Methods for synthesizing diethyl carbonate from ethanol and supercritical carbon dioxide by one-pot or two-step reactions in the presence of potassium carbonate

Fabien Gasc, Sophie Thiebaud-Roux[*], Zephirin Mouloungui

1- Université de Toulouse; INP; LCA (Laboratoire de Chimie Agro-Industrielle); ENSIACET, 4 Allées Emile Monso, F-31029 Toulouse, France
2- INRA; LCA (Laboratoire de Chimie Agro-Industrielle); F-31029 Toulouse

[*] corresponding author. Tel: +33 5 62 88 57 01; fax: +33 5 62 88 57 30.
E-mail address: sophie.thiebaudroux@ensiacet.fr

Carbon dioxide sequestration was studied by synthesizing diethyl carbonate (DEC) from ethanol and CO_2 under supercritical conditions in the presence of potassium carbonate as a base. The co-reagent was ethyl iodide or a concentrated strong acid. This sequestration reaction occurs in two steps, which were studied separately and in a one-pot reaction. An organic-inorganic carbonate hybrid, potassium ethyl carbonate (PEC) is generated at the end of the first step. This intermediate was characterized and was found to be a target molecule for CO_2 capture. Different co-reactants, such as ethyl iodide and concentrated strong Brönsted acid, were compared in the second step and used to investigate the reactivity of the hybrid. With ethyl iodide as the co-reactant, one-pot DEC synthesis gave higher yields (46%) than two-step production. The supercritical CO_2 acts as a swelling solvent and compatibilizing agent in the reaction medium, favoring interactions between ethanol and CO_2 and between PEC and ethyl iodide. The use of a phase transfer catalyst (PTC) increased DEC production (yield 51%) without increasing the amount of diethyl ether (DEE) produced as a by-product (yield 2%).

Keywords:
Diethyl carbonate, diethyl ether, supercritical carbon dioxide, ethanol, potassium carbonate, one-pot process, two-step reaction, hybrid carbonate.

1. Introduction

Carbon dioxide is one of the greenhouse gases (together with CH_4, NO_x and CFCs) responsible for global warming. By 2005, CO_2 concentration in the atmosphere had increased from the 280 ppm level, thought to be present before the Industrial Revolution, to 379 ppm. Over the last 10 years (1995-2005) it has increased substantially, at a mean rate of 1.9 ppm.year^{-1} [1]. No single technology currently available could, if used alone, decrease worldwide emissions of CO_2 into the atmosphere to the level required by the Kyoto protocol. The most appropriate approach to reducing CO_2 emissions into the atmosphere is currently thought to involve selecting a certain number of technologies, each able to reduce emission by a given amount and to make use of the cumulative effects of these technologies to reach carbon dioxide emission targets [2]. A number of current technologies for recovering, binding and sequestering carbon dioxide are being developed with a view to increasing their efficiency, reliability and cost [3]. One of these methods is the geological sequestration of CO_2 by the carbonation of minerals rich in calcium, magnesium, sodium and potassium. In nature, this process is exceedingly slow (100,000 years), so various experiments have been carried out to optimize the conversion of carbon dioxide into its solid stable form: mineral carbonate [4].

The sequestration of CO_2 into organic carbonates uses up only limited amounts of the total amount of CO_2 produced, but is nonetheless of real interest to the scientific community. CO_2 has been exploited as a substitute for phosgene [5] or carbon monoxide [6, 7] in the synthesis of various organic carbonates, and particularly in the carbonation of epoxides [8, 9] or alcohols [10]. These processes were reviewed by Shaikh *et al.* [11], and more recently, by Sakakura *et al.* [12]. However, from the perspective of green chemistry, the most attractive method [13] is the use of an alcohol and carbon dioxide as synthons.

However, several studies on the synthesis of dimethyl carbonate from alcohol and CO_2 have shown the major problem to be the rate of conversion of methanol, due to the thermodynamic limitations of the reaction and deactivation of the homogeneous catalysts (e.g. tin complexes: distannoxanes) [14-18] and heterogeneous catalysts (e.g. zirconium oxide: ZrO_2) [19-22]. The only means of improving methanol conversion to date has been to use a co-reactant, such as methyl iodide, in the presence of basic catalysts [23-26]. Potassium carbonate has been reported to be the most effective base tested. In 2001, Fujita *et al.* [27] reported a study of the reaction conditions required for the synthesis of DMC and proposed a reaction mechanism in which DMC and dimethyl ether (DME) were produced by parallel pathways. Increasing CO_2 pressure to 80 bar results in an increase in DMC yield with the amount of catalyst or methyl iodide added.

Carbon dioxide can also be sequestrated into a hybrid organic-inorganic carbonate. The existence of such hybrids and their synthesis have been known since the 1960s [28]. Indeed, although alkyl hydrogen carbonates are not stable at room temperature, metal salts (e.g. of Li, Na, K, Mg and Ba) may be obtained by saponifying dialkylcarbonate [29] or by bubbling dried CO_2 through a solution containing dry methanol and sodium [30].

In this study, we investigated two carbon dioxide sequestration reactions for DEC synthesis (Figure 1). The first of these reactions can be broken down into two steps:
   a. Preparation of two potassium salts: potassium ethylcarbonate (PEC) as a hybrid carbonate and potassium bicarbonate ($KHCO_3$), according to an ionic pathway (Figure 1a).
   b. Alkylation of PEC in the presence of ethyl iodide (EtI) or acidified ethanol (EtOH/H^+) to obtain DEC (Figure 1b). EtI and EtOH/H^+ are co-reagents in the O-alkylation of PEC giving rise to an electrophilic alkyl group.

The second one reaction involves the direct mixing of ethanol, supercritical CO_2 and ethyl iodide in a one-pot process (Figure 1c). The best yields reported for ethanol conversion to date have not exceeded 0.6% [27].

a. $CH_3CH_2OH + CO_2 + K_2CO_3 \longrightarrow CH_3CH_2O\text{-}C(=O)\text{-}O^- K^+ + KHCO_3$

b. $CH_3CH_2O\text{-}C(=O)\text{-}O^- K^+$

$\xrightarrow{CH_3CH_2I} CH_3CH_2O\text{-}C(=O)\text{-}O\text{-}CH_2CH_3 + KI$

$\xrightarrow{CH_3CH_2OH\,/\,H^+} CH_3CH_2O\text{-}C(=O)\text{-}O\text{-}CH_2CH_3 + H_2O$

c. $CH_3CH_2OH + CO_2 + K_2CO_3 \xrightarrow{CH_3CH_2I} CH_3CH_2O\text{-}C(=O)\text{-}O\text{-}CH_2CH_3 + KI + KHCO_3$
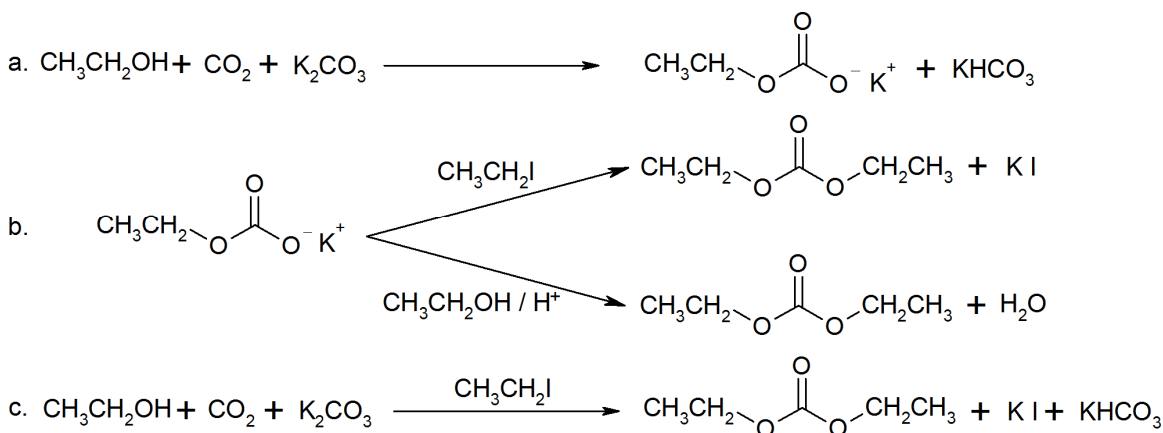
Figure 1: DEC synthesis from ethanol, carbon dioxide, potassium carbonate and a co-reactant

In this work, we used ethanol rather than methanol, and we assessed its reactivity with supercritical carbon dioxide. Ethanol was preferred over methanol as it is a highly abundant, non toxic biomolecule used in the production of biofuel and because it participates in the advantageous cycle reducing the greenhouse effect. For these reasons, carbon dioxide sequestration with ethanol is in keeping with most green chemistry principles. However, ethanol is less reactive than methanol, as it is less acidic [31].

2. Experimental procedures

Dimethyl and diethyl carbonates (99%), ethyl iodide ($\geq$ 99%), potassium carbonate ($\geq$ 99%) and Aliquat 336 (trioctylmethylammonium chloride, 88%) were all purchased from Sigma-Aldrich, France. Before use, potassium carbonate was dried for 48 hours at 104 °C. Anhydrous absolute ethanol was purchased from API, France. Compressed carbon dioxide was used in a specific installation purchased from Top-Industrie, France, and described in Figure 2.
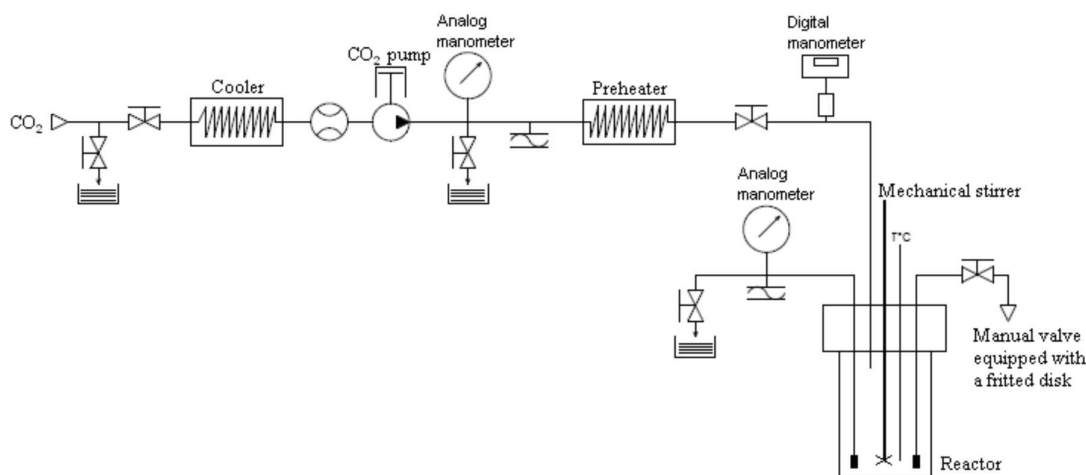
Figure 2: Experimental setup for reactions in supercritical CO_2

All experiments in the presence of supercritical CO_2 were carried out in a stainless steel autoclave with an internal volume of 200 ml equipped with a mechanical stirrer and a heating collar cooled by a vortex. The CO_2 is introduced into the reactor via a pneumatic pump, after heating to the required temperature. Pressure and temperature are kept constant with the aid of pressure and temperature regulators. All the parameters (temperature $\pm$ 0.1 °C, pressure $\pm$ 0.1 bar, stirring speed *ca.* 700 rpm, volume of CO_2 introduced $\pm$ 0.01 ml) were monitored and recorded. After the reaction, the reactor was cooled to *ca.* 10 °C by a vortex and bled via a manual valve equipped with a fritted disk.

Typical procedures are described below:

For the mixed carbonate synthesis method (procedure A), two different procedures were used for the first step:

Procedure A1: Ethanol (340 mmol) and K_2CO_3 (340 mmol) were loaded into the reactor. The autoclave was then heated to 100 °C and CO_2 was injected to the desired pressure with stirring. The desired pressure (*ca.* 80 bar) was reached within one minute.

Procedure A2: Ethanol (340 mmol) and K_2CO_3 (340 mmol) were loaded into the reactor. CO_2 was then injected into the reactor to a pressure of *ca.* 20 bar at room temperature. The autoclave was heated to 100°C at a rate of 5 °Cmin^{-1}. The pressure obtained was about 50 bar. Finally, CO_2 was injected to the desired pressure, with stirring.

For assessment of the reactivity of the mixed carbonate with a co-reactant (procedure B), experiments were carried out in a three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. The solid hybrid carbonate obtained during procedure A (30 g), was introduced in ethanol (50 ml) and the co-reactant solution was then via a dropping funnel once the desired temperature had been reached. The reaction was performed at 110 °C or -80 °C for 3 hours. Finally, once cold, the reaction medium was filtered to obtain a liquid phase and a solid, which was dried for 24 h in a vacuum at 104 °C.

For the one-pot reaction (procedure C), ethanol (856 mmol), C_2H_5I (107 mmol) and K_2CO_3 (107 mmol) were loaded into the reactor, into which CO_2 was then injected at a pressure of *ca.* 20 bar at room temperature. The autoclave was heated to 100 °C and CO_2 was injected to the desired pressure, with stirring.

The collected liquid phase was analyzed by infrared spectroscopy (JASCO, FT/IR 460 plus) and gas chromatography. Synthesized DEC and ethyl iodide were quantified with DMC as the internal standard. Methanol was used as the internal standard for diethyl ether (DEE) quantification. The solid hybrid carbonate was analyzed by infrared spectroscopy with FT-IR, CPMAS ^{13}C NMR (Bruker Avance 400WB) and by evaluating solid mass-gain.

The mass-gain MG(%) of the solid at the end of the reaction was determined as follows:

$$MG(\%) = \frac{m_1 - m_0}{m_0} \times 100 \qquad (1)$$

where m_0=mass of introduced K_2CO_3 (g), m_1= mass of dried solid phase (g). The theoretical mass-gain TMG(%) was defined by equation (2):

4

$$TMG(\%) = \frac{(n_{Et} \times M_{(EtOH+CO_2)})}{m_0} \times 100 \qquad (2)$$

where m_0 is the mass of introduced solid (g), n_E is the number of moles of introduced ethanol (mol), and $M_{(EtOH+CO_2)}$ is the molar weight of EtOH + the molar weight of CO_2 (gmol^{-1}).

The TMG(%) should be 65% if all the ethanol introduced has reacted with K_2CO_3 and CO_2 according to the reaction described in Figure 1a. We consider that the $KHCO_3$ formed to be in the solid phase, because it is insoluble in ethanol.

3. Results and discussion

For validation of the mechanism of this carbon dioxide sequestration reaction, in which PEC is formed as an intermediate (Figure 1), the two reaction steps were studied separately and then in a one-pot reaction.

3.1. Two-step reaction method

3.1.1. Carbon dioxide sequestration into a hybrid organic-inorganic carbonate (PEC)

Our research, based on green chemistry principles, led us to perform carbon dioxide sequestration in safer conditions (without the cogeneration of hydrogen gas), using ethanol and potassium carbonate.

The reactivity of carbon dioxide with ethanol and potassium carbonate was demonstrated by determining the mass-gain of the solid obtained after reaction (Table 1). Theoretically, the maximum mass-gain is 65% for a total sequestration reaction.

Entry	Base	Molar ratio (EtOH/K$_2$CO$_3$)	Temperature (°C)	Pressure (bar)	Time (min)	Mass-gain (%)
1	KHCO$_3$	1/1	100	80	180	-3
2	K$_2$CO$_3$	1/0.125	100	80	60	-3
3	K$_2$CO$_3$	1/1	100	80	5	8
4	K$_2$CO$_3$	1/1	100	80	20	10
5	K$_2$CO$_3$	1/1	100	80	45	11
6	K$_2$CO$_3$	1/1	100	80	60	14
7	K$_2$CO$_3$	1/1	100	80	120	56
8	K$_2$CO$_3$	1/1	100	80	180	58
9	K$_2$CO$_3$	1/1	100	80	360	61
10*	K$_2$CO$_3$	1/1	100	80	20	61
11	K$_2$CO$_3$	1/1	100	50	60	10

Operating conditions: 100°C and 80 bars with Procedure A1 or Procedure A2 (entry 10*).

Table 1: Effect of reaction time on the mass-gain of the solid product

An EtOH/K$_2$CO$_3$ molar ratio of 1/1 was required to respect the stoichiometry of the reaction, making it possible to obtain PEC and KHCO$_3$ (entry 2). During this reaction, the organized structure of the Lewis and Brönsted base (K$_2$CO$_3$) is disrupted by an exchange of the hydroxyl group proton from ethanol with the potassium cation.

As shown in Table 1, PEC yield was maximal in the presence of K_2CO_3 (entries 3 to 9), peaking two hours into the reaction. We accelerated the rate of reaction for this step by modifying the operating conditions for procedure A1 (section 2). With the second procedure, A2, a total reaction time of 30 minutes was required for sequestration of the carbon dioxide into PEC. With this method, the ethanolate generated from the ionic exchange between the base and ethanol is in contact with gaseous CO_2 during heating (*ca.* 10 minutes) and the reaction can start in subcritical CO_2 conditions. The mass gain in these conditions is slightly smaller than that in supercritical conditions (entry 6), when the reaction occurs with gaseous CO_2 (entry 11). Furthermore, the potassium bicarbonate ($KHCO_3$) produced did not react with ethanol and carbon dioxide due to a loss of the organized structure (monoclinic phase) of potassium carbonate [32]. Indeed, although potassium is complexed with eight oxygens in potassium carbonate and potassium bicarbonate, the additional hydrogen bonding in $KHCO_3$ results in dimeric bicarbonate units $[HCO_3]_2^{2-}$ capable of bidentate complexation [30]. Thus, hydrogen bonding controls the formation of complexes between the carbonate units and changes the structure established by van der Waals forces in K_2CO_3. It leads to a solid mass loss of 3% due to manipulation (entry 1 Table 1): potassium bicarbonate is not an efficient base for the sequestration of CO_2 in PEC synthesis.

The solid product containing PEC was initially characterized by infrared spectroscopy. Its FT-IR spectrum is shown in Figure 3, together with those of commercial potassium carbonate and commercial potassium bicarbonate.
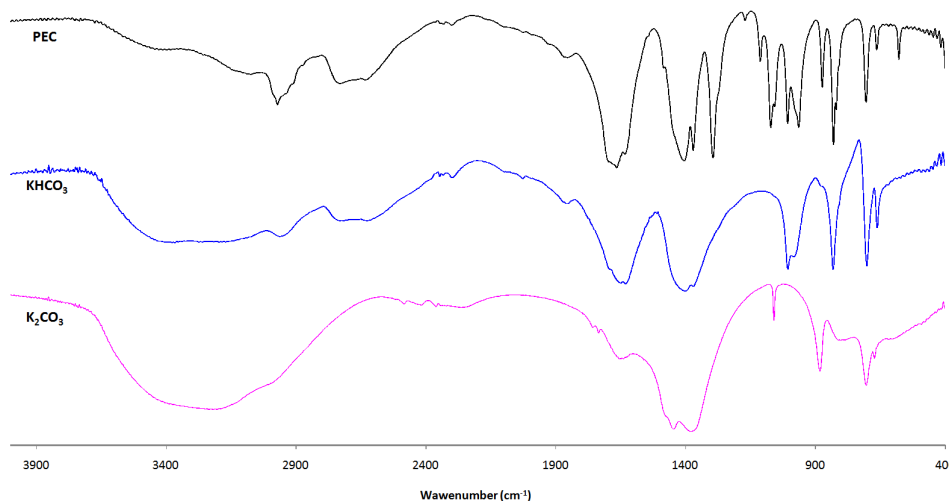

Figure 3: FTIR spectra of othe btained intermediate solid, KHCO$_3$ and K$_2$CO$_3$.

The characteristic absorption bands identified for the three products are shown in Table 2. A large O-H band is visible for K_2CO_3 and $KHCO_3$. Potassium carbonate is very hygroscopic and deliquesces rapidly. The hydration form of K_2CO_3 is known to depend on the synthesis procedure [32] (Figure 4). In the monoclinic structure, K_2CO_3 consists of $K_2CO_3 \cdot 1.5\ H_2O$ and traces of anhydrous carbonate. The active sites in its structure are H_2O, CO_3^{2-} and K^+.

$$K_2CO_3 \rightleftharpoons K_2CO_3 \cdot 0.5\ H_2O \rightleftharpoons K_2CO_3 \cdot 1.5\ H_2O \rightleftharpoons K_2CO_3 \cdot 5\ H_2O$$
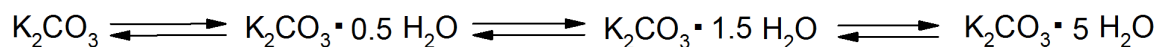
Figure 4: Potassium carbonate hydration form [22]

Stretching C-H bands (1294 and 874 cm^{-1}) and bending bands (2634 and 2971 cm^{-1}), characteristic of the presence of alkyl chains, were observed in the analyzed solid. Moreover, the presence of an organic carbonate was revealed by two large bands: one at *ca.* 1660 cm^{-1} (composite of 4 bands), corresponding to C=O vibration in the carbonate group, and the other at *ca.* 1400 cm^{-1} (a composite of two bands), corresponding to C-O vibration in the carbonate group. The C=O wavelength for the intermediate was lower than that for diethyl carbonate (1760 cm^{-1}) because PEC is an organic salt. Gatehouse *et al.* [33] showed that the separation of the C=O and C-O bands increases along the following series: basic salt < carbonate complex < organic acid < organic carbonate.

This difference between the C=O wavelengths of different compounds results from the structure and coordination of the molecules (Figure 5) [34]. The C-O distances and bond angles are between different carbonate molecules may differ considerably, due to the presence of different interactions in each structure [35]. For K$_2$CO$_3$, the CO$_3$ group coordinates one of the K atoms in a bidentate manner, and the other in a unidentate manner [36], whereas it coordinates K exclusively in a bidendate manner in PEC and KHCO$_3$, because of the resonance phenomenon (Figure 5).
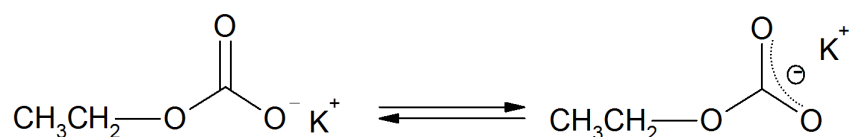

Figure 5: Resonance in potassium ethyl carbonate

These features account for the intensity of the characteristic band for the C=O bond in PEC falling below 1760 cm^{-1} and the intensity of the ether bond (C-O) exceeding 1376 cm^{-1}.

Vibration	Wavenumber (cm^{-1})		
	K$_2$CO$_3$	KHCO$_3$	Intermediate solid product
ν O-H	3218	3377	3417
ν_{as} C-H			3073
ν_{as} C-H			2971
ν O-H + ν_s C-H		2726	2730
ν O-H + ν_s C-H		2627	2634
ν_{as} C=O		1855	1853
ν_{as} C=O		1693	1698
ν_{as} C=O			1681
ν_{as} C=O	1655	1649	1665
ν_{as} C=O	1638	1631	1632
ν_s C-O	1446	1402	1406
ν_s C(-O)$_2^-$ + δ C-H	1378	1369	1371

δ C-H			1294
ν_{as} C-C(=O)-O			1171
ν_{as} C-O-C			1112
ν_{as} O-C-C			1072
δ C-O + δ C-H	1059	1006	1007
OCO_2	883	982	980
ν C-C			964
δ C-H			874
δ C-O		832	831
δ C-H			820
δ_{as} CO_2	704	701	704
O-C-O + δ OH	673	662	664

Table 2: Main IR bands of the intermediate solid obtained, commercial KHCO₃ and commercial K₂CO₃

Comparison of the IR spectra obtained for the commercial potassium carbonate, commercial potassium bicarbonate and the reaction product led to the identification of PEC and KHCO₃ in the solid product. For confirmation of this qualitative composition, we carried out CPMAS ¹³C NMR analysis. In our case, cross-polarization to study ¹³C functionality (CPMAS ¹³C NMR) was not quantitative, because of the poor signal-to-noise ratio. In Figure 6, two singlets can be observed, corresponding to the presence of an ethyl chain: at 15 ppm for the methyl group and 60 ppm for the CH₂ bound to oxygen. The other two signals correspond to the carbonyl group: one signal at 161 ppm is ascribed to the carbonyl group of KHCO₃ and the other, at 158 ppm, is ascribed to PEC.
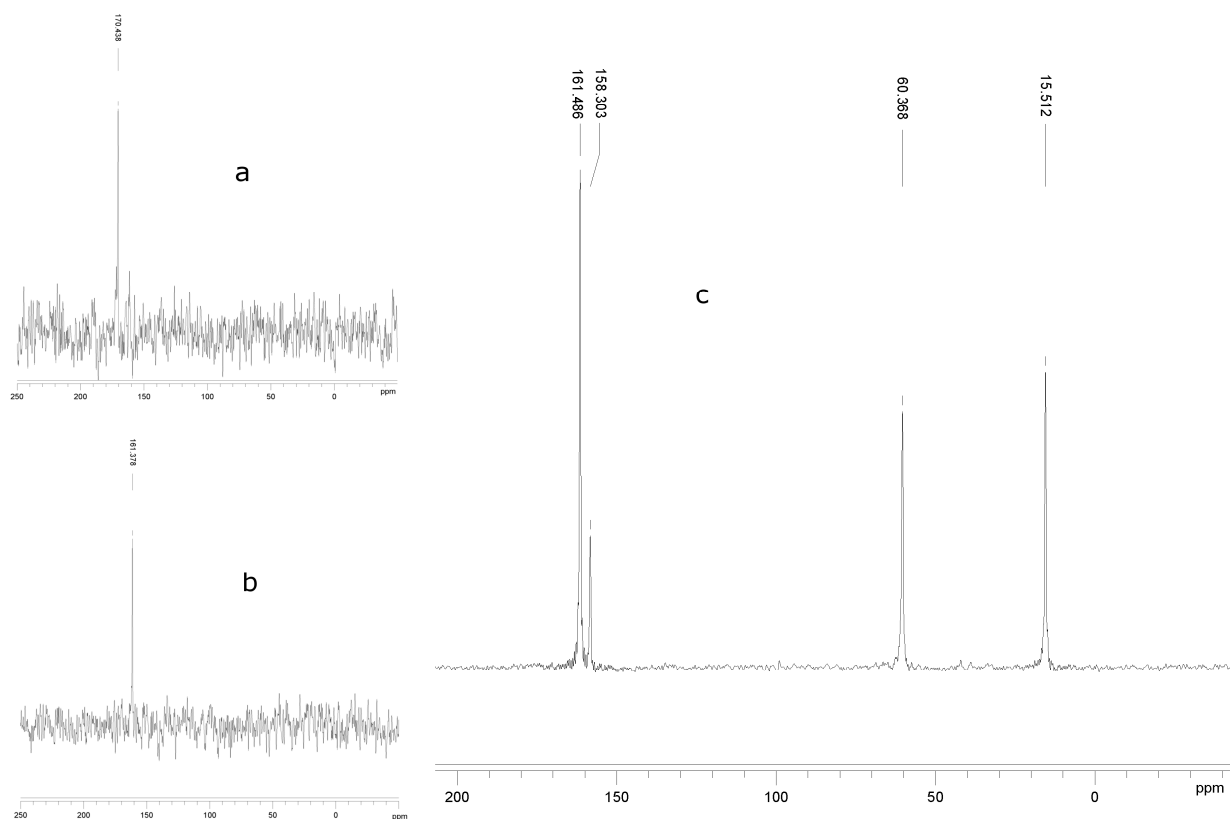

Figure 6: CPMAS ¹³C NMR spectra of K₂CO₃ (a), KHCO₃ (b) and the solid phase (c)

8

Correlations of the results of these analyses with mass-gain allowed us to draw conclusions concerning the sequestration of CO_2 in PEC and the exchange of protons and potassium cations between ethanol and potassium carbonate to form $KHCO_3$.

In this study, CO_2 was sequestrated by reaction with an equimolar amount of ethanol and potassium carbonate to produce a hybrid organic-inorganic carbonate. This hybrid can be used as a nucleophilic reagent for further reactions.

3.1.2. Reactions with the hybrid carbonate (PEC)

The second step of the carbon dioxide sequestration reaction to produce DEC from PEC was studied by PEC alkylation with iodoethane in ethanol and by PEC alkylation with ethanol in an acidic medium for ethanol dehydration (Figure 1b). The use of an acid rather than an alkyl halide for the second step of the reaction is advantageous as it is cheaper and less toxic and requires less effluent treatment at the end of the reaction. The number of co-reactant moles was at least as high as that for ethanol in the first step, given that ethanol reacted fully with CO_2 and K_2CO_3. The amount of acid used was determined on the basis of requirements for neutralization of the bases ($KHCO_3$ formed and, possibly, K_2CO_3) present in the solid particles obtained in the first step and ethanol dehydration. All reactions (entry 12-20) took place in a biphasic solid-liquid medium. The best results were obtained when iodoethane was used as the co-reagent (Table 3).

Entry	Reactant	n_{EtOH} (mmol)	$n_{meq\,H+}$ or n_{EtI} (mmol)	T (°C)	t (h)	n DEC (mmol)	n DEE (mmol)	% Yield DEC (K_2CO_3 basis)
12	EtI / EtOH	1800	206	110	4	7.1	3.5	5
13	EtI / EtOH / PTC[a]	1800	206	110	4	22.8	3.2	25
14	PTSA[b]	1800	45	110	3	0.4	0.3	0.3
15	H_2SO_4[c]	1800	400	110	3	0.1	0.2	0.1
16	H_2SO_4[c]	1800	3600	110	3	3.6	42.0	2.7
17	H_3PO_4[d]	1800	4000	110	3	0.2	0	0.1
18	HCl[e]	1800	3300	110	3	2.8	3.9	2
19	H_2SO_4[c]	1800	3600	- 80	3	3.1	17.4	2.3
20	HCl[e]	1800	3300	- 80	3	0	2.5	0

DEE: diethyl ether, DEC: diethyl carbonate, [a] PTC: 14 mmol Aliquat 336 (trioctylmethyl chloride), [b] PTSA: p-toluene sulfonic acid ($\geq$ 98.5%), [c] H_2SO_4 ($\geq$ 98%), [d] H_3PO_4 ($\geq$ 85%), [e] HCl ($\geq$ 37%).

Table 3: Effect of the co-reactant on the formation of DEC from the PEC synthesized (Table 1, entry 8)

DEC was synthesized with a low yield (5%) in the presence of iodoethane. Infrared analysis on the solid phase at the end of the reaction with EtI indicated the persistent presence of PEC. This second step of the reaction, using EtI, is probably the limiting step. The presence of diethyl ether (DEE) at the end of the reaction may result from nucleophilic attacks on the protonated alcohol CH_3-CH_2-O^+H_2 by ethanol [37]. A phase transfer catalyst was used to promote the reaction between reactants in the solid (PEC) and liquid (ethyl iodide) phases. As expected, the addition of Aliquat 336 to the reaction medium as a phase transfer catalyst increased yield from 5 to 25% (entry 13). The addition of this catalyst favors contact between the two phases, as shown in the reaction mechanism proposed in Figure 7.
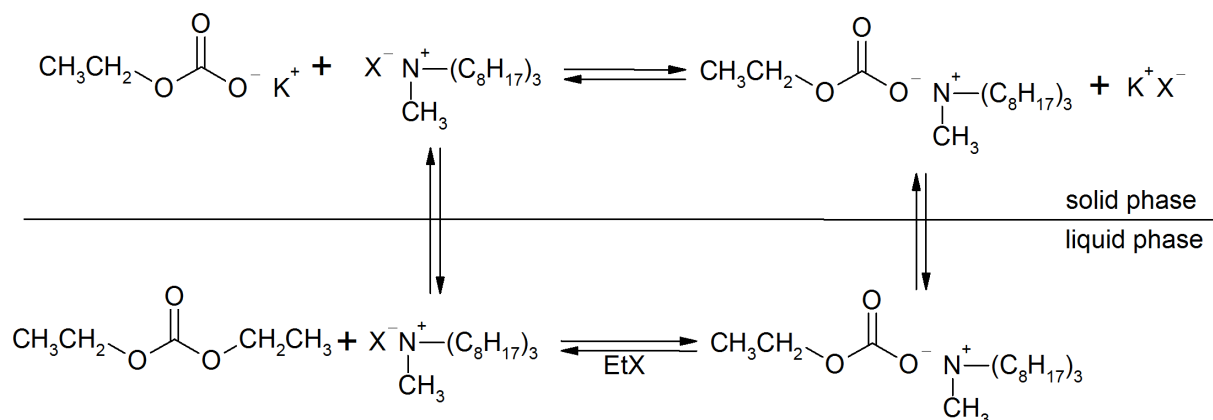
Figure 7: Mechanism of phase transfer catalysis at the solid/liquid interface

We tested several Brönsted acids (entries 14-18), but only concentrated strong acids produced DEC, through attacks on the ethyl carbonate anion of protonated ethanol (CH_3-CH_2-O^+H_2). Thus, although PEC is more basic than ethanol, concentrated strong Brönsted acids protonate a small fraction of ethanol to form CH_3-CH_2-O^+H_2, which is transformed by an SN_2 reaction with PEC into DEC and H_2O. The yields of DEC synthesis were low, probably due to competition with PEC protonation for formation of the monoethyl ester of carbonic acid [$CH_3CH_2OC(O)OH$] [38]. This molecule reacts with the hydroxy moiety OH^-, as described by Dibenedetto et $al.$ [39]. This results in carbon dioxide being inserted into potassium bicarbonate (Figure 8). The monoethyl ester of carbonic acid is not easily decarboxylated to form ethanol and CO_2 as this reaction has a very high dissociation energy [39].
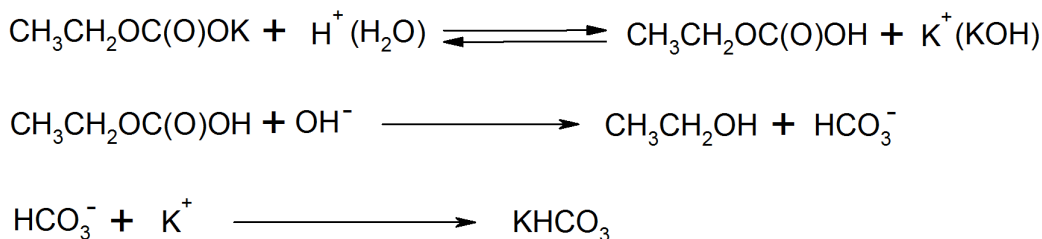

Figure 8: Reaction of PEC in an acidic medium

The use of concentrated strong acids also leads to the production of larger amounts of diethyl ether, due to the SN_2 reaction between ethanol and protonated ethanol (CH_3-CH_2-O^+H_2). Whatever the temperature, this reaction predominates, preventing the further sequestration of carbon dioxide (entries 15-20).

Finally, this two-step synthesis method leads to the capture of CO_2 in DEC. The first step involves the production of hybrid carbonate (PEC) from non toxic raw materials (ethanol, K_2CO_3, CO_2) and the second step consists of the reaction of PEC with ethyl iodide. In the presence of PTC, the global yield of PEC is 25%, based on the initial amount of K_2CO_3. Unfortunately, the use of a concentrated acid with the hybrid results in competition between potassium bicarbonate synthesis through the release of ethanol and organic carbonate synthesis. However, carbon dioxide is sequestered in both these reactions.

3.2. Carbon dioxide sequestration into an organic carbonate

Carbon dioxide can be sequestered in the form of organic carbonate via the one-pot synthesis of DEC. The synthesis of dimethyl carbonate from an alcohol (methanol) and an alkyl halide (iodomethane) has been studied by several authors. The optimum conditions for the synthesis of DMC are reported in Table 4. Only Fujita *et al.* [27] used these conditions for DEC production. Given the low yields obtained, we have modified some experimental parameters (entries 5 and 6).

| Entry	Reactant	n ROH (mmol)	n RX (mmol)	Molar ratio (ROH/RX/K$_2$CO$_3$)	T (°C)	P (bar)	t (h)	% Yield DAC (RX basis)
1 [23]	MeOH/MeI	192	24	64/8/1	100	>> 50 (n.a.[a])	2	50
2 [27]	MeOH/MeI	200	24	67/8/1	70	80	4	17
3 [27]	EtOH/EtI	200	24	67/8/1	70	80	4	0.6
4 [24]	MeOH/MeI	3730	160	64/3/1	90	70	n.a.[a]	53
5	EtOH/EtI	846	108	64/8/1	110	80	5	8
6	EtOH/EtI	846	108	8/1/1	110	80	5	46

ROH: alcohol, RX: alkyl halide, DAC: dialkyl carbonate, [a] n.a.: not available

Table 4: Effect of the experimental conditions on the yield of DAC

The use of equimolar amounts of potassium carbonate and iodoethane increased DEC yield by a factor of six (Table 4), indicating that K$_2$CO$_3$ is a reactant and not a catalyst. Its reaction with ethanol generates a deactivated base: KHCO$_3$.K$_2$CO$_3$ can be regenerated by reaction with potassium iodide (figure 10d) or downgraded in the presence of hydrogen iodide. Ethyl iodide is a reactant and not a catalyst, as proposed by Fang *et al.* [23] and by Cai *et al.* [25]. Ethyl iodide is soluble in ethanol, which is considered to be the solvent. Ethyl iodide should be less reactive with the organic-inorganic carbonate hybrid than methyl iodide, according to the SN$_2$ mechanism. There is greater steric hindrance with ethyl iodide and the electrophilic character of the alkyl group of ethyl iodide dissolved in ethanol is less marked than that of methyl iodide dissolved in methanol, due to the lower dissociation power of ethanol than of methanol [31].

However, the mixture of ethanol and ethyl iodide is swollen [40] by the CO$_2$, increasing the reactivity of the different species, for example, the reactivity of EtOH with CO$_2$ and that of PEC with EtI. The reaction medium is triphasic at the start of the reaction. It consists of supercritical CO$_2$, a liquid mixture of ethanol and ethyl iodide. As observed by Fujita *et al.* [27], CO$_2$ is then solubilized in the liquid phase and swells the volumes of both reactants. This increases reactivity.

Kinetic studies (Figure 9) showed that the production of DEC and DEE increased rapidly with time over the first two hours, reaching a maximum after five hours of reaction.
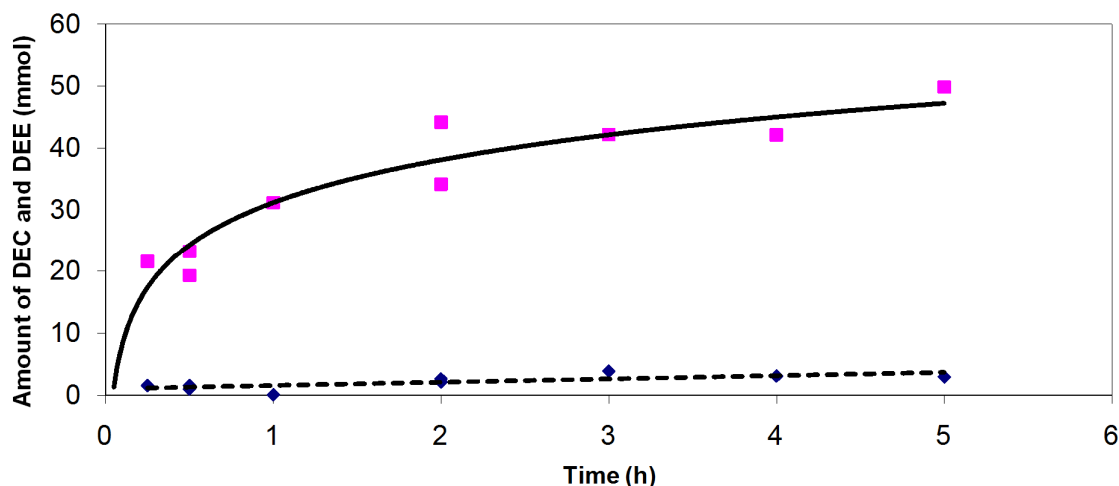
DEE: diethyl ether, DEC: diethyl carbonate

Figure 9: Concentration-time profiles for DEC (straight line) and DEE (dotted line)

An analysis of the two phases obtained at the end of the reaction provided insight into the reasons for the limited amount of diethyl carbonate produced (less than 50%). These two phases had the following characteristics:

1. The orange color of the liquid phase recovered after 5 hours of reaction was correlated with its UV absorbance, indicating the presence of iodine. Iodine is released when ethyl iodide consumption exceeds the sum of the amounts of DEC and DEE produced (see Table 5). There may be two reasons for this excess consumption. Ethyl iodide may be broken down by heat to generate hydrogen iodide (HI) and then iodine [41], or it may be dehydrohalogenated by EtO^-K^+ as a strong base, according to an E_2 mechanism (Figure 10b).

2. The infrared spectrum of the solid obtained after 5 hours reaction was the same as that obtained at the end of the first step. Thus, the PEC produced did not react completely with ethyl iodide to form DEC.

Other experiments were performed to increase yields and to study the proposed reaction mechanism further (Table 5).

Entry	Reactant	Molar ratio	T (°C)	P (bar)	t (h)	n DEE (mmol)	n DEC (mmol)	Conversion EtI (%)	% Yield DEC (EtI basis)
6	EtOH / EtI / K$_2$CO$_3$	8/1/1	110	80	5	3.0	50	97.6	46
7 [a]	EtOH / EtI / K$_2$CO$_3$	8/1/1	110	0	5	15	0.1	86.7	0.1
8	EtI / K$_2$CO$_3$	2/1	110	80	5	n.d. [d]	0.4	82.5	0.2
9 [b]	EtOH / EtOK / EtI	6/1/1	110	80	5	8.9	32	95.5	30
10	MeOH / EtI / K$_2$CO$_3$	8/1/1	110	80	5	n.d. [d]	0.1	98.7	0.1 (*ca.* 14) [e]
11 [c]	EtOH / EtI / K$_2$CO$_3$ / PTC	8/1/1/0.2	110	80	5	2.6	55	99.5	51

DEE: diethyl ether, DEC: diethyl carbonate, [a] without CO$_2$, [b] 24% w/w EtOK in EtOH, [c] PTC: Aliquat 336, [d] not detected, [e] relative % of ethyl methyl carbonate (EMC).

Table 5: Effect of operating conditions on yield and selectivity of the reaction

Entries 7-8 (Table 5) show that the carbonyl group introduced during the formation of DEC comes from carbon dioxide and not from potassium carbonate. Without CO_2, the main product formed was diethyl ether, rather than DEC, as indicated in the proposed mechanism (Figure 10). The very small amount of DEC produced in this case indicates that the carbonate ion of K_2CO_3 is involved in the reaction, but does not make a significant contribution. Without ethanol, only a very small amount of DEC can be produced by the O-alkylation of potassium carbonate with two equivalents of ethyl iodide in supercritical carbon dioxide (entry 8).
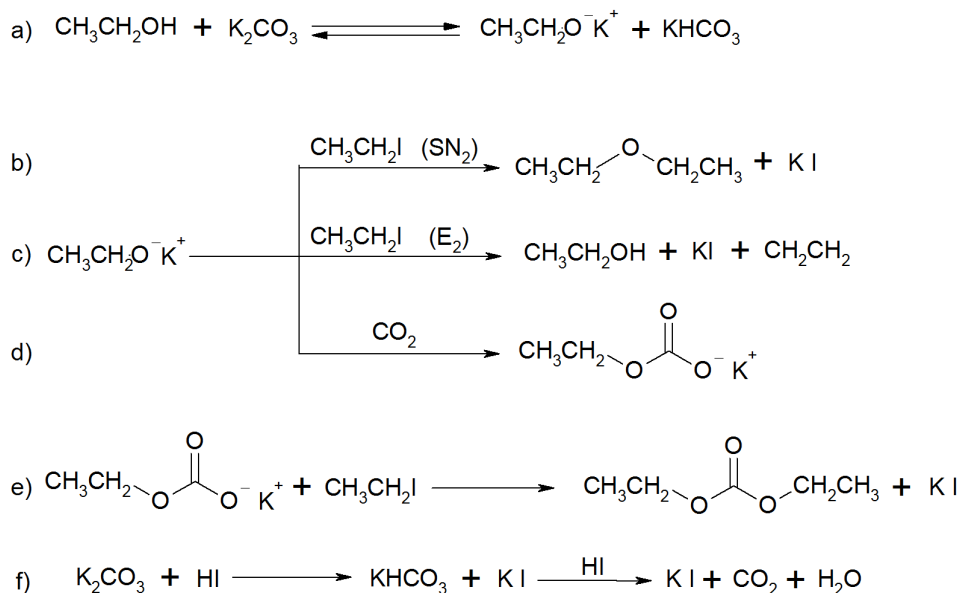
a) $CH_3CH_2OH + K_2CO_3 \rightleftharpoons CH_3CH_2O^- K^+ + KHCO_3$

b) CH_3CH_2I (SN_2) $\rightarrow$ $CH_3CH_2\text{-}O\text{-}CH_2CH_3 + KI$

c) $CH_3CH_2O^- K^+$ ⸻ CH_3CH_2I (E_2) $\rightarrow$ $CH_3CH_2OH + KI + CH_2CH_2$

d) CO_2 $\rightarrow$ $CH_3CH_2\text{-}O\text{-}C(=O)\text{-}O^- K^+$

e) $CH_3CH_2\text{-}O\text{-}C(=O)\text{-}O^- K^+ + CH_3CH_2I \longrightarrow CH_3CH_2\text{-}O\text{-}C(=O)\text{-}O\text{-}CH_2CH_3 + KI$

f) $K_2CO_3 + HI \longrightarrow KHCO_3 + KI \xrightarrow{HI} KI + CO_2 + H_2O$

Figure 10: Proposed reaction mechanism: competition between carbonate and ether formation

The basicity of the catalyst affects the reaction process rather than the carbonate ions [23]. Potassium carbonate basicity leads to the formation of ethanolate (EtO^-), which carries out nucleophilic attack on CO_2, generating PEC. The presence of the ethanolate at the start of the reaction (entry 9, Table 5) led to the formation of larger amounts of ether, due to competition between the parallel reactions (Figure 10b-d). More diethyl ether was produced because the concentration of ethanolate is higher in the reaction medium when a solution of potassium ethanolate in ethanol is used at the start of the reaction. However, in the experimental conditions used for entry 6 (Table 5), the ethanolate reacted with carbon dioxide as soon as it was produced. As demonstrated in the study of the first step of the reaction, PEC production was complete after 20 minutes of reaction at 100°C.

The mechanism shown in Figure 10 was confirmed by the production of a mixed organic carbonate (ethyl methyl carbonate, EMC) with methanol and ethyl iodide (containing two different alkyl chains).

As expected from the results of the study of the second step, the use of a phase transfer catalyst resulted in a small increase in DEC production, with no change in the amount of DEE produced (entry 11 and 6). Aliquat 336 was less effective in the one-pot reaction than in the two-step reaction (Figure 7), because its role in the one-pot reaction is secondary, with interaction phenomena due to the swelling of the reactants playing a much more important role. Similar quantities of DEE were produced in the presence and absence of Aliquat 336. This CTP did not affect the reaction of ethanolate with ethanol, because this reaction occurred in a homogeneous liquid medium.

Comparison of the yields of DEC produced when EtI was used as a co-reactant in the one-pot and two-step reactions showed that the one-pot synthesis reaction gave the best results. Thus, performing

the entire reaction in a supercritical CO_2 medium accelerates the rate of the DEC formation. The supercritical CO_2 solubilized in the liquid phase containing ethanol and ethyl iodide favors interactions between EtOH and CO_2 and between PEC and ethyl iodide by swelling the reactants. It therefore acts as a compatibilizing agent and a swelling solvent.

4. Conclusion

We studied the synthesis of diethyl carbonate (DEC) from ethanol and supercritical CO_2 in the presence of potassium carbonate and a co-reagent (ethyl iodide or concentrated acidic alcoholic solution) by two processes: a direct "one-pot" procedure and an indirect two-step procedure. The two-step procedure led to the isolation of a reaction intermediate, potassium ethyl carbonate (PEC), which was characterized by infrared spectrometry and ^{13}C NMR. This hybrid carbonate was then used as a nucleophilic agent for the second step of the reaction, the O-alkylation of PEC to generate DEC.

Studies of the synthesis of DEC with EtI showed that the second step was limiting for the synthesis of DEC. We also identified other reactions competing with the O-alkylation reaction of PEC (SN_2), such as the etherification of ethanolate (produced by the reaction of ethanol with the base K_2CO_3) and the EtI dehydrohalogenation reaction, according to an E_2 elimination mechanism.

The reaction of PEC with a concentrated alcoholic solution of a strong acid as a co-reactant made it possible to prepare DEC for the first time. Admittedly, the yields obtained with this method were low, but this method is more compatible with the principles of green chemistry. It will be used in future studies based on superacids and polyoxygenated reagents such as orthoesters or ketals.

The study of the effect of the operating conditions for each of the procedures on the yield and selectivity of the reaction (diethyl carbonate versus diethyl ether) showed that the one-pot procedure favored the synthesis of DEC. Indeed,
 the O-alkylation of PEC is favored when the reaction occurs in supercritical carbon dioxide, because the reactants are in the swelling solvent, CO_2. The use of a PTC increased the production yield of DEC without increasing the amount of DEE produced. However, the one-pot synthesis procedure is too inefficient for industrial use. Further work, involving an exhaustive study of the reaction with a PTC, is required to increase reaction yields.

In this study, carbon dioxide was captured in two forms: an organic carbonate and an organic-inorganic hybrid that could be reused without purification for the synthesis of organic carbonates.

References

[1]   B. Metz, Carbon dioxide capture and storage, IPCC special report. ed., IPCC, 2006.

[2]   M. Aresta,A. Dibenedetto, Utilisation of CO_2 as a chemical feedstock: opportunities and challenges, Dalton Transactions (2007) 2975-2992.

[3]   H. J. Herzog, What future for carbon capture and sequestration?, Environmental Science and Technology 35 (2001) 148A-153A.

[4]   M. Kharoune, J. Lavoie,Y. Comeau, Use of alkaline materials for sequestering and recycling of carbon dioxide, Patent CA 2 469 974, 2005.

[5]   A. G. Heyden, Patent DE 109933, 1900.

[6]   U. Romano, R. Tesei, M. M. Mauri,P. Rebora, Synthesis of dimethyl carbonate from methanol, carbon monoxide, and oxygen catalyzed by copper compounds, Industrial & Engineering Chemistry Product Research and Development 19 (1980) 396-403.

[7]   U. Romano, N. Dimuzio,F. Rivetti, Dimethyl carbonate, Patent BE 80-203043 886495, 1981.

[8]   B. M. Bhanage, S.-i. Fujita, Y. Ikushima,M. Arai, Synthesis of dimethyl carbonate and glycols from carbon dioxide, epoxides, and methanol using heterogeneous basic metal oxide catalysts with high activity and selectivity, Applied Catalysis, A: General 219 (2001) 259-266.

[9]   J.-S. Tian, C.-X. Miao, J.-Q. Wang, F. Cai, Y. Du, Y. Zhao,L.-N. He, Efficient synthesis of dimethyl carbonate from methanol, propylene oxide and CO_2 catalyzed by recyclable inorganic base/phosphonium halide-functionalized polyethylene glycol, Green Chemistry 9 (2007) 566-571.

[10]   D. Ballivet-Tkatchenko, O. Douteau,S. Stutzmann, Reactivity of Carbon Dioxide with n-Butyl(phenoxy)-, (alkoxy)-, and (oxo)stannanes: Insight into Dimethyl Carbonate Synthesis, Organometallics 19 (2000) 4563-4567.

[11]   A.-A. G. Shaikh,S. Sivaram, Organic Carbonates, Chemical Reviews (Washington, D. C.) 96 (1996) 951-976.

[12]   T. Sakakura, J.-C. Choi,H. Yasuda, Transformation of Carbon Dioxide, Chemical Reviews (Washington, DC, United States) 107 (2007) 2365-2387.

[13]   P. T. Anastas,M. M. Kirchhoff, Origins, current status, and future challenges of green chemistry, Accounts of Chemical Research 35 (2002) 686-694.

[14]   S. Sakai, T. Fujinami, T. Yamada,S. Furusawa, Reaction of organotin alkoxides with carbon disulfide, carbony sulfide, or carbon dioxide, Nippon Kagaku Kaishi (1975) 1789-1794.

[15]   N. Yamazaki, S. Nakahama,F. Higashi, Chemical reactions of carbon dioxide, Kenkyu Hokoku - Asahi Garasu Kogyo Gijutsu Shoreikai 33 (1978) 31-45.

[16]   J. Kizlink, Synthesis of dimethyl carbonate from carbon dioxide and methanol in the presence of organotin compounds, Collection of Czechoslovak Chemical Communications 58 (1993) 1399-1402.

[17]   J. Kizlink,I. Pastucha, Preparation of dimethyl carbonate from methanol and carbon dioxide in the presence of Sn(IV) and Ti(IV) alkoxides and metal acetates, Collection of Czechoslovak Chemical Communications 60 (1995) 687-692.

[18]   D. Ballivet-Tkatchenko, T. Jerphagnon, R. Ligabue, L. Plasseraud,D. Poinsot, The role of distannoxanes in the synthesis of dimethyl carbonate from carbon dioxide, Applied Catalysis, A: General 255 (2003) 93-99.

[19]   K. Tomishige, Y. Ikeda, T. Sakaihori,K. Fujimoto, Catalytic Properties and Structure of Zirconia Catalysts for Direct Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide, Journal of Catalysis 192 (2000) 355-362.

[20]   Y. Ikeda, T. Sakaihori, K. Tomishige,K. Fujimoto, Promoting effect of phosphoric acid on zirconia catalysts in selective synthesis of dimethyl carbonate from methanol and carbon dioxide, Catalysis Letters 66 (2000) 59-62.

[21]   K. Tomishige, T. Sakaihori, Y. Ikeda,K. Fujimoto, A novel method of direct synthesis of dimethyl carbonate from methanol and carbon dioxide catalyzed by zirconia, Catalysis Letters 58 (1999) 225-229.

[22]   T. Zhao, Y. Han,Y. Sun, Novel reaction route for dimethyl carbonate synthesis from CO_2 and methanol, Fuel Processing Technology 62 (2000) 187-194.

[23]   S. Fang,K. Fujimoto, Direct synthesis of dimethyl carbonate from carbon dioxide and methanol catalyzed by base, Applied Catalysis, A: General 142 (1996) L1-L3.

[24]   F.-h. Cao, D.-y. Fang, D.-h. Liu,W.-y. Ying. Catalytic esterification of carbon dioxide and methanol for the preparation of dimethyl carbonate. in ACS Symposium Series. 2003, 159-167.

[25]   Q. Cai, C. Jin, B. Lu, H. Tangbo,Y. Shan, Synthesis of Dimethyl Carbonate from Methanol and Carbon dioxide using Potassium Methoxide as Catalyst under Mild Conditions, Catalysis Letters 103 (2005) 225-228.

[26]   Z. Hou, B. Han, Z. Liu, T. Jiang,G. Yang, Synthesis of dimethyl carbonate using CO_2 and methanol: enhancing the conversion by controlling the phase behavior, Green Chemistry 4 (2002) 467-471.

[27]   S.-i. Fujita, B. M. Bhanage, M. Arai,Y. Ikushima, Synthesis of dimethyl carbonate from carbon dioxide and methanol in the presence of methyl iodide and base catalysts under mild conditions: effect of reaction conditions and reaction mechanism, Green Chemistry 3 (2001) 87-91.

[28]   R. Howe, Carbonic Acid and its Derivatives, in Rodd's chemistry of carbon compounds, Elsevier Publishing Co., Editor. 1965: New York. p. 268.

[29] A. Adam,V. Cirpus, Crystal structure of potassium monomethylcarbonate, Zeitschrift fuer Anorganische und Allgemeine Chemie 620 (1994) 1702-1706.

[30] M. Kunert, P. Wiegeleben, H. Gorls,E. Dinjus, Novel arrangement of methyl carbonate units: x-ray crystal structure of sodium methyl carbonate, Inorganic Chemistry Communications 1 (1998) 131-133.

[31] J. Murto, Nucleophilic reactivity of alkoxide ions towards 2,4-dinitrofluorobenzene and the acidity of alcohols, Acta Chemica Scandinavica 18 (1964) 1043-1053.

[32] L. Carbonnel, R. Cohen-Adad,A. P. Rollet, The water-potassium carbonate system, Compt. rend. 248 (1959) 413-416.

[33] B. M. Gatehouse, S. E. Livingstone,R. S. Nyholm, The infrared spectra of some simple and complex carbonates, Journal of the Chemical Society (1958) 3137-3142.

[34] K. Nakamoto, Infrared spectra of inorganic and coordination compounds, (1963) 169-171.

[35] I. Nitta, Y. Tomiie,C. H. Koo, Crystal structure of potassium bicarbonate, Acta Crystallographica 5 (1952) 292.

[36] J. S. Ogden,S. J. Williams, Matrix isolation studies on cesium, rubidium, and potassium carbonates. The shape of molecular potassium carbonate, Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1981) 456-462.

[37] T. D. Fridgen,T. B. McMahon, Enthalpy Barriers for Asymmetric SN2 Alkyl Cation Transfer Reactions between Neutral and Protonated Alcohols, Journal of Physical Chemistry A 107 (2003) 668-675.

[38] G. A. Olah,A. M. White, Stable carbonium ions. LXIV. Protonated carbonic acid (trihydroxycarbonium ion) and protonated alkyl (aryl) carbonates and hydrogen carbonates, and their cleavage to protonated carbonic acid and carbonium ions. The possible role of protonated carbonic acid in biological carboxylation processes, Journal of the American Chemical Society 90 (1968) 1884-1889.

[39] A. Dibenedetto, M. Aresta, P. Giannoccaro, C. Pastore, I. Papai,G. Schubert, On the existence of the elusive monomethyl ester of carbonic acid [$CH_3OC(O)OH$] at 300 K: ^{1}H- and ^{13}C NMR measurements and DFT calculations, European Journal of Inorganic Chemistry (2006) 908-913.

[40] K. N. West, C. Wheeler, J. P. McCarney, K. N. Griffith, D. Bush, C. L. Liotta,C. A. Eckert, In Situ Formation of Alkylcarbonic Acids with CO_2, Journal of Physical Chemistry A 105 (2001) 3947-3948.

[41] A. Maccoll, Heterolysis and the Pyrolysis of Alkyl Halides in the Gas Phase, Chemical Reviews (Washington, D. C.) 69 (1969) 33-60.