibrosis, broncopneumonia, and congenital birth defects. Two possible alternatives to the use of halogenated compounds and VOCs as solvents is the use of carbon dioxide (CO₂) and Ionic Liquids (ILs), which have some very attractive benefits such as solubility and recyclability.

BACKGROUND

Carbon Dioxide (CO₂)

CO₂ is available as a relatively cheaply recovered by-product from ammonia plants and natural gas wells. Furthermore, CO₂ is nontoxic, nonflammable, and chemically benign. It also does not contribute to the formation of smog or deplete the stratospheric ozone. However, CO₂ is a greenhouse gas. Thus CO₂ is partly responsible for global climate change; which is the gradual increased warming of the earth's climate due to anthropogenic chemicals in the atmosphere. Scientists have predicted some of the consequences of global warming to be an increase in rainfall amounts in already rainy areas; the making of arid climates even drier; and the melting of polar ice caps, which could raise sea levels 48 cm by 2100.⁵ Other compounds known to contribute to global warming include methane, nitrous oxide, hydrofluorinated carbons (HFCs), perfluorinated carbons (PFCs) and sulfur hexafluoride (SF₆) (**Figure 1**).

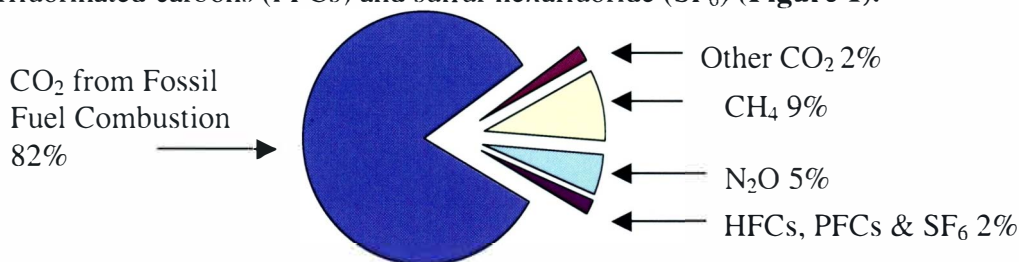


Figure 1: Anthropogenic Greenhouse Gas Emissions in the U.S. by Gas Type

Source: Energy Information Administration (Washington, D.C. 2002)

To aid in the reduction of global warming caused by CO₂, its gaseous form is recovered as mentioned above and used as a reactant and/or solvent by converting it into a subcritical or supercritical state. It is converted into a subcritical state by increasing the pressure exerted on it and maintaining a temperature below its critical point. The critical point is the highest point in both temperature and pressure on the liquid-vapor coexistence curve of its phase diagram. The critical temperature (T_c) of a substance is the temperature above which a distinct liquid phase of the substance cannot exist regardless of the pressure applied. The critical pressure (P_c) is the pressure above which a substance can no longer exist in gaseous phase. Therefore, a pure substance is considered to be in the supercritical state if its temperature and pressure are above the critical point (**Figure 2**).

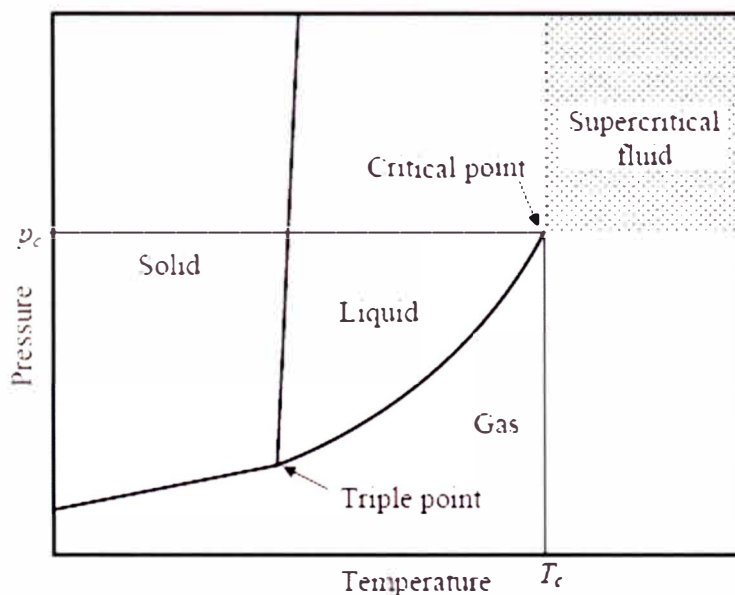


Figure 2. Generic Temperature-Pressure Phase Diagram of a Substance⁶

Above critical temperature ($T_c = 31^\circ\text{C}$) and pressure ($P_c = 72.9\text{ atm}$; 73.86 bar; 7.29 MPa, 1071.3 psi) of CO_2 , but below the pressure required to condense it into a solid ($< 5000\text{ atm}$) a supercritical fluid (SCF) is formed.²

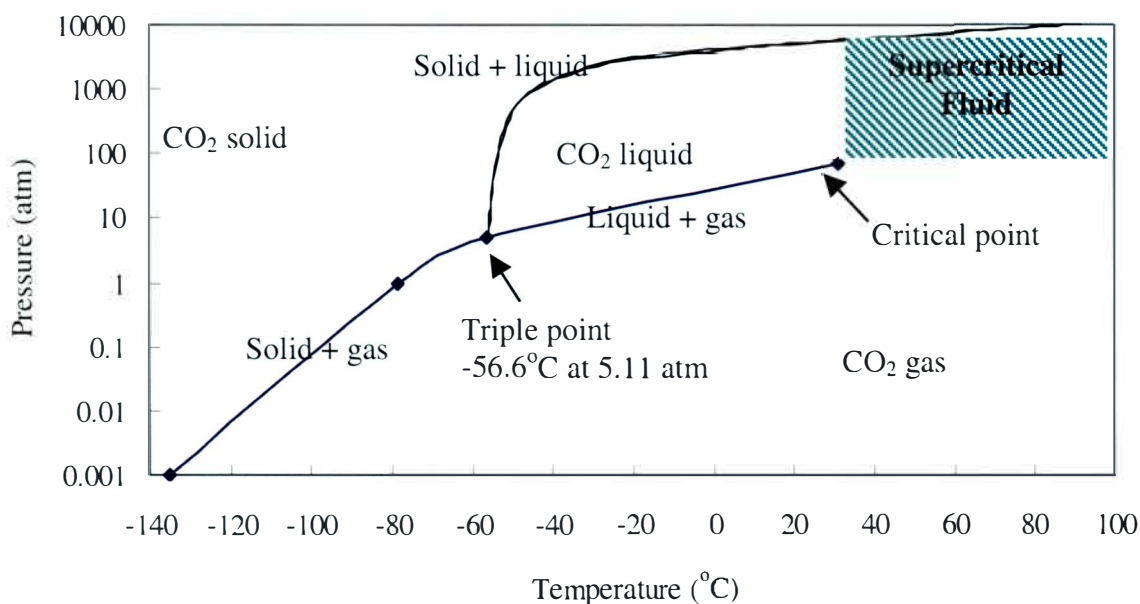


Figure 3: Temperature-Pressure Phase Diagram of Pure CO_2 ²

One of the attractive features of using a supercritical fluid is the ability to continuously “tune” its bulk physical properties, like density, viscosity and diffusivity coefficient, with small changes in temperature and pressure. As an example, **Figure 4** represents the density-pressure relationship for supercritical CO_2 (scCO_2) along four isotherms.

Isotherms closer to CO_2 's T_c have a larger degree of non-linearity, while those at higher temperatures are more linear. Examination of the 323 K isotherm demonstrates that at moderately high pressure (200 bar), the solvent density is liquid-like (0.8 g/mL) and comparable to many organic solvents. As pressure is reduced, the change in the bulk

solvent density is gradual in the high-pressure regime, and then decreases sharply as the pressure is lowered below 150 bar to the compressible region. At higher temperatures further removed from the T_c , solvent densities are lower and decrease more gradually from high to low pressure

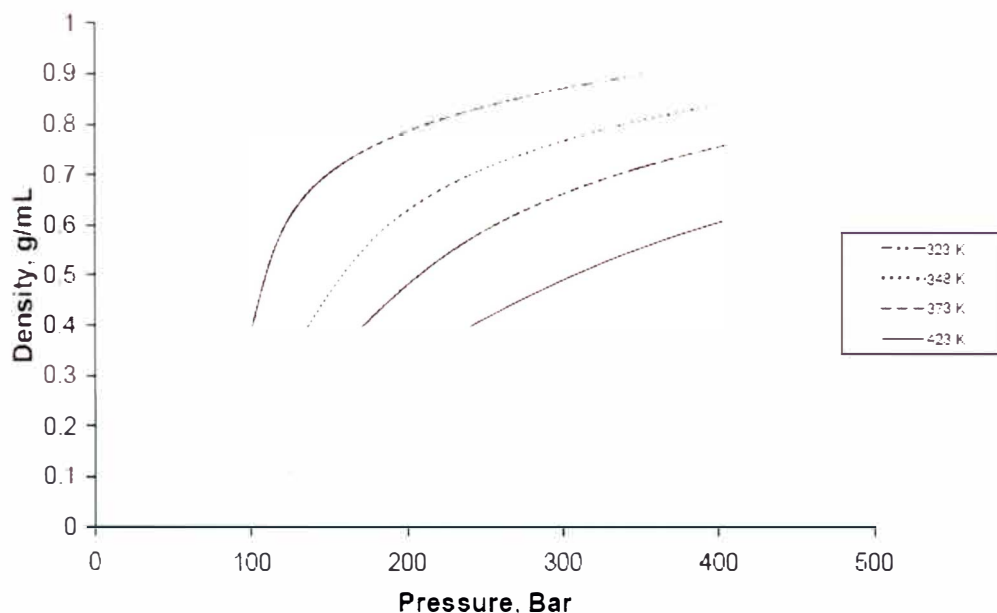


Figure 4: Density-Pressure Isotherms of Pure CO₂⁵²

Thus **Figure 4** illustrates the tremendous potential to control bulk density dependent properties of supercritical fluids. However, chemical reactivity in SCFs may also be influenced by local and solvent microstructure, in addition to the nature of the bulk solvent properties.

SCF have properties that are intermediate between liquids and gases. The densities, viscosities and diffusion coefficients of solutes of SCF fall between those found in liquids and gases. Comparisons of these values are found in **Table 1**. The most noticeable and

important feature of SCFs is that they have a high isothermal compressibility like a gas, and have the solvating power of a liquid, particularly at higher density.

Table 1: Comparison of Properties of Gases, SCF and Liquids⁷

	Density, g/mL	Diff. Coeff., cm ² /s	Viscosity, g/cm-s
Gas	0.001	0.1	0.0001
SCF	0.1 to 1.0	0.001	0.001 to 0.0001
Liquid	1.0	0.00001	0.01

Applications of CO₂

For decades, CO₂ has been used as a practical alternative to a variety of solvent based processes. The major commercial application of CO₂ in its supercritical state so far has been in the decaffeination of coffee and tea. For example, SKW/Trostberg runs a tea decaffeination plant in Meunschmeunster, Germany and General Foods has a coffee decaffeination facility in Houston, Texas. Other processing applications include the extraction of pharmaceutical compounds,⁸ various health supplements,⁸ as well as flavors and fragrances.⁹ For example, in 1992 Aryn Teja *et al.*¹⁰ showed that Taxol, a promising anti-cancer agent, can be extracted with scCO₂ from the bark of *Taxus brevifolia*, a slow growing variety of the yew tree. ScCO₂ extracts of celery, ginger, paprika, rosemary, sage and vanilla are also currently available commercially.

Other uses of scCO₂ can be found in the dry cleaning industry and in the cleaning of precision machinery: oils have high solubilities in CO₂; ¹¹ in the extraction of metals from solutions, soils and other solid matrices using metal chelates; and in material processing, e.g. the UNICARB[®] system, which is a process of spray painting and coating.

More recently, the catalytic transformation of CO₂ into useful organic compounds has received much attention, because of both environmental and economic factors.

Ionic Liquids (ILs)

Room temperature ionic liquids (RTIL) are organic salts that are liquid at (or close to) ambient temperature. They were formerly known as ‘room temperature molten salts’, but the term molten salts evoked an image of high temperature, viscous and highly corrosive media.¹² Other than liquid polymers, both RTIL and molten salts have a large liquidus range that perhaps no other molecular solvent can match with difference only in where the liquidus range is on the temperature scale. Most ionic liquids are liquids at room temperature.

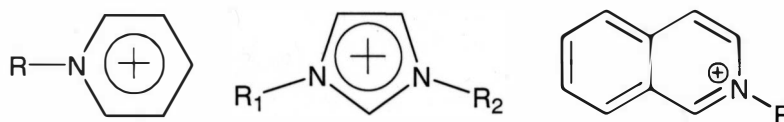
RTIL have interesting properties^{5,11} that make them attractive for use as solvents or catalysts, which serve as their underlying principle: (a) They are non-volatile owing to their lack of vapor pressure hence eliminate evaporation and containment problems. (b) They are thermally, chemically and electrochemically stable. (c) As stated earlier, they have a large liquidus range owing to the combination of non-volatility and thermal stability. (d) They dissolve a good number of organic and inorganic compounds as well

as gases such as H_2 , CO_2 and O_2 . (e) Their immiscibility with some organic solvents provides a non-aqueous, polar alternative for two-phase systems. (f) They are referred to as 'designer solvents' since some of their properties can be easily adjusted by a suitable choice of cation/anion. (g) They have the potential to be highly polar but non-coordinating solvents since they are composed of weakly coordinated ions. (h) Highly acidic ionic liquids, those containing chloroaluminate ions, are potential non-volatile replacements for hazardous acids such as HF in acid catalyzed reactions. These acids have been shown to possess Hammett acidities up to -18 .¹⁴

Many RTIL have been synthesized with some realizing more applications than others. The so-called 'red oil' (Heptachlorodialuminate salt) formed during Friedel-Crafts reaction was the first documented ionic liquid to be observed. Although this red-oil ionic liquid was patented as a useful material, no major industrial uses are known to date.¹⁵ Ethylammonium nitrate, described in 1914, was synthesized by the addition of concentrated nitric acid to ethylamine yielding a pure salt, which was a liquid at room temperature with a melting point of 12°C .⁴ Studies of N-alkylpyridinium chloroaluminates as electrolytes for electroplating aluminum were carried out in the late 1940s but it was not until the late 1970s that they were later revisited.¹³ However, their widespread application was hindered by the high reactivity of the chloroaluminate anion towards water. Other ionic liquids that are stable towards water were developed more recently with the first among these being 1-ethyl-3-methylimidazolium tetrafluoroborate (emimBF_4 or $[\text{C}_2\text{-MIM}]^+\text{BF}_4^-$), which was reported by Wilkes *et al.*¹⁶ in 1992. Following this, Fuller *et al.*¹⁷ synthesized the corresponding hexafluorophosphate salt, which was also

stable towards hydrolysis. This led to the preparation of a host of other ILs made up of various cations and anions. Some examples are shown in **Figure 5**.

Cations:



Anions:

Cl^- , Br^- , $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{SbF}_6]^-$, $[\text{NO}_3]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{Al}_2\text{Cl}_7]^-$, $[\text{NO}_3]^-$, $[\text{NO}_2]^-$, $[\text{SO}_4]^{2-}$

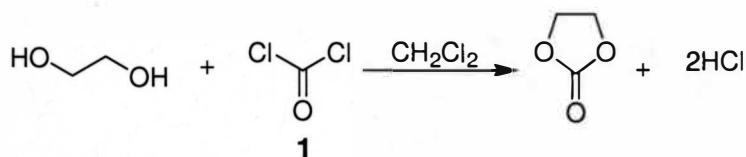
Figure 5: Structures of Cations and Anions That Make Up ILs

Organic Carbonates

The production of both molecular carbonates (world market equal to 80 Kt per year) and polymers (1.1 Mt per year), have gained increasing market demand in the past few decades. Organic molecular carbonates find extensive applications¹⁸ as monomers that are used as biodegradable material, aprotic polar solvents, fuel additives, and intermediates in the synthesis of agrochemicals such as herbicides and disinfectants as well as in the preparation of cosmetics and personal care products¹⁸ hydraulic fluids additives,⁴ and in textiles dyes.¹⁹

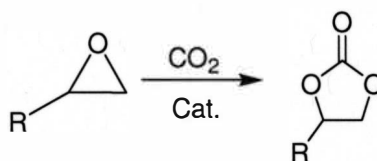
Conventional synthesis of organic carbonates is based on the use of highly toxic phosgene [**1**] as a starting material (**Scheme 1**), with the end production of large amounts of chlorinated waste products, which poses a large environmental impact.

Scheme 1



In the search for environmentally benign processes, several alternative routes to cyclic carbonates have been developed. The formation of cyclic carbonates represents one of the few uses of CO₂ in synthesis as a C₁ feedstock (**Scheme 2**).

Scheme 2



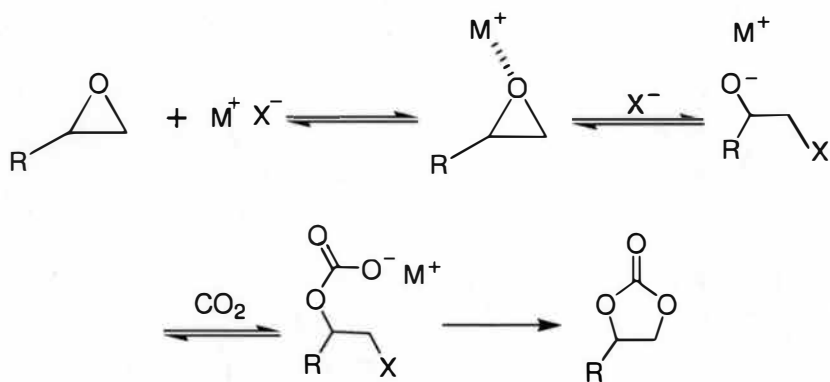
This represents a 100% atom economic reaction with a maximum incorporation of the starting material and reagents in the product. B.M. Trost³ developed the concept of atom economy in a consideration of 'how much of the reactants end up in the final product'. It was also determined by R.A. Sheldon³ and is given by:

$$\% \text{ atom economy} = \frac{\text{FW of atoms utilized}}{\text{FW of reactants used in the reaction}}$$

The coupling of CO₂ with epoxides has been shown to occur using various catalysts forming cyclic carbonates and/or polycarbonates. These catalysts vary from simple alkali metal salts to complex organometallic complexes. In 1969, Inoue *et al.*²⁰ discovered that polycarbonates could be synthesized from epoxides and CO₂ catalyzed by Et₂Zn/H₂O.

This led to a search for better catalysts to produce polycarbonates but instead many catalysts were found to produce only monomeric species, that is, cyclic carbonates, while others gave a combination of both monomeric and polymeric species. They were also faced with low yields and insufficient turnovers. Alkali metal salts have been used alone and in conjunction with crown ether to catalyze the reaction of CO₂ and epoxides. Rokicki *et al.*¹⁹ have studied a variety of alkali metal salts in the presence of crown ethers. After 24 hrs at 120°C and 40 atm of CO₂, high yields of cyclic carbonates were obtained (**Scheme 3**). Under these conditions the catalytic activity was found to increase with increasing anion nucleophilicity and cation diameter.

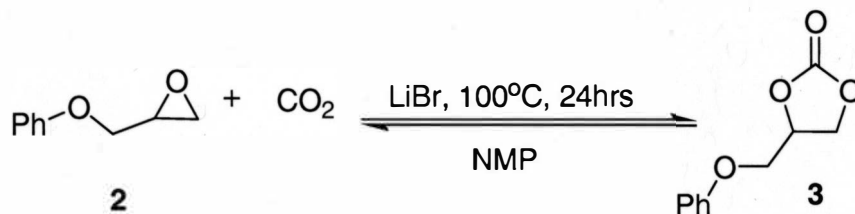
Scheme 3



In 1993 Kihara *et al.*²¹ reported that only halide salts showed a high activity under atmospheric pressure and were more effective than onium salts. 2,3-Epoxypropyl phenyl ether (11 mmol) [2] was used as the model epoxide, and 5mol% of the catalyst was added in 11 mL of N-methylpyrrolidone (NMP) and heated at 100°C for 24 hours at 1 atm of CO₂. 73% pure 4-(phenoxyethyl)-1,3-dioxolane-2-one [3] was obtained after recrystallization from ethanol (**Scheme 4**). The catalytic activity of the halides was seen to be consistent with the order of nucleophilic reactivity in aprotic solvents, which is, I⁻ <

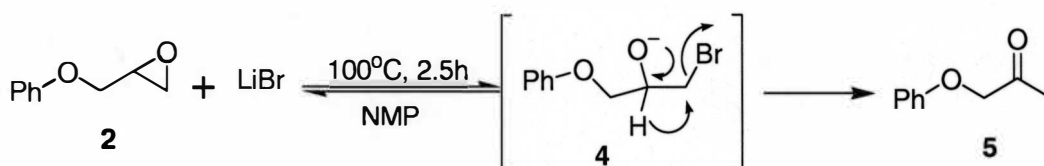
$\text{Br}^- < \text{Cl}^-$ while the cation order of activity was $\text{PhCH}_2\text{N}^+\text{Me}_3 < \text{Na}^+ < \text{Li}^+$, which is in order of the Lewis acidity of the cation, but opposite from the results obtained by Rocicki *et al.*¹⁹ as mentioned earlier.

Scheme 4



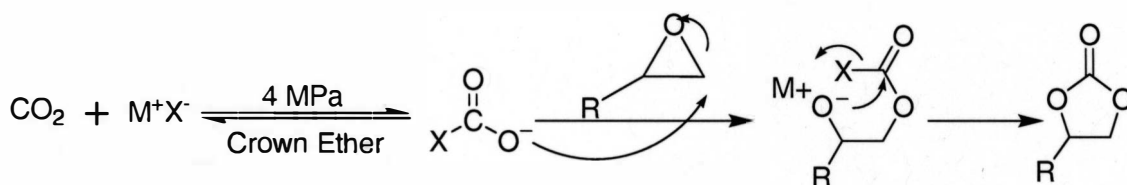
The reaction mechanism was as seen in **Scheme 3**, which they confirmed by the reaction of the epoxide with LiBr in the absence of CO_2 at 100°C for 2.5 hrs in NMP yielding 20 % 1-Phenoxy-2-propanone [**5**] as the sole product (**Scheme 5**). Thus the presence of key intermediate [**4**] was proven indirectly.

Scheme 5



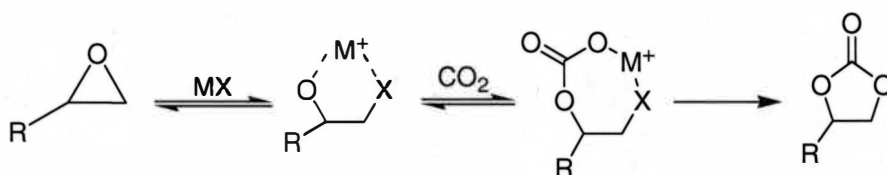
Highly nucleophilic anions such as acetate, cyanide, phenolate and thiophenolate showed no catalytic activity in the epoxide- CO_2 reaction at atmospheric pressure, probably due to their low leaving ability.²¹ However, carboxylate and phenolate anions have been shown to catalyze the same reaction in the presence of crown ether under high-pressure conditions¹⁹ indicating the existence of another mechanism (**Scheme 6**).

Scheme 6



Although non-nucleophilic anions such as p-toluene-sulfonate and perchlorate exhibit higher leaving ability, they showed no catalytic activity.²² Investigations by Sako *et al.*²² revealed that the alkali metal halides shown to have high catalytic power in aprotic polar solvent under atmospheric pressure,²¹ behaved differently in scCO_2 . Generally the order of catalytic activity was found to be $\text{LiBr} > \text{LiI} > \text{NaI} > \text{KI} \gg \text{LiCl}, \text{NaCl}, \text{KCl}$. The iodide salts showed highest activity while the chlorides showed no activity at all under supercritical conditions. It was suggested that the dissolving power of the catalysts in the different solvents contributed to the disparity of results. Two reaction pathways were identified: one for the catalyst dissolving model (shown in **Scheme 3**) and the other for the solid catalyst model (**Scheme 7**). However, it was not determined which of the pathways was appropriate in the case of a supercritical solvent.

Scheme 7



Sako *et al.*²² also proposed that the reaction proceeded rapidly and completely in the supercritical state while it hardly occurred in the vapor-liquid state. The product was selectively separated from the supercritical mixture of reactants and product by

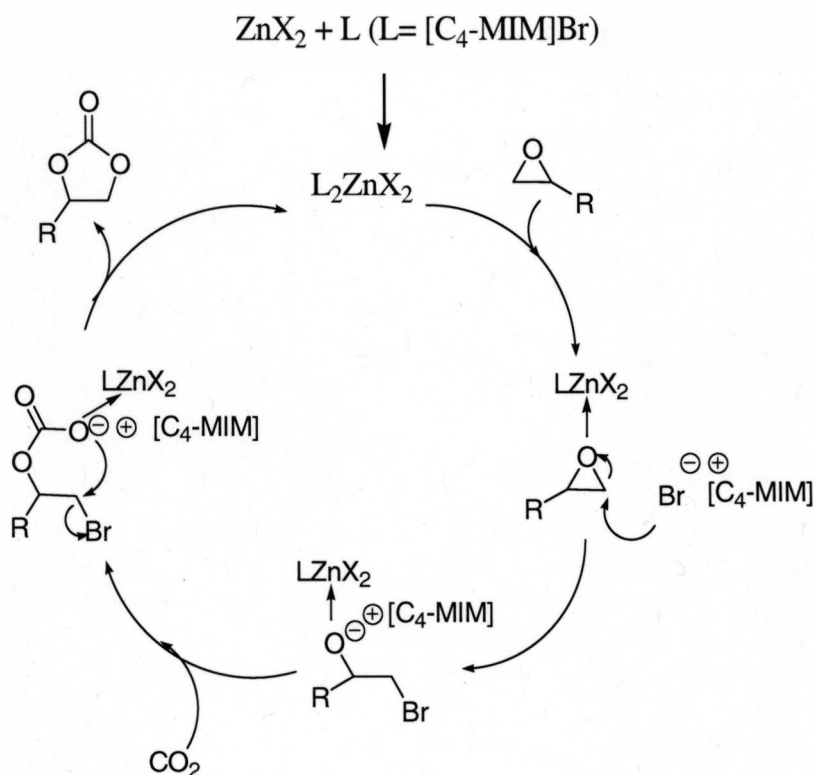
condensation into a product separation vessel whose temperature and pressure were lower than those of the reactor.

More recently, RTIL have been investigated as potential catalysts for the CO₂-epoxide coupling without using additional organic solvents. In 2001, Peng *et al.*²³ reported that 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄ or [C₄-MIM]⁺BF₄⁻) catalyzed the CO₂-propylene oxide coupling with a 100% conversion. The reaction was carried out at 110°C for 6 hours at pressures between 1.5 and 4.5 MPa. Other RTIL consisting of 1-butyl-3-methylimidazolium [C₄-MIM]⁺ or N-butyl-pyridinium [C₄-Py]⁺ cations and Cl⁻, [BF₄]⁻ or [PF₆]⁻ were investigated and the results showed that the catalytic activities were strongly influenced by both cations and anions. [C₄-MIM]⁺[PF₆]⁻ showed the lowest catalytic activity followed by [C₄-Py]⁺[BF₄]⁻, and when [C₄-MIM]⁺Cl⁻ was added to [C₄-MIM]⁺[PF₆]⁻, the yield increased remarkably.

As far as the mechanism is concerned, a new pathway was conjectured.²³ Since the non-nucleophilic BF₄⁻ and PF₆⁻ ions cannot form a covalent bond with the epoxide, it was suggested that a CO₂-propylene oxide complex was formed and activated by the [C₄-MIM]⁺ cation. The choice of the anion contributed greatly to the physicochemical properties of the cation resulting in an enhancement or inhibition of its interaction with the CO₂-propylene oxide complex, hence the difference in catalytic activities. The product was separated from the ionic liquid by simple distillation and the catalyst was recyclable.

Much more recent, in 2004, Li *et al.*²⁴ employed the $\text{ZnX}_2'/[\text{C}_4\text{-MIM}]^+\text{X}''^-$ catalytic system to form cyclic carbonates in excellent yields under mild conditions. Li *et al.*²⁴ investigated the carboxylation of propylene epoxide with CO_2 at a reaction pressure of 1.5 MPa, heated at 100°C for 1 hour. Trace reactions occurred in $\text{ZnCl}_2/[\text{C}_4\text{-MIM}]^+\text{BF}_4^-$ and $\text{ZnCl}_2/[\text{C}_4\text{-MIM}]^+\text{PF}_6^-$, while only 38% product was obtained when $\text{ZnCl}_2/[\text{C}_4\text{-MIM}]^+\text{Cl}^-$ was employed. $[\text{C}_4\text{-MIM}]^+\text{Br}^-$ showed the highest activity as a co-catalyst with yields as high as 98%. However, when it was used alone, only 8% yield was obtained. The $\text{ZnCl}_2: [\text{C}_4\text{-MIM}]^+\text{Br}^-$ ratio of 1:6 (0.05 mol %) was found most favorable. A plausible mechanism for the chemical fixation of CO_2 was proposed (**Scheme 8**).

Scheme 8



Other reaction systems reported in the literature employed catalytic systems such as Nb (V) compounds in organic solvents²⁵, $\text{Re}(\text{CO})_5\text{Br}$ in a solvent-free system²⁶, and phenol

in the presence of catalytic amounts of various organic bases such as 4-dimethylaminopyridine (DMAP).²⁷ When styrene oxide was employed as the model epoxide in these systems, long reaction times of between 12 and 48 hrs even at temperatures ranging from 110 to 135°C and average pressures of 3.5 to 5.5 MPa were required to give decent yields of 68 to 96%.

It is evident from all the cited literature that the reaction pressure affects the catalytic performance of various catalysts. Few catalysts were found to efficiently catalyze the coupling reaction of CO₂ and styrene oxide [6], and those that did catalyze the reaction had to be used in high quantities. We have therefore embarked on the search of a simple, versatile, efficient and environmentally friendly catalyst for the conversion of styrene oxide [6] to styrene carbonate (4-phenyl-1,3-dioxolan-2-one) [7].

OBJECTIVE

The uses of CO₂ in synthetic and industrial applications represent an important goal in the minimization of its emission as its output continues to rise. New strategies aimed at recovering and utilizing CO₂ have assumed increased importance. The chemical fixation of CO₂ to epoxides is a particularly well-studied reaction, which represents a successful utilization of CO₂. Its simple operation, high yield, and harmless nature of the reagents contribute to its attractive features. Numerous catalytic systems have been developed for this transformation. However, while the advances have been significant, most of them suffer from low catalyst stability/reactivity, air sensitivity, and the need for co-catalysts or solvents/ co-solvents. Also, the systems continue to use traditional methods such as

solvent extraction or distillation to recover the product and/or catalyst. Therefore, it is our goal to develop a reaction system that is both economically and environmentally attractive for the chemical fixation of CO₂ to styrene oxide [6] to form styrene carbonate [7]. We seek to develop a catalyst that is stable, which does not need any solvents or co-catalysts but gives high yields, and one that can be separated from product using scCO₂.

In an effort to achieve these objectives, several catalytic reaction systems have been investigated under a variety of reaction conditions. The following is a short outline of the Results and Discussion section presented below.

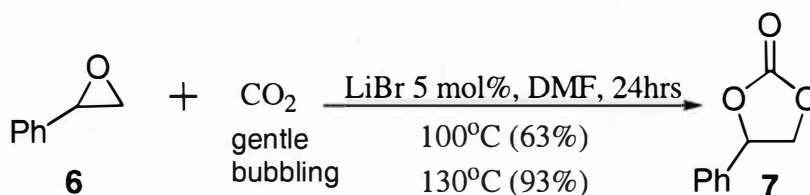
- Initial experiments explored the reaction efficiency of styrene oxide with 1 atm CO₂ in conventional organic solvent using an alkyl halide catalyst at varied temperatures.
- Utilizing high-pressure techniques to modify the conventional reaction system, the influence of CO₂ concentration at pressures between 1 MPa and 30 MPa was explored.
- Next, solvent-free reaction conditions were investigated using ammonium salts and ILs as catalysts.
- The data presented below will then describe a catalytic reaction system and reaction conditions that fulfill the objectives stated above.
- The observed results will be discussed in terms of CO₂ pressure/concentration effects and phase behavior.

RESULTS AND DISCUSSION

Conventional Synthesis Using an Alkyl Halide Catalyst

Styrene carbonate [7] was synthesized using Kihara *et al.*'s²¹ most successful reaction conditions in the synthesis of 4-phenoxy-1,3-dioxolan-2-one [3] from 2,3-epoxypropyl phenyl ether [2] (1 atm CO₂, 100°C, 24 hrs, 5 mol% LiBr, NMP. In our case, commercially available styrene oxide [6] was chosen as the model epoxide since it was one of the least studied epoxides and DMF was used as the reaction solvent (**Scheme 9**).

Scheme 9



Gaseous CO₂ was administered via a syringe in a gentle bubbling manner. The styrene carbonate [7] produced in the reaction mixture had a tendency to block the syringe and interrupt the CO₂ flow resulting in non-reproducible % yields ranging from 36% to 63%. This problem was overcome by exploring higher reaction temperatures where a maximum yield of 93% was obtained at 130°C, under otherwise identical conditions. The crude product was obtained by precipitation in water and recrystallized from ethanol.

Modification of Conventional Synthesis

To improve these reaction conditions we sought to synthesize styrene carbonate [7] under supercritical conditions. Styrene oxide [6], DMF, and the catalyst were charged into a 90 cm³ high pressure reactor and CO₂ was introduced using a high pressure syringe pump. The reaction was carried out at various temperatures, pressures and times giving yields as depicted in **Table 2**. We used GC-MS to determine the % conversion. The product was recovered by precipitation in water and characterized by M.P, ¹H NMR, ¹³C NMR, IR and GC-MS, and compared to literature data.²⁵

Table 2: Temperature, Pressure, and Time Dependence of % Conversion of Styrene Carbonate [7] Using LiBr as Catalyst

MPa ^a	1	5	10	15	18	20	25	30
100°C ^b (4hrs)	56.5	58.5	69.9	51.5	33.7	26.8	20.0	15.0
100°C ^b (8hrs)	65.6	66.1	73.2	66.4	51.5	49.3	47.2	40.0
130°C ^b (4hrs)	90.2	90.8	94.1	88.1	86.2	83.2	80.7	73.4

^a ±0.2 MPa; ^b ±1°C; ^c 6% estimated confidence level

The results obtained so far proved that the reaction rate was accelerated under pressures higher than atmospheric conditions. 94% of styrene carbonate [7] was obtained in 4 hrs at 130°C and 10 MPa compared to 93 % in 24 hrs under atmospheric conditions. As the pressure increased from 1 MPa to 10 MPa, the product yield increased. However, further increase in pressure led to a decrease in conversion. While an increase the reaction time afforded slightly higher % conversions, increase in temperature from 100 to 130°C

increased the % conversion significantly and at less time. **Figure 6** shows a plot of pressure verses % conversion for the data in **Table 2**.

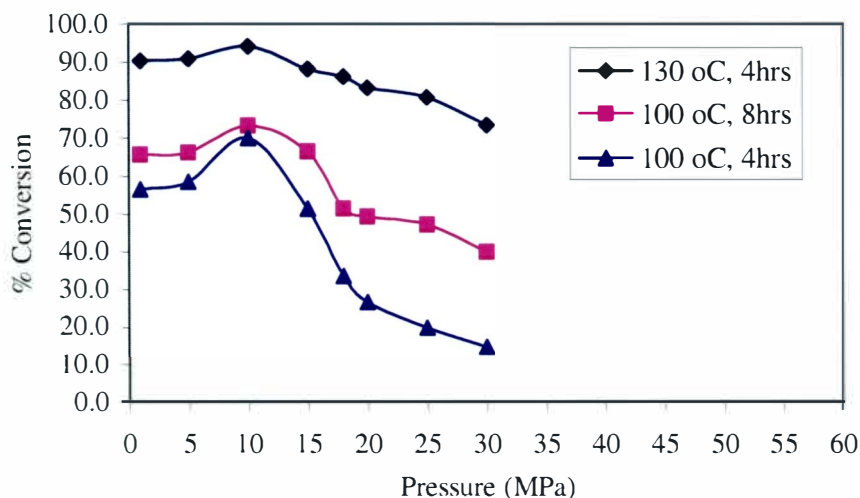


Figure 6: Temperature, Pressure, and Time Dependence of % Conversion of Styrene Carbonate [7] Using LiBr Catalyst

Solvent-Free Synthesis Using an Alkyl Halide Catalyst

The first step toward a ‘greener’ synthetic route was to exclude the toxic solvent from the reaction. In Sako *et al.*’s procedure,²² 2-methyloxirane or 2,2-dimethyloxirane were reacted with CO₂ using 1mol % LiBr catalyst at various temperatures from 50°C to 120°C at pressures of 6, 8, 10, and 12 MPa for 2 hrs without any solvent. Product yield varied from as low as 5% to as high as 95% in a narrow temperature range. Following the steps of Sako *et al.*²² we sought to synthesize styrene carbonate [7] in the absence of the solvent DMF. However, only a trace amount of product was obtained and it did not improve even when the reaction time was increased to 6 hrs, and the pressure was raised

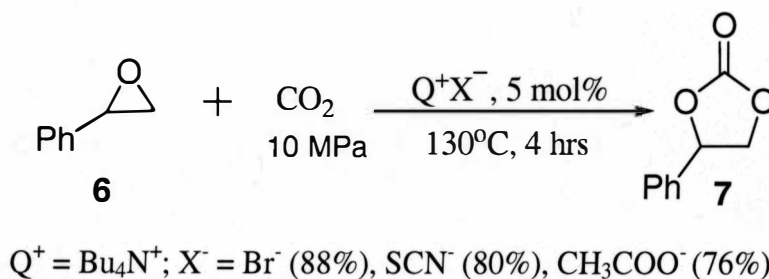
to 26 MPa. Since the lower molecular weight epoxides used by Sako *et al.*²² have higher solubility a single epoxide/scCO₂ phase was obtainable. This was not the case using higher molecular weight styrene oxide [6].

Therefore the lower reactivity of styrene oxide [6] may have been a result of poor mixing ratios of reactants since alkali metal salts have little or no solubility in CO₂. In order to achieve a better mixing ratio of reactants, catalysts with melting points lower than our reaction temperature and possibly better solubility in CO₂ were investigated without the aid of a solvent.

Solvent-Free Synthesis Using Quaternary Ammonium Salts

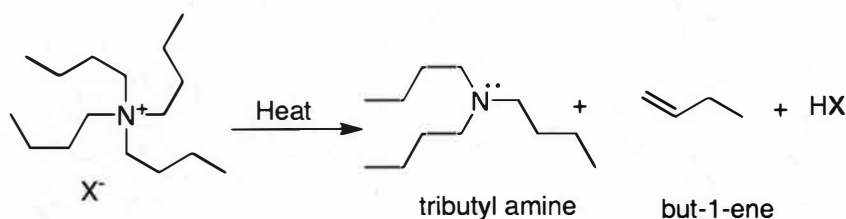
Styrene oxide [6] was reacted with CO₂ in the presence of a quaternary ammonium salt to give styrene carbonate [7] in high yields (Scheme 10).

Scheme 10



Quaternary ammonium salts proved to be more efficient catalysts in the absence of a solvent compared to the alkali metal salts probably due to better solubility in CO₂. Although the yields were pretty good, the ammonium salt decomposed via Hoffman elimination (**Scheme 11**) to form tributyl amine and 1-butene as detected and determined by GC-MS. Other side products were also formed when the acetate (CH₃COO⁻) and thiocyanate (SCN⁻) anions were used.

Scheme 11



In addition to these shortcomings, the solubility of the quaternary ammonium salts in supercritical carbon dioxide was a hindrance to the feasibility of selective supercritical fluid extraction without catalyst contamination.

Ionic Liquids in Synthesis

Blanchard *et al.*²⁸ first suggested the possibility of combining ILs and scCO₂. They noted that ILs have no solubility in CO₂ whereas CO₂ dissolved in the IL giving way to the use of scCO₂ to extract organic solutes without any cross contamination. At the same time,

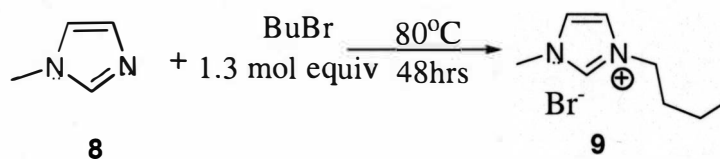
the use of RTILs as environmentally benign media for synthesis and catalysis was reported.⁴

Peng *et al.*²³ reported that $[\text{C}_4\text{-MIM}]^+[\text{BF}_4]^-$ (100% conversion) displayed a better catalytic efficiency than $[\text{C}_4\text{-MIM}]^+[\text{PF}_6]^-$ (11.3% conversion) in the synthesis of propylene carbonate from propylene oxide. To determine the generalities of using these ILs as catalysts, reactivity of styrene oxide **[6]** with CO_2 was explored at 3 MPa, 110°C, for 6 hrs in the presence of $[\text{C}_4\text{-MIM}]^+[\text{PF}_6]^-$ (used as purchased from Sachem). ^1H NMR detected no product. The IL was further purified by dissolving in methylene chloride and washed with small portions of deionized water until neutral. It was rotavaped and dried at 120°C *in vacuo* for 48 hrs. Using the purified IL, a wide range of reaction conditions were examined ranging from 1 MPa to 30 MPa at temperatures of 100, 115 and 130°C. ^1H NMR detected trace amounts of products or nothing. Based on these results and the findings of Peng *et al.*²³, the possibility of using $[\text{C}_4\text{-MIM}]^+[\text{PF}_6]^-$ as catalyst for the carboxylation of styrene oxide **[6]** was abandoned.

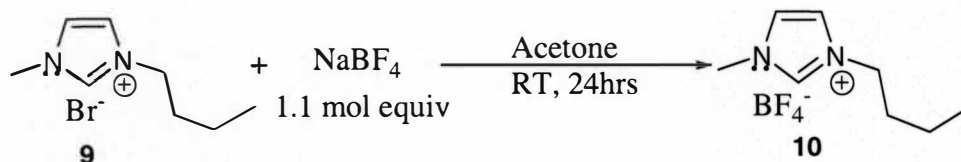
In turn, the catalytic efficiency of $[\text{C}_4\text{-MIM}]^+[\text{BF}_4]^-$ in the reaction of styrene oxide **[6]** with CO_2 was investigated. $[\text{C}_4\text{-MIM}]^+[\text{BF}_4]^-$ was synthesized by quaternization of 1-methylimidazole **[8]** with butyl bromide in a 1:1.3 molar ratio respectively to form $[\text{C}_4\text{-MIM}]^+\text{Br}^-$ **[9]** (Scheme 12). It was stirred and refluxed at 80°C for 48 hrs, and the reaction monitored by ^1H NMR until no alkylimidazole was observed. Washing with ethyl ethanoate and heating *in vacuo* removed any remaining starting material. The next step involved a metathesis reaction between IL **[9]** and a 1.1 molar equivalent of NaBF_4 in acetone at room temperature for 24 hrs to form $[\text{C}_4\text{-MIM}]^+[\text{BF}_4]^-$ **[10]** (Scheme 13).

After the workup, 92% of IL [10] was obtained and analyzed by ^1H NMR. The presence of halide ions was checked using the AgNO_3 in ethanol test.^{12,29}

Scheme 12



Scheme 13



IL [10] was used to catalyze the addition of CO_2 to styrene oxide [6] at pressures ranging from 0 MPa to 30 MPa; at temperatures of 100, 115, and 130°C. As with $[\text{C}_4\text{-MIM}]^+ [\text{PF}_6]^-$, only trace amounts of product could be detected by ^1H NMR.

In order to determine if the apparent non-nucleophilicity of $[\text{BF}_4]^-$ was a property related to the IL, NaBF_4 was used as a catalyst in the carboxylation process. No product was obtained. This relates to the results obtained by Sun *et al.*²⁴ when they coupled ILs bearing the non-nucleophilic anions $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$ with zinc halides and obtained low styrene carbonate [7] yields of 5 and 1 %, respectively. These results indicate that more

nucleophilic anions are needed to efficiently catalyze the cycloaddition of CO₂ to styrene oxide [6].

In order to utilize a nucleophilic anion while maintaining the ‘greenness’ of the process, IL [9], the precursor in the synthesis of IL [10], was employed as catalyst. Thus styrene oxide [6] was reacted with CO₂ in the presence of catalytic amounts of [C₄-MIM]⁺X⁻, where X⁻ is Cl⁻, Br⁻, or I⁻. Various pressure and temperature conditions were examined as recorded in **Table 3** and illustrated in **Figure 7**.

Table 3: % Conversion^c Using IL Catalysts at Various Temperature and Pressure Conditions

MPa ^a	[C ₄ -MIM] ⁺ Br ⁻ 100°C ^b (4hrs)	[C ₄ -MIM] ⁺ Br ⁻ 115°C ^b (4hrs)	[C ₄ -MIM] ⁺ Br ⁻ 130°C ^b (4hrs)	[C ₄ -MIM] ⁺ Br ⁻ 130°C ^b (1hrs)	[C ₆ -MIM] ⁺ I ⁻ 130°C ^b (1hrs)
1	57.6	78.3	95.1	70.2	90.3
5	65.0	83.3	96.5	72.3	92.8
10	75.6	85.6	99.4	77.3	96.7
15	61.0	79.6	88.4	61.9	86.8
20	52.7	69.2	83.3	49.3	72.4
25	42.7	66.4	81.9	38.6	67.8

^a ±0.2 MPa; ^b ±1°C; ^c 6% estimated confidence level

A consistent CO₂ pressure effect was observed for all [C_n-MIM]⁺X⁻ catalysts used at the three different temperatures (100, 115, and 130°C) investigated. It was observed that the yield increased with increase in pressure up to 10 MPa, and a further increase in pressure

past 10 MPa led to a decrease in yield. A rationale for the influence of CO₂ pressure on the observed reactivity is presented below

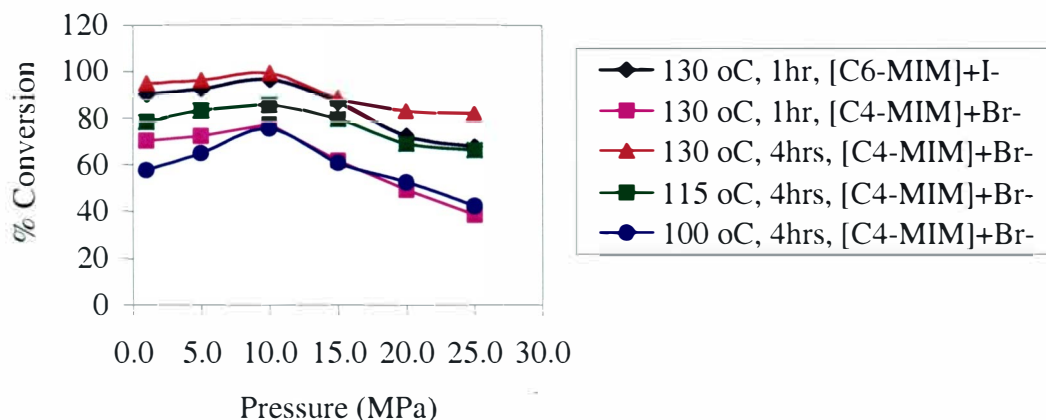


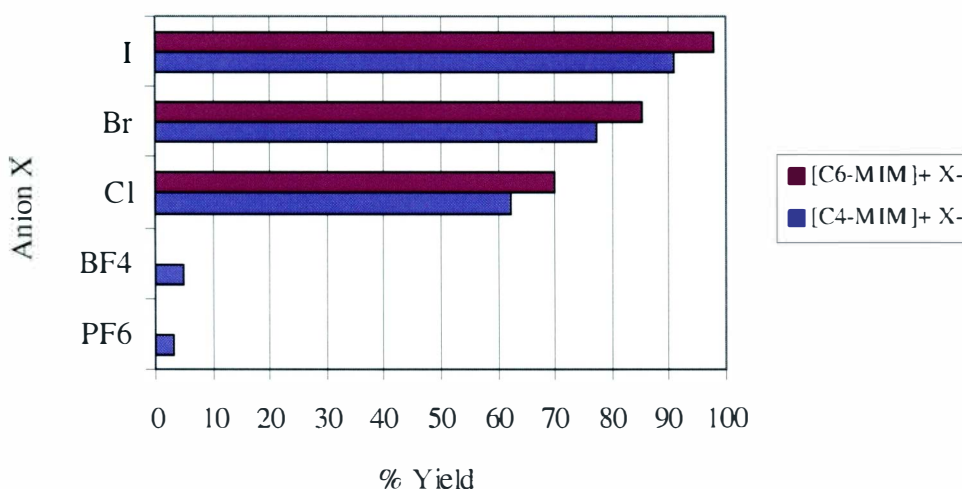
Figure 7: % Conversion Using IL Catalysts at Various Temperature and Pressure Conditions

The catalytic activity of the halides was examined at 10 MPa for 1 hr and the order of reactivity was found to be $I^- > Br^- > Cl^-$ in accordance with the nucleophilic strength of these anions in polar protic solvents. This closely corresponds with the results obtained by Sako *et al.*²² when the reaction was carried out in scCO₂. It was interesting to note that these halide catalysts have the same solubility properties as [C₄-MIM]⁺[BF₄]⁻.^{29,30} Among many other solvents, both the BF₄⁻ and halide ILs are soluble in water and insoluble in CO₂.

The % conversion of styrene oxide at the optimum conditions (130oC, 10 MPa, 1hr) was examined using all the ILs and the results are as shown in **Table 4** and **Figure 8**.

Table 4: Anion Reactivity and Cation Chain Length Effect

Anion X ⁻	% Conversion	
	[C ₄ -MIM] ⁺ [X] ⁻	[C ₆ -MIM] ⁺ [X] ⁻
PF ₆ ⁻	3.0	-
BF ₄ ⁻	5.0	-
Cl ⁻	62.4	69.8
Br ⁻	77.3	85.2
I ⁻	91.0	97.8

**Figure 8:** Anion Reactivity and Cation Chain Length Effect

Chain Length Effect

From **Figures 7 and 8** we notice that the lengthening of the alkyl chain on the cation leads to higher yields implying increased catalytic efficiency. This was also demonstrated by Kawanami *et al.*³¹ starting with [C₂-MIM]⁺[X]⁻, where X⁻ is NO₃⁻, [CF₃SO₃]⁻, [PF₆]⁻ or BF₄⁻, in the carboxylation of propylene oxide with scCO₂ at 14 MPa, 100°C for 2 hours. [BF₄]⁻ was found to be the most effective anion giving 61% yield. Using BF₄⁻ as the anion, a series of ionic liquids with different alkyl chain length from C₂ to C₈ were investigated. It was observed that the yield increased with lengthening of the alkyl chain.

This is consistent with our observations for the C₄ and C₆ IL results presented in **Figures 7 and 8**. It is apparent that an increase in alkyl chain length of the IL catalyst is beneficial to the carboxylation of epoxides using IL catalysts. This is most likely due to an increase in the solubility of CO₂ and epoxide, which results in a more favorable reactant/CO₂/catalyst ratio. This will be discussed further below.

Influence of Reaction Parameters

Figure 7 shows the influence of pressure, temperature and time on the yield of carbonate. As expected, the carbonate yield decreased with decrease in temperature. It is worth noting that the average temperature of 115°C had on average 80% conversion using [C₄-MIM]⁺Br⁻ although a longer reaction time of 4 hrs was needed. Conversions above 90% were obtained at 130°C, 10 MPa, for 1 hr using [C_n-MIM]⁺I⁻.

In order to ascertain the influence of pressure on the activity, two more reactions were carried out at lower pressures of 0.25 and 0.5 MPa. In the absence of CO₂, no product was obtained. When the pressure was increased to 0.25 MPa, 11% product was formed. Further increases in pressure led to a sharp increase in conversion to 57% at 0.5 MPa and 90% at 1 MPa followed by a gradual increase in conversion up to 97% at 10 MPa. Subsequently, a gradual decrease in yield was observed with increase in pressure beyond 10 MPa as recorded in **Table 5**. **Figure 9** illustrates this phenomenon.

Table 5: Effect of Pressure on Carbonate Conversion at 130°C Using $[\text{C}_6\text{-MIM}]^+\text{I}^-$ for 1 hr

Pressure (MPa)	0	0.25	0.5	1	5	10	15	20	25
% Conversions	0	11.1	56.9	90.3	92.8	96.7	86.8	72.4	67.8

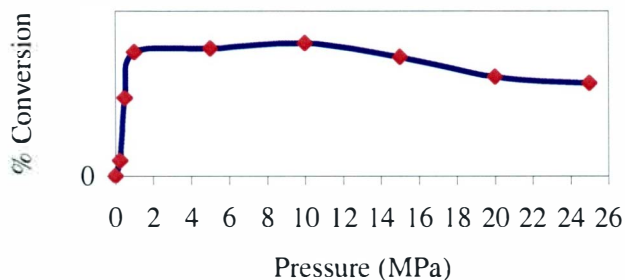


Figure 9: Effect of Pressure on Carbonate Conversion at 130°C Using $[\text{C}_6\text{-MIM}]^+\text{I}^-$ for 1 hr

Phase Behavior

Understanding the phase behavior of the reaction mixture at different pressures may provide a plausible explanation for the trends observed. Using UV-vis spectroscopy we examined the solubility of styrene oxide, styrene carbonate and $[\text{C}_4\text{-MIM}]^+\text{I}^-$ in CO_2 at various temperature and pressure conditions. The compounds were charged into a 2.25 mL optical cell equipped with sapphire windows and CO_2 was charged to the desired pressure.

IL solubility in CO_2 was first investigated by UV-vis analysis and was compared to its solubility in dichloromethane (DCM). The lack of absorption maxima at pressures between 1 and 25 MPa in **Figure 10** verifies the lack of IL in the CO_2 phase despite the

increase of pressure. Conversely, in DCM, an absorption maxima was observed at 360 nm corresponding to $\pi \rightarrow \pi^*$ transitions. These results are consistent with literature results^{28,33} for $[\text{C}_4\text{-MIM}]^+\text{BF}_4^-$ and $[\text{C}_4\text{-MIM}]^+\text{PF}_6^-$ in that the ILs did not dissolve in CO_2 .

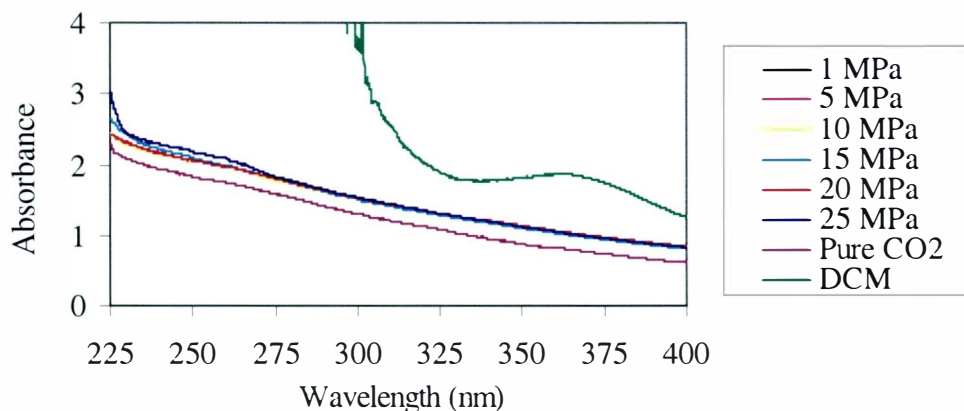


Figure 10: Comparison of UV-vis Absorption Spectra Observed for $[\text{C}_6\text{-MIM}]^+\text{I}^-$ in CO_2 vs. DCM at RT

Figure 11 shows the UV-vis spectrum of 0.5 μL of styrene oxide in CO_2 at room temperature (RT). The absorbance of the epoxide increases with increase in pressure implying that increasing the CO_2 pressure raises the solubility of styrene oxide in the CO_2 phase. Extensive studies of the extraction of organic compounds using scCO_2 have consistently shown that the solubility of organic compounds at higher pressures is generally higher even at low temperatures.³² Increase in pressure leads to increase in density hence a ‘liquid-like’ state is attained which dissolves compounds better than the ‘gas-like’ state.

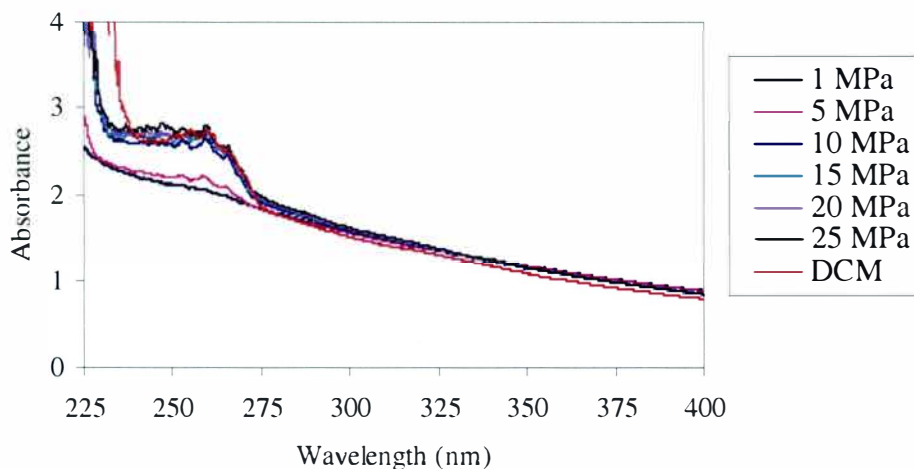


Figure 11: UV-vis Spectra of Styrene Oxide in CO₂ at RT

The epoxide solubility at reaction temperatures (100, 115, and 130°C) was also examined (**Figures 12**), and was found to be high. We know that density decreases with increase in temperature at constant pressure. Although we did not keep the pressure exactly constant, by using the density-pressure isotherms from **Figure 3** we know that the increase in temperature led to a decrease in density. However, even in the more ‘gas-like’ state (**Figure 12(a)**), epoxide solubility was high.

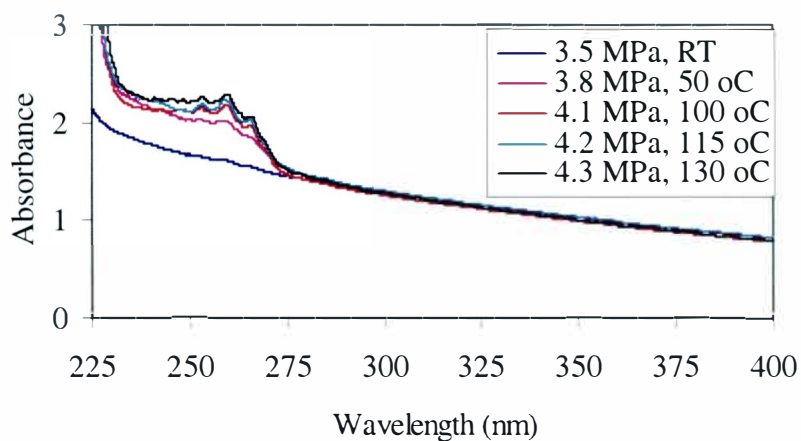


Figure 12(a): UV-vis Spectra of Styrene Oxide in CO₂ at Low Pressures

As expected, solubility of styrene oxide in CO₂ increased at higher pressures as evidenced by the increase in absorbance (**Figure 12(b)**).

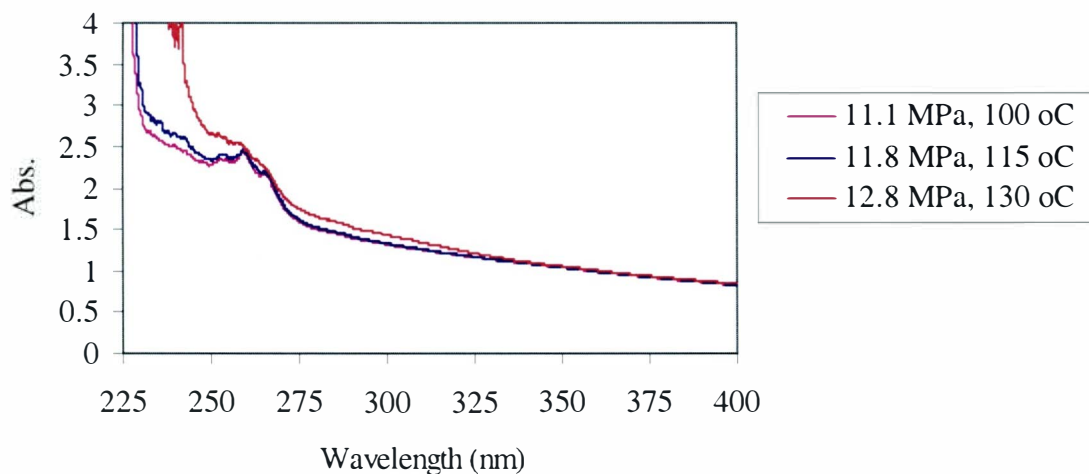


Figure 12(b): UV-vis Spectra of Styrene Oxide in CO₂ at Medium Pressures

To fully prove the solubility of epoxide in CO₂ even in the presence of ILs, styrene oxide, carbonate and IL were charged into an optical cell followed by CO₂. The results of the UV-vis analysis were in accordance to those previously reported in **Figures 10 and 12**.

However, the specific $\pi \rightarrow \pi^*$ transitions of styrene oxide and styrene carbonate were not visible due to their overlap (**Figure 13**). The styrene carbonate UV-vis spectra can be found in the Appendix. This shows that the presence of the IL did not hinder the epoxide solubility in CO₂ although it may have reduced it or slowed it down to some extent.

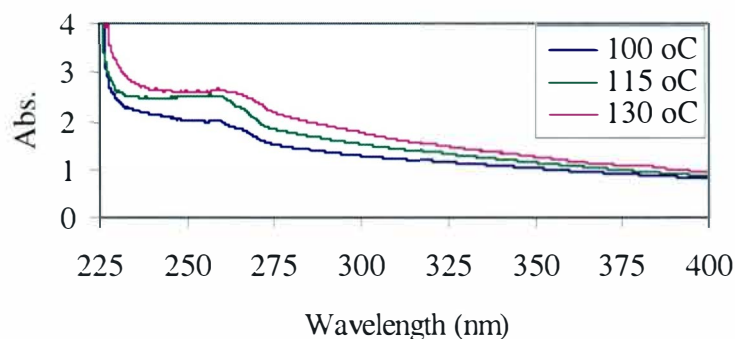


Figure 13: Uv-vis Spectra of Reaction Mixture at Reaction Temperatures

Blanchard and Brennecke³³ carried out an extensive study on the extraction of organic compounds from ILs using scCO₂ and reported that intermolecular interactions between organics and [C₄-MIM]⁺[PF₆]⁻ did not limit the degree to which the solute was separated from the IL. Both volatile and non-volatile organics displayed recoveries greater than 95%.

So far, we have tried to establish the phase behavior of the reactants. The reaction system may essentially be considered as a two-phase system:

- (1) A CO₂-rich phase, that depending on pressure, may consist of gaseous CO₂ or scCO₂ that may contain some amounts of styrene oxide and styrene carbonate, but not IL.

- (2) An IL/styrene oxide (IL/SO)-rich phase that may contain CO₂ and styrene carbonate.

Pressure and temperature will influence the composition of each phase.

We believe that the lack of IL in the CO₂ phase and the increase in epoxide solubility in the same phase with increase in pressure has a significant effect on the yields observed. Moreover, it has been reported that CO₂ is highly soluble in ILs.²⁹ For example, the solubility of CO₂ in [C₄-MIM]⁺[PF₆]⁻ may be as high as 0.8 mol fraction CO₂, at 13.6 MPa.³³ Unlike in organic solvents, ILs do not expand to a great degree when CO₂ is added. Studies have shown that the partial molar volumes for ILs remain almost equal to their pure component values.³⁴ At CO₂ mol fractions below 0.49, the experimental partial molar volume for CO₂ in [C₄-MIM]⁺[PF₆]⁻ is nearly constant at 29 cm³/mol, while the values calculated from solubility data by Cadena *et al.* at 25°C, were 34 for acetonitrile, 47 for ethanol and 79 cm³/mol for ethyl acetate.³⁵ These results indicate that the overall organization of the IL is relatively unperturbed by the addition of CO₂ due to its strong interionic interactions. Thus the dissolved CO₂ fills the interstices in the fluid without much expansion. Therefore, we believe that it is in the IL/SO rich phase that the reaction occurs

So how do these solubility factors relate to the yields observed at the different pressures?

We can visualize three pressure regions: (1) from 0 to 1 MPa, where increase in pressure leads to a sharp increase in yield; (2) from 1 to 10 MPa, where the yield continues to rise

very gradually with increase in pressure; and (3) from 10 to 25 MPa, where yield decreases with increase in pressure. **Figure 14** illustrates this phenomenon.

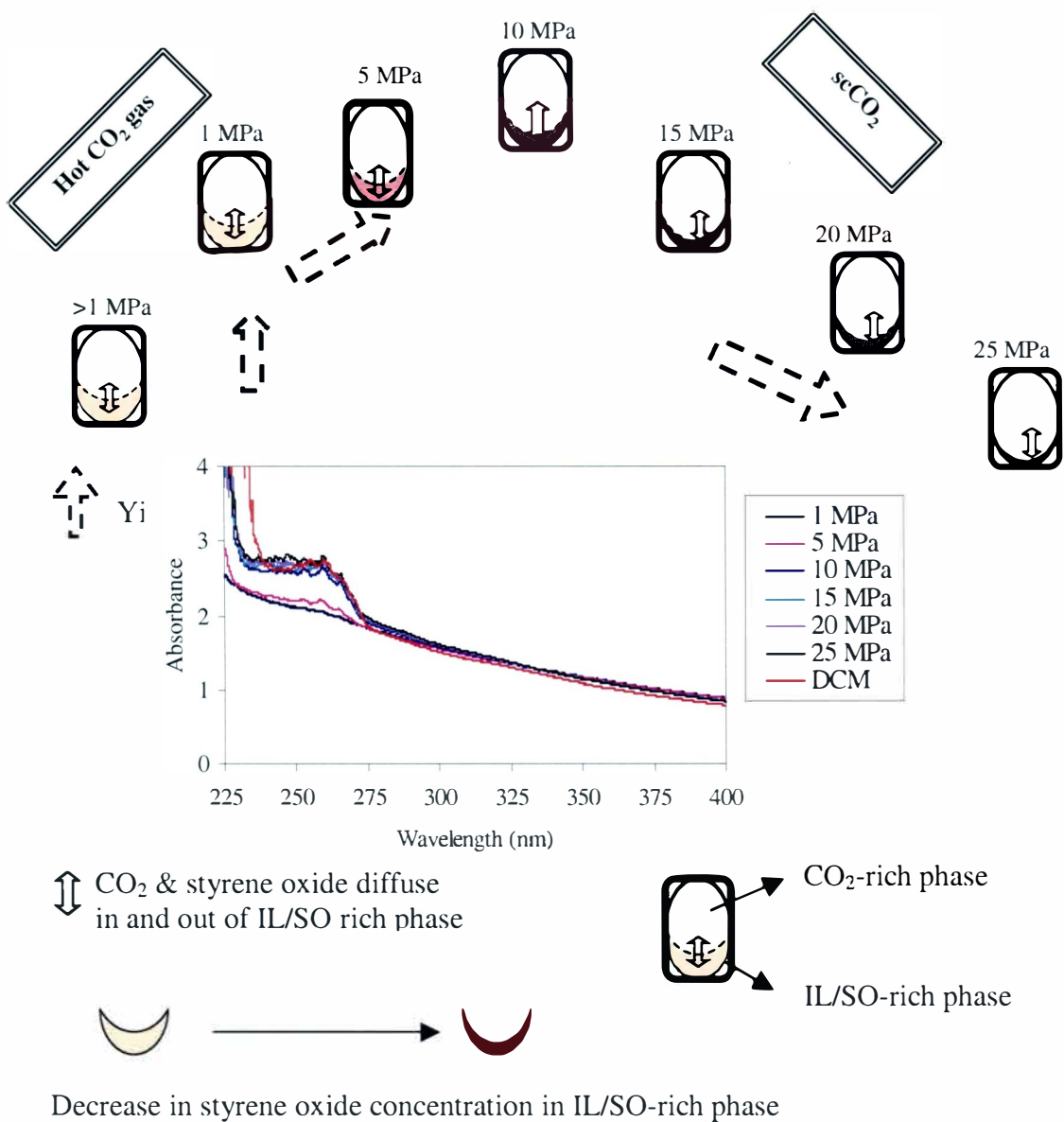


Figure 14: Illustration of Phase Behavior at Different Pressures with **Figure 11** as Insert

At pressures below 10 MPa, the amount of CO₂ dissolving in the IL/SO rich phase increases with increase in pressure. As seen in **Figure 8** and illustrated in **Figure 14**, as the pressure rises from 0.25 to 1 MPa, the yield rises sharply from 11% to 90% due to increased concentration of CO₂ in the IL/SO rich phase and drives the reaction forward, which occurs homogenously in this phase. Between pressures of 1 and 10 MPa, the rise in yield is very gradual. When the reaction pressure is raised to 5 MPa, the amount of dissolved CO₂ in IL increases slightly. However, as evidenced by the UV-vis spectrum of styrene oxide in CO₂ at low pressures [**Figure 12(a)**], the amount of styrene oxide in the CO₂-rich phase also increases indicating a reduced amount of the epoxide in the IL/SO-rich phase. However, it should always be kept in mind that at any given pressure and temperature, the system will be in equilibrium. This may be a contributing factor in reducing the rate at which the yield rose. Although further increase in pressure to 10 MPa led to increased solubility of styrene oxide in CO₂-rich phase, a maximum yield of 97% was obtained in 1 hr. We therefore propose that at this condition, an optimum reactant ratio exists for high conversion to styrene carbonate.

We also observed that when the pressure rose above 10 MPa, the yield dropped steadily. This is indicative of the continued withdrawal of the oxide from the IL/SO-rich phase as the CO₂ density increases. The same trend was observed by Sun *et al.*³⁶ We believe that the reduced yield at high pressure is a dilution effect in the IL/SO phase from an excessively increased CO₂ quantity.

Local Density Augmentation

Another factor that plays a key role in reaction enhancement in SCFs is local density augmentation. This phenomenon has also been referred to as “clustering”, “local density enhancement”,³⁷ and “molecular charisma”.^{38,39} Clustering occurs when supercritical solvent molecules are attracted to a solute in dilute solutions, leading to the creation of regions in space near the solute molecule where the local density differs from the bulk density. Experimental,⁴⁰⁻⁴² theoretical⁴³ and simulation^{44,45} studies have been carried out to investigate this occurrence. Although it was originally suggested that the augmented density was related to the isothermal compressibility, the maximum in the local density augmentation was shown to be below the highest isothermal compressibility (**Figure 15**).⁴⁶

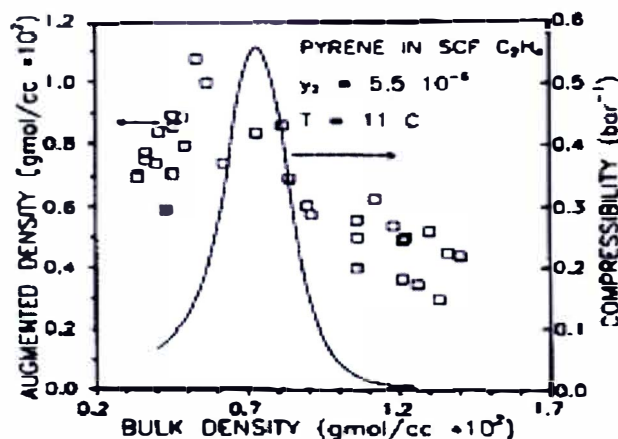


Figure 15: The Augmented Density Around Pyrene in Ethylene at 11°C as Measured by Fluorescence Spectroscopy (open squares). Also Shown is the Bulk Isothermal Compressibility (solid line).⁴⁶

Local density augmentation may be as much as two to three times the bulk density and exhibits a maximum at fluid densities of one-third to four-fifths of the critical density.⁴⁴ Keeping in mind that the fluid densities calculated in Table 3 are those of pure CO₂, we

may speculate about the possibility of local density augmentation, or local concentration effects influencing the reaction system under study. This could potentially explain the maximum yield observed consistently at the 10 MPa region of the three reaction temperatures. We have assumed that the critical density (d_c) of the reaction system is equal to the d_c of pure CO₂, which is 0.428 g/cm³. Augmented densities, therefore, are highest at pressures ranging from 0.142 to 0.342 g/cm³. Using the analytic equation of state used in constructing the IUPAC CO₂ density data,^{48,51} density values were acquired for the reaction temperatures and pressures used (Table 6).

Table 6: Calculated CO₂ Densities in g/cm³ of Various Reaction Conditions

MPa	1	5	10	15	20	25
100°C	0.016	0.084	0.195	0.342	0.491	0.596
115°C	0.016	0.079	0.177	0.299	0.417	0.533
130°C	0.015	0.075	0.164	0.269	0.380	0.479

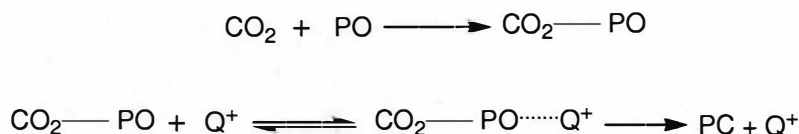
If indeed the local density augmentation occurs at one-third to four-fifths of the critical density (as mentioned above), then, for the three reaction temperatures, density values that lie in the range that exhibits highest augmentation densities were found to be at 10 and 15 MPa only. All the other pressure values had far less or far higher densities than the range specified above. We believe that this phenomenon may have had a contribution to the reaction yield observed at 10 MPa for all the reaction temperatures. However, the lower yield observed at 15 MPa may be as a counter-effect of withdrawal of styrene epoxide from the IL/SO phase, thus depleting one of the reactants necessary for carbonate formation.

The overall rate of reaction depends on several factors including the concentration of the phases present, the concentration of the reacting species, the activity of the catalytically active species, and the reaction kinetics in these phases.

PROPOSED MECHANISM

As presented in the background section, there has been several reaction mechanisms proposed. Three distinct mechanisms are:

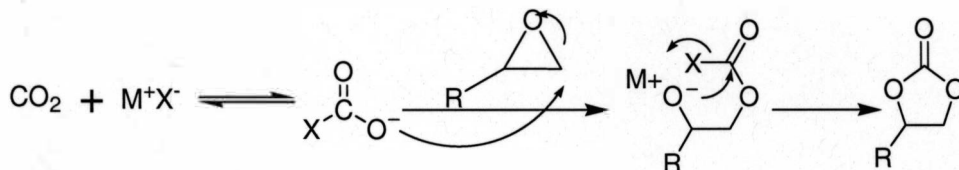
- (1) Based on non-nucleophilic anions e.g. BF_4^- , PF_6^- , as proposed by Peng *et al.*²³ where by a CO_2 -propylene oxide complex is formed since the anions cannot form covalent bonds with the epoxide. The interaction of this complex with the IL cation leads to the formation of propylene carbonate and the IL cation is regenerated.



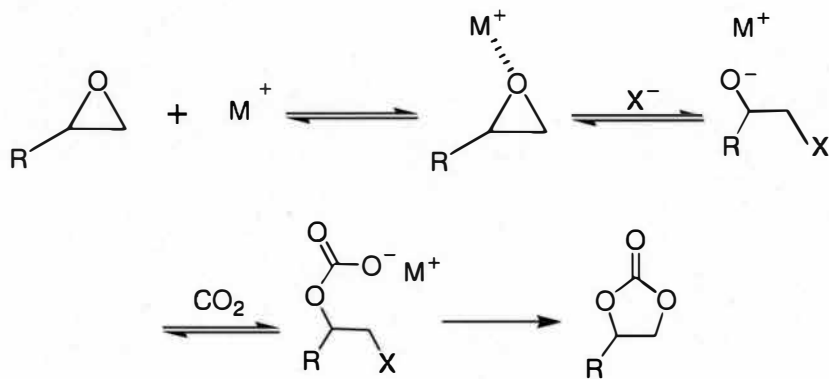
Where PO = Propylene Oxide, Q^+ = IL cation, PC = Propylene Carbonate,
 $\text{CO}_2\text{---PO}$ = $\text{CO}_2\text{---PO}$ complex.

- (2) Based on highly nucleophilic anions such as carboxylate and phenolate anions, as proposed by Rokicki *et al.*¹⁹ in the presence of crown ether under high pressure conditions. Due to its high nucleophilicity, the anion is able to attack CO_2 forming an oxide which opens the epoxide ring. Another attack of the alkoxide on the

carbonyl carbon leads to cyclization of the carbonate and elimination of the nucleophile.



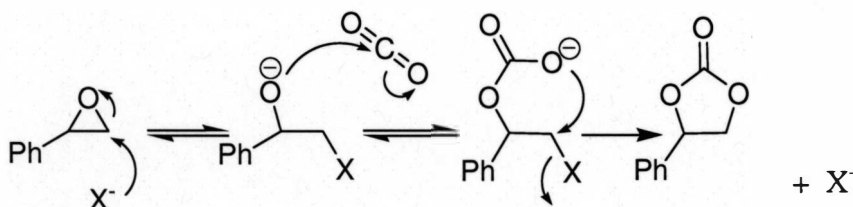
- (3) Based on metal salts e.g. LiBr, Na I, as proposed by Kihara *et al.*²¹ The metal cation associates with the epoxide oxygen making the carbons on the ring more electrophilic leading to the attack by the nucleophile and formation of an alkoxide. The alkoxide is a strong nucleophile which can now attack the CO₂ and follow the cyclization process into a carbonate.



Based on our studies and the results we have obtained so far, we believe that the mechanism follows an S_N2 type reaction when ILs with halide anions are used as catalysts. As we have already established, the more nucleophilic anion and better leaving group, I⁻, gave the best results. Therefore, it is possible the anion plays the primary role of

initiating the reaction leading to the formation of the alkoxide anion, which being strongly nucleophilic, attacks the carbon on the CO₂. Cyclization and easy elimination of the anion leads to the formation of styrene carbonate and regeneration of the catalyst.

We have however, not thoroughly studied the role of the cation and therefore cannot state its role in our proposed mechanism. Therefore, we propose the following mechanism:



SUMMARY AND CONCLUSION

Some of our primary objectives for this work were (a) to synthesize styrene carbonate using pressurized CO₂, (b) to eliminate organic solvents from the system, and (c) to develop an efficient, economical, and thermally stable catalyst.

We have determined that both temperature and pressure have a significant effect on the carboxylation of styrene oxide with CO₂. The influence of CO₂ pressure at 100, 115, and 130°C has been investigated and the optimum conditions have been established as 130°C at 10 MPa. This is a supercritical state by definition, even though it is below the critical density. VOCs previously employed in this reaction have been replaced by non-toxic scCO₂ in the reaction process and water is used in the product recovery process.

Previously, $[\text{C}_4\text{-MIM}]^+\text{X}^-$ ($\text{X}=\text{halide}$) catalysts have been reported to give extremely low yields and have therefore been used as co-catalysts with metal halides. We have proven that it is not necessary to do so and that high yields are obtainable at appropriate reaction conditions. In scCO_2 , the order of anion reactivity has been shown to be $\text{I}^- > \text{Br}^- > \text{Cl}^- \gg \text{BF}_4^-, \text{PF}_6^-$, which shows the importance of nucleophilicity of anion. This may indicate that the rate-determining step involves the nucleophilic attack of the anion. The order of cation activity is $[\text{C}_6\text{-MIM}]^+ > [\text{C}_4\text{-MIM}]^+ > [\text{NBu}_4]^+$. It is probable that a further increase in the alkyl chain length on the cation may demonstrate even better catalytic activities since more CO_2 may be dissolved in a higher molecular weight IL than a smaller one.

We have developed a versatile catalyst, $[\text{C}_n\text{-MIM}]^+\text{I}^-$, since it can be used at pressures ranging from 1 to 10 MPa with high yields. It is also easy to synthesize (65 secs by the application of microwave technology) and does not require the use of toxic organic solvents for styrene carbonate.

The feasibility of product separation and recovery by manipulation of temperature and pressure has been studied. By using UV-vis spectroscopy, the solubility studies of styrene oxide, styrene carbonate and IL in CO_2 have been investigated. Styrene oxide displays a high solubility even at low temperatures and pressures such as 50°C and 3.8 MPa respectively. On the other hand, styrene carbonate shows minimal solubility at low pressures of 4.7 MPa even at high temperatures of 130°C [Appendix]. A slightly higher solubility was observed at pressures above 10 MPa. ILs did not show any absorbance in

CO₂, which is consistent with reports made for [C₄-MIM]⁺BF₄⁻.^{33,34} Although we did not experiment on the product separation and recovery using scCO₂, from our results so far we strongly believe that it is feasible and it will contribute to the cost-effectiveness of this process.

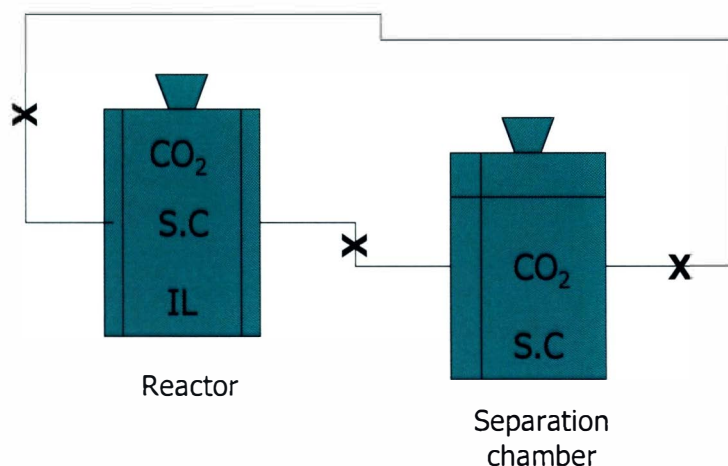
We have also determined how many phases there are in the system, in which phase the reaction is taking place and proposed the reaction mechanism based on the results.

It is clear that the study and results presented here could be highly relevant for the further development of truly environmentally benign processes based on CO₂ serving as both solvent and a cheap C₁ component.

FUTURE WORK

The selective condensation of styrene carbonate by tuning temperature and pressure conditions should be further explored. So far, only Sako *et al*²² have attempted to isolate a cyclic carbonate, 4-methyl-1,3-dioxolan-2-one, from the reaction mixture by tuning temperature and pressure. From the UV-vis data of styrene carbonate in CO₂ [Appendix], it is clear that styrene carbonate is not readily soluble in CO₂ at low pressures of approximately 4 MPa compared to higher pressures of about 11 MPa.

Therefore, we propose the following scheme for product recovery.



After the reaction is complete, the CO₂-rich phase is discharged into the separation chamber leaving the ionic liquid in the reactor. The pressure in the separation chamber is reduced to allow the carbonate to separate from the CO₂. However, the pressure is not fully decompressed in order to save the costs of compressing again to reaction pressure. The CO₂ is then recycled back into the reactor.

ILs are generally referred to in a 'green' context. However, little is known about their biodegradability and toxicology. So far, few studies have been carried out, with the most recent being done by Garcia *et al.*⁴⁹ They suggest that the incorporation of an ester in the side chain of the imidazolium cation significantly increases biodegradability. More studies need to be carried out to ascertain the environmental friendliness of these attractive compounds.

Further extension of the alkyl chain length of the 1-alkyl-3-methylimidazolium cation should be investigated for increased catalytic activity. Also, this reaction system should

be tested on other epoxides with varied substituents and yields compared to literature data.

EXPERIMENTAL METHODS

Reagents and Solvents

All the reagents and solvents used in this project were obtained from Aldrich, Acros, Sachem and Lancaster chemical companies. They were of 98% + purity and other than $[C_4\text{-MIM}]^+\text{PF}_6^-$, they were used without further purification. All the solvents used were of reagent grade. CO_2 (SFC grade) was obtained from Air Products and used without further purification.

High Pressure Equipment

The High Pressure Reactor (HPR) used as our reaction vessel was a custom built cylindrical stainless steel reaction vessel having *ca.* 79 mL capacity. The lid of the vessel was threaded and the base notched to fit a standard vice. An open-ended wrench was used to tighten the lid and the vessel was sealed with a Teflon washer. It was fitted with inlet and exit valves, a Noshok (Germany) 5000 psi pressure gauge and High Pressure (HIP) rupture disk. Heat was supplied using Omegalux, Omega (Stanford, CT) heating tape that was regulated using a variable voltage regulator. The external temperature of the reaction vessel was monitored using an Omega model HHII digital thermometer and a type K thermocouple.

For UV-vis analyses, a high-pressure stainless steel optical cell fitted with suprasil quartz or sapphire windows was used. It had approximately 2.54 mL capacity and 1.7 cm optical pathlength. Pressure was monitored by a precision digital pressure gauge, model 901A Heise obtained from Dresser Industries (Newtown, CT). The system temperature was controlled to $\pm 0.2^{\circ}\text{C}$ and monitored with a platinum resistance thermometer (Omega RTD probe) Model CN-6070A that made direct contact with the samples, coupled with a Watlow Firerod (Omega, 150W) cartridge heater.

In order to deliver CO_2 to the HPR or optical cell, special equipment was used consisting of the following components: a CO_2 gas cylinder fitted with a diptube, a model 260D ISCO (Lincoln, NE) high-pressure syringe pump thermostated with a water jacket and a Fisher Scientific (Pittsburgh, PA) ISOTEMP 1006s heater/chiller re-circulation bath. To connect to the HPC or optical cell, HIP (Erie, PA) 1/16" stainless steel high-pressure tubing and HIP line valves fitted with Teflon o-rings were used.

Instruments for Characterization of Compounds

Melting points, reported in degree Celcius, were determined in open capillary tubes using a Mel-Temp instrument. ^1H Nuclear Magnetic Resonance (NMR) and ^{13}C NMR spectra were obtained from a 400 MHz Jeol Eclipse NMR spectrometer, using TMS at an internal standard. Samples to be analyzed were dissolved in deuterated solvents such as chloroform, dichloromethane, or dimethyl sulfoxide. Infrared (IR) spectra were recorded

using Bruker Equinox 55 and Perkin Elmer 1710 Fourier Transform Infrared Spectrometers. UV-vis data was collected using a Shimadzu UV-2101PC scanning spectrophotometer equipped with a halogen lamp for the visible region and a deuterium lamp for the UV region. The product mixture was also analyzed by Hewlett Packard 6890 series Gas Chromatography (GC) system equipped with a flame ionized detector and a BPX5 capillary column (30m x 0.25mm x 0.25 μ m), and Hewlett Packard 5973 Mass Selective detector.

Synthesis of Styrene Carbonate Under Atmospheric CO₂ Pressures

This procedure was adapted from Kihara *et al.*'s²¹ experimental methods. A solution of 1.32 g (1.25 mL, 11 mmol) of styrene oxide and 0.047g (5 mol% of styrene oxide) in 11 ml DMF was heated at 100°C for 24 hrs. CO₂ was gently bubbled into the reaction mixture and closely monitored due to irregularities in the CO₂ flow. The mixture was then poured into 100 mL of water and precipitates were washed thoroughly with water. Recrystallization of the crude product was done in ethanol to obtain 36 to 63% of 4-phenyl-1,3-dioxolan-2-one. MP: 54.0-55.5°C (lit. 55-56°C);²⁵ ¹H NMR (CDCl₃, 400 MHz) δ 7.36-7.43 (m, 5H, aromatic H), 5.67 (t, 1H, J_c = 8.06 Hz), 4.79 (t, 1H, J_b = 8.42 Hz), 4.34 (dd, 1H, J_{Ha-Hb} = 8.42 Hz, J_{Ha-Hc} = 8.06 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 155.0, 135.9, 129.8, 129.3, 126.0, 78.1, 71.3; IR (KBr Pellet) 3054 cm⁻¹ (m, aromatic C – H), 2986 cm⁻¹ (m, SP³ C – H), 1815 cm⁻¹ (s, lactone C=O), 1265 cm⁻¹ (vs, C_{sp2}-O), 1165 and 1069 cm⁻¹ (m, C_{sp3}-O); GC-MS 164 (*M*⁺), 119, 105, 90, 77, 64, 51.

Synthesis of Styrene Carbonate in the HPR Using LiBr as Catalyst

This is a modification of the synthetic procedure previously discussed using atmospheric conditions. 11 mmol styrene oxide, 0.55 mmol LiBr and 11 mL DMF were charged to the HPR and a minimum amount of CO₂, well below the reaction pressure, was introduced. The HPR was heated to the reaction temperature (+/- 1°C) and the pressure adjusted to the reaction pressure. The starting time of the reaction was defined as the time of achievement of reaction conditions. Various reaction parameters were examined. At 100°C, reaction times of 4 and 8 hrs were used while at 130°C only 4 hr reaction time was used. Reactions were carried out at pressures of 1, 5, 10, 15, 18, 20, 25, and 30 MPa. After the reaction time passed, the HPR was left to cool to RT and the pressure reduced to atmospheric pressure, and subsequently opened. 10 µL of the reaction mixture was added to 10 mL DCM for GC-MS analysis while the rest of the mixture was transferred into 100 mL of water. Precipitates were filtered, washed thoroughly with water and recrystallized from ethanol. Crude yields were well within 10% of the GC yields. Products were analyzed by MP, IR, GC-MS, ¹H NMR and ¹³C NMR and the results were as previously reported.

Synthesis of Styrene Carbonate Using LiBr Catalyst in the Absence of Solvent

This procedure was adapted from Sako et al's²² methods. 5.16g (42 mmol) of styrene oxide was added to the HPC followed by 0.037g of LiBr which corresponds to 1 mol % of styrene oxide. A minimum amount of CO₂ was added and the temperature raised to required reaction temperatures, after which the pressure was adjusted accordingly.

Reaction pressures between 6 and 26 MPa at temperatures from 50 to 120°C for 2 to 6 hrs were applied. The HPR was allowed to cool down to RT and depressurized. 10 μ L of reaction mixture was analyzed by GC-MS while the rest of the mixture was poured into 100 mL of water. A trace amount of product was obtained and was analyzed as previously stated.

Synthesis of Styrene Carbonate Using Quaternary Ammonium Salts as Catalysts

5 mol % of the appropriate quaternary ammonium salt was charged into the HPR along with 11 mmol styrene oxide and pressurized with 5 MPa of CO₂. After the reaction temperature of 130°C was attained, the pressure was adjusted to 10 MPa and the reaction run for 4 hrs. The HPR was then allowed to cool to RT and depressurized. 10 μ L of reaction mixture was analyzed by GC-MS while the rest of the mixture was poured into 100 mL of water. Precipitates were collected by filtration, washed with water and recrystallized from ethanol. Crude and GC yields were within 10% of each other. The product was analyzed as previously stated.

Synthesis of [C₄-MIM]⁺BF₄⁻ by Conventional Heating

This procedure follows the literature procedure.¹² The first step is a quaternization reaction to form a halide salt followed by anion metathesis. 47.8 mL of 1-methylimidazole is combined with 1.3 molar equivalent of butyl bromide (83.96 mL) in a round-bottomed flask. The mixture was heated with stirring under a reflux attached to a

CaCl₂ drying tube, at 60°C for 24 hrs. ¹H NMR was used to monitor the reaction progress to ensure that the starting materials, especially 1-methylimidazole, were consumed. After the reaction was complete, the excess butyl bromide was removed by heating the reaction product *in vacuo* at 75°C for 1 hr and analyzed by ¹H NMR. A suspension of 0.46 mols of the halide salt, [C₄-MIM]⁺Br⁻, and 1.1 molar equivalent of NaBF₄ in acetone was stirred at RT for 24 hrs giving [C₄-MIM]⁺BF₄⁻ and NaBr. After this, the insoluble NaBr was removed by filtration. The acetone layer was stirred with neutral alumina to remove any traces of NaBr and finally dried by heating at 120°C for 24 hrs. [C₄-MIM]⁺BF₄⁻ was produced in 98% yield with a light yellow hue. ¹H NMR (DMSO-d, 400 MHz) δ 8.9 (s, 1H, aromatic H), 7.65 (d, 1H, aromatic H), 7.59 (d, 1H, aromatic H), 4.15 (t, 2H, methylene), 3.85 (s, 3H, *N*-methyl), 1.78 (p, 2H, methylene), 1.26 (s, 2H, methylene), 0.89 (t, 3H, methyl); ¹³C NMR (DMSO-d, 100 MHz) δ 137.1, 124.1, 122.8, 48.9, 36.4, 31.9, 19.2, 13.8.

Synthesis of [C_n-MIM]⁺X⁻, where X⁻ = Cl⁻, Br⁻ or I⁻ and n = 4 or 6 by Microwave Irradiation

This is a modification of Varma *et al*'s procedure.⁵⁰ Reactions were carried out in a Panasonic Microwave equipped with Inverter Technology (Model NN-S752BF – 1300W). To synthesize [C₄-MIM]⁺Br⁻, a solution of 1.4 mL (0.018 mols) of 1-methylimidazole and 2.4 mL (0.022 mols, 1.2 molar equivalent) butyl bromide were mixed thoroughly in a vortex (Fischer, Model 231) for 15 secs. The solution was heated intermittently at 260 W for 30s +15s + 15s + 15s + 15s +15s, with 10s mixing. The resulting IL was cooled, washed with 4ml ethyl ether 3 times to remove unreacted material and dried *in vacuo* at 75°C (88%). ¹H NMR (DMSO-d, 400 MHz) δ 9.45 (s, 1H,

aromatic H), 7.92 (d, 1H, aromatic H), 7.83 (d, 1H, aromatic H), 4.23 (t, 2H, methylene), 3.91 (s, 3H, *N*-methyl), 1.75 (p, 2H, methylene), 1.20 (s, 2H, methylene), 0.84 (t, 3H, methyl); ^{13}C NMR (DMSO-*d*, 100 MHz) δ 137.1, 124.1, 122.8, 48.9, 36.4, 31.9, 19.2, 13.8. The rest of the IL halide salts, other than the chloride salt, were synthesized in a similar manner, using 0.018 mols of 1-methylimidazole and 1.2 molar equivalent of the appropriate alkylhalide. However, the reaction times and yields differed as follows:

- $[\text{C}_4\text{-MIM}]^+\text{T}^-$: (260 W) 30s + 15s + 15s + 15s (95 %)
- $[\text{C}_6\text{-MIM}]^+\text{T}^-$: (260 W) 30s + 15s + 10s + 10s (98%)
- $[\text{C}_6\text{-MIM}]^+\text{Br}^-$: (260 W) 30s + {(130 W) 15s + 15s + 15s}(92%)

A molar ratio of 1:2.2 (1-chlorohexane) was used for the synthesis of the halide salt due to its low leaving ability hence low reactivity, thus requiring longer reaction times.

- $[\text{C}_6\text{-MIM}]^+\text{Cl}^-$: (260 W) [30s x 12] + 15s + 15s + 15s (86%).

$[\text{C}_6\text{-MIM}]^+\text{X}^-$ was analyzed as follows: ^1H NMR: (CD_2Cl_2 , 400MHz) δ 10.0 (s, 1H, aromatic H), 7.36 (d, 1H, aromatic H), 7.31 (d, 1H, aromatic H), 4.27 (t, 2H, methylene), 4.05 (s, 3H, *N*-methyl), 1.90 (p, 2H, methylene), 1.31 (m, 6H, methylene), 0.87 (t, 3H, methyl); ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 137.0, 123.4, 121.9, 50.2, 36.9, 31.1, 30.1, 25.9, 22.4, 13.8.

Synthesis of Styrene Carbonate Using ILs as Catalysts

The procedure used when quaternary ammonium salts were used as catalysts was employed. A mixture of 11mmol styrene oxide and 5mol % of the appropriate IL catalysts was charged into the HPR and pressurized with minimal CO_2 . When reaction temperatures were achieved (100, 115, 130°C), the pressure was adjusted to the reaction

pressure (0.25 MPa to 25 MPa). Once again, the starting time was defined as the time all the reaction parameters were achieved. After the reaction time was over, the HPC was allowed to cool and depressurized. For all the reactions, 10 μ L of the reaction mixture was analyzed by GC-MS in 100 mL of DCM. When $[\text{C}_4\text{-MIM}]^+\text{PF}_6^-$ was used as catalyst, trace amounts of product were visible by NMR but attempts to extract it using various organic solvents such as ethyl ether or toluene were futile due to the minute amounts of product and high solvent power of the IL. The rest of the ILs used, $\{[\text{C}_4\text{-MIM}]^+\text{BF}_4^-$, $[\text{C}_4\text{-MIM}]^+\text{Br}^-$, $[\text{C}_6\text{-MIM}]^+\text{Br}^-$, $[\text{C}_4\text{-MIM}]^+\text{Cl}^-$, $[\text{C}_6\text{-MIM}]^+\text{Cl}^-$, $[\text{C}_4\text{-MIM}]^+\text{I}^-$, $[\text{C}_6\text{-MIM}]^+\text{I}^- \}$, are water-miscible, hence, pure product crystals were obtained by precipitation in water. Product was analyzed by MP, IR, GC-MS, ^1H NMR and ^{13}C NMR, and results are as reported above.

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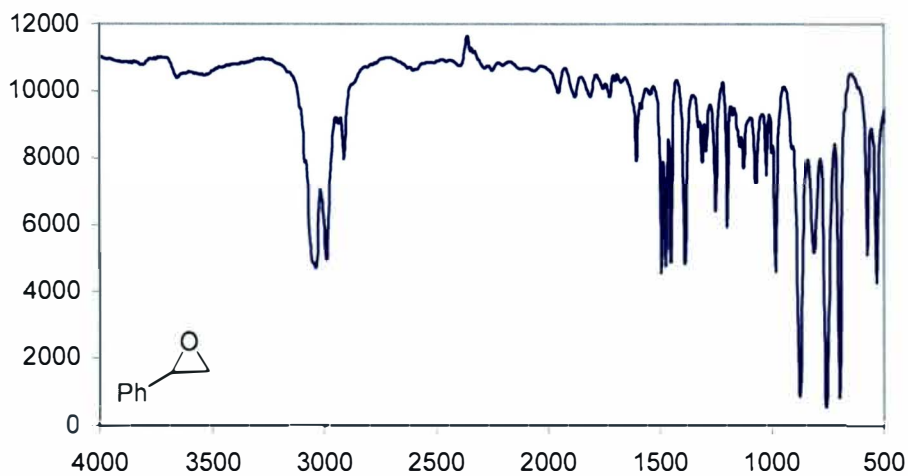
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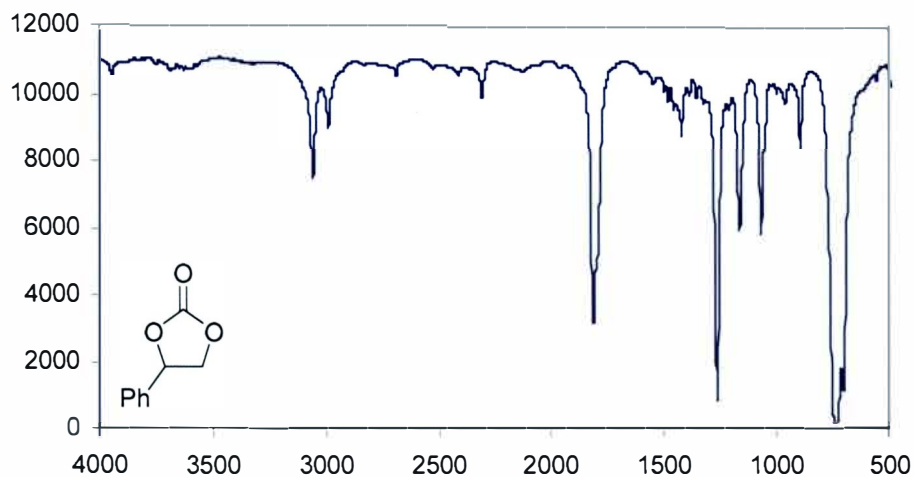
APPENDIX

IR, ^1H NMR, ^{13}C NMR, UV-vis, GC-MS

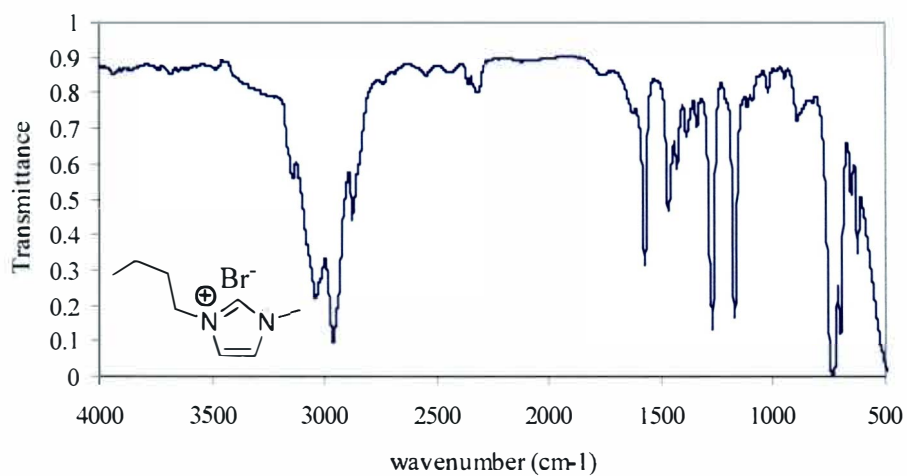
A. IR OF STYRENE OXIDE



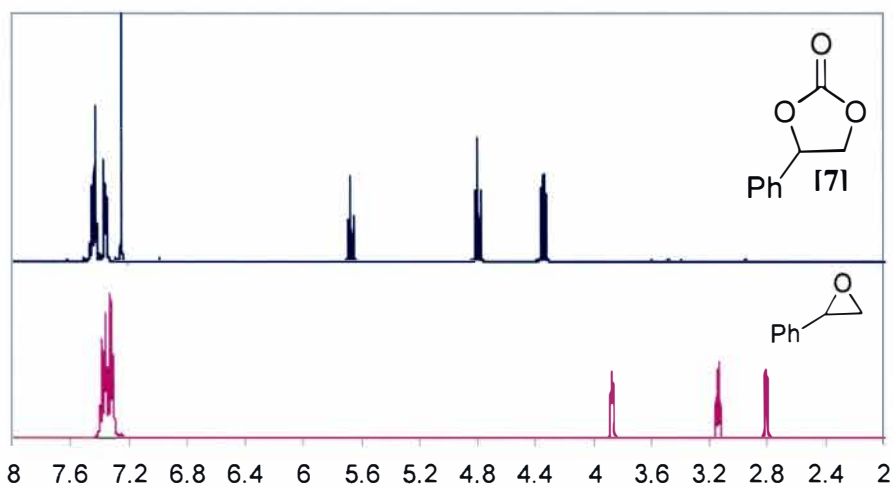
B. IR OF STYRENE CARBONATE [7]



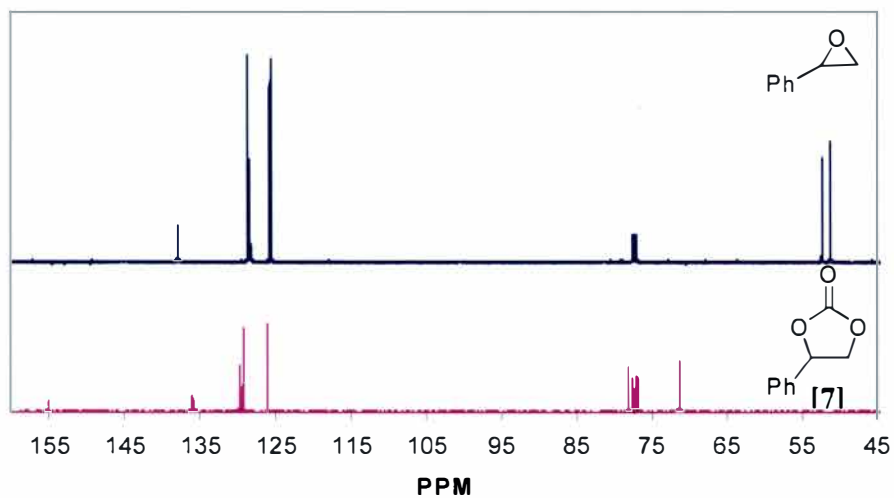
C. IR OF $[C_4\text{-MIM}]^+\text{Br}^-$



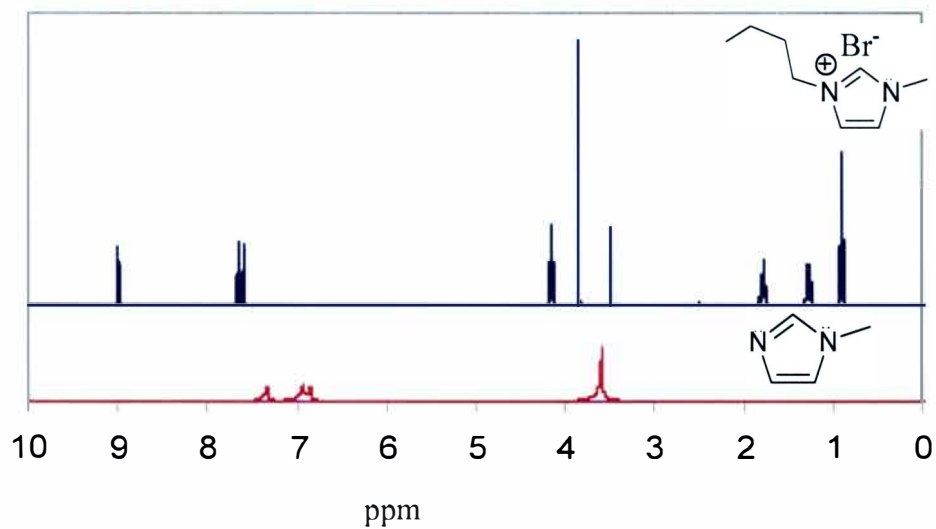
D. ^1H NMR



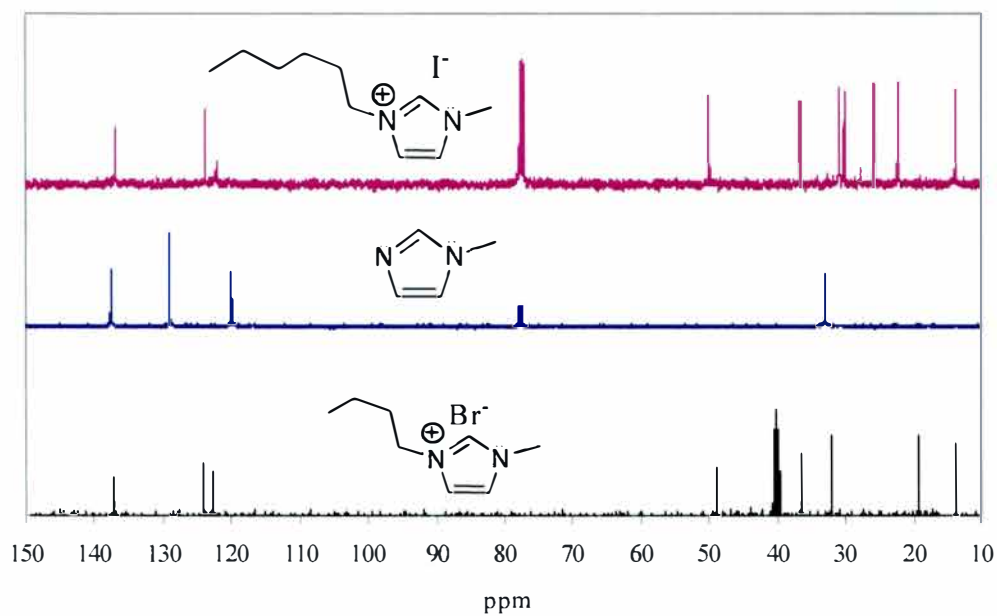
E. ^{13}C NMR



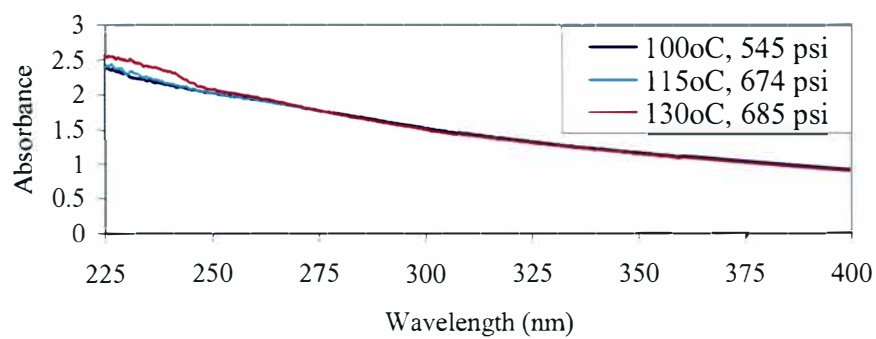
F. ^1H NMR OF $[\text{C}_4\text{-MIM}]^+\text{Br}^-$ AND METHYLIMIDAZOLE



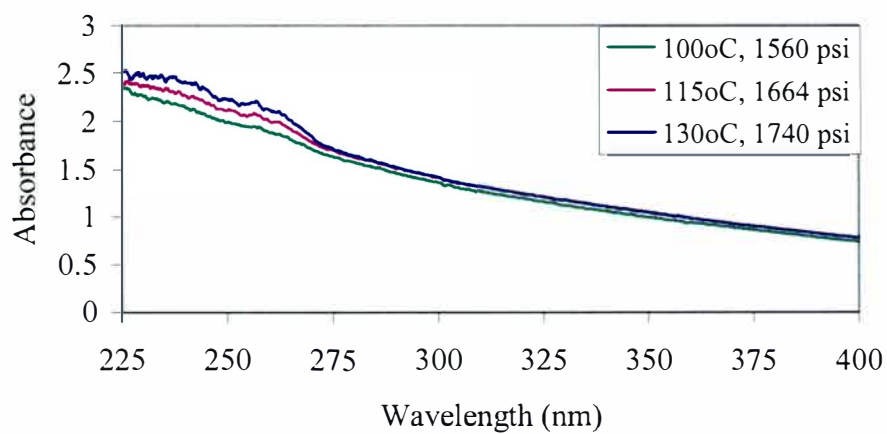
G. ^{13}C NMR OF $[\text{C}_4\text{-MIM}]^+\text{Br}^-$, $[\text{C}_6\text{-MIM}]^+\text{I}^-$ AND METHYLIMIDAZOLE



H. UV-VIS OF STYRENE CARBONATE [7] AT LOW PRESSURE



I. UV-VIS OF STYRENE CARBONATE [7] AT HIGHER PRESSURES



J. GC/MS OF STYRENE CARBONATE [7]

