



Short Communication

Propylene carbonate synthesis from propylene glycol, carbon dioxide and benzonitrile by alkali carbonate catalysts

E. Da Silva ^a, W. Dayoub ^a, G. Mignani ^b, Y. Raoul ^c, M. Lemaire ^{a,*}^a Laboratoire Catalyse, Synthèse et Environnement, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS), CNRS, UMR 5246, Université Claude Bernard Lyon 1, bat. CPE, 43 boulevard du 11 novembre 1918, 69622, Villeurbanne, France^b RHODIA, Centre de Recherche et de Technologie de Lyon (CRTL), 85 avenue Frères Perret, 69190, Saint-Fons, France^c SOFIPROTEOL, 11 rue de Monceau CS 60003, 75378 Paris cedex 08, France

ARTICLE INFO

Article history:

Received 14 November 2011

Received in revised form 24 July 2012

Accepted 28 August 2012

Available online 19 September 2012

Keywords:

Alkali carbonate

Carbon dioxide

Homogeneous

Glycol carbonate

Dehydrating agent

ABSTRACT

The synthesis of propylene carbonate from propylene glycol and carbon dioxide in the presence of various catalysts has been reported. Benzonitrile has been used as both solvent and dehydrating agent. Under optimal conditions, the best results were obtained in the presence of alkali carbonate catalysts. The propylene carbonate yield could reach up to 20% with a propylene-1,2-glycol conversion of 44%.

© 2012 Published by Elsevier B.V.

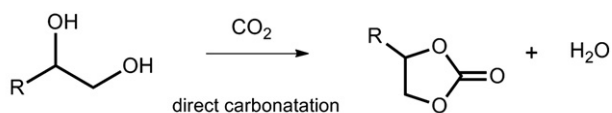
1. Introduction

The formation of polyol carbonate from carbon dioxide is probably one of the most interesting pathways in terms of synthetic method and atom economy [1]. New syntheses for the conversion and valorization of polyols [2–4] have been realized and especially for the formation of glycerin carbonate [5] as a main compound of battery electrolyte, surfactant, intermediate reactant and propylene carbonate as new green solvents or triphosgene substitute [6]. The carbonatation of diols gave low yields due to the presence of water molecules formed during the reaction [7,8] and thus inducing a possible catalyst poisoning and a reversible reaction (Scheme 1).

Due to the difficulty of this synthetic route and the urgent need for enhancing new methodologies, efforts on direct carbonatation of monoalcohols or glycol derivatives have been done. Methods for the synthesis of DMC from carbon dioxide and orthoesters [9,10] or acetal derivatives [11–13] have been developed by Sakakura et al. using organotin compounds as catalysts. Nowadays, tin catalysts remain as the best catalysts for DMC production from carbon dioxide but the process has not been applied for industrial process due to harsh conditions: high temperature, high pressure, until 300 atm. and the use of tin catalysts. The role of Sn-catalysts or other metal oxides in the synthesis of DMC has been widely detailed in the literature [14–18]. About glycol derivatives, the synthesis of five-membered rings such as ethylene

carbonate and propylene carbonate can be obtained by direct carbonatation of ethylene glycol (EG) or propylene glycol (PG) in the presence of carbon dioxide. He et al. described an effective synthesis of propylene carbonate with remarkable selectivity catalyzed by organotin compounds [19]. However, conversion and yield are very low and show the limit of using tin catalyst. Another example was described in the presence of magnesium catalysts and scCO_2 without any solvent or additives showing high selectivity but a very low yield [20]. Recently, the formation of carbonate compounds from carbon dioxide and alcohol compounds has been done by using dehydrating reagent to remove water produced during the reaction. Acetonitrile is a nitrile solvent commonly used as a dehydrating agent giving acetamide and acetic acid in the presence of water molecules. Several works tend to optimize the reaction conditions in the presence of this solvent. The first example of propylene or ethylene carbonate has been obtained using cerium based catalysts or a mixture of cerium and zirconium oxides and carbon dioxide in supercritical media showing high selectivity but limited by reaction equilibrium [21,22]. Alkali carbonates were used to catalyze propylene carbonate synthesis from PG and CO_2 with a conversion of 30–40% and a selectivity of average 60% for PC [23]. A series of zinc oxide [24] or modified acetate catalysts [25] present similar results than those described with alkali carbonates. Related with the basicity of catalysts, a series of organic bases such as TBD (triazabicyclodecene), DBU (diazabicycloundecene) and TEA (triethylamine) were employed for PC synthesis where the yield reached average 15% with 60% of selectivity [26]. Under optimal conditions performed by various groups, acetonitrile remains a major drawback due to its cost, low boiling

* Corresponding author. Tel.: +33 4 72 43 14 07; fax: +33 4 72 43 14 08.
E-mail address: marc.lemaire@univ-lyon1.fr (M. Lemaire).



R = H, CH₃, nAlkyl, -CH₂OH

Scheme 1. Direct carbonatation of glycol derivatives.

point, its toxicity and high polarity. Moreover such nitrile is weakly compatible with CO₂ system. In this article, we describe a synthetic route of formation of propylene carbonate from PG and CO₂ over different sources of heterogeneous or homogeneous catalysts. Acetonitrile is substituted by benzonitrile and other industrially available nitrile or dinitrile acting as both solvent and dehydrating agent. As reported for CO₂-expanded ethanol, benzonitrile can increase the solubility of carbon dioxide in propylene glycol at high temperature and pressure [27]. PC yield was improved and the reaction conditions in Benzonitrile + CO₂ + Propylene Glycol were optimized. The reactions were investigated in details by GC and GC/MS analyses. We have reported the mechanism by identifying intermediate and byproduct compounds. This is the first example reported of propylene carbonate formation in the presence of benzonitrile.

2. Experimental part

2.1. Chemical reagents

Propylene-1,2-glycol (Acros, 99%) was dried at 110 °C at 100 mbar during 4 h and stored under nitrogen. Propylene-1,3-glycol (Acros, 99%), ethylene glycol (Acros, 99%), phenol (Acros, 99+%), octane-1,2-diol (Aldrich, 98%), and pentafluorophenol (Acros, 99+%) were used for reaction without further purification. All the products were purchased: benzamide (purity 99%), adiponitrile, glutaronitrile, succinonitrile, cyanamide and isobutyronitrile having a purity >98% from Acros; benzonitrile (99+%), tetrahydrofuran and ethanol in p.a. grade from Sigma-Aldrich; carbon dioxide from Air Liquide France (purity 99.998%, moisture 3 ppm, oxygen 2 ppm, 4.95 MPa).

2.2. Preparation of catalysts

Anhydrous alkali carbonates were obtained from various industrial companies and directly used without further purification. Metal oxides were given by Rhodia Electronics and Catalysis (La Rochelle, France) and calcinated at 500 °C during 2 h (increment rate 2 °C/min during 4 h) using a Nabertherm apparatus.

2.3. Reaction apparatus and conditions

Reactor was previously heated at 150 °C during 2 h to remove water molecules and cooled down at room temperature under carbon dioxide atmosphere. The reaction was carried out in a 100 mL stainless-steel reactor provided by PARR instrument. The autoclave is equipped with a mechanical stirrer, internal thermal probe and a manometer up to 20 MPa. A solution of PG (100 mmol) and benzonitrile (100 mmol) was stirred at 1000 rpm in the presence of catalysts (5%mol) as a typical process. Carbon dioxide was introduced into the reactor to replace air at 5 MPa at room temperature. The mixture was heated at 175 °C showing 8 MPa pressure. The 10 MPa pressure is adjusted with a pump. Reaction was stopped after 18 h by cooling down the reactor to room temperature and then slowly depressurized. Tetraethyleneglycol was added to the crude mixture as an internal standard for quantitative analysis. The reaction mixture was analyzed by GC apparatus using tetrahydrofuran or ethanol as solvent.

2.4. GC and NMR analyses

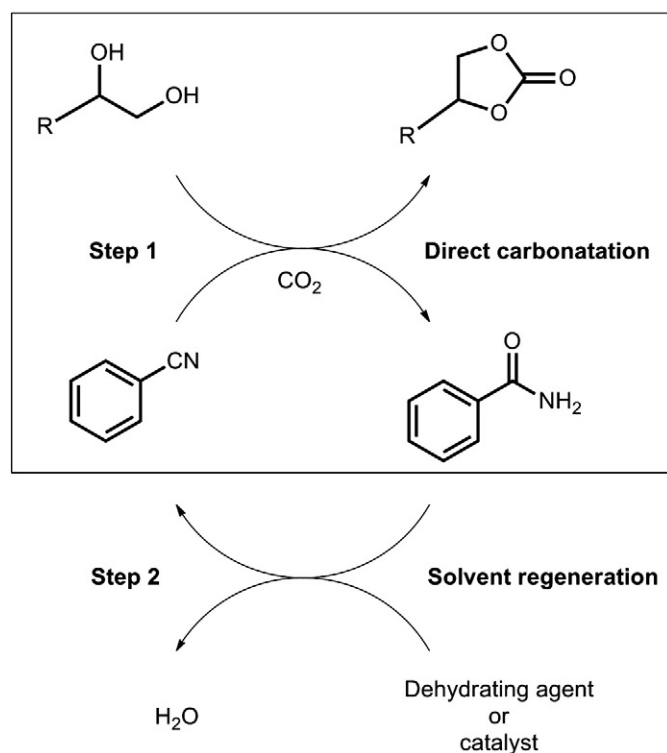
All reaction media were analyzed by gas chromatography (SHIMADZU GC-14A) equipped with a temperature-programmed injector. The injector temperature was maintained at 250 °C. The compounds were separated on a RESTEK Stabilwax column (30 m long, i.d. 0.32 mm, 0.5 μm) as polar stationary phase (Crossbond® Carbowax® polyethyleneglycol). The column temperature was maintained at 40 °C for the first minute and then raised up to 250 °C by 15 °C/min. Nitrogen was employed as vector gas. The outlet of the column was connected to a hydrogen flame ionization detector maintained at 250 °C. CR6-A Chromatopac integrator was used for data acquisition. Samples were prepared in THF or ethanol. GC–MS were measured with focus DSQ electronic ionization with stabilwax column. The characterization of PGB molecules has been done by nuclear magnetic resonance. NMR spectra were recorded with a Bruker ALS or DRX 300 spectrometer (¹H: 300 MHz, ¹³C: 75 MHz).

3. Results and discussion

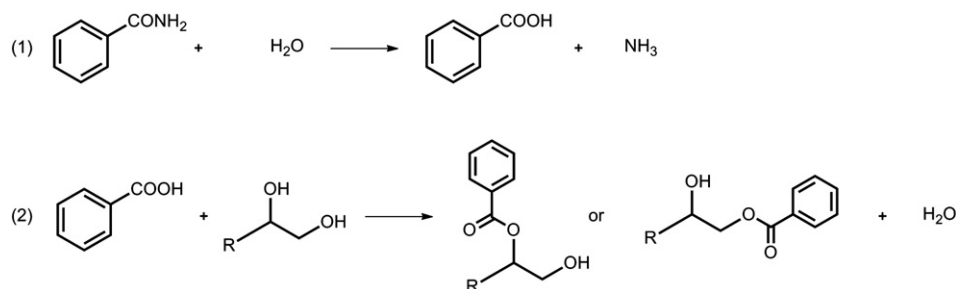
3.1. PC synthesis from PG and C₆H₅CN

As shown Scheme 2, the synthetic route to alkylene carbonate is based on: (step 1) direct carbonatation of glycol derivatives and water formation; benzonitrile was hydrated to benzamide in the presence of water molecules; (step 2) the benzonitrile could be easily regenerated from benzamide by flash vacuum pyrolysis as described by McNab [28]. In our work, we focused on the optimization of step 1 using propylene glycol as reference.

Propylene carbonate is synthesized in the presence of propylene glycol (100 mmol) and benzonitrile (100 mmol) under CO₂ supercritical conditions at 10 MPa, 448 K for 18 h in the presence of catalytic amount of various catalysts (5% mol). As detailed in Scheme 1, benzamide is formed by the hydration of benzonitrile in the presence of water molecules provided from the following reaction: PG + CO₂ gives PC + H₂O. Depending on the reaction conditions, ester



Scheme 2. Synthesis of PC from PG and CO₂.



Scheme 3. Eq. (1): hydrolysis of benzamide to benzoic acid; Eq. (2): formation of two monoesters from benzoic acid and PG.

derivatives from propylene glycol such as PG-1-B (propylene glycol-1-benzoate) and PG-2-B (propylene glycol-2-benzoate) were also observed and characterized by GC–MS technique. To confirm the presence of ester derivatives, we synthesized PGB with a ratio of 40/60 for PG-1-B and PG-2-B following the procedure described in the literature [29]. The PGB formation can be explained by esterification process between benzoic acid and PG as shown in Scheme 3. However, benzoic acid as benzamide hydration product has never been observed in reaction mixture and only an esterified product was obtained.

As shown in Fig. 1, the synthesis of PC in the presence of benzonitrile is quite selective showing PGB and benzamide as byproducts. All peaks have been characterized and analyzed by GC–MS. A broad peak is observed for both PGB having approximately the same retention time. The yield and ratio of each product were analyzed by GC and the results are summarized in Table 1. Without addition of nitrile solvent, propylene carbonate formation is not observed at all, pointing out that dehydrating agent is essential for catalysis. In addition, benzamide was not detected in the absence of PG demonstrating that it was formed in the presence of water molecules provided from PC synthesis. In the absence of carbon dioxide, no PC formation and PG conversion were observed assuming that carbonate group was provided from CO₂ and not

from carbonate catalysts. The best result is observed using 5%mol of potassium carbonate giving 20% and 24% of yields for PC and PGB, respectively (Table 1, entry 1). The conversion of PG reached 44% with TON of 4. Extending the reaction time until 62 h (entry 2), PG conversion increased partially up to 57% showing limitations of the reaction. Nowadays, this value is the best conversion reported but PC selectivity dropping from 45% to 33%. To enhance the PC selectivity, ammonium carbonate was added into the reaction system to afford benzamide hydration [23] and not to produce PGB (entry 4). Unfortunately in this case, no significative effect was shown. At 473 K, PC yield drops until 9% with a low selectivity reaching 20% (entry 3). That implied a possible demixing between benzonitrile and supercritical carbon dioxide and/or an unstability of propylene carbonate at high temperature.

Replacing potassium carbonate by a more basic one such as cesium carbonate (entry 6), similar result was observed in terms of conversion, yield and selectivity for both products. Using 15%mol of catalyst (entry 7), the activity of cesium carbonate decreased seriously where PC yield was only 13%. The yield dropped in comparison to that obtained with 5%mol of catalyst. The quantity of PG was not enough to solubilize all the carbonate catalyst giving a heterogeneous mixture and decreasing the mass transfer process.

Moreover, alkali carbonates such as sodium or lithium carbonates have little solubility in benzonitrile/PG mixture showing a very low activity for PC synthesis (entries 8–9). The reaction activity can be resumed by the basicity and the size of counterion where high activity is done in the following order: K ≈ Cs > Na > Li. To raise basicity of

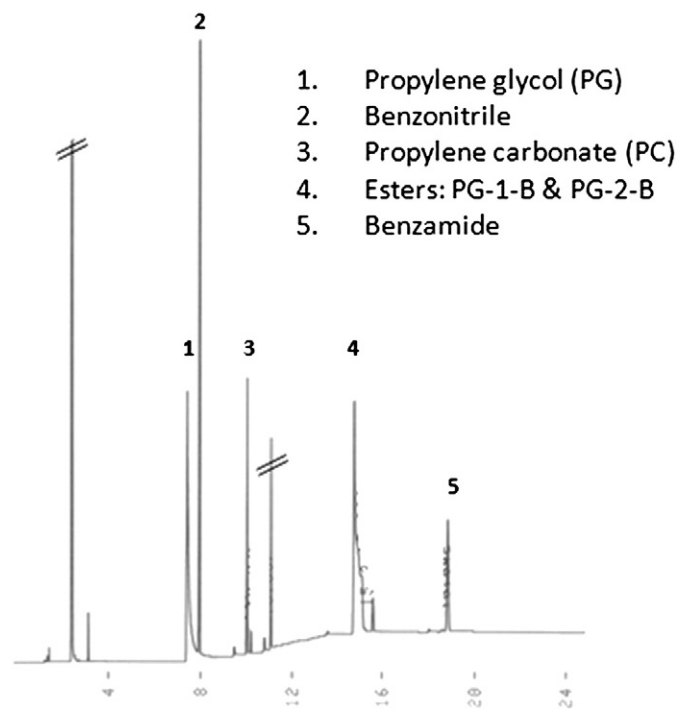


Fig. 1. GC-chromatogram (stabilwax column) of reaction mixture done in THF under standard conditions. Retention times are omitted for clarity and double line represents the solvent.

Table 1
PC synthesis from PG and CO₂ under standard conditions.

Entry	Cat.	PG _{conv} (%)	Yield PC (%)	Yield PGB (%)	Selectivity PC (%)	Selectivity PGB (%)	TON
1	K ₂ CO ₃	44	20	24	45	55	4.0
2	K ₂ CO ₃	57 ^a	19	38	33	67	3.8
3	K ₂ CO ₃	45 ^b	9	36	20	80	1.8
4	K ₂ CO ₃	38 ^c	13	25	34	66	2.6
5	K ₂ CO ₃	30 ^d	13	18	42	58	2.6
6	Cs ₂ CO ₃	44	17	28	37	63	3.4
7	Cs ₂ CO ₃	31 ^e	13	18	42	58	2.6
8	Na ₂ CO ₃	22	8	14	36	64	1.6
9	Li ₂ CO ₃	6	4	2	–	–	0.8
10	MgCO ₃	1	Traces	Traces	–	–	–
11	CaCO ₃	2	Traces	Traces	–	–	–
12	La ₂ (CO ₃) ₃	1	Traces	Traces	–	–	–
13	Al ₂ (CO ₃) ₃	2	Traces	Traces	–	–	–

Reaction conditions: PG (100 mmol), Benzonitrile (Bn, 100 mmol), 5% mol catalyst, CO₂ 10 MPa, temperature 448 K, time 18 h; Y_{PGB} = yield of PG-1-B + PG-2-B; yield (Y) and conversion determined by GC; TON (turn-over number) = (mol of substrate converted to propylene carbonate/mol of catalyst).

^a 62 h reaction time.

^b Reaction done at 473 K.

^c 5%mol of (NH₄)₂CO₃ was added.

^d 5%mol 18-crown-6 was added.

^e 15%mol catalyst.

K₂CO₃, 18-crown-6 ether was added to the reaction (entry 5) but no increasing performance was observed.

Using di- or trivalent carbonates such as magnesium, calcium, aluminum or lanthanum (entries 10–13) leads to a very low conversion and only traces of PC were detected by GC analysis. Several metal oxides such as La₂O₃, Al₂O₃ (96%) and Al₂O₃/BaO mixture (78:22) were evaluated for PC synthesis in the same conditions. However, all data gave low activity with PG conversion below 3%. In some cases, PC and PGB have been detected. Other catalysts such as CeO₂ (99.5%) and CeO₂/ZrO₂ mixture (58:42) did not increase the conversion. These results are coherent with those observed in the presence of Ce-catalysts in acetonitrile [30]. For all cases, we noted that the reaction occurred to be very slow in heterogeneous mixture.

3.2. Nitrile solvents screening

Other nitrile solvents have been studied in order to evaluate the efficiency of the dehydrating agent. Data are summarized in Table 2. Mononitrile solvents such as acetonitrile, cyanamide and isobutyronitrile were used. Acetonitrile is a common solvent and widely tested for PC synthesis from PG and CO₂ with PC. In terms of efficiency, benzonitrile presented better conversion and PC yield than acetonitrile (Table 2, entries 1–2). Cyanamide and isobutyronitrile did not perform the reaction at all. Benzonitrile presents a better choice compared to acetonitrile in terms of solubility. Indeed, high-pressure vapor–liquid equilibria for CO₂ + benzonitrile at high temperature and pressure have been studied by Whalter and Maurer showing good compatibility and miscibility between them [31]. Using benzamide as co-solvent, only 8% of PG conversion occurred with a yield of 2% and 4% for PC and PGB, respectively. Benzamide is less dehydrating than benzonitrile.

Dicyanated solvents were also tested such as adiponitrile, glutaronitrile and succinonitrile in order to raise the dehydrating effect by introducing two cyano groups. Two of them bearing short alkyl chains (entries 4–5) generated polymers which are difficult to characterize by GC. In the case of adiponitrile (entry 3), PG conversion was similar to that with benzonitrile but showed a better selectivity for PC with 27% of yield. The high selectivity can be explained by the fact that water molecules were trapped faster than with monocyano solvents. Byproducts correspond to adiponitrile hydration and ester derivatives with a global yield of 17%.

3.3. Alcohol screening

The efficiency of the reaction has been extrapolated to other glycols like propylene-1,3-glycol (PG_{1,3}), ethylene glycol (EG) and octane-1,2-diol (OG) for formation of alkylene carbonate. For PG_{1,3} and EG, only traces of corresponding carbonate have been observed with a glycol conversion below 3% inducing the difficult implement for cyclic carbonation having hydroxyl groups in terminal position. For OG compound with long alkyl chain, less polar and less hydroscopic than PG, the synthesis of octylene carbonate has been performed under standard conditions giving OC yield of 10%. The OC yield was lower

than this achieved for PC but suggested that the formation of alkylene carbonate is easier when the molecule presents both primary and secondary alcohols. For higher polyol such as glycerol having three hydroxyl groups, we never observed the formation of glycerin carbonate under these conditions. Recently, Tomishige et al. used benzonitrile to substitute acetonitrile for direct carbonation of monoalcohols (methanol, ethanol, propanol, isopropyl and benzyl alcohols) to dialkyl carbonate in the presence of CeO₂ as catalyst [32,33]. In our work, we were also interested on direct transformation of phenol to diphenylcarbonate (DPC) as phosgene substitute. DPC has never been seen under our experimental conditions. Pentafluorophenol was also used to increase solubility in CO₂ but no conversion was observed.

3.4. Other parameters

The best result was obtained with a 1:1 ratio of Benzonitrile/PG. Decreasing 5 times the concentration of PG with respect to benzonitrile and CO₂, the values of PG conversion and PC yield remained unchanged. That implied that increasing CO₂ molar fraction into alcohol/benzonitrile mixture did not affect the activity of the reaction inducing limitation process. Moreover, the maximum PG conversion was obtained when the pressure value was 10 MPa under supercritical conditions. Increasing the CO₂ pressure up to 15 MPa at 448 K, the PG value dropped until 24% showing a heterogeneous solution after cooling down at room temperature. Decreasing pressure until 6 MPa, PG conversion was similar to that obtained with a much higher pressure. Indeed under non-supercritical conditions (gaseous/liquid phase), the reactivity is lower than supercritical conditions where all substances are soluble giving a homogeneous solution. The supercritical medium considerably accelerated the rate of PC formation.

3.5. Mechanism proposal

Up to now, the real challenge was to convert totally PG to PC. Unfortunately, complete conversion of PG into desired final compound could be limited either by the stability of desired product or the formation of byproducts. Indeed, we synthesized a mixture of PGB in a 70/30 ratio (PG-2-B and PG-1-B respectively) and the carbonation of this mixture was performed in the presence of K₂CO₃ and CO₂ at 10 MPa and 448 K. We observed the formation of PG with a PGB conversion of 2% as shown in Scheme 4. In this case, the formation of PC was not detected and PGB appeared not to be an intermediate. In parallel, benzoic acid was detected by GC technique as hydration ester product. Applying optimal conditions, pure propylene carbonate was converted to PG with 1% inducing a high stability of alkylene carbonate in supercritical conditions. Indeed, the formation of PGB appears to be the main limitation of the reaction.

It is worth to mention that propylene carbonate and ester derivatives have a good stability in supercritical carbon dioxide. If the starting compounds were not dried, we observed an increasing value of conversion up to 10 and 20%. In this paper, the value of 44% of PG conversion is the highest we have observed. Of course, it would be interesting to focus on the selectivity of the reaction in favor of alkylene carbonate. Thermodynamic studies are on going to provide insights on the mechanism of hydration and esterification processes but this is another work which will be done in due course.

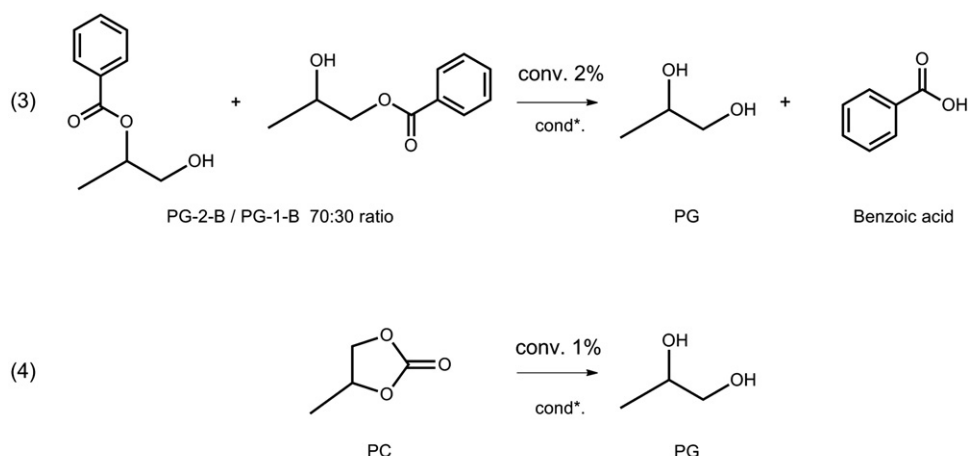
4. Conclusion

The reaction of PG + CO₂ + Benzonitrile showed relatively good conversion in supercritical media but suffered of limitations due to the presence of intermediate ester derivatives and side reactions collapsing the yield of PC. Benzonitrile plays the role of dehydrating agent and co-solvent and seems to be the best solvent for this transformation. Basic alkali carbonates like potassium and cesium give the best result for PC synthesis. Under optimal reaction conditions, the

Table 2
Effect of nitrile solvents on PC synthesis.

Ent.	Solvent	PG _{conv} (%)	Y _{PC} (%)	Y _{byproduct} (%)	TON
1	Benzonitrile	44	20	24	4
2	Acetonitrile	34	12	22	2.4
3	Adiponitrile	44	27	17	5.4
4	Glutaronitrile	Polymerization			
5	Succinonitrile	Dark polymer: degradation			
6	Cyanamide	1	–	trace	–
7	Isobutyronitrile	5	1	2	0.2

Reaction conditions: PG (100 mmol), Benzonitrile (Bn, 100 mmol), 5% mol K₂CO₃, CO₂ 10 MPa, temperature 448 K, time 18 h.



*Cond.: starting compound (100 mmol), benzonitrile (100 mmol), K_2CO_3 (5% mol), Pressure CO_2 (10MPa), Temp. 448K, 18h.

Scheme 4. Hydrolysis of esters and propylene carbonate under optimal reaction conditions.

production of PC is limited by the reaction equilibrium. The future challenge is to find an alternative process to remove water molecules from the system while limiting formation of side products.

Acknowledgment

E.D.S. and W.D. acknowledge SOFIPROTEOL industry for financial support. We thank F. Albrieux, C. Duchamp and N. Henriques from the Centre de Spectrométrie de Masse (ICBMS UMR-5246), for the assistance and access to the Mass Spectrometry facilities. We thank E. Rohart from Rhodia Electronics and Catalysis (La Rochelle, France) for lanthanum catalysts.

References

- [1] T. Sakakura, K. Kohno, *Chemical Communications* (2009) 1312–1330.
- [2] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, *Angewandte Chemie International Edition* 46 (2007) 4434–4440.
- [3] C.-H. Zhou, J.N. Beltrami, Y.-X. Fan, G.Q. Lu, *Chemical Society Reviews* 37 (2008) 527–549.
- [4] C. Vriet, 2005, *Généralisation de la carbonatation aux substrats polyhydroxylés. Synthèse de carbonates cycliques, linéaires et mixtes, à partir d'érythritol, de xylitol et de sorbitol*. Thesis (PhD), Université de Toulouse.
- [5] B. Schöffner, F. Schöffner, S.P. Verevkin, A. Börner, *Chemical Reviews* 110 (2010) 4554–4581.
- [6] I. Vauthey, F. Valot, C. Gozzi, F. Fache, M. Lemaire, *Tetrahedron Letters* 41 (2000) 6347–6350.
- [7] M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, *Journal of Molecular Catalysis A: Chemical* 257 (2006) 149–153.
- [8] J. George, Y. Patel, S. Muthukumar Pillai, P. Munshi, *Journal of Molecular Catalysis A: Chemical* 304 (2009) 1–7.
- [9] T. Sakakura, J.-C. Choi, Y. Saito, T. Masuda, T. Sako, T. Oriyama, *The Journal of Organic Chemistry* 64 (1999) 4506–4508.
- [10] T. Sakakura, Y. Saito, M. Okano, J.-C. Choi, T. Sako, *The Journal of Organic Chemistry* 63 (1998) 7095–7096.
- [11] T. Sakakura, J.-C. Choi, Y. Saito, T. Sako, *Polyhedron* 19 (2000) 573–576.
- [12] K. Kohno, J.-C. Choi, Y. Ohshima, A. Yili, H. Yasuda, T. Sakakura, *Journal of Organometallic Chemistry* 693 (2008) 1389–1392.
- [13] J.-C. Choi, L.-N. He, H. Yasuda, T. Sakakura, *Green Chemistry* 4 (2002) 230–234.
- [14] J. Kizlink, I. Pastucha, *Collection of Czechoslovak Chemical Communications* 60 (1995) 687–692.
- [15] D. Ballivet-Tkatchenko, T. Jerphagnon, R. Ligabue, L. Plasseraud, D. Poinot, *Applied Catalysis A: General* 255 (2003) 93–99.
- [16] D. Ballivet-Tkatchenko, R. Burgat, S. Chambrey, L. Plasseraud, P. Richard, *Journal of Organometallic Chemistry* 691 (2006) 1498–1504.
- [17] D. Ballivet-Tkatchenko, S. Chambrey, R. Keiski, R. Ligabue, L. Plasseraud, P. Richard, H. Turunen, *Catalysis Today* 115 (2006) 80–87.
- [18] D. Ballivet-Tkatchenko, O. Douteau, S. Stutzmann, *Organometallics* 19 (2000) 4563–4567.
- [19] Y. Du, D.-L. Kong, H.-Y. Wang, F. Cai, J.-S. Tian, J.-Q. Wang, L.-N. He, *Journal of Molecular Catalysis A: Chemical* 241 (2005) 233–237.
- [20] Y. Du, L.-N. He, D.-L. Kong, *Catalysis Communications* 9 (2008) 1754–1758.
- [21] K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. Li, K. Kunimori, *Catalysis Letters* 95 (2004) 45–49.
- [22] K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. Li, K. Kunimori, *Green Chemistry* 6 (2004) 206–214.
- [23] S. Huang, S. Liu, J. Li, N. Zhao, W. Wei, Y. Sun, *Catalysis Letters* 112 (2006) 187–191.
- [24] S. Huang, S. Liu, J. Li, N. Zhao, W. Wei, Y. Sun, *Catalysis Letters* 118 (2007) 290–294.
- [25] X. Zhao, N. Sun, S. Wang, F. Li, Y. Wang, *Industrial and Engineering Chemistry Research* 47 (2008) 1365–1369.
- [26] S. Huang, J. Ma, J. Li, N. Zhao, W. Wei, Y. Sun, *Catalysis Communications* 9 (2008) 276–280.
- [27] I.-H. Lin, C.-S. Tan, *Journal of Chemical and Engineering Data* 53 (2008) 1886–1891.
- [28] J.A. Campbell, G. McDougald, H. McNab, L.V.C. Rees, R.G. Tyas, *Synthesis* 20 (2007) 3179–3184.
- [29] H. Sharghi, M.H. Sarvari, *Tetrahedron* 59 (2003) 3627–3633.
- [30] M. Honda, S. Kuno, N. Begum, K.-I. Fujimoto, K. Suzuki, Y. Nakagawa, K. Tomishige, *Applied Catalysis A: General* 384 (2010) 165–170.
- [31] D. Walther, G. Maurer, *Journal of Chemical and Engineering Data* 38 (1993) 247–249.
- [32] M. Honda, S. Kuno, S. Sonehara, K.-I. Fujimoto, K. Suzuki, Y. Nakagawa, K. Tomishige, *ChemCatChem* 3 (2011) 365–370.
- [33] K. Suzuki, K. Fujimoto, K. Tomishige, *Jpn. Kokai Tokkyo Koho JP 2010077113*.