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To cite this version:

Fabien Gasc, Sophie Thiebaud-Roux, Zephirin Z. Mouloungui. Methods for synthesizing diethyl carbonate from ethanol and supercritical carbon dioxide by one-pot or two-step reactions in the presence of potassium carbonate. Journal of Supercritical Fluids, 2009, 50 (1), pp.46-53. 10.1016/j.supflu.2009.03.008. hal-02669095

HAL Id: hal-02669095
https://hal.inrae.fr/hal-02669095
Submitted on 31 May 2020

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

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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].
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 (≥ 99%), potassium carbonate (≥ 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.
All experiments in the presence of supercritical CO₂ 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 CO₂ 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 ± 0.1 °C, pressure ± 0.1 bar, stirring speed ca. 700 rpm, volume of CO₂ introduced ± 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 K₂CO₃ (340 mmol) were loaded into the reactor. The autoclave was then heated to 100 °C and CO₂ 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 K₂CO₃ (340 mmol) were loaded into the reactor. CO₂ 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 °C min⁻¹. The pressure obtained was about 50 bar. Finally, CO₂ 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), C₂H₅I (107 mmol) and K₂CO₃ (107 mmol) were loaded into the reactor, into which CO₂ was then injected at a pressure of ca. 20 bar at room temperature. The autoclave was heated to 100 °C and CO₂ 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 ¹³C 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:

\[ MG(\%) = \frac{m_1 - m_0}{m_0} \times 100 \]  

(1)

where \( m_0 \) = mass of introduced K₂CO₃ (g), \( m_1 \) = mass of dried solid phase (g). The theoretical mass-gain TMG(%) was defined by equation (2):
\[
TMG(\%) = \frac{n_E \times M_{(\text{EtOH}+\text{CO}_2)}}{m_0} \times 100
\]  

(2)

where \(m_0\) is the mass of introduced solid (g), \(n_E\) is the number of moles of introduced ethanol (mol), and \(M_{(\text{EtOH}+\text{CO}_2)}\) 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\(_2\)CO\(_3\) 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.

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

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 K₂CO₃ (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 CO₂ during heating (ca. 10 minutes) and the reaction can start in subcritical CO₂ conditions. The mass gain in these conditions is slightly smaller than that in supercritical conditions (entry 6), when the reaction occurs with gaseous CO₂ (entry 11). Furthermore, the potassium bicarbonate (KHCO₃) 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 KHCO₃ results in dimeric bicarbonate units [HCO₃]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 K₂CO₃. 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 CO₂ 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.

![FTIR spectra](image)

**Figure 3: FTIR spectra of obtained intermediate solid, KHCO₃ and K₂CO₃.**

The characteristic absorption bands identified for the three products are shown in Table 2. A large O-H band is visible for K₂CO₃ and KHCO₃. Potassium carbonate is very hygroscopic and deliquesces rapidly. The hydration form of K₂CO₃ is known to depend on the synthesis procedure [32] (Figure 4). In the monoclinic structure, K₂CO₃ consists of K₂CO₃,1.5 H₂O and traces of anhydrous carbonate. The active sites in its structure are H₂O, CO₃²⁻ and K⁺.
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 bidentate manner in PEC and KHCO\(_3\), because of the resonance phenomenon (Figure 5).

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\(^{-1}\).

<table>
<thead>
<tr>
<th>Vibration</th>
<th>K(_2)CO(_3)</th>
<th>KHCO(_3)</th>
<th>Intermediate solid product</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν O-H</td>
<td>3218</td>
<td>3377</td>
<td>3417</td>
</tr>
<tr>
<td>ν(_{as}) C-H</td>
<td></td>
<td>3073</td>
<td></td>
</tr>
<tr>
<td>ν(_{as}) C-H</td>
<td></td>
<td>2971</td>
<td></td>
</tr>
<tr>
<td>ν O-H + ν(_s) C-H</td>
<td>2726</td>
<td>2730</td>
<td></td>
</tr>
<tr>
<td>ν O-H + ν(_s) C-H</td>
<td>2627</td>
<td>2634</td>
<td></td>
</tr>
<tr>
<td>ν(_{as}) C=O</td>
<td>1855</td>
<td>1853</td>
<td></td>
</tr>
<tr>
<td>ν(_{as}) C=O</td>
<td>1693</td>
<td>1698</td>
<td></td>
</tr>
<tr>
<td>ν(_{as}) C=O</td>
<td></td>
<td>1681</td>
<td></td>
</tr>
<tr>
<td>ν(_{as}) C=O</td>
<td></td>
<td>1655</td>
<td>1665</td>
</tr>
<tr>
<td>ν(_{as}) C=O</td>
<td></td>
<td>1638</td>
<td>1632</td>
</tr>
<tr>
<td>ν(_s) C-O</td>
<td>1446</td>
<td>1402</td>
<td>1406</td>
</tr>
<tr>
<td>ν(_s) C(-O)(_2)^- + δ C-H</td>
<td>1378</td>
<td>1369</td>
<td>1371</td>
</tr>
</tbody>
</table>
 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 KHCO$_3$ in the solid product. For confirmation of this qualitative composition, we carried out CPMAS $^{13}$C NMR analysis. In our case, cross-polarization to study $^{13}$C functionality (CPMAS $^{13}$C 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 CH$_2$ bound to oxygen. The other two signals correspond to the carbonyl group: one signal at 161 ppm is ascribed to the carbonyl group of KHCO$_3$ and the other, at 158 ppm, is ascribed to PEC.

Table 2: Main IR bands of the intermediate solid obtained, commercial KHCO$_3$ and commercial K$_2$CO$_3$

\[
\begin{array}{cccc}
\text{δ C-H} & 1294 \\
v_{\text{as}} C-C(=O)-O & 1171 \\
v_{\text{as}} C-O-C & 1112 \\
v_{\text{as}} O-C-C & 1072 \\
\text{δ C-O + δ C-H} & 1059 & 1006 & 1007 \\
OCO_2 & 883 & 982 & 980 \\
v C-C & 964 \\
δ C-H & 874 \\
δ C-O & 832 & 831 \\
δ C-H & 820 \\
δ_{\text{as}} CO_2 & 704 & 701 & 704 \\
O-C-O + δ OH & 673 & 662 & 664 \\
\end{array}
\]

Figure 6: CPMAS $^{13}$C NMR spectra of K$_2$CO$_3$ (a), KHCO$_3$ (b) and the solid phase (c)
Correlations of the results of these analyses with mass-gain allowed us to draw conclusions concerning the sequestration of CO₂ in PEC and the exchange of protons and potassium cations between ethanol and potassium carbonate to form KHCO₃.

In this study, CO₂ 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 CO₂ and K₂CO₃. The amount of acid used was determined on the basis of requirements for neutralization of the bases (KHCO₃ formed and, possibly, K₂CO₃) 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-reactant (Table 3).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant</th>
<th>n_{EtOH} (mmol)</th>
<th>n_{meq H+ or n_{EtI}} (mmol)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>n DEC (mmol)</th>
<th>n DEE (mmol)</th>
<th>% Yield DEC (K₂CO₃ basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>EtI / EtOH</td>
<td>1800</td>
<td>206</td>
<td>110</td>
<td>4</td>
<td>7.1</td>
<td>3.5</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>EtI / EtOH / PTC</td>
<td>1800</td>
<td>206</td>
<td>110</td>
<td>4</td>
<td>22.8</td>
<td>3.2</td>
<td>25</td>
</tr>
<tr>
<td>14</td>
<td>PTSA</td>
<td>1800</td>
<td>45</td>
<td>110</td>
<td>3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>15</td>
<td>H₂SO₄</td>
<td>1800</td>
<td>400</td>
<td>110</td>
<td>3</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>16</td>
<td>H₂SO₄</td>
<td>1800</td>
<td>3600</td>
<td>110</td>
<td>3</td>
<td>3.6</td>
<td>42.0</td>
<td>2.7</td>
</tr>
<tr>
<td>17</td>
<td>H₃PO₄</td>
<td>1800</td>
<td>4000</td>
<td>110</td>
<td>3</td>
<td>0.2</td>
<td>0</td>
<td>0.1</td>
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<tr>
<td>18</td>
<td>HCl</td>
<td>1800</td>
<td>3300</td>
<td>110</td>
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<td>2</td>
</tr>
<tr>
<td>19</td>
<td>H₂SO₄</td>
<td>1800</td>
<td>3600</td>
<td>-80</td>
<td>3</td>
<td>3.1</td>
<td>17.4</td>
<td>2.3</td>
</tr>
<tr>
<td>20</td>
<td>HCl</td>
<td>1800</td>
<td>3300</td>
<td>-80</td>
<td>3</td>
<td>0</td>
<td>2.5</td>
<td>0</td>
</tr>
</tbody>
</table>

DEE: diethyl ether, DEC: diethyl carbonate, PTC: 14 mmol Aliquat 336 (triocylmethyl chloride), PTSA: p-toluene sulfonic acid (≥ 98.5%), H₂SO₄ (≥ 98%), H₃PO₄ (≥ 85%), HCl (≥ 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 CH₃-CH₂-O⁺H₂ 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.
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$_2$O. The yields of DEC synthesis were low, probably due to competition with PEC protonation for formation of the monoethyl ester of carbonic acid [CH$_3$CH$_2$OC(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].

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$_2$CO$_3$, 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$_2$CO$_3$. 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

![Figure 7: Mechanism of phase transfer catalysis at the solid/liquid interface](image)

![Figure 8: Reaction of PEC in an acidic medium](image)
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).

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

ROH: alcohol, RX: alkyl halide, DAC: dialkyl carbonate, 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.
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 EtOK⁺ as a strong base, according to an E₂ 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).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant</th>
<th>Molar ratio</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>t (h)</th>
<th>n DEE (mmol)</th>
<th>n DEC (mmol)</th>
<th>Conversion EtI (%)</th>
<th>% Yield DEC (EtI basis)</th>
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</thead>
<tbody>
<tr>
<td>6</td>
<td>EtOH / EtI / K₂CO₃</td>
<td>8/1/1</td>
<td>110</td>
<td>80</td>
<td>5</td>
<td>3.0</td>
<td>50</td>
<td>97.6</td>
<td>46</td>
</tr>
<tr>
<td>7 a</td>
<td>EtOH / EtI / K₂CO₃</td>
<td>8/1/1</td>
<td>110</td>
<td>0</td>
<td>5</td>
<td>15</td>
<td>0.1</td>
<td>86.7</td>
<td>0.1</td>
</tr>
<tr>
<td>8</td>
<td>EtI / K₂CO₃</td>
<td>2/1</td>
<td>110</td>
<td>80</td>
<td>5</td>
<td>n.d. d</td>
<td>0.4</td>
<td>82.5</td>
<td>0.2</td>
</tr>
<tr>
<td>9 b</td>
<td>EtOH / EtOK / EtI</td>
<td>6/1/1</td>
<td>110</td>
<td>80</td>
<td>5</td>
<td>8.9</td>
<td>32</td>
<td>95.5</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>MeOH / EtI / K₂CO₃</td>
<td>8/1/1</td>
<td>110</td>
<td>80</td>
<td>5</td>
<td>n.d. d</td>
<td>0.1</td>
<td>98.7</td>
<td>0.1 (ca. 14) e</td>
</tr>
<tr>
<td>11 c</td>
<td>EtOH / EtI / K₂CO₃ / PTC</td>
<td>8/1/1/0.2</td>
<td>110</td>
<td>80</td>
<td>5</td>
<td>2.6</td>
<td>55</td>
<td>99.5</td>
<td>51</td>
</tr>
</tbody>
</table>

DEE: diethyl ether, DEC: diethyl carbonate, a without CO₂, 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 CO₂, 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 K₂CO₃ 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).

![Figure 10: Proposed reaction mechanism: competition between carbonate and ether formation](image)

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 CO₂, 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$_2$CO$_3$) 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.
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