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ARTICLE TYPE

Insights on recyclable catalytic system composed of task-specific ionic liquids for the chemical fixation of carbon dioxide

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5

A series of imidazolium-based ionic liquids (ILs) were synthesised and used as a single component and metal-free homogeneous catalysts to convert a renewable, inexpensive and non-toxic CO_2 feedstock into useful products. The cycloaddition of carbon dioxide to

10 epoxides to produce cyclic carbonate was evaluated. A detailed investigation was carried out on a variety of factors that affected the reactivity and selectivity, such as the catalyst structures (nature of cation and anion). The effect of reaction parameters (temperature, reaction time, CO_2 uptake and catalyst amount) on the catalytic performance was also investigated in detail. High conversions and selectivities could be achieved under mild pressure condition (5 bar) using 1-*n*-butyl-3-methylimidazolium bromide. A synergetic effect of the acidic and basic sites as well as suitable hydrogen-bonding strength is considered crucial for the reaction to proceed smoothly. This

15 protocol was found to be applicable to a disubstituted epoxide. Furthermore, the straightforward synthesis of cyclic carbonates by direct oxidative carboxylation from olefins was achieved using only 1-*n*-butyl-3-methylimidazolium bromide as a catalyst.

Introduction

From the standpoint of environmental protection and resource utilisation, continuous efforts have been directed towards the

20 fixation and utilisation of carbon dioxide. Therefore, CO_2, which has the advantages of being non-toxic, abundant and economical, can be considered as a C1 building block in organic synthesis.[1] One promising conversion of CO_2 into useful chemicals is its insertion into epoxides to form cyclic carbonates (Scheme 1).[2]

25 These carbonates can be used as electrolytes for batteries, aprotic polar solvents, valuable starting materials for polymerisation reactions and intermediates in organic synthesis.[3]
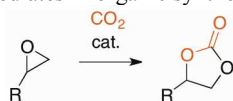
Scheme 1 Conversion of CO_2 into cyclic carbonate from epoxide

30 Many catalytic systems have been developed for the cycloaddition of carbon dioxide to oxiranes. However, homogeneous catalyst systems[4] suffer from problems such as separation of catalysts and low cost effectiveness of the catalyst synthesis process. Alternatively, heterogeneous catalytic

35 conditions[5] can be adopted to overcome these problems, but these catalysts have some disadvantages, such as low catalytic activity and/or selectivity, and high-pressure requirements. Therefore, the development of a highly efficient catalyst for the chemical fixation of carbon dioxide under mild conditions remains a

40 challenge.

Ionic liquids (ILs) have received a lot of interest during the past few years because they possess important features, such as the negligible vapour pressure, unique solvation properties, as well as catalytic activity and selectivity. It has been reported that

45 various kinds of catalytic reactions have smoothly performed in ionic liquids, which can act itself as catalytic active species.[6] Although the fixation of CO_2 with epoxides catalysed by imidazolium salts has been successfully achieved,[7] the presence of a co-catalyst, as quaternary onium salts,[7a] Lewis acid,[7f] base,[7h]

50 polymer[7i] or silica support[7j] is required. Furthermore, high pressure (higher than 10 bar) is generally required to achieve high yields.[7] Interestingly, phosphonium iodide salts are effective tandem catalysts for the industrial production of methylethylene glycol via sequential epoxide carbonation and carbonate

55 hydrolysis.[8] In this context, it appears that simple halides can promote the carbonation of epoxides, presumably via a nucleophilic-base-like catalysis.[9] Therefore, it is reasonable to assume that the fine-tuning of IL basicity-nucleophilicity by playing with the electronic-steric features of both cation and

60 anions may generate recyclable catalytic systems in which the IL may display the role of catalyst and support. For this purpose, we have systematically investigated a series of ILs as catalyst for the cycloaddition of CO_2 with epoxides. We focused our study on imidazolium ILs as catalysts. For toxicity and biodegradability

65 reasons,[10] we prepared low molecular weight and mainly mono or free halogenated catalysts. We studied the effects of cations and anions on the yield and selectivity of cyclic carbonate synthesis as well as the effect of reaction parameters in the catalytic activities. From these results, the mechanism of the catalytic

70 system was theoretically addressed. The scope of the cycloaddition with other epoxide substrates was also considered. Finally, the direct synthesis of cyclic carbonates from olefin instead of epoxides was tested with same imidazolium salt catalysts.

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Result and discussion

Investigation of catalysts

The conversion of styrene oxide into styrene carbonate was selected as the model reaction since the reaction could be easily monitored by ^1H NMR spectroscopy. Furthermore, the conversion of styrene oxide to styrene carbonate is more difficult due to its lower reactivity of β-carbon atoms compared to propylene oxide and ethylene.[7a] In order to check the steric-electronic influence of the IL through relation structure/catalytic activity, a series of imidazolium salts containing different N-substituents associated with a variety of anions (Figure 1) was used as media and catalyst for the carbonation of styrene oxide.
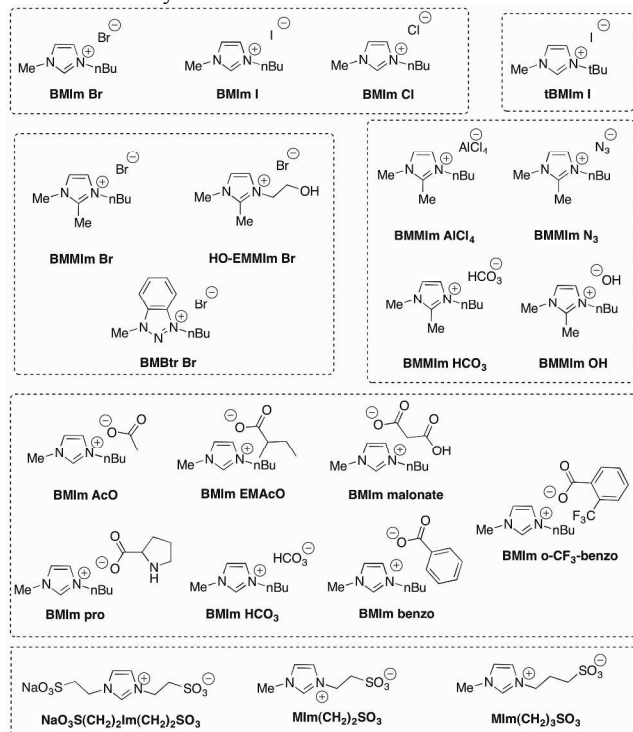

Fig. 1 Imidazolium salts prepared and used in this study

The cycloaddition reaction of CO_2 with styrene oxide was initially investigated at 150°C in autoclave reactor under 5 bar for 4-24 h without any solvent or co-catalyst. The results were summarised in Table 1.

First of all, no reaction occurred without any catalyst under this condition (Entry 1). In the cases of ILs, the anions show a crucial influence on the yield and selectivity of the reaction. No reaction occurs in the presence of KI, indicating that the anion alone does not allow the reaction (Entry 2) and that the imidazolium counterion plays an important role as well. Indeed, several research groups investigated the synergetic effects between acidic and basic functional groups of catalysts.[11] They pointed out that an epoxide is activated by acid functional groups through the O atom of epoxide, whereas in the basic functional groups, the epoxide is activated through effective nucleophilic attack on the sterically less hindered carbon atom of the epoxide. In the particular case of ILs, the coordination of both cationic and anionic moieties hence promoted the reaction by dual activation of the epoxide and carbon dioxide (Figure 2).

Firstly, halide anions (Br⁻, I⁻ and Cl⁻) have been tested (Entries 3-5). Optimal performances were obtained for 1-butyl-3-methylimidazolium salts: **BMIm Br** and **BMIm I**. However, both yield and selectivity decreased to 46% in the case of Cl⁻ (Entry 5). This activity might be attributed to their nucleophilicity, which is high enough to enable further ring-opening of the epoxide to form reactive intermediates shown in Schemes 3 and 4.

Table 1 Comparison of CO_2 and styrene oxide cycloaddition over several catalysts

Entry	Cat.(mol%)	Time(h)	Yd(%)[a]	Sel.(%)[a]	Conv.(%)[a]
1	none	24	-	-	-
2	KI	24	3	99	3
3	BMIm Br	4	99(29)[b]	99(99)[b,c]	99(29)[b]
4	BMIm I	4	99	99	99
5	BMIm Cl	4	46	46[c]	99
6	tBMIm I	4	77	87[d]	88
7	BMMIm Br	4	94(39)[b]	99(99)[b]	94(39)[b]
8	HO-EMMIm Br	4	99(55)[b]	99(99)[b]	99(55)[b]
9	BMBtr Br	4	79	79[e]	99
10	BMMIm AlCl₄	4	67	67[e]	99
11	BMMIm N₃	4	68	68	99
12	BMMIm HCO₃	4	68	77[e]	88
13	BMMIm OH	4	-	-	27[c]
14	BMIm AcO	6	36	61[e]	59
15	BMIm AcO/AcOH	6	41	42[e]	98
16	BMIm EMAcO	6	38	44[e]	87
17	BMIm malonate	6	64	74[e]	87
18	BMIm pro	6	60	60[e]	99
19	BMIm HCO₃	4	70	75[e]	93
20	BMIm benzo	6	22	33[e]	67
21	BMIm benzo/benzoic acid	6	32	36[e]	89
22	BMIm o-CF₃-benzo	6	53	58[e]	92
23[f]	NaO₃S(CH₂)₂Im(CH₂)₂SO₃	24	31	99	31
24	MIm(CH₂)₂SO₃	6/24	43/99	99/99	43/99
25	MIm(CH₂)₃SO₃	6	-	-	-

Reaction conditions: 3.34 mmol styrene oxide, CO_2 (5 bar), 10 mol% catalyst, 150 °C. [a]Determined by ^1H NMR spectroscopy. [b](%) for 1 mol% catalyst. [c]Styrene 1,2 diol identified as a by-product. [d]Phenylacetaldehyde identified as a by-product.[e]Styrene 1,2-diol identified as a by-product and unidentified additional by-products [f]Under 8 bar.

Another important factor is the good leaving ability that is essential for ring closure, which is an SN2-type reaction on sp3 carbon. This can explain the lower activity and selectivity of weaker Cl nucleophiles and less efficient leaving groups compared to Br/I.
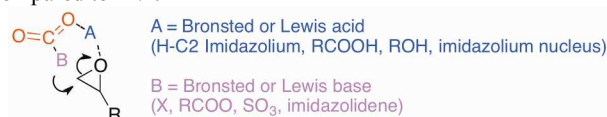

Fig. 2 Synergetic effect of catalyst

The influence of the steric hindrance in position 1 of the imidazolium nucleus was then investigated. A t-Bu bulky group replaced the n-Bu N-substituent. Indeed, it was previously reported that t-butylimidazolium salts are good precursors of imidazolidenes.[12] These species have proved their ability to react with carbon dioxide to afford imidazolium carboxylates, which can act as CO_2 delivery agents (see further scheme 2).[13] However, in the synthesis of styrene carbonate (Entry 6), this CO_2 activation mode does not seem favourable (or does not occur) because both yield and selectivity declined to 77% and 87% respectively. Phenylacetaldehyde has been identified as a

by-product, provided by isomerisation of styrene oxide in the presence of *t*-**BMIm I** (the ^{1}H NMR spectrum of the reaction mixture before the addition of CO_2 has shown aldehyde formation). This can be explained by the stronger acidity of the
5 H-C2 when the lateral chain is *t*-Bu substituted.

Various mechanisms were proposed to explain the catalytic activity of imidazolium-based ionic liquids.[14] The most largely accepted explanation suggests a first step in which CO_2 molecules are coordinated to the C2 position of the imidazolium
10 ring.[15] To confirm the influence of this hydrogen, a methyl group replaced the H-C2 and Br was first chosen as the anion source. Surprisingly, good yields (94% and 99%) and complete selectivity were obtained (Entries 7 and 8). With lower catalyst loading, the yield decreased to 39%for Me-C2 imidazolium
15 (Entry 7), which is still slightly higher than the corresponding H-C2 with the equal low catalyst amount (Entry 3). This activity was improved to 55% by the presence of a hydroxyl group in the lateral chain of imidazole (Entry 8). This indicates that the reaction is not only based on activation of the CO_2 molecules by
20 the imidazolium C2 position, as often reported in the literature.[15] Other cations, such as benzo(1,2,3)triazole and anions like $AlCl_4$, N_3 and HCO_3 have been evaluated but gave lower selectivities than imidazolium bromide salts (Entries 9-12). With OH as the anion, the conversion decreased to 27% and only styrene 1,2 diol
25 was identified (Entry 13). This means that after the nucleophilic attack of a hydroxyl group on the epoxide, the cyclic carbonate will never be formed under our conditions; only hydrolysis by-products will be formed.

In addition, several imidazolium carboxylates have been
30 synthesised and studied. These salts are known for their basic properties[16] and have already shown good CO_2 uptake.[17] As a matter of fact, a potential H-bonding interaction of the H-C2 of imidazolium ring with the carboxylate anion has been described affording the corresponding carbene precursor of imidazolium
35 carboxylate zwitterion after reaction with CO_2 (Scheme 2).[18]
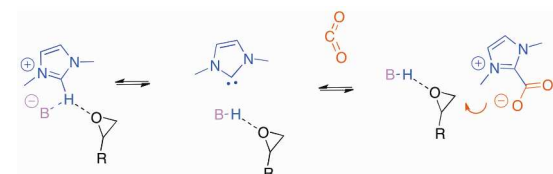
Scheme 2 Proposed pathway through an imidazolidene intermediate.

In the case of **BMIm AcO**, moderate conversion (59%), yield (36%) and selectivity (61%) were obtained (Entry 14). The
40 styrene 1,2-diol or carboxylate addition products were identified as by-products (Scheme 4). Compared to halides, the basic character of carboxylate anions seems unfavourable for the conversion of epoxide to carbonate. To investigate the possibility of carbene formation, we added an excess of acid (Entries 15 and
45 21) and observed a better conversion of up to 98% (**BMIm AcO**/AcOH) and 89% (**BMIm benzoate**/benzoic acid); unfortunately, the selectivity was in favour of hydrolysis, which indicates that those ILs can act as efficient nucleophilic catalysts without the imidazolidene intermediate. According to the
50 literature,[19] the carboxylic acid acts as a Brønsted acid to activate the epoxide ring-opening, which explains the better conversion observed. With higher electron density on the carboxylate,

2-methylbutanoate gave a higher conversion (87%) than acetate (59%) but lower selectivity (44%) (Entry 16). This result shows
55 again that a balance has to be found between the nucleophilicity and hydrolisability. Considering the favourable effect of acid addition in the conversion, we prepared the hydrogenomalonate (Entry 17). Its free COOH function allowed good conversion, better selectivity up to 74% and a yield of 64%. The prolinate has
60 been also tested and afforded complete conversion, 60% selectivity and 64% yield (Entry 18). As the hydrogenomalonate, the nitrogen of pyrrolidine can play a role of H-donor too. In the same way, the presence of a hydroxyl group provided by the bicarbonate anion (Entry 19) allows similar results but a slightly
65 higher yield (70%). Aromatic carboxylates were also prepared, giving low yields and selectivities although good conversions (Entries 20-22). However, the presence of a withdrawing group such as CF_3 in the aromatic moiety improved the selectivity and yield, to 58% and 53%, respectively (Entry22). This can be
70 attributed to the better hydrolysis ability afforded by aromatic functionality.

In this investigation, imidazolium sulfonates were studied as zwitterionic-type imidazolium salts. Ohno *et al.* revealed that zwitterionic-type ILs based on alkylimidazolium sulfonates are
75 useful in electrochemical applications due to their ion conductive properties and hydrophilicity.[20] Some are solid at room temperature, which can be an advantage for reuse of the catalyst. In our study, they were found to be less efficient, but totally selective (Entries 23-25). Only two have shown activities, but
80 longer reaction times are required (Entries 23 and 24). Those zwitterions are weak nucleophiles but present good stability. Their high melting points compared to the other ILs used can also explain these low yields. Furthermore, because their component cations and anions are both covalently tethered, this can be a
85 disadvantage in the mechanism where both cation and ion moieties play a role at the same time. This hypothesis is verified because the reaction is influenced by the size of the chain between the cation and the anion. Only a distance of two carbons has shown activity. This result confirms the dual activation of
90 IL-based catalysts in the ring opening of the epoxide and/or activation of carbon dioxide.

Effect of reaction conditions in the catalytic activity

The influence of reaction conditions on the formation of styrene carbonate from styrene oxide was investigated using one of the
95 most active and selective salts, **BMIm Br** (Table 2).

Table 2 Effects of reaction conditions in cycloaddition of CO_2 with styrene oxide catalysed by **BMIm Br**

Entry	Cat.(mol%)	Time(h)	Temp.(°C)	Yd(%)[a]	Sel.(%)[a]	Conv.(%)[a]
1	10	4	100	70	99	70
2	10	6	100	91	99	91
3	10	20	100	89	99	89
4	10	4[b]	100	41	85[c]	48
5	10	4[d]	100	79	99	79
6	10	2	150	96	99	96
7	5	4	150	30	99	30
8	10	4	150	90[e]	99	99
9	10	4	150	99[f]	99	99

Reaction conditions: 3.34 mmol styrene oxide, 5 bar CO_2. [a] Determined by ^{1}H NMR spectroscopy. [b] CO_2 uptake with 8 bar at rt for 20 h before styrene oxide addition under atmospheric air pressure. [c] Styrene 1,2-diol identified as by-product. [d] Same procedure than *b* but 5 bar of CO_2 was added after addition of styrene oxide. [e] Isolated yield. [f] After 3 runs.

The pressure range studied (5-8 bar) was chosen to correspond to the pressures that can be accommodated by standard stainless steel reactors, thus avoiding the capital costs associated with constructing specialised high-pressure reactors.

5 The influence of time was first investigated (Entries 1-3). As can be seen (Entry 2), the yield increased to 91% within 6 h of reaction time. Further extending the reaction time had no apparent effect on the reaction (Entries 3). Furthermore, the effect of CO_2 pre-solubilisation in IL before the addition of epoxide was
10 tested. We found that a pre-uptake of CO_2 by **BMIm Br** (8 bar, 20 h) is sufficient to yield 41% of styrene carbonate in 4h of reaction under atmospheric air (Entry 4). However, under this condition, the selectivity of styrene carbonate decreased to 85% compared to entry 3. By the addition of 5 bar of CO_2 after uptake
15 (Entry 5), the selectivity is total and the yield improved to 79% in comparison with entry 4. With temperature rising to 150°C (Entry 6), only 2 h already allowed a yield of 96%.The catalyst loading was also studied under this last condition (Entries 7 and 8), but the yield and selectivity decreased drastically as the catalyst
20 loading was reduced to 5 mol%. The easy separation of the product was verified and a simple extraction with ethyl acetate provided the pure carbonate with a yield of 90% (Entry 8). Finally, the recyclability of the imidazolium catalyst was tested. After 3 runs, neither conversion nor a decrease in selectivity was
25 observed (Entry 9).

Mechanism

Effect of water in diol formation

Due to the formation of styrene 1,2-diolin some conditions studied, the mechanism of this by-product formation was
30 evaluated. It can be provided at three steps: hydrolysis of epoxide, alkoxide or cyclic carbonate (Scheme 3). The presence of water under different conditions was investigated and the results are summarised in Table 3.
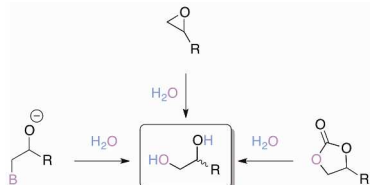
35 **Scheme 3** Proposed pathway of styrene 1,2-diol formation through hydrolysis

First of all, reaction parameters as temperature and pressure were tested independently on the styrene oxide without catalyst, with or without water. None of them led to hydrolysis (Entries 1 and
40 2). Two ILs were tested. With Br as anion (Entries 3-7), it is worth noting that presence of water benefits on the conversion to carbonate, increasing from 24 to 49% with water amount from entry 4 to 7. No diol was observed until a higher amount of water was used (Entry 7). In this last case, the conversion was enhanced
45 mostly in favour of diol formation.

Table 3 Effect of water on CO_2 and styrene oxide cycloaddition over styrene 1,2-diol formation

Entry	Cat.	T (h)	P.(bar)	H₂O(μL)	Conv.(%)[a]	Yd pdt(%)[a]	Yd Diol(%)[a]
1	-	4	-	-/20	0	-	0
2	-	4	5	-/20	0	0	0
3	BMIm Br[b]	4	-	20	0	-	0
4		4	5	-[c]	24	24	0
5		4	5	-	29	29	0
6		4	5	20	44	44	0
7		4	5	150	85	49	36
8	BMIm OAc[d]	4	-	20	30	-	30
9		6	5	-	59[f]	36	14
10		6	5	20	97[f]	22	63
11[e]	-	4	5	20	0	-	0

Reaction conditions: Styrene oxide (3.34 mmol),. [a] Identified by ^{1}H NMR. [b] Cat (1 mol%). [c] Addition of MgSO₄ (20 mg). [d] Cat (10 mol%). [e] Cyclic carbonate was used as substrate. [f] Styrene 1,2-diol identified as by-product and unidentified addition by-products.

are known to be strongly hygroscopic and acyl group easily hydrolyzed. Indeed in the case of OAc anion, the addition of
50 water even under atmospheric pressure provided the formation of diol with 30% of yield (Entry 8). Under CO_2,the addition of water increased the conversion from 59 to 97% but selectively for hydrolysis (Entries 9 and 10).At this step the growing of diol formation can also be coming from the hydrolysis of acetate
55 group itself. Finally, the hydrolysis of the final cyclic carbonate was tested and does not occur under our conditions (Entry 11). This study has shown that the by-product 1,2-diol is provided by hydrolysis of alkoxide. Moreover, carboxylate anion shows higher capacity of hydrolysis than halogens.
60

Hypotheses

Considering the coupling reactions of epoxides and CO_2 described[7,14]and our experiment results, a proposed general mechanism is illustrated in Scheme 4. In **cycle1**, the epoxide,
65 activated by an acidic center (H-C2 imidazolium, H-donor group, electron deficient imidazolium nucleus). Through this "Lewis acid" type activation, the isomerization of the epoxide to aldehyde by 1,2 H-shift is possible. However, as a main reaction, the activated epoxide **I** is attacked by the nucleophilic center
70 (halide, carboxylate, sulfonate, imidazolidene) to produce the required alkoxide intermediate **II**. At this stage, depends on the IL anion used and the presence of water, hydrolysis can occur to give corresponding monoalcohol and/or diol by-products as observed experimentally. Without this step of hydrolysis, the
75 cycle is followed by carbonation of alkoxide **II** with $CO_2$to form acyclic carbonate **III** that leads to the cyclic carbonate and regenerate the catalyst. In **cycle2**, the nucleophilic center (which can be the NHC in the case of imidazolium carboxylate or *t*-**BMIm**, scheme 2) attacks CO_2 to form intermediate **IV**. This
80 carboxylate compound is added to the epoxide via nucleophilic attack through complex **V** and generates the alkoxide **VI**. Then an intramolecular cyclic substitution nucleophile provides the final carbonate.
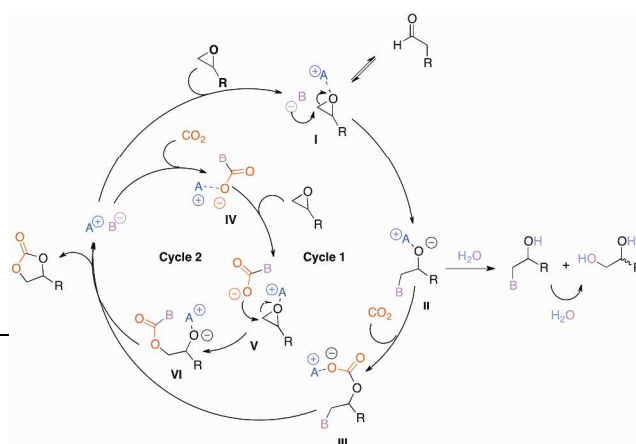
Scheme 4 Proposed mechanism

*Calculation on **BMIm Br** and styrene oxide*

To prove these hypotheses, a preliminary density functional
theory (DFT) computational study was carried out in the
Gaussian 09[21] program package using the ωB97XD functional
with the 6-31G(d,p) basis set. All of the species participating the
cycloaddition reaction were fully optimised using tight
convergence criteria and the energies of all species take into
account the zero-point energy (ZPE). Energies are relative to the
sum of the isolated reactants, which is taken to be zero. The
minima connecting the transitions states were found by means of
the intrinsic reaction coordinate (IRC) method and all of the
extremes were verified through vibrational analysis. The results
shown are with respect to the cycloaddition of styrene oxide in
the presence of **BMIm Br** (Figure 3). First of all, only **cycle 1**was
observed in this case. Initially **complex 1** was formed, which is
more stable than the isolated reactants by 14.22 kcal.mol^{-1}. Here,
the H-C2 of imidazolium ion was facing the O of oxirane (2.168
Å). This complex reacts via the transition state **TS 1** (with an
imaginary vibration frequency of 490i cm^{-1}), where the
coordination O/H-C2 is conserved (O-H: 1.676 Å) and through a
relatively low energy barrier of 26.93 kcal.mol^{-1} (compared to the
non-catalysed reaction of about 54 kcal.mol^{-1}). [22] The
corresponding opened-ring intermediate, **Int. 1**, lying 13.99
kcal.mol^{-1} lower in energy compared to the isolated reactants,

was then found with the anti-addition in the less substituted C of
the epoxide through deprotonation of the H-C2 by the O. After
the introduction of CO$_2$, the presence of a new intermediate, **Int.
2**, was observed due to interactions of the highly positive C of
CO$_2$ with the highly negative O of epoxide (2.710 Å) and was
20.72 kcal.mol^{-1}more stable with respect to the isolated reactants.
Transition state **TS 2** (235i cm^{-1}) characterises the next step in
which the formation of a new bond between the O of epoxide and
the C of CO$_2$ (2.023 Å) is followed by a 7.18 kcal.mol^{-1} energy
barrier while the H goes back to C2 of imidazolium. This leads to
the corresponding acyclic carbonate, **Int. 3**, as expected which is
17.27 kcal.mol^{-1} below the reactants where the new C-O bond is
1.447 Å. Cyclization is then possible through an intramolecular
cyclic SN2-type reaction via **TS 3** (502i cm^{-1}) with a barrier of
10.77 kcal.mol^{-1}. The breaking C-Br bond associated to **TS 3** is
2.394 Å, while the forming O-C bond is 1.999 Å. The resulting
product-like intermediate, **complex 2**, is then formed and is 40.24
kcal.mol^{-1} lower in energy than the isolated reactants. The overall
reaction to the isolated products is exothermic by 17.35
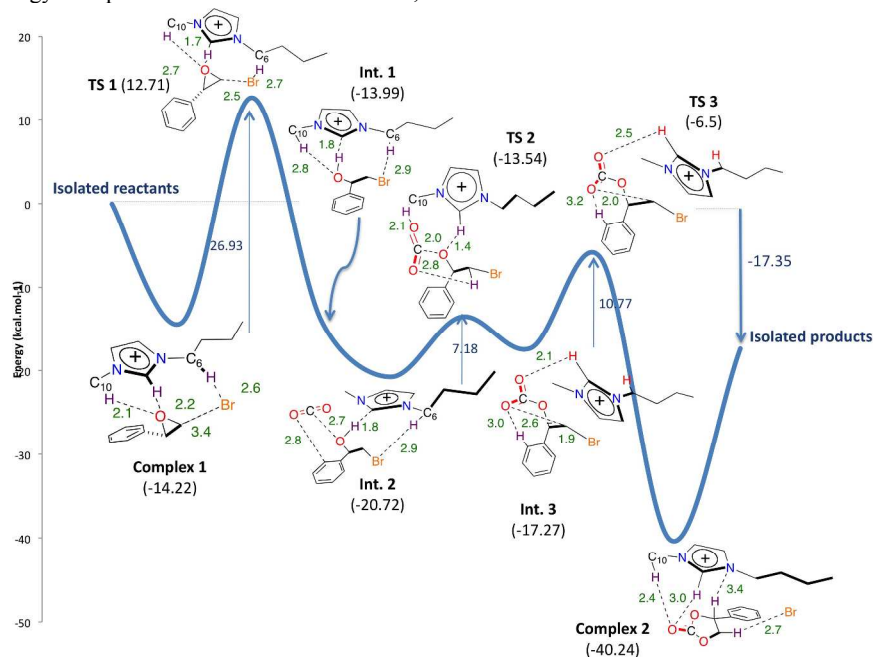kcal.mol^{-1} showing that this path is thermodynamically
favourable.

Fig. 3 Energy profile for the cycloaddition of CO$_2$ on styrene oxide catalysed by **BMIM Br**

Encouraged by the successful results of CO$_2$-fixation using
terminal epoxide, we next extended the scope of this catalytic
system.

Cycloaddition of CO$_2$ to internal epoxide

In order to study the feasibility of using the catalysts studied for
other epoxides, the cycloaddition of CO$_2$ to cyclohexene oxide
was examined (Scheme 5). The cyclohexene oxide was selected

as a disubstituted and cyclic epoxide, which needs harsher
conditions due to its bicyclic hindered structure. **BMIm Br** stays
active (85% of conversion) and selective (99%) but higher
pressure (8 bar) and reaction time (24 h) were required.
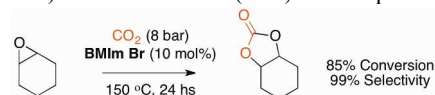
Scheme 5 Effective cycloaddition of CO_2 with cyclohexene oxide catalysed by **BMIm Br**

Direct synthesis of cyclic carbonate from styrene

The epoxides used as substrates in the reaction with carbon dioxide are typically prepared by the catalytic oxidation of alkenes.[23] The development of a process for the synthesis of cyclic carbonates from alkenes would be attractive both from the point of view of sustainability and for industrial application. This route would require a multifunctional catalyst that is able to promote the oxidation of alkenes to epoxides and the following reaction of the latter with CO_2 to yield carbonates. Few studies of catalysts for the direct synthesis of carbonates from alkenes have been reported,[24] but these systems are still far from optimal and future research efforts should aim at achieving higher activity whilst minimising the formation of side-products of the epoxidation reaction, controlling selectivity towards the desired carbonate.

This process has been evaluated with some imidazolium salts presented previously. Once more, the best results were obtained for **BMIm Br**. The reaction was effective as a one-pot reaction as well as two consecutive steps (Scheme 6) under low pressure (5 bar) without solvent or co-catalyst addition. *t*ert-Butyl hydroperoxide (TBHP) was found to be the best oxidant under these conditions. The one-pot reaction allowed 90% conversion with 40% selectivity against 99% conversion with 63% selectivity for the two steps version in a single reactor. This reaction is under investigation and will be published later.
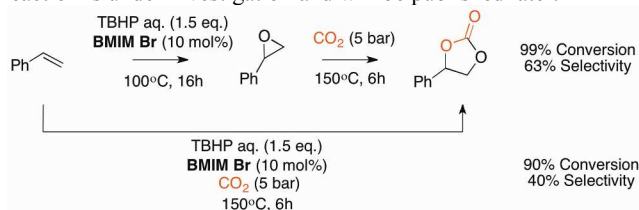
Scheme 6 Direct synthesis of cyclic carbonate from olefin

Conclusions

In summary, a simple and mild pressure condition (5-8 bar) for CO_2 fixation to epoxides using simple halide imidazolium salts as catalysts and solvent has been disclosed. Structural modifications of cation and anion moieties have shown that the first step of ring opening is crucial in the reactivity. This has been confirmed by DFT calculation obtained for **BMIm Br** salt (Fig. 3 and cycle 1 of scheme 4).In this step, an H-donor part (H-C2 of imidazolium, hydroxyl or carboxylic acid) can activate the epoxide but the presence of a good nucleophile (Br, I, $AlCl_4$ or N_3)is sufficient to achieve complete conversion. Concerning the selectivity, the sensibility to hydrolysis and the leaving group ability of the nucleophile, which opened the epoxide ring, is important to avoid by-product formation before CO_2 insertion.

Moreover, the conversion of disubstituted epoxide was observed to be effective under similar mild conditions. Taking advantage of this solvent-free process, a direct oxidative conversion of CO_2 to carbonate from olefin was investigated. The preliminary results are promising. This approach represents an environmentally friendly example of the catalytic conversion of carbon dioxide into value-added chemicals by employing simple ionic liquids as

catalysts. Further mechanistic studies by NMR and FTIR are under investigation.

Experimental

Materials and instruments

CO_2 (99.99%) was purchased from ALPHAGAZ™ and used as received.^{1}H NMR (400 and 500 MHz) and ^{13}C NMR (101 and 125.7 MHz) spectra were obtained as solutions in either $CDCl_3$, CD_3ODor D_2O. Chemical shifts were reported in parts per million (ppm, δ). All spectra were recorded in a Varian spectrometer at ambient temperature. For ^{1}H NMR spectra, multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), p (pintuplet), m (multiplet), br (broad), or a combination of these.

Preparation of imidazolium halides

These salts were prepared according to the literature.[25]

1-Butyl-3-methylimidazolium bromide (**BMIm Br**).[26] Colourless oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ ppm 0.93-1.00 (m, 3H); 1.35-1.46 (m, 2H); 1.91-1.98 (m, 2H); 4.16 (s, 3H); 4.41 (t, *J* = 7.3 Hz, 2H); 7.79 (t, *J* = 1.7 Hz, 1H); 7.86 (t, *J* = 1.7 Hz, 1H); 10.19 (s, 1H).

1-Butyl-3-methylimidazolium iodide (**BMIm I**).[26] Yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ ppm); 4.16 (s, 3H); 4.40 (t, *J* = 7.2 Hz, 2H); 7.73 (d, *J* = 1.5 Hz, 1H); 7.77 (d, *J* = 1.5 Hz, 1H[-]); 9.81 (s, 1H).

1-Butyl-3-methylimidazolium chloride (**BMIm Cl**).[25] White solid (82%). ^{1}HNMR (300 MHz, D_2O) δ ppm 0.89 (t, *J* = 7.4 Hz, 3H); 1.22-1.35 (m, 2H); 1.82 (qp, *J* = 7.4 Hz, 2H); 3.86 (s, 3H); 4.17 (t, *J* = 7.2 Hz, 2H); 7.40 (d, *J* = 2.0Hz, 1H); 7.45 (d, *J* = 2.0, 1H).

1-*tert*-Butyl-3-methylimidazolium iodide (*t***BMIm I**). [27] White solid. ^{1}HNMR (400 MHz,$CDCl_3$) δ ppm 1.75 (s, 9H); 4.19 (s, 3H); 7.50 (s, 1H); 7.57 (s, 1H), 10.14 (br, 1H).

1-Butyl-2,3-dimethylimidazolium bromide (**BMMIm Br**). [28] Yellow solid (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.96 (t, 3H, *J* = 7.3 Hz). 1.35-1.45 (m, 2H), 1.78-1.85 (m, 2H), 2.84 (s, 3H), 4.05 (s, 3H), 4.25 (t, 2H, *J* = 7.4 Hz), 7.59 (d, 1H, *J* = 1.9 Hz), 7.79 (d, 1H, *J* = 1.9 Hz).

1-(2-Hydroxyethyl)-2,3-dimethylimidazolium bromide (**HO-EMMIm Br**). [29] Brown solid (99%). ^{1}HNMR (400 MHz, CD_3OD) δ ppm 2.69 (d, 3H, *J* = 3.5 Hz), 3.86 (d, 3H, *J* = 3.2 Hz), 4.00 (m, 2H), 4.34 (m, 2H), 7.43 (d, 1H, *J* = 1.4 Hz), 7.48 (d, 1H, *J* = 1.4 Hz).^{13}C NMR (125.7 MHz, CD_3OD) δ ppm 10.3; 35.6; 51.9; 61.4; 122.5; 123.6; 146.7.

Preparation of 1-Butyl-3-methylbenzo[d][1,2,3]triazolium bromide (BMBTr Br)

This salt was prepared according to the literature.[30]Orange oil. ^{1}HNMR (500 MHz, CD_3OD) δ ppm 1.04 (t, *J* = 7.4 Hz, 3H), 1.47-1.54 (m, 2H), 2.13-2.19 (m, 2H), 4.69 (s, 3H), 5.05 (t, *J* = 7.2 Hz, 2H), 8.02 (dd, *J* = 6.6, 3.0 Hz, 2H), 8.30-8.31 (m, 1H), 8.33-8.39 (m, 1H).

Preparation of other 1-butyl-2,3-dimethylimidazolium salts

1-Butyl-2,3-dimethylimidazolium aluminium (IV) chloride (**BMMIm AlCl₄**) was prepared according to the literature.[31] White solid (99%). ^{1}HNMR (400 MHz, CDCl₃) δ ppm 0.93 (t, 3H, J = 7.2 Hz), 1.32-1.38 (m, 2H), 1.72-1.80 (m, 2H), 2.77 (s, 3H), 4.00 (s, 3H), 4.18 (t, 2H, J = 6.9 Hz), 7.45 (s,1H), 7.75(s,1H).^{13}C NMR (125.7 MHz, CD₃OD) δ ppm 10.3; 35.6; 51.9; 61.4; 122.5; 123.6; 146.7.

1-Butyl-2,3-dimethylimidazolium azide (**BMMIm N₃**) was prepared according to literature.[32] Orange oil (95%).^{1}H NMR (400 MHz, CDCl₃) δ ppm 0.97 (t, 3H, J = 7.3 Hz), 1.38 - 1.44 (m, 2H), 1.79–1.89 (m, 2H), 2.80 (s, 3H), 3.99 (s, 3H), 4.23 (t, 2H, J = 7.4 Hz), 7.54 (d, 1H, J = 1.6Hz), 7.63 (d, 1H, J = 1.4 Hz).

1-Butyl-2,3-dimethylimidazolium hydrogencarbonate (**BMMIm HCO₃**) was prepared according to the literature.[33] White solid (94%).^{1}H NMR (400 MHz, CDCl₃) δ ppm 0.86 (t, 3H, J = 7.2 Hz), 1.25-1.30 (m, 2H), 1.76-1.62 (m, 2H), 2.76 (s, 3H), 3.91 (s, 3H), 4.12 (t, 2H, J= 4.2 Hz), 7.44 (s, 1H), 7.68 (s, 1H).

1-Butyl-2,3-dimethylimidazolium hydroxide (**BMMIm OH**) was prepared according to literature.[34]Brown oil (96%). ^{1}H NMR (400 MHz, CDCl₃) δ ppm 0.97 (t, 3H, J = 7.4 Hz), 1.36-1.40 (m, 2H), 1.79-1.84 (m, 2H), 2.80 (s, 3H), 4.03 (s, 3H), 4.22 (t, 2H, J = 7.4 Hz), 7.52 (d, 1H, J = 1.6 Hz), 7.79 (d, 1H, J = 1.6 Hz).

Preparation of other 1-butyl-3-methylimidazolium carboxylates

These salts were prepared according to the literature.[35] 3-Butyl-1-methylimidazolium hydroxide (**BMIm OH**) aqueous solution was prepared from an aqueous solution 0.1 mol.L⁻¹ of 3-butyl-1-methylimidazolium chloride (**BMIm Cl**) using anion exchange resin (AMBERLITE IRA400OH (SUPELCO) previously prepared with a solution1 mol.L⁻¹ of NaOH). The chloride exchange is monitored with AgNO₃ solution test (AgCl precipitate detection). The **BMIm OH** aqueous solution was then neutralised with equal molar corresponding acids. After removing water by evaporation under reduced pressure, the viscous liquid was dried in vacuum under vigorous stirring for 2 days at 80°C.

1-Butyl-3-methylimidazolium acetate (**BMIm AcO**).[35] Colourless oil. ^{1}H NMR (400 MHz, CDCl₃) δ ppm 0.96 (t, J = 7.4 Hz, 3H); 1.32-1.42 (m, 2H); 1.86 (p, J = 7.4 Hz, 2H); 1.97 (s, 3H); 4.06 (s, 3H); 4.29 (t, 2H), 7,28 (s, 1H); 7.34 (s, 1H); 11.01 (s, 1H).

1-Butyl-3-methylimidazolium2-methylbutanoate (**BMIm EMAcO**). Colourless oil. ^{1}H NMR (400 MHz, CDCl₃) δ ppm 0.87-0.98 (m, 6H); 1.06-1.11 (m, 3H); 1.31-1.40 (m, 3H); 1.63-1.71 (m, 1H); 1.85 (q, J = 7.0 Hz, 2H); 2.16-2.21 (m, 1H); 4.07 (s, 3H); 4.29 (t, J = 7.0 Hz, 2H); 7.24 (d, J = 7.0 Hz, 2H);11.02 (s, 1H). ^{13}C NMR (101 MHz, CDCl₃) δ ppm 12.5; 13.4; 18.3; 19.5; 28.1; 32.2; 36.3; 45.1; 49.6; 121.2; 122.9; 140.2; 183.5.

1-Butyl-3-methylimidazolium hydrogenomalonoate (**BMIm malonate**).[35] ^{1}H NMR (400 MHz, CDCl₃) δ ppm 10.37 (s, 1H), 8.41 (br, OH), 7.43 (s, 1H), 7.37 (s, 1H), 4.27 (t, J = 7.33Hz, 2H), 4.04 (s, 3H), 3.09 (s, 2H), 1.91-1.83 (m, 2H), 1.47-1.27 (m, 2H), 0.96 (t, J = 7.36Hz, 3H).

1-Butyl-3-methylimidazolium prolinate (**BMIm pro**).[36] Yellow oil. ^{1}H NMR (400 MHz, CDCl₃) δ ppm 0.95 (t, J = 7.4 Hz, 3H); 1.28-1.43 (m, 2H); 1.59-1.78 (m, 2H); 1.78-1.93 (m, 3H); 2.10

(m, 1H); 2.80 (d, J = 6.7 Hz, 1H); 3.10 (d, J = 6,7 Hz, 1H); 3.55 (s, 1H); 4.05 (s, 3H); 4.29 (t, J = 7.3 Hz, 2H); 7.35 (s, 1H); 7.45 (s, 1H); 10.80 (s, 1H).

1-Butyl-3-methylimidazoliumhydrogen carbonate (**BMImHCO₃**).[37] Colourless oil. ^{1}H NMR (500 MHz, CDCl₃) δ ppm 0.95 (t, 3H, J = 7.3 Hz); 1.33-1.41 (m, 2H); 1.87-1.93 (m, 2H); 4.11 (s, 3H); 4.34 (t, 2H, J = 7.3 Hz); 7.61 (s, 1H); 7.76 (s, 1H); 10.3 (s, 1H). ^{13}C RMN (101 MHz, CDCl₃) δ ppm13.2; 19.2; 31.9; 36.2; 49.5; 121.9; 123.6; 137.5.

1-Butyl-3-methylimidazolium benzoate (**BMIm benzo**).[38] Colourless oil. ^{1}H NMR (400 MHz, CDCl₃) δ ppm 0,80 (t, J = 7.4 Hz, 3H); 1.13-1.22 (m, 2H); 1.66 (p,J = 7.3 Hz, 2H); 3.91 (s, 3H); 4.08 (t, J = 7.4 Hz, 2H); 7.16 (s, 1H); 7.25-7.33 (m, 4H); 7.99 (m, 2H); 10.17 (s, 1H).

1-Butyl-3-methylimidazolium 2-(trifluoromethyl)benzoate (**BMIm oCF3-benzo**). Colourless oil. ^{1}H NMR (400 MHz, CDCl₃) δ ppm 0.87-0.92 (m, 3H); 1.23-1.33 (m, 2H); 1.72-1.81 (m, 2H); 3.95 (d, J = 5,9 Hz, 3H); 4.16 (t, J = 6.7 Hz, 2H); 7.26 (d, J = 7.4, 2H); 7.37 (s, 1H); 7.44 (t, J = 7.4 Hz, 1H); 7.53-7.59 (m, 2H); 10.49 (s, 1H). ^{13}C NMR (101 MHz, CDCl₃) δ ppm 13.3; 19.3; 31.9; 36.0; 32.1; 36.1; 49.4; 121.4; 123.2; 125.5; 125.9 (2C); 126.6 (2C); 131.4; 139.0; 142.4; 173.1.

Preparation of imidazolium sulfonates

Sodium 1,3-(diethanesulfonate) imidazolium (**NaO₃S(CH₂)₂Im(CH₂)₂SO₃**) [39] was prepared according to a previous procedure.[40] White solid.^{1}H NMR (400 MHz, D₂O): δ ppm8.99 (s, 1H), 7.63 (2s, J = 1.3 Hz, 2H), 4.67 (t, J = 6.5 Hz, 4H), 3.48 (t,J = 6.5 Hz, 4H).

1-Methyl-3-(3-sulphonatoethyl)imidazolium (**MIm(CH₂)₂SO₃**) was prepared according to a previous procedure.[40] White solid. ^{1}H NMR (400 MHz, D₂O): δPPM 8.82 (s, 1H), 7.58 (s, 1H), 7.47 (s, 1H), 4.64 (t, J = 6.3 Hz, 2H), 3.93 (s, 3H), 3.47 (t, J = 6.3 Hz, 2H).

1-Methyl-3-(3-sulfonatopropyl)imidazolium (**MIm(CH₂)₃SO₃**) was prepared by a modification of Ohno's procedure.[41] White solid. ^{1}H NMR (400 MHz, D₂O): δ ppm 8.79 (s, 1H), 7.56 (s, 1H), 7.49 (s, 1H), 4.40 (t, J = 7.2 Hz, 2H), 3.93 (s, 3H), 2.96 (t, J = 7.2 Hz, 2H), 2.36 (p, J = 7.2 Hz, 2H).

Synthesis of styrene carbonate

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 CO₂ 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 ^{1}H NMR spectroscopy to determine the conversion, yield and selectivity to styrene carbonate.

Styrene carbonate[42] ^{1}H NMR (400 MHz,CDCl₃) δ ppm 4.31 (td, J

= 7.8,3.8Hz,1H); 4.82 (td, J = 8.2, 2.3Hz, 1H); 5.7 (t, J=7.9Hz, 1H); 7.35-7.41 (m, 5H).

Cyclohexene carbonate[43] ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 1.40-1.45 (m, 2H); 1.58-1.64 (m, 2H); 1.88-1.92 (m, 2H); 4.7 (t, J =3.6Hz, 2H).

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Notes and references

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† Electronic Supplementary Information (ESI) available: [1]H/ [13]C spectra and optimised geometries. See DOI: 10.1039/b000000x/

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ARTICLE TYPE

Graphical abstract

Insights on recyclable catalytic system composed of task-specific ionic liquids for the chemical fixation of carbon dioxide

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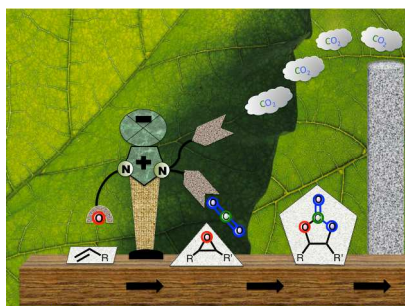
Several imidazolium ionic liquids displays high 15 efficiency as a catalyst for the sequencial oxidation of alkene and carboxylation of epoxide.

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