

Phosphonium-based ionic liquids: economic and efficient catalysts for the solvent-free cycloaddition of CO₂ to epoxidized soybean vegetable oil to obtain potential bio-based polymers precursors

A. Centeno-Pedraza¹, J. Perez-Arce¹, S. Prieto-Fernandez¹, Z. Freixa^{2,3}, E.J. Garcia-Suarez^{3,4,*}

¹TECNALIA, Basque Research and Technology Alliance (BRTA), Alava Technology Park, Leonardo da Vinci 11, 01510 Vitoria-Gasteiz, Spain.

²University of Basque Country UPV/EHU, Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country (UPV-EHU), 20080 Donostia-San Sebastián, Spain.

³IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, 48009 Bilbao, Spain.

⁴Center for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510 Vitoria-Gasteiz, Spain.

*corresponding authors: esuarez@cicenergigune.com

Abstract

A series of phosphonium-based ionic liquids have been prepared in one step in a simple way from inexpensive feedstocks. The prepared ionic liquids have been successfully tested as catalysts in the solvent-free cycloaddition reaction of CO₂ to an epoxidized soybean oil to obtain carbonated soybean oil that can be potentially employed as bio-monomer in the synthesis for bio-based polymers. The catalytic performance of these ionic liquids was compared to the widely used and benchmark catalyst in CO₂ cycloaddition to epoxides reaction, namely tetrabutylammonium bromide at different reaction conditions. The influence of some reaction parameters such as temperature, CO₂ pressure, reaction time and catalyst amount was studied. It has been found that the solubility of the prepared ionic liquids in the reaction media (epoxidized soybean oil) is a key factor that limits the catalytic performance of some of the synthesized ionic liquids. All prepared ionic liquids have shown higher thermal stability than the benchmark catalyst and three of them have shown superior catalytic performance. The best results in terms of conversion and selectivity have been obtained with dodecyltriphenylphosphonium bromide (**5**) achieving almost full conversion (99.8 %) and excellent selectivity (84.0 %) after 5 hours reaction at 160 °C and 40 bar of CO₂. Outstanding results compared to those reported in the literature with similar catalysts in the solvent-free CO₂ cycloaddition to an epoxidized soybean oil to obtain the corresponding carbonated oil have been achieved. Considering the facile synthesis of catalyst **5**, the large availability and low-cost of the feedstocks and its catalytic performance it can be considered a valuable and green alternative for CO₂ fixation to epoxidized vegetable oil.

1. Introduction

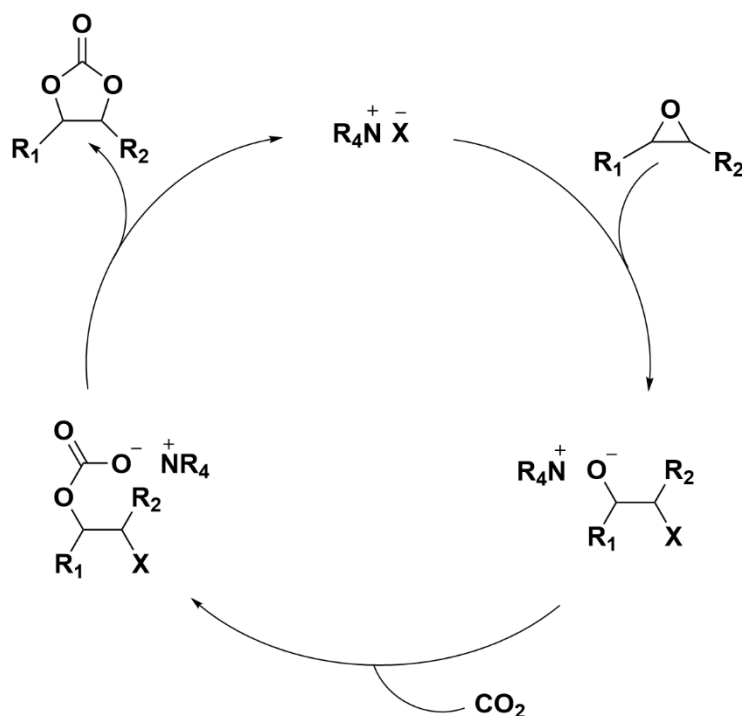
The excessive use of petrochemical resources is considered one of the main concerns of today's society.¹ One of the major causes, among others, is the rise of CO₂ emissions linked mainly to the human consumption of finite petrochemicals to produce energy, commodity and fine chemicals. Hence, scientists are focused on the development of processes in accordance to the green chemistry principles.² To achieve this ambitious goal, the finding of an abundant, largely available, renewable, low cost and non-toxic feedstock has raised as an important worldwide challenge. In this context, the storage and chemical utilization of CO₂, a greenhouse gas with low toxicity and anthropogenic produced in large amounts, has attracted considerable attention as a promising C1 building block source.³⁻⁶ In fact, some value-added products are already produced using CO₂ as feedstock, e.g., methanol,^{7,8} urea,⁹ salicylic acid¹⁰ among others. Noteworthy, the obtention of cyclic carbonates by atom economic cycloaddition reaction between CO₂ and epoxides is of great interest. As a matter of fact, cyclic

carbonates are key compounds in the synthesis of daily use polymers such as non-isocyanate polyurethanes, polycarbonates etc.^{11,12} Nevertheless, still most of the epoxides employed in the preparation of cyclic carbonates are obtained from non-renewable fossil sources.¹³⁻¹⁷ Therefore, to obtain fully renewable cyclic carbonates from CO₂, biomass derived epoxides are needed. Among biomass-derived epoxides, those from vegetable oils are of special interest due to their availability and easy preparation.¹⁸ In addition, the carbonated vegetable oils produced by cycloaddition of CO₂ to epoxidized vegetable oils offer a range of properties that makes them potentially applicable in several industries focused in the generation of bio-based products.¹⁹ Among the possible applications of carbonated vegetable oils several could be highlighted: monomers for polyesters, polycarbonates and polyurethanes synthesis, industrial lubricants, fuel additives and plasticizers.^{17,20,21} One of the plausible applications of carbonated vegetable oils with a major growth potential is their use as monomers in the synthesis of non-isocyanate polyurethanes (NIPUs) by polyaddition or polycondensation reaction with diamines.²²⁻²⁴ Indeed, the preparation of NIPUs using cyclic and/or linear carbonates and diamines will avoid the use of the highly toxic isocyanate monomers which handling and use is becoming more restrictive through European regulation.²⁵ Unfortunately, there are some drawbacks hampering the use of epoxidized vegetable oils and CO₂ as feedstocks to produce carbonated vegetable oils able to be employed as monomers in the synthesis of NIPUs. These drawbacks are the low reactivity of both the oxirane groups of the vegetable oil, mainly due to steric impediments, and the CO₂ molecule that due to its high stability is considered almost an inert molecule. Therefore, the production of carbonated oils by cycloaddition reaction of CO₂ with epoxidized vegetable oils remains a challenge.^{26,27} These inherent problems associated to the low reactivity of the feedstocks could potentially be overcome by designing the appropriate catalytic systems or catalyst. In fact, several reports on the cycloaddition reaction of CO₂ to sterically hindered oleochemical internal epoxides have been reported employing different catalytic systems under moderate reaction conditions, such as combination of quaternary ammonium and phosphonium salts with metal complexes²⁸⁻³⁴ or hydrogen bond donors,^{35,36} crown ether complexes,^{21,37,38} ionic liquids,^{21,39,40} deep eutectic solvents⁴¹ and organocatalysts.⁴² Among the catalysts employed, probably the tetra-*n*-butylammonium bromide [TBA][Br] ionic liquid is the most widely investigated and studied one.¹⁹ However, with this catalyst high temperatures (> 100 °C), high CO₂ pressures (> 25 bar), high amounts of catalyst (2-7 mol%) and long reaction times (typically > 24 h) are required in order to obtain good conversion and selectivity towards the desired carbonated product. Consequently, the research on new more effective, efficient, cheaper and more thermally robust catalysts is highly demanded.

Ionic liquids (ILs) are a class of compounds formed exclusively by ions with multiple applications, among them in catalysis, e.g. homogeneous, heterogenized homogeneous catalysis, biphasic systems etc.^{43,44} ILs possess several inherent properties that make them special, among other are noteworthy good thermal and chemical stability, low toxicity, negligible vapor pressure, good solubility and easily functionalization for a chosen application.^{45,46} Nevertheless, their use as catalysts in the cycloaddition reaction of CO₂ with epoxidized vegetable oils is limited and has not been widely reported with the exception of the above-mentioned IL ([TBA][Br]).^{21,39}

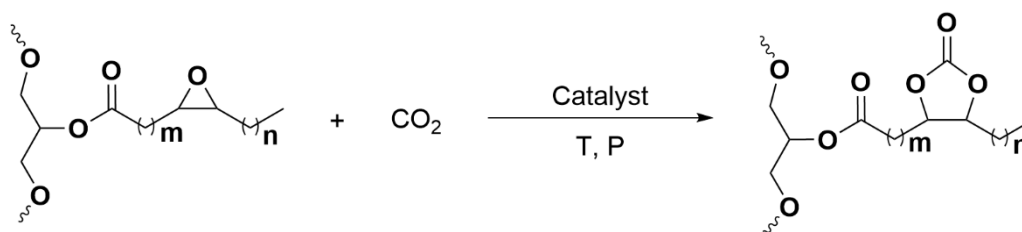
The carbonation reaction mechanism proposed elsewhere in the scientific literature is show in **scheme 1**, in the first step the formation of an alkoxide intermediate takes place by the oxirane opening by a nucleophile species. This is followed by the attack of the alkoxide intermediate to the CO₂ molecule forming an alkyl carbonate compound. Finally, the cyclic carbonate is obtained after an intramolecular ring-closure.²⁹ Considering the

reaction mechanism, it is clear that the opening of the epoxide is a key step in the cycloaddition reaction otherwise the reaction does not take place. The opening of the epoxide can be achieved 1) by using a good nucleophile species which could be also a good leaving group to allow the formation of the carbonated product, 2) by using a hydrogen bond donor compound to increase the electrophilicity of the carbons in the epoxide ring or 3) by the combination of 1 and 2. In this regard, the bromide anion fulfils both conditions a good nucleophile and good-moderate leaving group.⁴⁷ In addition, Br⁻ nucleophilicity could be modified depending on the steric hindrance and rigidity of the selected cation which allows or not the Br⁻ to be close to the electron deficient carbon modifying the electrostatic interaction between them.



Scheme 1. General mechanism of CO₂ cycloaddition to an epoxide catalyzed by a tetralkylammonium halide salt.

Due to previously described reasons and taking into account the reaction mechanism, in this work a series of economic and easy to prepare and to isolate ionic liquids based in phosphonium cation (triphenylphosphonium and tricyclohexylphosphonium) and a halogen anion (bromide or iodide) have been designed, prepared, fully characterized and tested in the cycloaddition reaction of CO₂ to a reference epoxidized soybean oil (ESBO) to obtain the corresponding carbonated soybean oil (CSBO) (**scheme 2**). The influence of the cation and the anion on the performance of the ionic liquid and several reaction parameters such as reaction temperature, catalyst concentration, total pressure and reaction time are studied and deeply discussed. The results in terms of conversion and selectivity to the carbonated desired product have been compared with the most used and reference catalyst [TBA][Br] for the studied reaction.



Scheme 2. General cycloaddition reaction of CO₂ to an epoxidized vegetable oil.

2. Experimental

2.1 Materials

All compounds were used as received unless otherwise stated. 1-bromobutane (99%), 1-bromooctane (99%), 1-iodooctane (98%), 1-bromododecane (97%), 1-bromohexadecane (97%) 1-bromoeicosane ($\geq 97\%$) tetraphenylphosphonium bromide (97%) and tricyclohexylphosphine ($\geq 98\%$) were purchased from Sigma-Aldrich. 4-bromobutyric acid (98%) and 3-bromopropanol were purchased from Fluorochem. 8-bromooctanoic acid ($> 97\%$) was purchased from TCI. Triphenylphosphine (99%) and 1-methylimidazole (99%) were purchased from Across Organics. Tetrabutylammonium bromide (98 %) was purchased from Fluka. Toluene (EssentQ), *n*-pentane (99%), diethyl ether (EssentQ, stabilized by BHT), hexane (EssentQ, fraction from petroleum) and ethyl acetate (EssentQ) were purchased from Scharlau. Epoxidized soybean oil (ESBO) containing 4.19 mmol/g of oxirane was kindly supplied by Hebron (Spain) and the CO₂ (Industrial grade, 99.8%) was purchased from Nippon gases.

2.2 Synthesis and characterization of the prepared ionic liquids

Ionic liquids were synthesized following similar procedures to those already reported in the scientific literature.^{48,49} In a typical synthesis phosphonium based ionic liquids were prepared as follows, in a 100 mL Fischer-Porter reactor under a positive nitrogen pressure, triphenylphosphine (TPP) or tricyclohexylphosphine (TCP) (19 mmol; 1.1 equiv.) was dissolved in toluene (25 mL). Then, 1 equivalent of the selected haloalkane ($C < C8$) compound was added dropwise and the mixture was heated at reflux temperature for 24 h. After, the excess of toluene was removed by decantation and the crude product was washed with toluene (3 x 40 ml) to remove non-ionic residues, and after was washed with *n*-pentane (2 x 40 ml). Finally, the solid residue was dried overnight under reduced pressure. Ionic liquids based on long alkyl chains ($C \geq C8$) were prepared likewise but reaction products were isolated by washing them with diethyl ether (3 x 40 ml) instead of toluene and/or pentane (see supporting information S1).

2.3 Characterization of the prepared ionic liquids

All prepared ionic liquids were characterized by complementary techniques:

Structural characterization was determined by means of nuclear magnetic resonance (NMR) in solution. ¹H and ³¹P{¹H} spectra were recorded on a Bruker 300 MHz spectrometer. Chemical shifts are reported in ppm (δ) referenced to the chemical shifts of residual solvents resonances (¹H), or 85% H₃PO₄ (³¹P{¹H}).

Thermal stability was evaluated by thermal gravimetric analysis (TGA) using either Mettler Toledo TGA/DSC 1 STARE System under nitrogen flow (50 mL min⁻¹). In a typical analysis the sample was heated from room temperature to 100 °C with a heating rate of 10 °C min⁻¹, and keep in isothermal conditions (100 °C, 1 h) to eliminate moisture and/or residual solvent, if any. Then, the sample was heated from 100 °C to 700 °C with at a

rate of 10 °C min⁻¹. Isothermal measurements were performed at 160 °C, 180 °C and 200 °C by heating the sample from room temperature to desired temperature at 10 °C min⁻¹. Once the desired temperature was reached it was kept for 12 h.

Melting points were measured using capillary melting point apparatus (STUART SMP30) or by differential scanning calorimetry (DSC) analysis carried out using Mettler Toledo DSC 2 STARe System. DSC Scans cycles consisted on heating the sample up to 200 °C followed by a cooling ramp from 200 °C and -80 °C and a subsequent heating ramp between -80 °C and 200 °C, both at 10 °C/min.

2.4 Catalytic tests

Catalytic experiments were carried out in a 100 mL stain-steel Autoclave. In a typical experiment the reactor was loaded with epoxidized soybean oil (ESBO, 25 g containing 104.7 mmol of oxirane) and the desired amount of the previously prepared ionic liquids as catalyst (mol% referred to the oxirane mol). Afterwards, reaction system was heated to the selected reaction temperature and subsequently purged with CO₂. Then, the reactor was loaded with CO₂ to the desired pressure which was considered as initial reaction time. After the selected reaction time, the reactor was cooled down to room temperature and then the pressure was slowly released. ESBO conversion into the carbonated soybean oil (CSBO) was determined by ¹H NMR spectroscopy. The conversion and selectivity values were calculated integrating the peaks corresponding to the cyclic carbonates (5.1-4.4 ppm); epoxides (3.25-2.8 ppm) and the unknown peak (2.4-2.3 ppm) and giving a total value to the area of 100% (supporting information S2). All the experiments were performed at least twice in order to check their repeatability. The products (unreacted ESBO, carbonated oil CSBO and unknown product) were isolated by flash chromatography on silica gel (SiO₂) employing hexane/ethyl acetate as eluent mixture.

2.5 Solubility test of the employed catalysts

A solubility test of the employed catalysts was performed in the epoxidized soybean oil (ESBO) used as reaction media. In a typical test, 5 mol % of the corresponding catalyst referred to the oxirane mol was added to 25 g of ESBO containing 0.105 mol of oxirane in a round bottom flask. The mixture, was heated at 120 °C for two hours. Catalyst's solubility in the ESBO reaction media was visually inspected.

3. Results and discussion

3.1. Synthesis and characterization of ionic liquids

Eleven phosphonium-based ionic liquids (ILs) (**figure 1 (1-11)**) were synthesized. The prepared ILs were rationally designed and selected on the bases of the cycloaddition mechanism described for [TBA][Br] ionic liquid (**Scheme 1**).²⁹ Consequently, bulky rigid aromatic cations such as triphenylphosphine (TPP) or bulky flexible aliphatic cations such as tricyclohexylphosphine (TCP) and Br⁻ and I⁻ as anions were selected. The catalytic performance of the presence of functional groups such as hydroxyl (-OH) and carboxyl (-COOH) and the length of the alkyl chain attached to the phosphorus atoms was also evaluated in the studied reaction. All of the ILs were prepared from inexpensive starting materials in one step and isolated and purified in a very simple way following slightly modified procedures from those found in the scientific literature.⁵⁰ The purity of the prepared ILs was confirmed by ¹H and ³¹P{¹H} NMR spectroscopy (see supporting information S3) and the thermal properties (melting and stability) were measured by TGA, DSC and/or capillary technique. Within the catalytic study the

synthesized ILs were compared with a commercially available IL (**figure 1 (12)**) used as benchmark in the CO₂ cycloaddition reaction with epoxidized vegetable oils to yield carbonated vegetable oils.

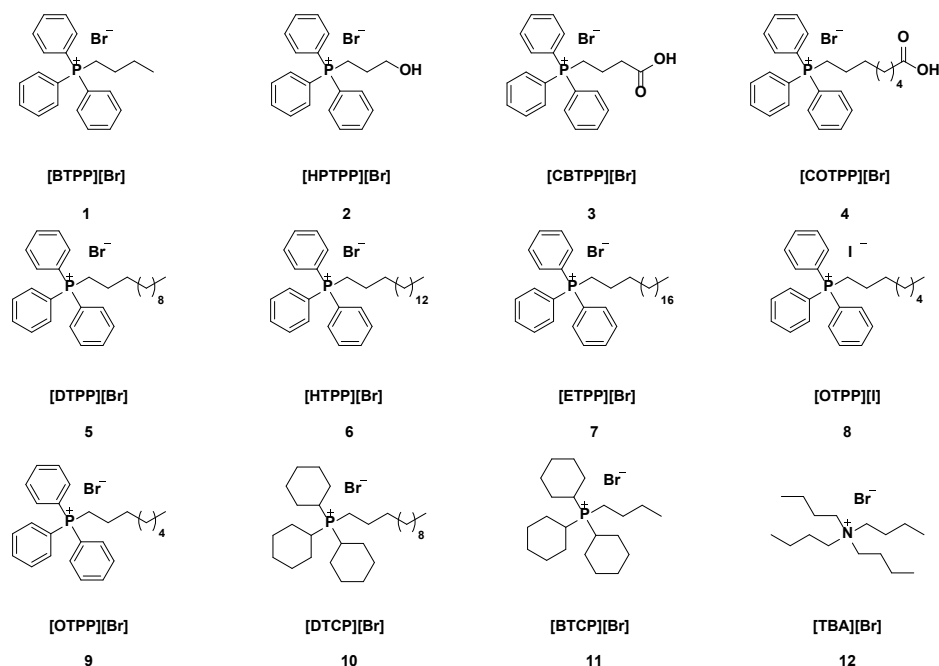


Figure 1. Prepared phosphonium-based ionic liquids (1-11) and the benchmark ionic liquid (12) employed in this work as catalysts in the cycloaddition reaction of CO₂ to epoxidized soybean oil.

The thermal stability of the prepared ionic liquids was determined by TGA. Decomposition onset temperature as well as melting points are shown in **table 1**. All prepared ILs possess high thermal stability within the range from 287 °C to 341 °C (see supporting information **S4**). Among them, the ILs bearing the tricyclohexylphosphine moiety were found slightly more thermally stable than the ones bearing the triphenylphosphine moiety (entry 1 vs. entry 11 and entry 5 vs. entry 10, **table 1**). It is worth noticing that the benchmark IL (**12**) (entry 12, **table 1**) shows lower thermal stability ca. 200 °C compared to all prepared ILs (1-12). This is in line with what is reported in the literature where phosphonium-based ILs are, in general, thermally more stable than ammonium-based counterparts.⁵¹

Table 1. Decomposition temperature (T_{onset}) and melting temperature (T_{m}) of the ionic liquids employed in this work.

entry	ionic liquid	T_{onset} (°C)	T_{m} (°C)
1	[BTPP][Br]	304	245-247
2	[HPTPP][Br]	329	237-239
3	[CBTPP][Br]	326	251-254
4	[COTPP][Br]	318	125-128
5	[DTPP][Br]	293	101-104
6	[HTPP][Br]	291	103-105
7	[ETPP][Br]	289	108-110
8	[OTPP][I]	304	73-76
9	[OTPP][Br]	294	32-34
10	[DTCP][Br]	337	4-6
11	[BTCP][Br]	341	150-153

3.2. Catalytic study

ILs **1 to 11** were tested in the solvent-free synthesis of carbonated soybean oil (CSBO) by cycloaddition of CO₂ to the corresponding epoxidized soybean oil (ESBO) at different reaction conditions. Their performance in the investigated reaction was compared as well with the widely employed in the cited reaction and commercially available ionic liquid (**12**).

3.2.1. Influence of the employed ionic liquid in the studied reaction

Initially, a screening to the different “ad hoc” designed ILs was done in selected standard conditions found elsewhere in the literature for the studied reaction, 20 bar CO₂ pressure, 120 °C, 5 mol% catalyst referred to oxirane mol and 2 hours reaction. The obtained results are shown in **figure 2**. As can be observed, 3 of the prepared ILs (**1, 2 and 4**) showed negligible or very low conversion (< 2 %) at the studied reaction conditions. On the other hand, 3 out of the 11 prepared ILs (**5, 6 and 7**) achieved higher conversions than the reference catalyst (**12**). The highest conversion among the tested ILs (45.6%) was obtained with the triphenyl phosphonium-based IL (**5**) bearing a 12-carbon length alkyl chain and a Br⁻ as anion. Slightly lower conversions 45.3% and 42.3% were also achieved with the ILs based on triphenyl phosphonium cation bearing an alkyl chain of 16 and 20 carbons length respectively and a Br⁻ as anion (**6 and 7**). Conversion closed to the benchmark catalyst (**12**), 37.9 % was achieved with IL (**9**) bearing an alkyl chain of 8 carbons. On the other hand, the other tested IL (**1**) based on the triphenyl phosphonium cation bearing a shorter alkyl chain (C4) showed negligible conversion. The presence of a functional group, -OH or -COOH, in the alkyl chain attached to the triphenyl phosphonium cation (**2, 3 and 4**) in the performance of the IL in the studied reaction was also investigated. It was expected, on the basis of the reaction mechanism, that the presence of these functional groups could improve the catalytic performance in terms of conversion because these groups could contribute to make more electrophilic the carbon in the epoxide groups due to interaction with the oxygen present in the epoxide ring and consequently facilitated its opening. Nevertheless, unexpected negligible or low conversion, < 10 %, was obtained. From the experimental results, it looks that the solubility of the ILs in the reaction media (epoxidized oil) is a key factor that strongly determines the performance of the studied catalyst in the investigated reaction conditions at 2 hours reaction time. The effect of the solubility was already evidenced in the work of V. dos Santos et al. by quantitative structure-property relationships modelling and exploratory analysis.⁵² It is evident that the reaction rate is strongly dependent on the solubility of the catalyst. Considering previous statement, a study of the solubility of the different tested ILs at 5 mol % in the ESBO, 120 °C and 2 hours was performed. It was observed that the benchmark catalyst (**12**) was completely soluble in the reaction media at the studied conditions while among the prepared catalysts only **5, 6, 7 and 10** were completely soluble under identical conditions. Therefore, only this set of catalysts can be fairly compared to the benchmark catalyst **12**. All the other prepared ILs showed partial (**3, 4, 8, 9 and 11**) or no solubility (**1 and 2**) at all in the studied reaction media and conditions. In fact, we do believe that the lack of solubility masks other effects that were expected to improve the catalytic performance such as alkyl length and/or the presence of -OH, -COOH functional groups in its catalytic performance. In fact, the effect of the catalyst solubility is very well evidenced in the catalytic performance if two similar ILs (**1 and 11**) are compared. The difference between them is the nature of the substituents on the phosphonium cation (aromatic vs. aliphatic). As shown in **figure 2**, with the first one a negligible conversion is obtained while with the second one the conversion increased up to

39.5 %. This different behaviour is attributed to the by far higher solubility of the IL (**11**) with the whole-aliphatic cation in a reaction media which has more affinity for aliphatic molecules.

As expected, it has been observed that increasing the length of the alkylic chain has a beneficial effect on the solubility of the IL in the substrate. Therefore, the use of IL with longer aliphatic chains (i.e. C12) in which the solubility is not compromised, permitted us to study the effect of the nature of the phosphonium substituents on the reaction rate. A comparison of catalysts **5** and **10** showed that triphenyl-substituted salt outperformed the analogue tricyclohexyl phosphonium (45.6 % vs. 38.5 %). The different reactivity can be attributed to the increased rigidity of the triphenyl phosphonium fragment compared to the more flexible tricyclohexyl counterpart. The more rigid cation keeps the anion (bromide and/or the alkoxide formed during the catalytic reaction) far from the phosphorus atom weakening the electrostatic interaction between anions and the cationic center, increasing the nucleophilic character of the anion and contributing to an easier and faster epoxide ring opening in the case of the bromide anion or facilitating the attack of the formed alkoxide to the CO₂ molecule to form the final cyclic carbonate.⁵³

Concerning the selectivity to the carbonated product, with most of the ILs studied a selectivity above 96 % was achieved. Only in the case of **4** and **8** the selectivity was compromised, 64.8 % and 86.0 % respectively. In fact, ¹H NMR analysis of the reaction mixtures at the end of the reactions showed the formation of an “unidentified” compound (see supporting information **S2**). Intrigued to identify this “unknown” product, a flash-chromatography column was performed to isolate and characterize it. ¹H NMR signals between 2.3 and 2.4 ppm were ambiguously assigned to this new “unidentified” product. Unfortunately, full characterization and the final identification of the “unknown” product was not successful. Nevertheless, considering the ¹H NMR spectra of the isolated “unknown” product (supporting information **S2**) and the group of signals between 4.0-4.6 ppm and between 5.2-5.4 ppm that are common in ESBO, CSBO and the “unknown” product think we do believe that the “unknown” product is not a decomposition one but derived with high probability from CSBO by reaction of the later with the alkoxide resulting from the epoxide ring opening. In summary and taking into account all factors that contribute to the activity and selectivity of the prepared ILs, the catalysts **5**, **6** and **7** yielded the best results in terms of conversion and selectivity outperforming the benchmark catalyst **12** at the same reaction conditions. Due to the slightly higher conversion achieved with catalyst **5**, this IL was selected to further study of other reaction parameters such as temperature, catalysts amount, pressure and time. The benchmark catalyst **12** was also investigated at the same conditions for comparative purposes.

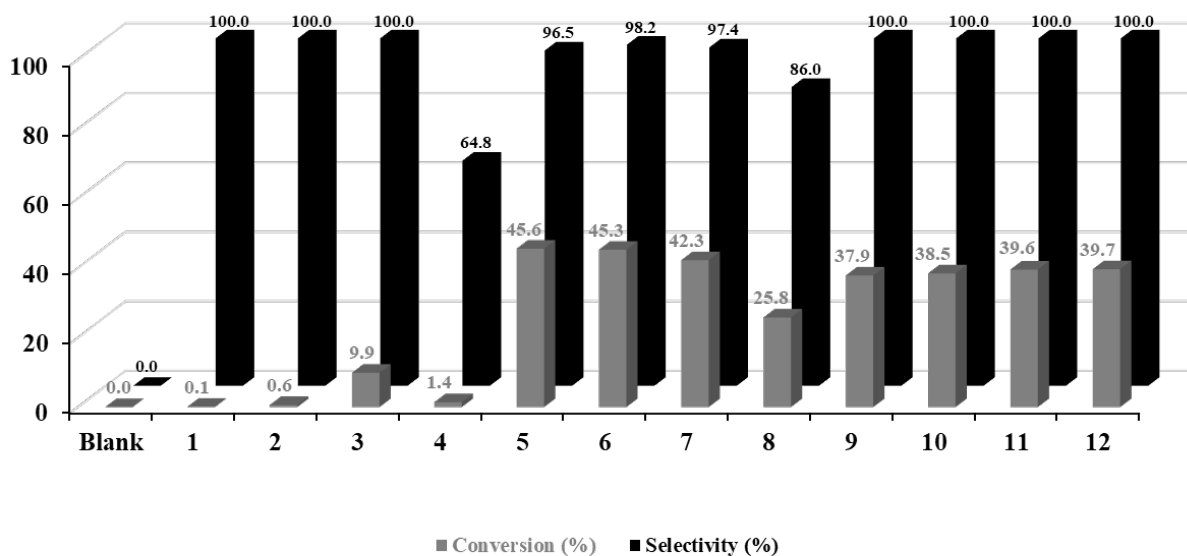


Figure 2. Conversion and selectivity of ESBO to CSBO after cycloaddition with CO₂ with the different ionic liquid tested as catalysts (1 to 12). Reaction conditions: temperature: 120 °C, CO₂ pressure: 20 bar, reaction time: 2 h, 5 mol% of catalyst referred to mol of oxirane.

3.2.2. Influence of the catalyst loading

The effect of the catalyst loading (in mol % related to oxirane groups) on the solvent-free cycloaddition reaction of CO₂ to the ESBO was investigated with the selected catalyst 5 and compared to the benchmark catalyst 12. The explored catalyst loadings were 1, 2 and 5 mol%, respectively. The obtained results are depicted in **figure 3**.

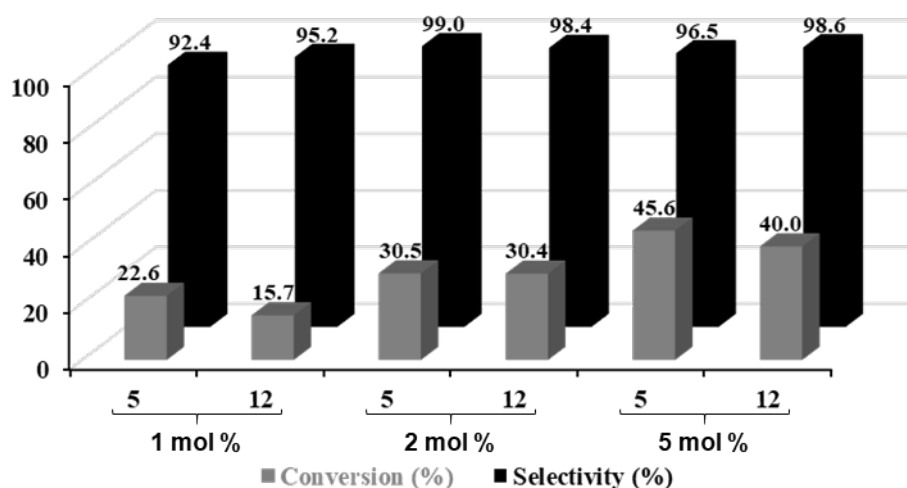


Figure 3. Conversion and selectivity of ESBO to CSBO after solvent-free cycloaddition with CO₂ at different mol % with catalysts 5 and the reference catalyst 12. Reaction conditions: temperature: 120 °C; CO₂ pressure: 20 bar; reaction time: 2 h; mol % is referred to oxirane mol.

As can be seen, with both tested catalysts the conversion increases almost linearly with the catalysts amount in the studied range of concentrations. On the other hand, the selectivity towards the carbonated product was superior at 2 mol % (> 99 %) with IL **5**. The prepared catalyst **5** showed in all cases better performance in terms of conversion than the benchmark catalyst **12**. In fact, catalyst **5** increases the conversion achieved by **12** in ca. 43.9 %, 0.3 % and 14 % at 1 mol%, 2 mol% and 5 mol% of catalyst respectively. The highest increment in conversion was obtained at 1 mol % (more than 43 % increment). The better performance of catalysts **5** could be attributed to an increase of the nucleophilic character of the bromide anion due to the presence of the more sterically hindered phosphonium cation and the weaker interaction between the cation and the anion.⁵³⁻⁵⁷

3.2.3. Influence of the temperature

Temperature is a key parameter in many catalytic reactions influencing both conversion and selectivity to desired product. The influence of the temperature was studied in the range 60-160 °C with 2 mol % of catalyst and at 2 h reaction time.

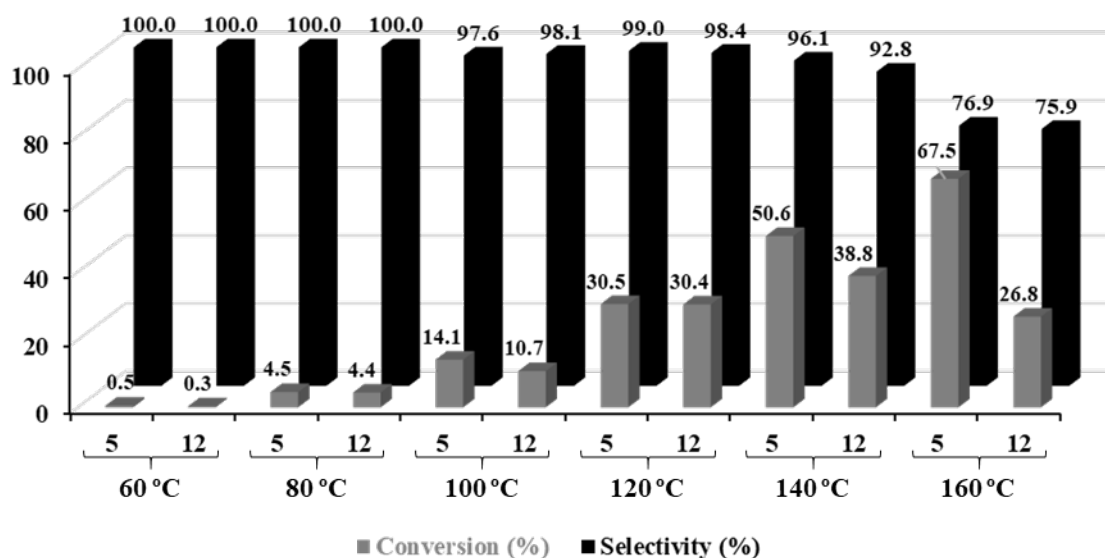


Figure 4. Conversion and selectivity of ESBO to CSBO after solvent-free cycloaddition with CO₂ at different temperatures with catalyst **5** and the reference catalyst **12**. Reaction conditions: catalyst amount: 2 mol % referred to oxirane mol; CO₂ pressure: 20 bar; reaction time: 2 h.

As can be observed in **figure 4**, the catalytic activity of **5** surpasses that of the benchmark IL (**12**) at all the studied temperatures. In the case of catalyst **5** a continuous increase on the activity with the raise of temperature was observed. On the other hand, with the benchmark catalyst (**12**) the highest conversion was obtained at 140 °C (38.8 %) while it decreased to 26.8 % at 160 °C. This result was somehow unexpected since the decomposition temperature of the benchmark catalyst (**12**) is reported to be 190 °C.⁵⁹ Therefore, it was decided to check the thermal stability of the two tested catalysts at the highest temperature studied by performing an isotherm thermogravimetric analysis at 160 °C for 12 h. As suspected, the benchmark catalyst (**12**) starts degrading after less than one hour at 160 °C while the prepared catalyst **5** shows negligible or no degradation after 12 hours at 160 °C (**figure 5**). This finding ambiguously explains why the conversion with **12** decreases when the temperature

increases from 140 °C to 160 °C, and constituted a clear advantage of IL **5** compared to the benchmark catalyst (**12**) for scale-up processes at high temperatures.

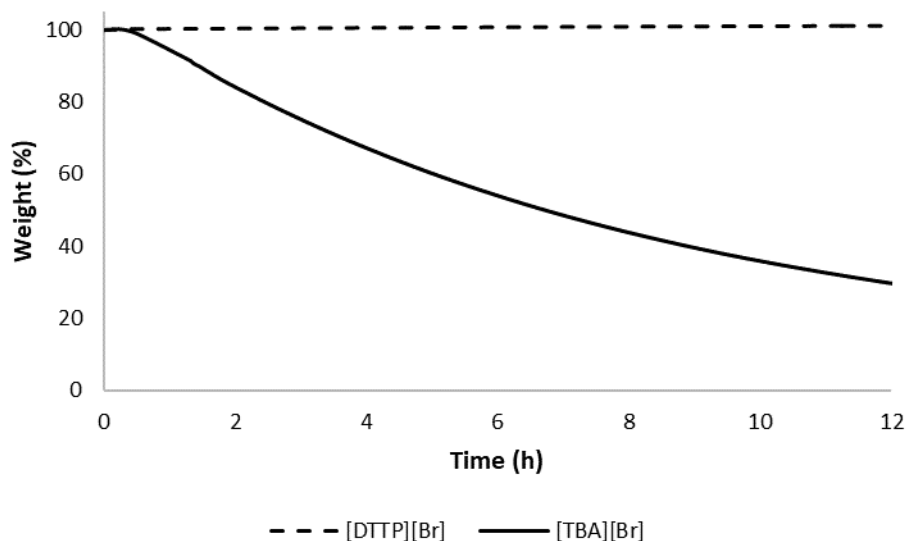


Figure 5. Catalysts **5** ([DTTP][Br]) and **12** ([TBA][Br]) isothermal thermogravimetric analysis at 160 °C. With both catalytic systems the selectivity towards CSBO decreases significantly at temperatures ≥ 140 °C, which indicates that the further decomposition of CSBO towards an unidentified product is favoured.

3.2.4. Influence of the pressure

The effect of CO₂ pressure was investigated between atmospheric pressure and 40 bar at 120 °C and 2 hours reaction time (**figure 6**). The results obtained showed that with both catalytic systems the activity increases when rising the CO₂ pressure. This indicates a positive contribution of the CO₂ partial pressure on the rate-equation law. This result is in agreement with the proposed reaction mechanism and may indicate that attack of the alkoxide intermediate to CO₂ could be involved in the rate-determining step of the process. Nevertheless, a change in the rate determining step depending upon the total CO₂ pressure cannot be discarded. Unexpectedly, an increase of the selectivity towards CSBO was also observed at higher CO₂ pressures with both catalytic systems. This effect could be due to a stabilizing effect of CO₂ avoiding further transformation of the carbonated compounds. In general, catalyst **5** and the benchmark catalyst **12** showed similar behaviour with the pressure achieving slightly higher conversion within the whole range of CO₂ pressures studied when the prepared catalyst **5** was employed.

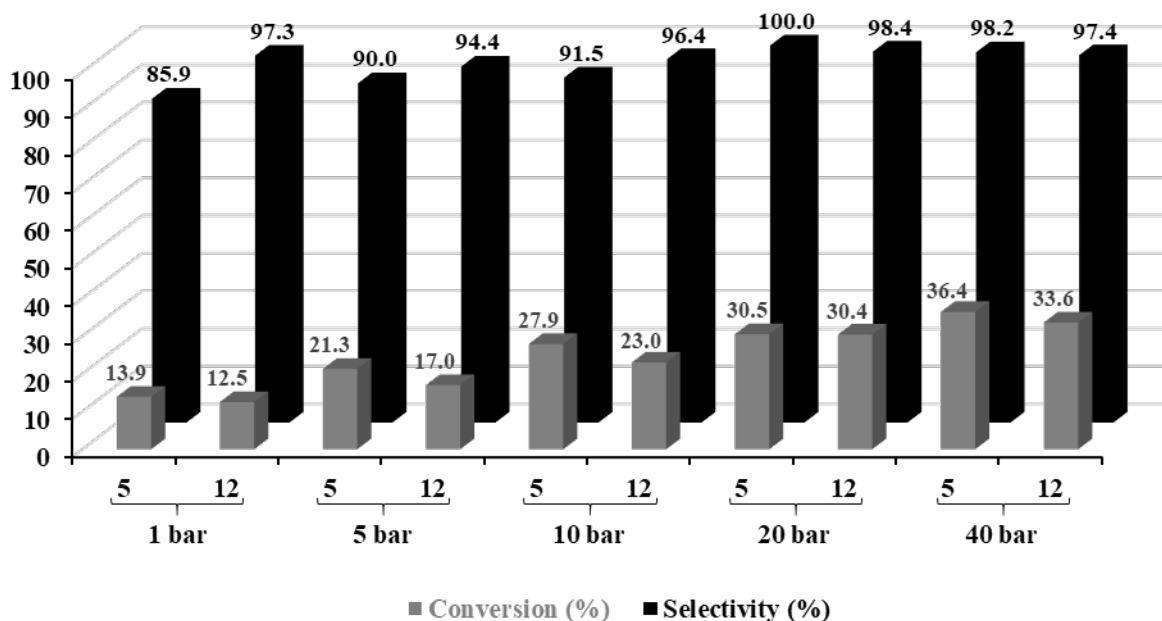


Figure 6. Conversion and selectivity of ESBO to CSBO after solvent-free cycloaddition with CO₂ at different pressure of CO₂ with catalyst **5** and the reference catalyst **12**. Reaction conditions: catalyst amount: 2 mol % referred to oxirane mol; temperature: 120 °C; reaction time: 2 h.

3.3 Influence of the reaction time

A study to follow the conversion of the ESBO and the selectivity towards the CSBO product with time was done with the prepared catalyst **5** at the optimized reaction conditions for this system (160 °C, 40 bar CO₂, 2 mol% catalyst with respect to oxirane mol). The results obtained are shown in **figure 7**. Under these conditions, full conversion was achieved after 5 h reaction although excellent conversions 90.5 % were already obtained after 3h. On the other hand, an excellent selectivity (≥ 84 %) was observed along the whole process despite the high reaction temperature employed that could contribute to further reaction of the carbonated product. These results show the potential of catalyst **5** that yield among the highest conversion of ESBO to CSBO reported in the literature so far, to the best of our knowledge. In summary, this catalyst that can be readily obtained from commercially available cheap feedstocks shows undoubtedly superior performance and stability in the solvent-free cycloaddition of CO₂ to ESBO reaction compared to the commercially available and widely used in this reaction benchmark catalyst **12**.

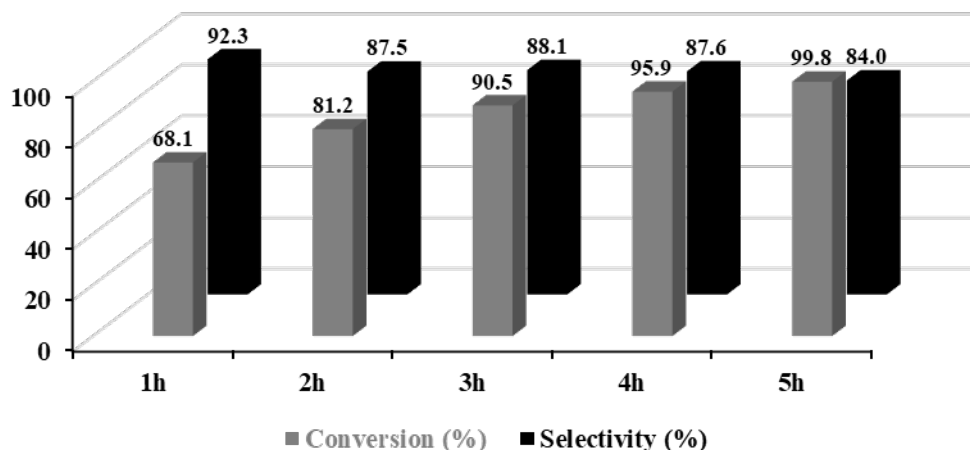


Figure 7. Conversion and selectivity of ESBO to CSBO after solvent-free cycloaddition with CO₂ at different reaction times with catalyst **5**. Reaction conditions: catalyst amount: 2 mol % referred to oxirane mol; temperature: 160 °C; CO₂ pressure: 40 bar.

4. Conclusions

In the present work, a series of eleven ILs were rationally designed and prepared to be employed as catalyst in the obtention of CSBO by solvent-free cycloaddition reaction of CO₂ to ESBO. Most of the ILs were prepared in one step and isolated in a straight-forward manner from economic and widely available feedstock materials, triphenylphosphine and the corresponding haloalkane. Three out of the eleven prepared ionic liquids showed better performance than the benchmark and widely used catalysts (**12**) in this reaction. It was evidenced that the solubility of the employed ionic liquid in the ESBO reaction media is a key factor in the catalyst performance. Additionally, it was shown that the length of the alkylic chain suffices to impart the desired solubility as long as it was of at least 8 carbon atoms-length. The rigidity and the steric hindrance of the substituents on the phosphonium cation was found to affect the nucleophilic character of the Br⁻ anion and therefore the catalyst performance that is improved in the case of the triphenylphosphonium (more rigid) compared to tricyclohexylphosphonium (more flexible). Practically full conversion > 99 % and excellent selectivity toward the carbonated product 84 % was obtained with 2 mol % of catalyst **5** at 160 °C, 40 bar CO₂ and after 5 hours reaction while, at the same reaction conditions, the benchmark catalyst **12** showed less than 27% conversion due to lack of thermal stability. In summary, at least three ionic liquids (**5**, **6** and **7**) with improved catalytic performance in terms of conversion and selectivity compared to the benchmark catalyst **12** in the solvent-free CO₂ cycloaddition to ESBO at moderated reaction conditions, 5h, 40 bar and 160 °C were encountered. Furthermore, these phosphonium-based ionic liquids were synthesized from commercially available and low-cost feedstocks (triphenylphosphine and bromoalkanes) in one step process and were easily isolated. The obtained CSBO can be employed as bio-based compounds with huge application in the field of biopolymers such as polyurethanes and polycarbonates. Further work, focused in the recovery and reuse of the prepared catalyst **5** is currently under progress.

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5. References

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