Application of ionic liquids in CO$_2$ valorisation

BACHELOR'S THESIS

JUNE 2022

Student: Francesc Xavier Lara Rimbau

Academic tutor: Jordi Riu Rusell

Professional tutor: Isabel Vicente Valverde

2021/2022

<u>Acknowledgements</u>

First of all, I would like to express my gratitude to Dra. Isabel Vicente for guiding me since the first day of the work. Thank you for your patience, support, advice and motivation you have given to me. Working with you these past couple of months has been such an enjoyable experience.

I would also to thank Dr. Aitor Gual for giving me the opportunity to work in a technological centre and believe in me since day one. Thank you for your commitment and dedication towards this work.

Also, I would like to thank all of the members of the UTQ in Eurecat Tarragona. Thank you for welcoming me as another member of the group and, special thanks to master student David Domingo, who has been a key pillar for carrying out this work.

Lastly, I would like to thank Prof. Jordi Riu for his advices during the meetings we had over the last months.

Table of contents

1) <u>Summary</u>

Reducing carbon emissions to mitigate global warming is the major environmental concern of current and future generations. Carbon dioxide use technologies are an opportunity not only to reduce the CO_2 emissions but to use them as feedstock.

In this work, a green ionic liquid catalytic system was designed for the transformation of CO_2 into high added value products, (cyclic carbonates) from epoxides or propargylic alcohols at mild conditions (45-150 ºC, 1-5 bar CO_2). Ionic liquids based on 3-butyl-1-methylimizadolium (BMI) were synthesized. Conversion and selectivity were determined by NMR analysis of the crude reaction mixture sample dissolved in $CDCl_3$.

La reducció de les emissions de carboni per mitigar l'escalfament global és la principal preocupació ambiental de les generacions actuals i futures. Les tecnologies d'ús del diòxid de carboni són una oportunitat no només per reduir les emissions de CO_2 sinó per utilitzar-les com a matèria primera.

En aquest treball es va dissenyar un sistema catalític de líquid iònic per a la transformació del CO_2 en productes d'alt valor afegit (carbonats cíclics) a partir d'epòxids o alcohols propargílics en condicions suaus (45-150 ºC, 1-5 bar CO_2). Es van sintetitzar líquids iònics basats en 3-butil-1-metilimidazoli (BMI). La conversió i la selectivitat es van determinar mitjançant l'anàlisi de RMN de la mostra bruta de la barreja de reacció dissolta en $CDCl_3$.

2) Goal

It has been estimated that up to 60% of Earth's temperature increase is due to CO_2 emissions. In just over 40 years the increase of CO_2 concentration in the atmosphere has gone from 1ppm/year (1960s) to 2ppm/year (2009). Europe has contributed up to 18.4% of cumulative worldwide CO_2 emissions between 1750 to 2006. However, according to the European low-carbon economy roadmap, Europe needs to reduce its emission by at least 80% below of 1990 levels by 2053. Based on these objectives, carbon dioxide use is an alternative to non-renewable carbon feedstocks.

The main goal of this study was the application of ionic-liquid catalytic systems for the obtention of cyclic carbonates by transformation of CO_2.

Our partial objectives were:

-   To synthesize and characterize ionic liquids based on 3-butyl-1-methylimizadolium (BMI).
-   To perform several anionic exchanges in order to obtain ionic liquids with soft basic anions.
-   To characterize the ionic liquids synthetized by ^1H NMR spectroscopy.
-   To test the ionic liquids as catalysts for the CO_2 conversion into cyclic carbonates using different substrates.
-   To discuss the effect of the cation and anion of the ionic liquids in the mechanism of the reactions for carboxylative cyclizations.

3) Introduction

3.1) Scope in which the work has been developed

This thesis has been developed at UTQ (Unitat de Tecnologies Químiques) in Eurecat Tarragona. The UTQ has a large experience on the development of catalytic systems for the transformation of CO_2 into added-value chemicals. The project in which this work has been developed is called "ACHIEVER".

ACHIEVER aims to advance in the technologies involving carbon capture and purification from industrial gaseous effluents, while transforming them into high added value products through biological and chemical conversions.

In the coming years, all the industries will have to reduce drastically their CO_2 footprint, meaning that they will have to cut their direct and indirect CO_2 emissions. Renewable energies won't be enough to satisfy the energy demand of the industrial sector, so carbon capture, use and storage will have to be adopted by all the industrial sectors. In this scenario, the development of technologies for producing high-added value products from carbon emissions is presented as an opportunity. Not only for reduction of greenhouse gas emissions but also for carbon recycling.

3.2) Ionic liquids

Ionic liquids (ILs) are salts formed by an anion and a cation with a melting temperature below 100ºC. These are characterized by having a steam pressure of virtually zero, low volatility and high chemical and thermal stability, which make ILs have multiple applications such as solvents, catalysts or catalytic supports. Basic ionic liquids especially have wide application in catalysis [1]. Lately, they have received significant attention due to such unusual properties as liquids, being considered as suitable substitutes for volatile organic solvents (VOC, which are one of the major waste sources in chemical synthesis). Due to their unique physicochemical properties, ionic liquids have seen a remarkable boost on their applications in several fields such as chemistry, materials science or chemical engineering. The evolution of the number of scientific contributions for the past decade (68.057 from 2010-2020) are displayed in Figure 1.
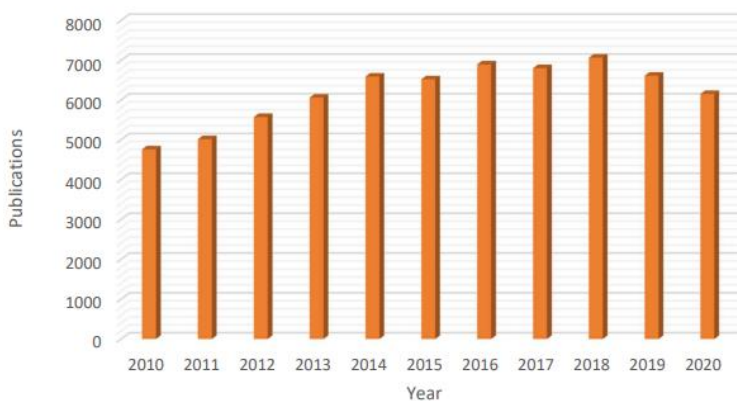
Figure 1. Yearly number of publications in the domain of ionic liquids in the 2010-2020 period [1]

Room temperature ionic liquids general physicochemical properties are summarized in Table 1.

Table 1. General characteristics of room temperature ionic liquids [2][3]

General Properties	Features
	Treated as liquid at ambient temperature
Low melting point	Wide temperature interval for applications
	Thermal stability
Non volatility	Flame retardancy
	High ion density
Composed by ions	High ion conductivity
	Designable/Tuneable
Organic ions	Unlimited combinations possible

It is worth mentioning that every ionic liquid does not always show the above properties since they have unlimited structural variations. Different combinations of cations and anions and the possibility to achieve modifications of cation/anion part offer access to ionic liquids with targeted properties.

Imidazolium-based ionic liquids such as 3-butyl-1-methylimidazolium (BMI) and 3-ethyl-1-methyl-imidazolium (EMI) are among the most studied ionic liquids due to their stability versus oxidative and reductive conditions, low viscosity and ease of synthesis. [4]

3.3) CO_2 sorption in ILs: IL with soft basic anions

Capturing CO_2 with ionic liquids is a promising option due to their unique properties (see Table 1). Imidazolium based ionic liquids are by far the most investigated ones. In most cases, they absorb CO_2 physically [5]. However, depending on the anion basicity, CO_2 can be chemically incorporated into the imidazolium cation. Since the selectivity and solubility of CO_2 can be tuned depending on the anion/cation of the ILs, they present great versatility in applications for CO_2 processing.

Several theories for the mechanism of CO_2-IL sorption have been proposed over the years[5]:

a) *IL free volume effect* – theoretical and experimental data demonstrated that CO_2 solubility increases with increasing the molecular weight, molar volume and free volume of ILs.

b) *Lewis acid-base interaction effect (anion theory)* – the solubility of CO_2 is linked to the interaction anion - CO_2 where the latter acts as a Lewis acid and the anion as a Lewis base; solubility is enhanced by the CO_2 localization closer to the anion.

c) *Strong interaction cation-CO_2* – several studies reported evidence of the CO_2 localisation near the cation's butyl-methyl groups of 1-n-butyl-3-methylimidazolium ILs as well as CO_2 being close to the anion. In this case, the IL structure suffers small changes due to the CO_2 solvation without disrupting the hydrogen bond contact ion pairs.

d) *Chemical interaction* – very common in amine solutions (to form carbamates) and imidazolium-based IL with carboxylate anions (activation of the C2 position in dialkyl imidazolium ILs, followed by reaction of this position with CO_2).

e) *Water influence* – the formation of bicarbonate in hydrated ILs can increment the gas solubility by the reaction between CO_2 and residual water in the IL.

Despite these studies, there is still a lack of understanding regarding the correlation between the IL structure and CO_2 sorption ability. Generally speaking, the last proposed theory focuses on a set of ionic liquids belonging to the same structural family.

In a recent study [5], some classical imidazolium-based ionic liquids with different stereo-electronic characteristics were synthetized and their ability to sorb CO_2 was tested. Together with NMR studies and MDS (molecular dynamics simulations), it allowed the

identification of cation-anion-CO_2 interactions and IL-CO_2 interactions that explain the ILs performances.

The solubility in ILs was tested in BMI and BMMI cations. The sorb quantity of these ionic liquids is expressed in molar fraction X_{CO2}. The results are included in Table 2.

Table 2. CO2 capture in BMI·X and BMMI·X ionic liquids with different anions. [5]

Entry	Ionic Liquid	X_{CO2}
1	BMI·Mal	0.60
2	BMI·Succ	0.59
3	BMI·neoPent	0.58
4	BMI·sBu	0.56
5	BMI·Oac	0.53
6	BMMI·Oac	0.33
7	BMI·HCO$_2$	0.51
8	BMMI·HCO$_2$	0.33
9	BMI·tBu	0.42
10	BMI·iBu	0.42
11	BMI·Pro	0.33
12	BMMI·Pro	0.42
13	BMI·HCO$_3$	0.30
14	BMMI·HCO$_3$	0.32
15	BMI·Br	0.25
16	BMMI·Br	0.23
17	BMI·Cl	0.23
18	BMMI·Cl	0.20
19	HOEMMI·Br	0.30

According to the results of Table 2, the sorption is not directly dependent on anion basicity but onto the different types of interaction between the IL and CO_2. The carboxylates (entries 1-10) present the highest CO_2 sorption capacities. Such high performances are probably the result of two factors: the formation of a C2-CO_2 bond promoted by carboxylate anions and the other by residual water reacting with CO_2. In Figure 2, the effect of C2 substitution for different groups (group 1 = RCO_2 anions, group 2 HCO_3/Pro anions and group 3 Br/Cl anions) is illustrated.
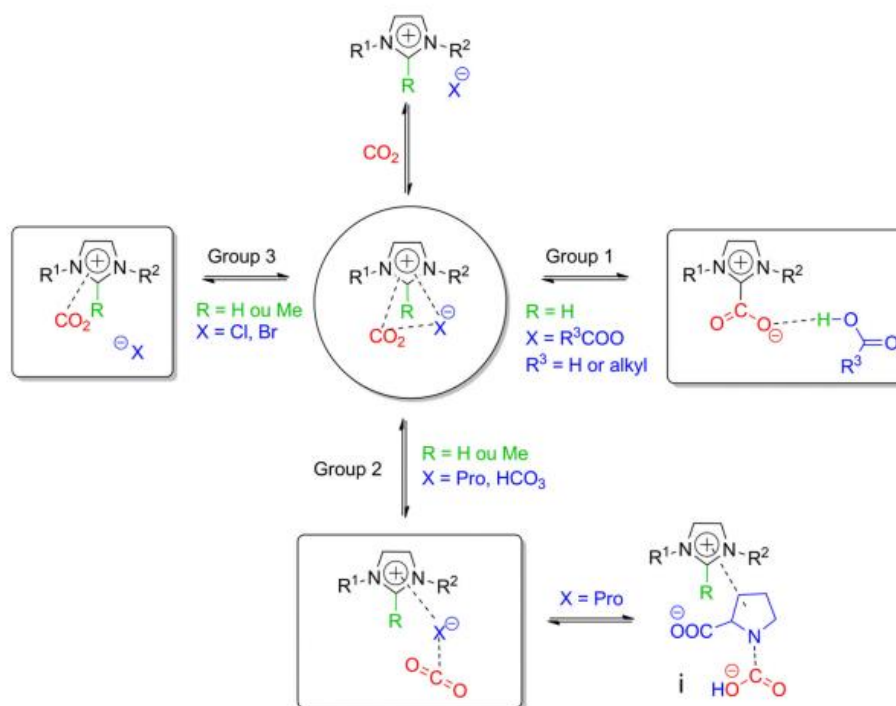
Figure 2. Effect of C2 substitution according to the group on the solubility of CO_2 [5]

The formation of 1-butyl-3-methylimizadolium-2-carboxylate (Figure 2, Group 1) exhibits the CO_2-C2 signal under 10 bar in ^{13}C NMR. This observation could explain the lower sorption capacities of BMMI (Me-C2) compared to BMI (H-C2) association with formate and acetate ions. The hygroscopic characteristic of carboxylates also positively influences CO_2 sorption, especially in the case of the anion OAc.

Observing the carboxylates presented, it is worth mentioning that the molar fraction of CO_2 increases with the number of carbon atoms in carboxylates: 4C (sBu, iBu, tBu) < 5C (neoPent). In the same carbon number carboxylates, the steric hindrance can interfere and the sorption capacities increase in the following order: iso = tert < sec. Since the steric hindrance hampers the cation-anion approximation, it is necessary an equal balance between the steric hindrance and the free volumed formed in the cavity by the IL to permit the CO_2 physisorption. Anions that are derived from dicarboxylic acids (e.g. malonate, succinate) promote higher CO_2 sorption probably due to the presence of two cations in their structure. The carboxylates are classified as both cationic and anionic influencers.

In the case of group 2 (Table 2, entries 11-14), the addition of water influences as the anions of this group can act as a neutral base and therefore, they strongly interact with CO_2 molecules. An experiment using BMI·Pro under 10 bar of CO_2 was performed and

neither the reaction between the C2 position of the imidazolium ring and CO_2 nor CO_2 freely dissolved was observed in natural abundance. Surprisingly, in the group 2 the BMMI present higher CO_2 sorption capacity than the BMI cation. Since the anions are weak bases, the C2 deprotonation does not occur under these studied conditions, thereby preventing the CO_2 additions at this position. Therefore, the C2 position must be protected so that the protic H of the anion becomes most acid and the molecule can act as a neutral base, promoting the interaction between the anion and CO_2. This group is classified as anionic influencers.

Group 3 (Table 2, entries 15-18), includes the ionic liquids that show lower CO_2 sorption capacity. No bonds at the C2 position of the cation are expected due to the inability of the anions to extract H2. Consequently, the sorption values obtained for both BMI and BMMI are quite similar. These types of anions are not basic enough to produce interactions with water and generate bicarbonate. Furthermore, anion-CO_2 bonds are not expected, suggesting that the sorption observed is mainly due to physisorption. For these reasons, these type of ILs are cationic influencers.

3.4) Recent examples of applications of IL with soft basic anions in CO_2 transformation to cyclic carbonates

The use of basic ILs as catalysts for the conversion of renewable CO_2 into value-added organic carbonates is highly significant in terms of environmental and economic issues. In terms of synthesis, the use of CO_2 as a primary feedstock has been very attractive for the synthesis of high added value chemicals. Due to the inherent thermodynamic and kinetic stability of CO_2, effective protocols and catalysts are still on the scope for potential CO_2 transformation reactions. [4]

a) Cyclic carbonates from alkynols: Mechanism and Results

The carboxylative cyclization of CO_2 and propargylic alcohols has evoked great interest since the resultant products, cyclic carbonates, are compounds with potential bioactivities for pharmaceutical chemistry and wide applications in organic synthesis.

Based on the principles of green chemistry, a catalyst exhibiting excellent activity as well as reusability is far more favourable for practical applications. Until now, most of the catalysts reported for these cyclizations do not possess recyclability. Although some

heterogeneous catalysts have been developed, these were applied under harsh conditions such as high CO_2 pressure, high catalyst loading and poor recyclability.

Ionic liquids combine excellent activity and outstanding reusability which can offer high solubility for homogeneous catalysis to dissolve the starting materials and high polar immiscibility, allowing the extraction of the products with low polar solvents in order to obtain reusability.

A green and recyclable AgI/OAc^- catalytic system was designed for the carboxylative cyclization of propargylic alcohols and CO_2 [4]. This proposed system converted different substrates, even hindered ones into the target cyclic carbonates at atmospheric pressure. The ionic liquids used were based on imidazolium ILs: EMI and BMI (see Figure 3).
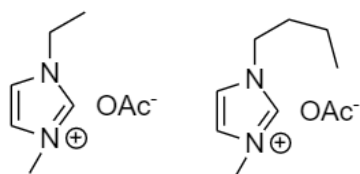
Figure 3. 1-Ethyl-3-methyl-imidazolium acetate (EMI·OAc) and 1-Butyl-3-methylimidazolium acetate (BMI·OAc)

The carboxylative cyclization of 2-methylbut-3-yn-2-ol and CO_2 (Scheme 1) was selected for the model catalytic reaction in order to explore the optimal reaction conditions (Table 3).
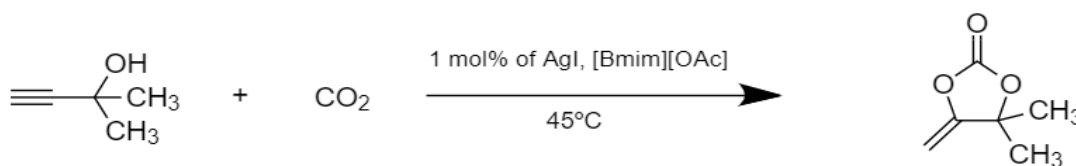
Scheme 1. Carboxylative cyclization of 2-methylbut-3-yn-2-ol

Table 3. Screening of reaction conditions[a]

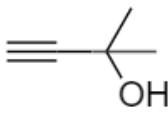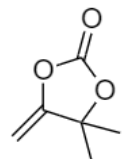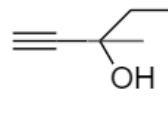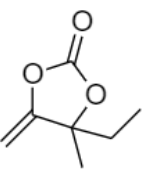| Entry	Ag salt	Ionic Liquid	Yield[b] (%)
1	AgI	-	0
2	-	EMI·OAc	0
3	AgI	EMI·OAc	91
4	AgBr	EMI·OAc	75
5	AgCl	EMI·OAc	48
6	Ag_2O	EMI·OAc	43
7	Ag_2WO_4	EMI·OAc	44
8	Ag_2CO_3	EMI·OAc	60
9	AgOAc	EMI·OAc	48
10	$AgNO_3$	EMI·OAc	58
11	$AgPF_6$	EMI·OAc	86
12	AgI	BMI·OAc	41
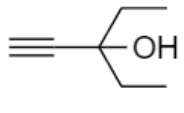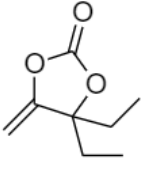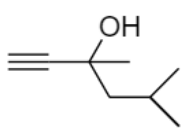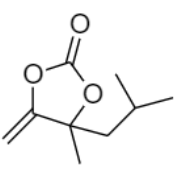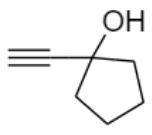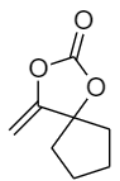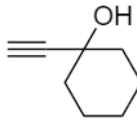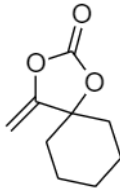
[a] *Reaction conditions: 0.05mmol of [Ag], 1ml of IL, 5mmol 2-methylbut-3-yn-2-ol, 1 bar CO_2 at 45ºC, 3h.*

[b] *Yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.*

Looking at Table 3, the combination of silver salts and ionic liquids provided good yields for the desired products (entries 3-12). AgI together with EMI exhibited the best catalytic performance (entry 3). In addition, iodide anion was exchanged by different halogens showing activities following the order of I>Br>Cl (entries 3-5). Furthermore, various anions were introduced and moderate yields were obtained (entres 6-11). Lastly, replacing the ethyl group of the cation for a n-butyl group led to a signficiant reduce in yield from 91% to 41%. Consequently, the optimal reaction conditions for the catalytic system were working at 45ºC at 1 bar of CO_2.

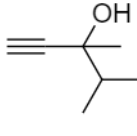Once the optimal reaction conditions were set, numerous propargylic alcohols with varios substituents were tested. The reactivity of the substrates was dependent on the steric hindrance of the substituents, hence indicating the different times of reaction for each substrate. The results are featured in Table 4.

Table 4. Screening of the substrates[a]

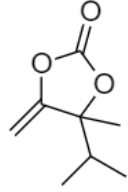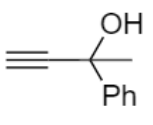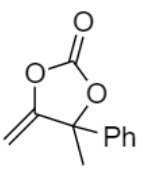| Entry	Substrate	Product	Time	Yield[b] (selectivity)
1			3h	93% (>99%)
2			4h	96% (>99%)
3			3h	91% (98%)
4			6h	99% (>99%)
5			8h	88% (99%)
6			6h	99% (>99%)
7			6h	97% (98%)
8			12h	44% (97%)

[a] *Reaction conditions: 0.05mmol of [Ag], 1ml of IL, 5mmol 2-methylbut-3-yn-2-ol, 1 bar CO_2 at 45ºC, 3h.*

[b] *Yields were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.*

Numerous propargylic alcohols were converted into the desired α-alkylidene cyclic carbonates with excellent yields. The catalytic system showed robust activities to challenging substrates (the ones with high steric hindrance) such as entry 8 where only 41% yield was obtained.

The activation of the hydroxyl group is considered the crucial step for the catalysis of the carboxylative cyclization. This can be accomplished thanks to the IL component of the system. The interaction between OAc⁻ and CO_2 is considered the possible CO_2 activation mechanism since OAc⁻ is in high concentration. A plausible mechanism for the carboxylative cyclization of propargylic alcohols and CO_2 catalyzed by the Ag/IL catalytic system is featured in Figure 4.
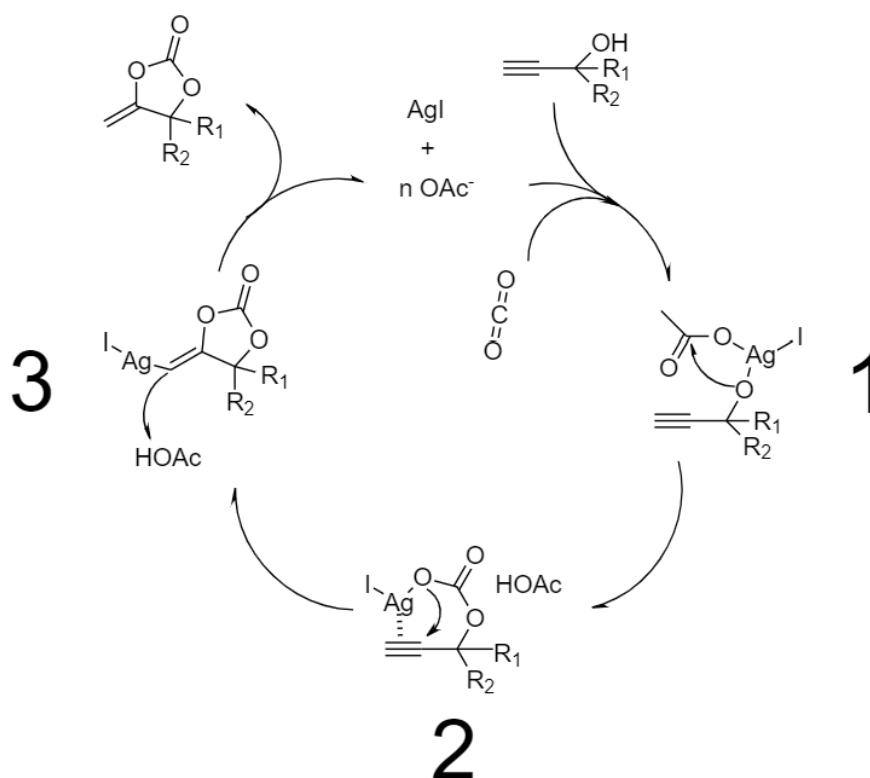
Figure 4. Proposed catalytic mechanism of the Ag/IL system (4)

The high concentration of OAc⁻ activates the hydroxyl group from the substrate, thus, enhancing its nucleophilicity to the silver atom. Carbon dioxide is induced by OAc⁻ and receives a partial negative charge which is followed by the positive silver centre and thus, the generation of intermediate 1. Afterwards the electrophilic attack of the carboxylic carbon atom on the hydroxyl oxygen atom occurs to give intermediate 2. The triple bond is activated by the silver atom to bring the connection of the adjacent oxygen and the carbon in the triple bond, which results in the formation of the five membered ring,

intermediate 3. Finally, the corresponding cyclic carbonate is obtained with the regeneration of the catalyst.

Concluding, different substrates were tested with the catalytic system proposed. However, in this study the effects of the anion of the imidazole in the catalytic system were not thoroughly studied, so this is one of the objectives to study in this thesis.

(b) Cyclic carbonates from epoxides: Mechanism and Results

Another promising conversion of CO_2 into useful chemicals is its insertion into epoxides to form cyclic carbonates. These types of carbonates can be used as electrolytes for batteries, aprotic polar 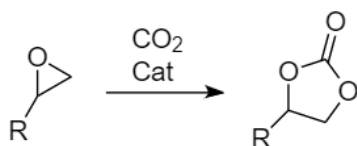solvents, valuable starting materials for polymerization reactions and as intermediates for organic synthesis. The general scheme of reaction is featured in Scheme 2.

Scheme 2. Conversion of CO_2 into cyclic carbonate from an epoxide

The fixation of CO_2 with epoxides catalysed by imidazolium salts has been achieved in the past via a nucleophilic-base-like catalysis [6]. Therefore, it is reasonable to assume that the tuning of IL-basicity nucleophilicity by playing with the electronic-steric features of both cation and anions may generate recyclable systems in which the IL displays both the catalyst and support role. In a recent study [7], imidazolium ILs are tested as catalysts. These ionic liquids are mainly derivatives of BMI and BMMI. Although in several studies, the use of dicationic imidazolium ionic liquids were also used for the conversion of carbon dioxide into cyclic carbonates from epoxides [8] [9]. The effects of both cations and anions on the yield and selectivity of cyclic carbonate synthesis were studied. From the results, the mechanism of the catalytic system was addressed.

The conversion of styrene oxide into styrene carbonate was selected as the model reaction. The cycloaddition reaction of CO_2 with styrene oxide was investigated at 150 ºC at 5 bar of CO_2. The results are summarized in Table 5.

Table 5. Comparison of CO_2 and styrene oxide cycloaddition with several catalysts[a]

Entry	Catalyst	Time (h)	Selectivity[b] (%)	Conversion[b] (%)
1	None	24	-	-
2	BMI·Br	4	99	99
3	BMI·I	4	99	99
4	BMI·Cl	4	46	99
5	tBMI·I	4	87	88
6	BMMI·Br	4	99	94
7	BMMI·AlCl$_4$	4	67	99
8	BMMI·HCO$_3$	4	77	88
9	BMMI·OH	4	-	27
10	BMI·AcO	6	61	59
11	BMI·EMAcO	6	44	87
12	BMI·Malonate	6	74	87
13	BMI·Pro	6	60	99
14	BMI·HCO$_3$	4	75	93
15	BMI·BA	6	33	67

[a] *Reaction conditions: 3.34mmol styrene oxide, 5 bar CO_2, 10% mol catalyst, 150ºC.*

[b] *Conversion and selectivity were determined by ^1H NMR spectroscopy.*

Several investigations have been made about the synergetic effects between acidic and basic functional groups of the imidazolium counterions as catalysts [10] (see Figure 5). The epoxide is activated by acid functional groups through the O atom of the epoxide, whereas in basic functional groups it is through the nucleophilic attack on the sterically less hindered carbon atom of the epoxide. In the case of these ILs, the coordination of both cationic and anionic moieties promote the reaction by the dual activation of the epoxide and CO_2 (Figure 6).
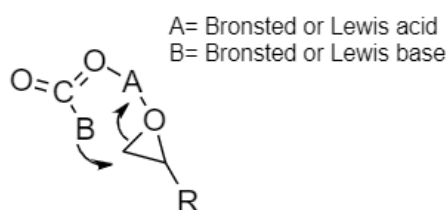

Figure 5. Synergetic effect of the catalyst
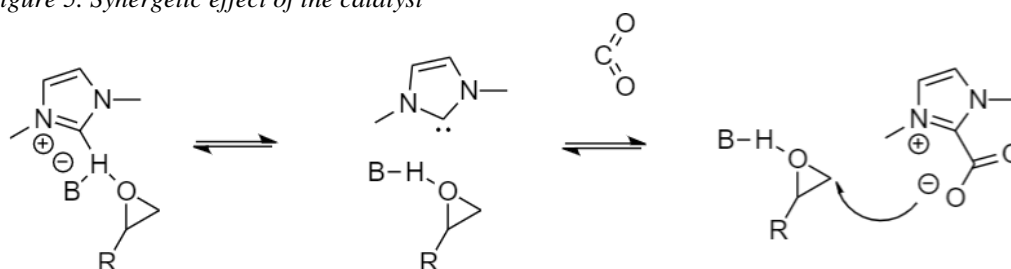
Figure 6. Proposed pathway through an imidazolidene intermediate

Halide anions (entries 2-4) were tested firstly and optimal performances were obtained for BMI·Br and BMI·I. The selectivity in the case of BMI·Cl decreased to 46% since Cl⁻ is a worst nucleophile, so the ring-opening of the epoxide is less favoured. Another important factor is the good leaving ability, which is essential for ring closure, a SN_2-type reaction on sp3 carbon. This can also explain the lower activity of Cl nucleophiles compared to Br/I.

The influence of the steric hindrance in was also investigated by replacing the n-butyl group of the cation with t-butyl group. Both selectivity and conversion decreased to 87% and 88%, respectively.

When OH was the anion, the conversion decreased to 27% and all the product formed was the styrene 1,2-diol. This means that, with these conditions, after the nucleophilic attack of the hydroxyl group on the epoxide, the cyclic carbonate will never be formed; only hydrolysis will occur.

In the case of BMI carboxylates, which are known for their basic properties, they showed a good CO_2 capture. BMI·OAc showed moderate conversion (59%) and selectivity (61%) as the styrene 1,2-diol was identified as a byproduct. Compared to halides, the basic character of carboxylate anions seems unfavourable for the conversion of epoxide to carbonate as they are weaker nucleophiles and moderate leaving groups.

Since styrene 1,2-diol was identified as the biggest byproduct, the effect of water in the mechanism was thoroughly investigated. In Figure 7, it can be observed that the formation of the diol is provided through either the hydrolysis of epoxide, alkoxide or cyclic carbonate.

Figure 7. Proposed pathway of the styrene 1,2-diol formation through hydrolysis

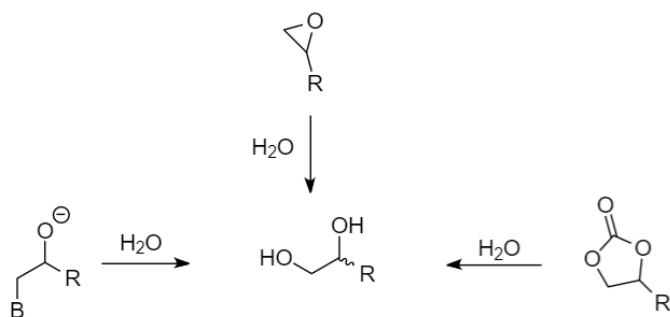With halides as the anion in ILs, the presence of water did not affect the conversion to carbonate. Since carboxylate anions are known to be strongly hygroscopic, the effect of water provides a higher conversion to the diol. Under CO_2, with the presence of water, increases conversion but the selectivity to the carbonate is reduced since more diol is being formed.

4) Experimental Part

4.1) General procedures

The solvents and reagents used were commercially purchased from Sigma-Aldrich and Thermo Fisher Scientific. CO_2 (99.9995%) was purchased from Air Liquide and was used as received.

Nuclear Magnetic Resonance (NMR) experiments were performed in a Bruker Aveance Neo 400 MHz spectrometer. ^1H NMR (401 MHz) and ^{13}C NMR (101 MHz) spectra were obtained as solutions in D_2O or $CDCl_3$. Chemical shifts were reported in parts per million (ppm, δ). For ^1H NMR spectra, multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or a combination of these.

4.2) General procedure for the ionic liquids synthesis

The BMI·Cl salts were synthetized according to the literature procedure [11]. The synthesis of 3-butyl-1-methyl imidazolium chloride (BMI) is straightforward. The reaction is a nucleophilic substitution that follows an SN_2 mechanism in which the lone pare of electrons of the nitrogen that does not form part of the aromatic system, attacks the electrophilic carbon of an alkyl halide. The reaction scheme of the synthesis is displayed in Scheme 3.
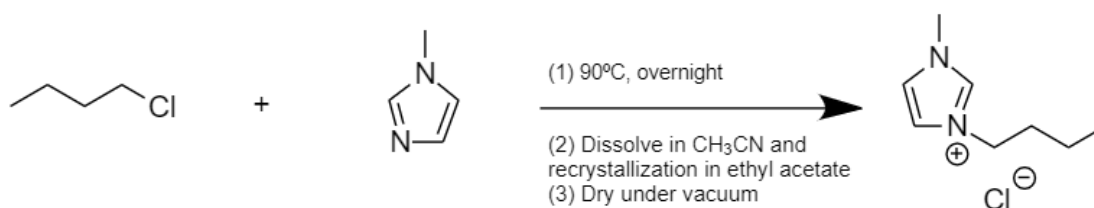
Scheme 3. BMI·Cl synthesis

In a two necked round bottom flask, 267 g of 1-chlorobutane and 237 g of 1-methylimidazole was mixed. The flask was heated at 90 ºC under reflux and magnetic stirring for 72 h. Then, the unreacted reagents were removed under reduced pressure. In order to purify more the final product, a recrystallization was performed: the product was solubilized in 450 mL of acetonitrile and it was added into 1.6 L of ethyl acetate in a 5 L Erlenmeyer flask drop by drop. To induce crystallization, some seeds of BMI·Cl previously synthesized were added. The product was characterized by ^{1}H NMR analysis.

The crystallized product, a white solid, was filtered. It was dried under vacuum for 24 h. 260 g of BMI·Cl was obtained with a yield of 55 %. The yield was lower than the expected due to problems with the recrystallization.
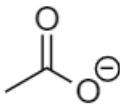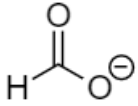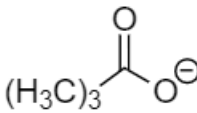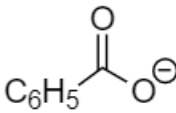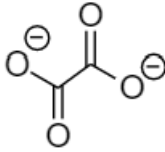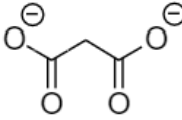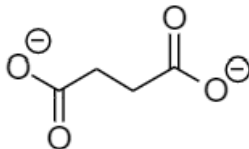
The synthesis scheme for BISCAT·Cl is featured in Scheme 4. In a 250ml round bottom flask with double neck, 57 g (0.57 mol) of 1,2-dichloroethane and 95g (1.15 mol) of 1-methylimidazole were mixed. The solution was heated under reflux at 90 ºC for 24h with magnetic stirring. After reaction time, the unreacted reagents were removed under reduced pressure. A white crystalline solid was obtained as product that was dried under vacuum leading to 130 g of 2,2-(ethanediyl)-bis-(1-methylimizadolium) chloride with a yield of 86 %. The product was characterized by ^{1}H NMR analysis.
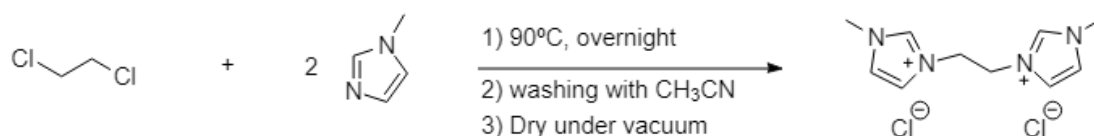
Scheme 4. BISCAT·Cl synthesis

Several anionic exchanges were performed to obtain the desired ionic liquids. The exchange schemes can be observed in Scheme 5 and in Scheme 6. The anions for which the chlorine ion was exchanged are listed in Table 6.

Table 6. Anions used for the anionic exchanges

Anion	Structure	pKa (acid)
Acetate		4.8
Formate		3.7
Pivalate		5.0
Benzoate		4.2
Oxalate		1.2, 4.2
Malonate		2.8, 5.0
Succinate		4.2, 5.4
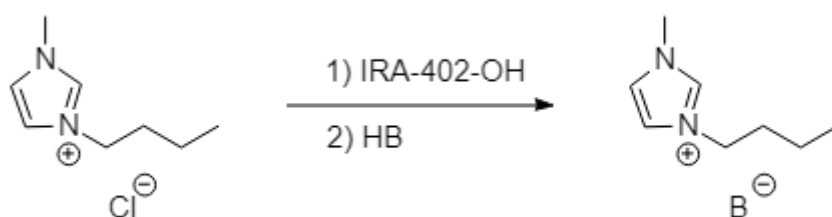
Scheme 5. Anionic exchange of BMI·Cl.
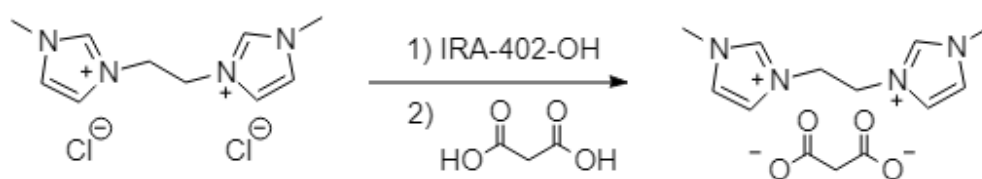
Scheme 6. Anionic exchange of BISCAT·Cl

To perform anionic exchanges on BMI·Cl/BISCAT·Cl, a column with resin was prepared. 70 g of resin Amberlite 402(Cl) was weighted and added to the column. Then, 200 mL of 1 M solution of NaOH (8 g NaOH needed) was passed through the column in order to exchange the chloride anions by hydroxyl anions; the exchange was monitored by analysing the pH of the outflow solution, that had a basic pH after the NaOH solution passed through the column. Afterwards, approximately 1L of MiliQ water was passed through to remove the excess of NaOH and to pull the NaCl formed, until the outflow solution had a neutral pH and no turbidity was observed when adding a $AgNO_3$ solution.

Then, a 500mL 0.1M solution of BMI·Cl /BISCAT·Cl was passed through the column so that the resin can retain the chloride ions, and the positively charged BMI/BISCAT was stabilized by the hydroxide anions. Then, 250ml of MiliQ water was passed through to ensure no IL remained on the column. Finally, the conjugate acid wanted for the counterion was added to the solution with the BMI (only malonic acid for BISCAT). The solution was stirred in an Erlenmeyer flask for 48h.

After, the water was removed under reduced pressure in a rotary evaporator. When finished, the resulting ILs were weighted and stored in vials. Each synthesized ionic liquid was characterized by ^{1}H NMR in deuterium oxide. All the exchanged ionic liquids were obtained in a >99% yield.

19

4.3) General procedure for the ionic liquid applications in catalysis

(a) Cyclic carbonates from epoxides

For the synthesis of styrene carbonate (Scheme 7) the reaction conditions were the same as the ones reported in the literature [7]. Catalysts (1–10 mol%) were charged in a Teflon™ insert with a magnetic stirrer bar. Styrene oxide (406 mg, 3.34 mmol) was added, and this Teflon™ insert was placed within a ca. 14 mL stainless steel autoclave, which was sealed and flushed 3 times at room temperature with Argon, vacuum and then CO_2 to remove the air from the vessel. The pressure was adjusted to 5 bar. The reaction was stirred at 100–150 °C for 2–24 h. After this reaction, the reactor was cooled to room temperature and the pressure was released. The autoclave was opened, and the contents were analysed by 1H NMR spectroscopy to determine the conversion, yield and selectivity to styrene carbonate. The experimental set-up can be observed in Figure 8.
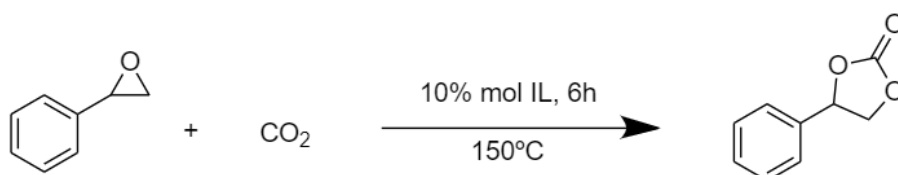
Scheme 7. Synthesis of styrene carbonate

Figure 8. Experimental set-up for the synthesis of styrene carbonate

(b) Cyclic carbonates from alkynols

For the synthesis of cyclic carbonates from alkynols, 2-methylbut-3-yn-2-ol was used as the primary substrate (Scheme 8Scheme 8). The reaction conditions were the same as the ones reported in the literature [4]. AgI (11.7 mg, 0.05 mmol, 1 mol %), IL1 (1 mL, 1.102 g, 6.474 mmol), a propargylic alcohol (5 mmol) were added in a glass insert and placed in a stainless steel autoclave. The system was quickly purged 3 times with N_2 and filled with 1 bar (g) of CO2. Then the mixture was stirred at 45 °C, for the required time. Upon completion, the pressure was released by opening the autoclave and the crude of reaction was analysed by ^{1}H NMR to determine the conversion and selectivity to the cyclic carbonate.
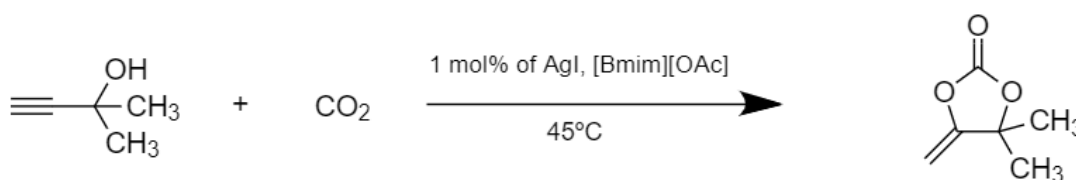
Scheme 8. Carboxylic cyclization of 2-methylbut-3-yn-2-ol

5) Results and discussion

5.1) Ionic liquid characterization by ^{1}H NMR

The ionic liquids synthetized were characterized by ^{1}H NMR spectroscopy in D_2O. The corresponding peaks for the imidazolium were assigned as well as the peaks characteristic for each anion. The signals obtained were compared to the Spectral Database for Organic Compounds (SBDS) [12].

The ^{1}H NMR signals obtained are in agreement with the reported ones, confirming the successful preparation of this IL structures in high purity (>99%) and moderated yields (55 to 99%).

In general, the ^{1}H NMR spectra displayed the signals typical of the three protons of the methyl imidazolium cation (position 6, 7 and 7') at 8.63 ppm, 7.31-7.43 ppm as a s, m respectively. The signals of the protons at the 7 and 7' coincided and appeared at the same chemical shift.

Also, in the ^{1}H NMR, the signals corresponding to the lateral alkyl chains were recorded for the methyl group at 3.86 ppm as a singlet, and for the butyl group at 0.80 ppm, 1.27-1.13 ppm, 1.64-1.82 ppm and 4.07 ppm as a t, m, m and t, respectively.

Concerning the anion group, the ^{1}H NMR also displayed the signals attributed to the different anions; acetate, formate, pivalate, malonate, succinate and benzoate. Whereas, no signals were recorded, as expected, for the chloride and oxalate anions.

For the biscationic IL, the ^{1}H NMR signals displayed also the three imidazolium protons of the imidazolium cations, but in this case, the lateral alkyl chain are the methyl group with a chemical shift of 3.99 ppm as a s and 1,2-ethylene group with a chemical shift of 4.64 ppm as a t.

Table 7. BMI·Cl ^{1}H NMR signals

Position	Signal predicted	Signal obtained
1	0.89 ppm (t, 3H)	0.80 ppm (t, J = 7.4 Hz, 3H)
2	1.22-1.35 ppm (m, 2H)	1.27 – 1.13 ppm (m, 2H)
3	1.82 ppm (m, 2H)	1.82 – 1.64 ppm (m, 2H)
4	4.17 ppm (t, 2H)	4.07 ppm (t, J = 7.1 Hz, 2H)
5	3.86 ppm (s, 3H)	3.77 ppm (s, 3H)
6	8.68 ppm (s, 1H)	8.63 ppm (s,1H)
7	7.25-7.34 ppm (m,2H)	7.31-7.43 ppm (m,2H)

Figure 9. BMI·Cl signal assignation

Table 8. BMI·OAc ¹H NMR signals

Position	Signal predicted	Signal obtained
1	0.89 ppm (t, 3H)	0.84 ppm (t, J = 7.4 Hz, 3H)
2	1.22-1.35 ppm (m, 2H)	1.12-1.32 ppm (m, 2H)
3	1.82 ppm (m, 2H)	1.70-1.82 ppm (m, 2H)
4	4.17 ppm (t, 2H)	4.12 ppm (t, J = 7.1 Hz, 2H)
5	3.86 ppm (s, 3H)	3.81 ppm (s, 3H)
6	8.68 ppm (s, 1H)	8.63 ppm (s,1H)
7	7.25-7.34 ppm (m,2H)	7.30-7.42 ppm (m,2H)
8	1.97 ppm (s,1H)	1.86 ppm (s,1H)

Figure 10. BMI·OAc signal assignation

Table 9. BMI·Form ¹H NMR signals

Position	Signal predicted	Signal obtained
1	0.89 ppm (t, 3H)	0.80 ppm (t, J = 7.4 Hz, 3H)
2	1.22-1.35 ppm (m, 2H)	1.06-1.35 ppm (m, 2H)
3	1.82 ppm (m, 2H)	1.51-1.86 ppm (m, 2H)
4	4.17 ppm (t, 2H)	4.07 ppm (t, J = 7.1 Hz, 2H)
5	3.86 ppm (s, 3H)	3.77 ppm (s, 3H)
6	8.68 ppm (s, 1H)	8.59 ppm (s,1H)
7	7.25-7.34 ppm (m,2H)	7.16-7.40 ppm (m,2H)
8	8.58 ppm (s, 1H)	8.31 ppm (s,1H)

Figure 11. BMI·Form signal assignaton

Table 10. BMI·Piv ^{1}H NMR signals

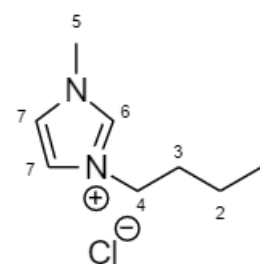| Position	Signal predicted	Signal obtained
1	0.89 ppm (t, 3H)	0.80 ppm (t, J = 7.4 Hz, 3H)
2	1.22-1.35 ppm (m, 2H)	1.30 – 1.12 ppm (m, 2H)
3	1.82 ppm (m, 2H)	1.84 – 1.60 ppm (m, 2H)
4	4.17 ppm (t, 2H)	4.07 ppm (t, J = 7.1 Hz, 2H)
5	3.86 ppm (s, 3H)	3.77 ppm (s, 3H)
6	8.68 ppm (s, 1H)	8.59 ppm (s,1H)
7	7.25-7.34 ppm (m,2H)	7.31-7.43 ppm (m,2H)
8	1.02 ppm (s, 9H)	0.98 ppm (s, 9H)

Figure 12. BMI·Piv signal assignation

Table 11. BMI·Ox ^{1}H NMR signals

Position	Signal predicted	Signal obtained
1	0.89 ppm (t, 3H)	0.80 ppm (t, J = 7.4 Hz, 6H)
2	1.22-1.35 ppm (m, 4H)	1.27 – 1.13 ppm (m, 4H)
3	1.82 ppm (m, 4H)	1.84 – 1.60 ppm (m, 4H)
4	4.17 ppm (t, 4H)	4.07 ppm (t, J = 7.1 Hz, 4H)
5	3.86 ppm (s, 6H)	3.77 ppm (s, 6H)
6	8.68 ppm (s, 2H)	8.59 ppm (s, 2H)
7	7.25-7.34 ppm (m, 2H)	7.30-7.35 ppm (m, 2H)

Figure 13. BMI·Ox signal assignation

Table 12. BMI·Mal ¹H NMR signals

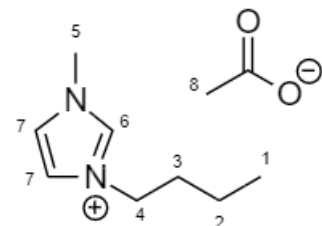| Position	Signal predicted	Signal obtained
1	0.89 ppm (t, 6H)	0.80 ppm (t, J = 7.4 Hz, 6H)
2	1.22-1.35 ppm (m, 4H)	1.30 – 1.07 ppm (m, 4H)
3	1.82 ppm (m, 4H)	1.88 – 1.61 ppm (m, 4H)
4	4.17 ppm (t, 4H)	4.07 ppm (t, J = 7.1 Hz, 4H)
5	3.86 ppm (s, 6H)	3.77 ppm (s, 6H)
6	8.68 ppm (s, 2H)	8.59 ppm (s, 2H)
7	7.25-7.34 ppm (m, 4H)	7.31-7.43 ppm (m, 4H)
8	3.40 ppm (s, 2H)	3.06 ppm (s, 2H)

Figure 14. BMI·Mal signal assignation

Table 13. BMI·Succ ¹H NMR signals

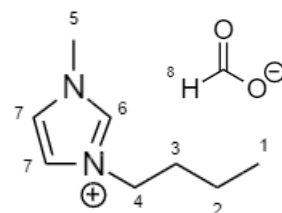| Position	Signal predicted	Signal obtained
1	0.89 ppm (t, 6H)	0.80 ppm (t, J = 7.4 Hz, 6H)
2	1.22-1.35 ppm (m, 4H)	1.29 – 1.09 ppm (m, 4H)
3	1.82 ppm (m, 4H)	1.93 – 1.62 ppm (m, 4H)
4	4.17 ppm (t, 4H)	4.07 ppm (t, J = 7.1 Hz, 4H)
5	3.86 ppm (s, 6H)	3.76 ppm (s, 6H)
6	8.68 ppm (s, 2H)	8.59 ppm (s, 2H)
7	7.25-7.34 ppm (m, 4H)	7.48-7.23 ppm (m, 4H)
8	2.25 ppm (s,4H)	2.32 ppm (s, 4H)

Figure 15. BMI·Succ signal assignation

Table 14. BMI·BA ^{1}H NMR signals

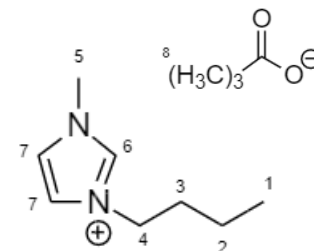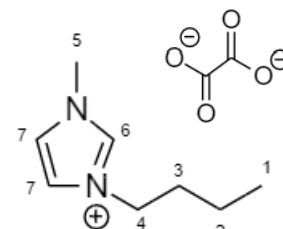| Position	Signal predicted	Signal obtained
1	0.89 ppm (t, 3H)	0.80 ppm (t, J = 7.4 Hz, 3H)
2	1.22-1.35 ppm (m, 2H)	1.30 – 1.12 ppm (m, 2H)
3	1.82 ppm (m, 2H)	1.84 – 1.60 ppm (m, 2H)
4	4.17 ppm (t, 2H)	4.07 ppm (t, J = 7.1 Hz, 2H)
5	3.86 ppm (s, 3H)	3.77 ppm (s, 3H)
6	8.68 ppm (s, 1H)	8.59 ppm (s,1H)
7	7.25-7.34 ppm (m, 2H)	7.31-7.43 ppm (m, 2H)
8	7.89-7.30 ppm (m, 5H)	7.82-7.34 ppm (m, 5H)
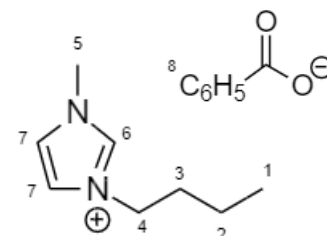
Figure 16. BMI·BA signal assignation

Table 15. BISCAT·Cl ^{1}H NMR signals

Position	Signal predicted	Signal obtained
1	3.94 ppm (s, 6H)	3.99 ppm (s, 6H)
2	7.93 ppm (s, 2H)	7.84 ppm (s, 2H)
3	7.22-7.24 ppm (m, 4H)	7.32-7.36 ppm (m, 4H)
4	4.72 ppm (t, 4H)	4.64 ppm (t, 4H)
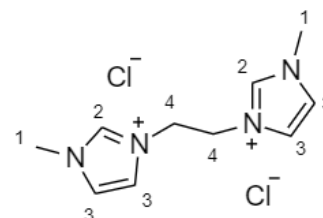
Figure 17. BISCAT·Cl signal assignation

Table 16. BISCAT·Mal ^{1}H NMR signals

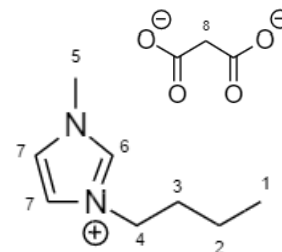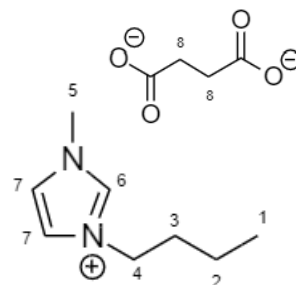| Position	Signal predicted	Signal obtained
1	3.94 ppm (s, 6H)	3.99 ppm (s, 6H)
2	7.93 ppm (s, 2H)	7.84 ppm (s, 2H)
3	7.22-7.24 ppm (m, 4H)	7.32-7.36 ppm (m, 4H)
4	4.72 ppm (t, 4H)	4.64 ppm (t, 4H)
5	3.40 ppm (s, 2H)	3.48 ppm (s, 2H)
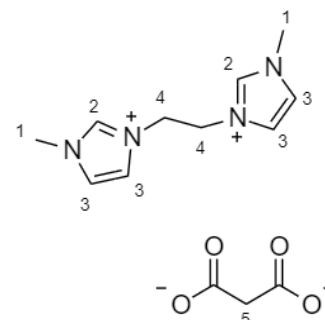
Figure 18. BISCAT·Mal signal assignation

In conclusion, in this thesis, a series of 7 monocationic imidazolium salt (1,3-methyl imidazolium) ILs bearing different basic anions derived from carboxylic acids (monoanionic and bianionic carboxylates). Furthermore, the preparation of 1 novel biscationic bisimidazolium salt IL bearing malonate anion was reported.

5.2) Ionic liquids applications in catalysis

(a) Cyclic carbonates from epoxides

The formation of cyclic carbonates from styrene oxide was explored by using ionic liquids as catalyst under the desired reaction conditions of pressure, temperature and reaction time. After reaction, the conversions and selectivities were determined by performing ^{1}H NMR analysis of the crude reaction mixture. The results of the carboxylation of styrene oxide are included in Table 17. First of all, the effect on the catalytic performance of the cation and anion combination in the IL catalysts was explored by performing experiments using the BMI cation and different anions. The obtained results revealed the effect of the anion on the conversion and selectivity of the reaction.

Table 17. Results of styrene oxide carboxylation
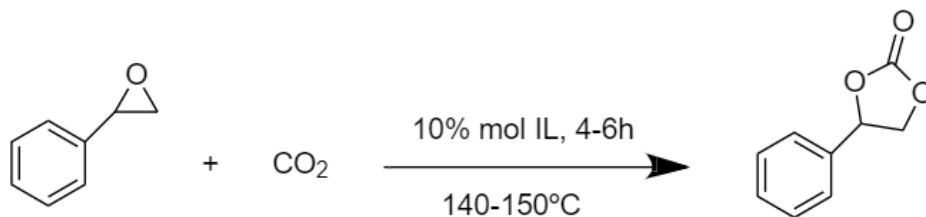
Entry	Ionic Liquid	Temp. (ºC)	Time (h)	Conv. (%)	Sel. (%)
1	Blank	150	6	-	-
2	[BMI·I]	150	4	99	90
3	[BMI·Mal]	150	6	99	5
4	[BMI·OAc]	140	6	99	1
5	[BMI·Form]	140	6	99	9
6	[BMI·BA]	140	6	99	1
7	[BMI·Mal]	140	6	99	<1
8	[BMI·Ox]	140	6	99	7
9	[BMI·Mal/BMI·I] (50/50) w/w	150	4	99	<1
10	[BMI·I]	150	6	99	63
11	[BMI·Mal/H$_2$O](1/67) mol	150	6	99	2

Reaction conditions: 3.34mmol (0.40g) of styrene oxide, 10%mol IL and CO$_2$ (5 bar). Conversion and selectivity were determined by ^{1}H NMR of the crude reaction mixture sample dissolved in CDCl$_3$.

BMI·I exhibited the best conversion and selectivity out of all the anions tested (entry 2 & 10) as expected. These results are in agreement to that reported in the literature [7], and it can be attributed to the outstanding properties of the iodide anion [I⁻] as nucleophile and leaving group. The selectivity to styrene carbonate decreased when increasing the reaction time from 4h to 6h (90% to 63%). Styrene 1,2-diol was observed as the major by-product. This observation suggested a possible decomposition of the cyclic carbonate under prolonged treatment at the reaction conditions.

The ILs bearing the BMI cation and anions derived from carboxylic acids (entries 3-8) resulted in quantitative conversions with very low selectivities to the cyclic carbonate product and high selectivities to the styrene 1,2-diol. These results are in agreement to that reported in the literature [7], where the authors explained this by the presence of remanent water in the IL, that promoted the formation of the diol since the anions derived from the carboxylic acids are much weaker nucleophiles and poorer leaving groups than the iodide anion, therefore, they do not promote the formation of the cyclic carbonate.

However, according to a previous study [13], water was used for the synthesis of cyclic carbonate by means of an acidic medium to favour the opening of the epoxide in presence of ILs such as BMI·I, and therefore, it seems no plausible that remanent water in the IL was enough for transforming the epoxide into the diol. In the above mentioned study that reported the effect of water, they have also observed that water addition has a positive effect on the product selectivity [13], and then, an experiment was conducted in presence of such molar ratio H_2O/IL (67/1) but no improvement of the selectivity was recorded.

Then, according to the idea that the combination of BMI·I/H_2O improved the catalyst activity and selectivity [13], our innovative idea was to explore the combination of both ILs, the BMI·I as a catalyst for promoting the formation of the cyclic carbonates, and the BMI with carboxylate anions which could have the same role of H_2O but with the advantages of the properties of the ionic liquids (non-volatile, easy recyclable and higher CO_2 solubility). Then, in the experiment displayed in entry 9, a test was performed by using a mixture of BMI·I and BMI·Mal (weight ratio of 1/1). The BMI·Mal was selected because this IL displayed the highest CO_2 solubility (see Table 2). However, poor results were obtained since the selectivity was <1%.

This result and the above ones makes us suspecting that the 1,2-diol could be a reaction product resulting from both, the reaction of remanent water with the styrene oxide and

also, the decomposition of the cyclic carbonate in the presence of the IL bearing basic anions. In fact, in the literature, they observed an improvement of the cyclic carbonate selectivity by tuning the medium acid-base properties using the proper ratio of BMI·AcO/AcOH. [13].

In order to know the origin of the formation of the styrene 1,2-diol, some additional experiments were carried out in order to know the reactivity of the carbonate and find an hypothesis to why the selectivity with basic anions was so low. Firstly, the reactivity of the BMI·Mal was tested with styrene oxide under N_2 (inert) atmosphere in order to know if the diol is obtained. In the second entry, the reactivity of the BMI·Mal with the cyclic carbonate (the one generated with BMI·I) under N_2 (inert) atmosphere was tested in order to know if the diol was obtained.

Table 18. Reactivity tests of the BMI·Mal
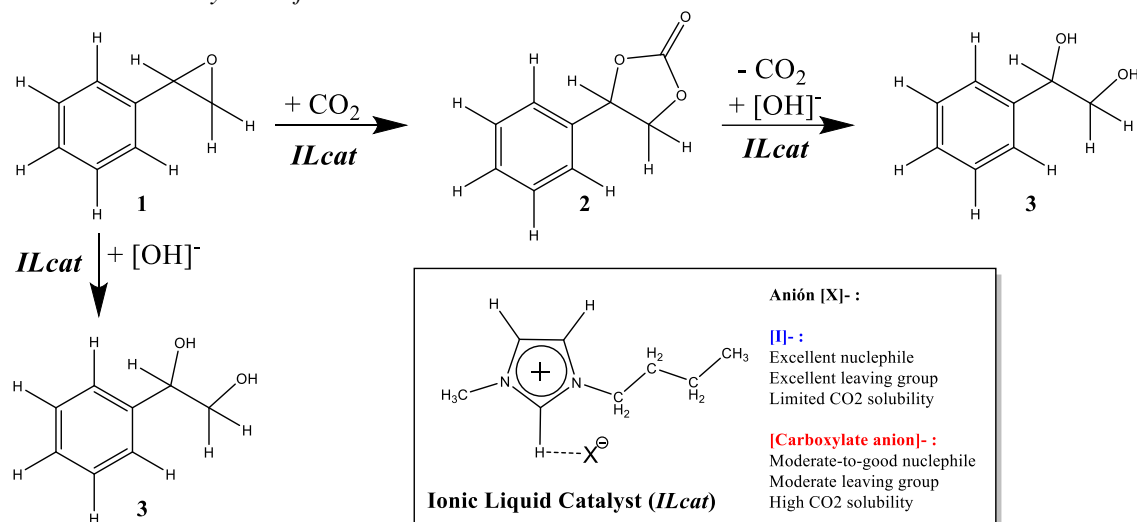
Entry	Test	Temp. (ºC)	Time (h)	Conv. (%)	Sel. (%)
1	[BMI·Mal] + styrene oxide	150	6	99	<1
2	[BMI·Mal] + cyclic carbonate	150	6	99	<1

Reaction conditions: 3.34mmol (0.40g) of substrate, 10% mol IL. Conversion and selectivity were determined by ^{1}H NMR of the crude reaction mixture sample dissolved in CDCl$_3$.

According to the results obtained in Table 18, it was observed that the formation of the diol could be from either the reaction of the epoxide with water or the decomposition of the carbonate. It remains to be known if the low selectivity obtained with the ionic liquids with basic anions is due to one or the other.

In summary [7], the formation of the diol comes from the reaction of epoxide with water (see Figure 7). However, there is also stated that the use of water with halides as anion such as BMI·I, high selectivity to carbonate was obtained. In our case, we performed an experiment (entry 9) in which a mixture of BMI·I and BMI·Mal was used and the major product obtained was the diol. This tendency could explain that the formation of the carbonate is catalyzed by BMI·I and its decomposition in situ is catalyzed by the basic media generated by BMI·Mal.

In conclusion, even though the ionic liquids with basic anion are thought to be the ideal media for these types of transformations of CO_2 thanks to their high capacity to absorb it, they are not suitable for this type of carbonates because they favour its decomposition. In the next chapter, the reaction to form cyclic carbonates from an alkynol is featured. Better selectivities are expected since these types of substrates and the derived cyclic carbonates are relatively less reactive and more stable, as all the carbons are secondary.

(b) Cyclic carbonates from alkynols

The formation of cyclic carbonates alkynols was explored by using AgI as catalyst and ionic liquids as reaction media under the desired reaction of pressure, temperature and reaction time. After reaction, the conversions and selectivities were determined by performing ^{1}H NMR analysis of the crude reaction mixture. The results of the carboxylation of 2-methyl-3-but-2-ynol (an alkynol) are featured in Table 19.

Table 19. Results of carboxylation of 2-methyl-3-but-2-ynol and CO₂
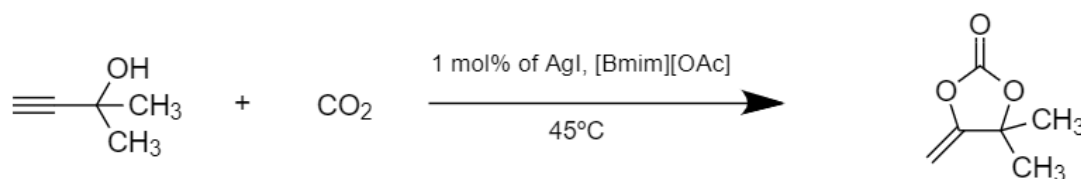
Entry	Ionic Liquid	Pressure (bar)	Temp. (ºC)	Time (h)	Conv. (%)	Sel. (%)
1	Blank	1	45	3	-	-
2	[BMI·OAc]	1	60	3	26	54
3	[BMI·OAc]	1	45	3	21	81
4	[BMI·OAc]	1	60	18	99	0
5	[BMI·OAc]	5	45	3	39	82
6	[BMI·OAc]	5	60	3	52	30
7	[BMI·Form]	1	45	3	4	5
8	[BMI·BA]	1	45	3	7	9
9	[BMI·IM]	1	45	3	6	85
10	[BMI·Mal]	1	45	3	28	83
11	[BMI·Succ]	1	45	3	20	41
12	[BISCAT·Mal]	1	45	3	<1	-

Reaction conditions: 5mmol substrate, 0.05mmol AgI. Conversion and selectivity were determined by ^{1}H NMR of crude reaction mixture sample dissolved in CDCl₃.

As mentioned in the introduction section, the reaction of an alkynol with CO_2 in order to obtain cyclic carbonates catalyzed by AgI in ionic liquids bearing acetate anions was already studied [4]. The effect of the different anions for the ionic liquid was not thoroughly studied and only it was used EMI as the cation. In our study, the innovation is the application for the first time of ionic liquids bearing 7 different anions. In Table 19, several experiments were performed with different basic anions and modifying the reaction conditions in order to obtain the highest selectivity to the cyclic carbonate. The first ionic liquid tested in order to obtain the optimal conditions was BMI·OAc in order to corroborate the reproducibility respect to the literature results [4].

The reaction conditions were optimized by exploring the effect of the:

- *Reaction temperature*. Entries 2 & 3 showed that increasing the temperature from 45 ºC to 60 ºC increased the conversion of the substrate but the selectivity towards the cyclic carbonate diminished significantly and increases the selectivity towards the α-hydroxyketone (acyloin). It should be highlighted that the α-hydroxyketone (acyloin) is a product resulting from the decomposition of the cyclic carbonate, formed by similar reaction mechanism to that operating for the formation of 1,2-diol by decomposition of cyclic carbonate derived from styrene oxide.

- *Reaction time.* In entry 4, the reaction time was increased to 18h in order to check the decomposition of the carbonate. Since the selectivity was 0%, the carbonate had fully been decomposed into the α-hydroxyketone (acyloin).

- *CO_2 pressure.* In entries 5 & 6, the pressure was increased to 5 bar and the conversion again was higher in the case of 60ºC compared to 45ºC. However, the selectivity towards the cyclic carbonate was significantly higher in the case of 45ºC.

Later, the IL with the soft basic anions were evaluated under optimal reaction conditions and the resulting reaction performances compared to that recording using BMI·OAc (entries 7 to 11). Among all the IL tested, BMI·Mal showed the highest overall yield (conversion x selectivity) and BMI·Succ the second highest. This tendency can be explained by their high ability to the sorption of CO_2 (see Table 2). Other soft basic anions such as formate, imidazolate and benzoate were tested but lower yields were obtained as they are weaker captors of CO_2.

Finally, a test performed with a different cation, ILs bearing bisimizadolium cations (BISCAT·Cl and BISCAT·Mal) were synthesised. As it was a dicationic, and according to the literature [8] [9], this kind of dicationic ILs displayed unique properties respect to monocationic ILs and they also displayed improved performance in the formation of cylic carbonates by cycloaddition of CO_2 with epoxides. Then, our innovative idea was the application of this kind of biscationic ILs as a reaction media for the synthesis of cyclic carbonates from alkynols. Surprisingly, the conversion obtained was very low (<1%) due to either, the catalyst deactivation under reaction conditions, or because a negative effect of this cation-anion combination in the CO_2 solubility. Among them, the Ag-catalyst deactivation by formation of (NHC)-Ag-I species is the most plausible according to the literature [14].

6) Conclusions and outlook

English

The present Bachelor's thesis was aimed towards the chemical transformation of CO_2 into added value chemicals, in this case, cyclic carbonates. The objectives planned for this thesis have been accomplished and the main conclusions are as follow:

- The experimental procedure for the synthesis of the ionic liquids has been accomplished. 8 ionic liquids bearing 3-butyl-1-methylimidazolium (BMI) cations and different anions (1 bearing chloride anions and 7 bearing anions derived from different carboxylic acids), and 2 ionic liquids bearing 1,2-bis(1-methyl-imidazolium) ethylene cation and different anions (1 bearing chloride anion and 1 novel IL bearing malonate anion) have been synthetized and characterized by ^{1}H NMR spectroscopy.

- The ionic liquids have been tested as catalysts for the synthesis of cyclic carbonates from CO_2 and selected substrates. In the case of the 2-methyl-3-butyn-2-ol (alkynol), the IL acts as reaction media and the AgI is the catalyst. Whereas, in the case of the and styrene oxide (epoxide), the IL acts as the catalyst.

- The mechanism for both reactions has been discussed alongside with the results obtained comparing it with previous studies suggesting that the cyclic carbonates are susceptible to be decomposed to the corresponding diol in the reaction media in presence of the ILs with basic anions.

- The effect of the anion and cation of the ionic liquids for the cyclic carboxylations in epoxides and alkynols has been discussed. In general, the IL bearing basic anions seems to have more promising application for the synthesis of cyclic carbonates from alkynols than from styrene oxide. In fact, for the first time, improvements of the catalytic performances in the cyclic carbonate synthesis from alkynols respect to the reference literature results have been recorder by using ILs bearing anion derived from biscarboxylic acids (attributed to the reported higher CO_2 solubility in BMI·Mal and in BMI·succ than in BMI·OAc) were reported. Furthermore, for the first time, the application of IL bearing bisimidazolium cation and malonate anion has been explored in the cyclic carbonate synthesis from alkynols revealing the deactivation of the catalyst, probably, by the formation of the NHC-Ag species.

- Reactivity tests were performed in order to obtain information regarding the formation of the by-products either by the decomposition of the substrate or by the decomposition of the cyclic carbonates under reaction conditions. Our results suggested that the side products (1,2-diol derived from styrene oxide and α-hydroxyketone (acyloin)) are also formed by the decomposition of the cyclic carbonate under reaction conditions, thus, the reaction time is a critical variable. Furthermore, this could be also the explanation for the highest selectivity achieved from the alkynols than from styrene oxide, since these types of substrates and the derived cyclic carbonates are relatively less reactive and more stable since all of the carbons are secondary.

As an outlook, based in the insights resulting from the results of this TFG, it is expected to continue developing efficient ILs for their application in CO_2 transformation processes for the production of added-value chemicals.

Català

El present treball de fi de grau va tenir com a objectiu la transformació química del CO_2 en productes químics de valor afegit, en aquest cas, carbonats cíclics. Els objectius previstos per a aquesta tesi s'han assolit i les principals conclusions són les següents:

- S'ha realitzat el procediment experimental per a la síntesi dels líquids iònics. 8 líquids iònics que porten cations 3-butil-1-metil-imidazoli (BMI) i diferents anions (1 que porta anions de clorur i 7 que porten anions derivats de diferents àcids carboxílics) i 2 líquids iònics amb 1,2-bis(1-metilimidazoli) amb catió d'etilè i diferents anions (1 amb clorur i 1 nou IL anió amb malonat) s'han sintetitzat i caracteritzats per espectroscòpia ^{1}H RMN.
- Els líquids iònics han estats provats com a catalitzadors per a la síntesi de carbonats cíclics a partir de CO_2 i substrats seleccionats. En el cas del 2-metil-3-butin-2-ol (alquinol), el líquid iònic actua com a medi de reacció i l'AgI és el catalitzador. Mentre que, en el cas de l'òxid d'estirè (epòxid), el líquid iònic actua com a catalitzador.
- S'ha discutit el mecanisme de les dues reaccions juntament amb els resultats obtinguts comparant-los amb estudis anteriors que suggereixen que els carbonats cíclics són susceptibles a descompondre's al diol corresponent en els medis de reacció en presència dels IL amb anions bàsics.

- S'ha comentat l'efecte de l'anió i el catió dels líquids iònics per a les carboxilacions cícliques tant en epòxids com en alquinols. En general, el líquid iònic que porta anions bàsics sembla tenir una aplicació més prometedora per a la síntesi de carbonats cíclics a partir d'alquinols que a partir de l'òxid d'estirè. De fet, per primera vegada, s'han registrat millores de les prestacions catalítiques en la síntesi de carbonats cíclics a partir d'alquinols respecte als resultats de la literatura de referència mitjançant l'ús de líquids iònics que contenen anions derivats d'àcids dicarboxílics (atribuïts a la major solubilitat de CO_2 en el BMI·Mal i BMI·Succ que en el BMI·OAc). A més, per primera vegada, s'ha explorat l'aplicació d'un líquid iònic amb un catió bisimidazoli i anió malonat en la síntesi cíclica de carbonats a partir d'alquinols revelant la desactivació del catalitzador, probablement, per la formació de l'espècie NHC-Ag.

- Es van realitzar proves de reactivitat per tal d'obtenir informació sobre la formació dels subproductes ja sigui per la descomposició del substrat o per la descomposició dels carbonats cíclics en les condicions de reacció. Els nostres resultats van suggerir que els productes secundaris (1,2-diol derivat de l'òxid d'estirè i α-hidroxicetona (aciloïna)) també es formen per la descomposició del carbonat cíclic en condicions de reacció, per tant, el temps de reacció es una variable crítica. A més, aquesta també podria ser l'explicació de la major selectivitat aconseguida a partir dels alquinols que de l'òxid d'estirè, ja que aquest tipus de substrats i els carbonats cíclics derivats són relativament menys reactius ja que tots els carbonis són secundaris.

Com a treball futur, basant-se en els coneixements derivats dels resultats d'aquest treball de fi de grau, es preveu continuar desenvolupant líquids iònics eficients per a la seva aplicació en processos de transformació del CO_2 per a la producció de productes químics de valor afegit.

7) Bibliography

(1) Tiago, G. A.; Matias, I. A.; Ribeiro, A. P.; Martins, L. M. Application of Ionic Liquids in Electrochemistry—Recent Advances. *Molecules* **2020**, *25* (24), 5812.

(2) Greer, A. J.; Jacquemin, J.; Hardacre, C. Industrial Applications of Ionic Liquids. *Molecules* **2020**, *25* (21), 5207.

(3) Ivanov, M. Y.; Prikhod'ko, S. A.; Bakulina, O. D.; Kiryutin, A. S.; Adonin, N. Y.; Fedin, M. V. Validation of Structural Grounds for Anomalous Molecular Mobility in Ionic Liquid Glasses. *Molecules* **2021**, *26* (19), 5828.

(4) Yuan, Y.; Xie, Y.; Zeng, C.; Song, D.; Chaemchuen, S.; Chen, C.; Verpoort, F. A Recyclable AGI/OAC− Catalytic System for the Efficient Synthesis of α-Alkylidene Cyclic Carbonates: Carbon Dioxide Conversion at Atmospheric Pressure. Green Chemistry **2017**, 19 (13), 2936–2940.

(5) Simon, N. M.; Zanatta, M.; Neumann, J.; Girard, A.-L.; Marin, G.; Stassen, H.; Dupont, J. Cation−Anion−Co2 Interactions in Imidazolium-Based Ionic Liquid Sorbents. *ChemPhysChem* **2018**, *19* (21), 2879–2884.

(6) Fogassy, G.; Pinel, C.; Gelbard, G. Solvent-Free Ring Opening Reaction of Epoxides Using Quaternary Ammonium Salts as Catalyst. *Catalysis Communications* **2009**, *10* (5), 557–560.

(7) Girard, A.-L., Simon, N., Zanatta, M., Marmitt, S., Gonçalves, P., & Dupont, J. (2014). Insights on recyclable catalytic system composed of task-specific ionic liquids for the chemical fixation of carbon dioxide. *Green Chem.*, *16*(5), 2815–2825. https://doi.org/10.1039/c4gc00127c

(8) Jiang, Y.; Wang, Z.; Xu, P.; Sun, J. *Crystal Growth & Design* **2021**, *21* (7), 3689–3698.

(9) Taheri, M.; Ghiaci, M.; Shchukarev, A. Cross-Linked Chitosan with a Dicationic Ionic Liquid as a Recyclable Biopolymer-Supported Catalyst for Cycloaddition of Carbon Dioxide with Epoxides into Cyclic Carbonates. *New Journal of Chemistry* **2018**, *42* (1), 587–597.

(10) Darensbourg, D. Catalysts for the Reactions of Epoxides and Carbon Dioxide. *Coordination Chemistry Reviews* **1996**, *153*, 155–174.

(11) Dupont, J.; Consorti, C. S.; Suarez, P. A.; de Souza, R. F. Preparation of 1-Butyl-3-Methyl Imidazolium-Based Room Temperature Ionic Liquids. Organic Syntheses 2003.

(12) Spectral database for organic compounds,SDBS. https://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi (accessed Jun 13, 2022).

(13) Sun, J.; Ren, J.; Zhang, S.; Cheng, W. Water as an Efficient Medium for the Synthesis of Cyclic Carbonate. *Tetrahedron Letters* **2009**, *50* (4), 423–426.

(14) Hayes, J. M.; Viciano, M.; Peris, E.; Ujaque, G.; Lledós, A. Mechanism of Formation of Silver *n*-Heterocyclic Carbenes Using Silver Oxide: a Theoretical Study. *Organometallics* **2007**, *26* (25), 6170–6183.