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Selective Formation of Trimethylene Carbonate (TMC): Atmospheric Pressure Carbon Dioxide Utilization

Benjamin R. Buckley,*[a] Anish P. Patel,[a] and K. G. Upul Wijayantha*[a]

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Carbon dioxide utilisation (CDU) is currently gaining increased interest due to the abundance of CO₂ and its possible application as a C₁ building block. We herein report the first example of atmospheric pressure carbon dioxide incorporation into oxetane to selectively form trimethylene carbonate (TMC), which is a significant challenge as TMC is thermodynamically less favoured than its corresponding co-polymer.

Introduction

Anticipated pressures on fossil fuel resources in the coming decades mean that raw materials for the chemical industry must be found that can reduce our reliance on fossil-fuel-based feedstocks.[1] Hence, the development of new production processes for chemical syntheses from renewable resources is a challenge that should be a priority for all major economies.[2] Research into/application of carbon dioxide utilization (CDU) technologies has recently gained increased interest.[3] CDU offers an attractive alternative to the well-established carbon dioxide storage (CCS) processes, however, scale of production means that CDU is unlikely to significantly reduce anthropogenic carbon dioxide emissions, but waste carbon dioxide under CDU protocols can be converted into useful chemicals or fuels.

Carbon dioxide is abundant, cheap and non-toxic when compared with other C₁ building blocks, such as phosgene, and has been used in the manufacture of salicylic acid, urea and cyclic carbonates for 50–100 years. However, because of the relative inertness of carbon dioxide these processes are significantly energy demanding with reactions taking place at high temperatures and pressures. Therefore, if CDU technologies are to become viable processes reliance on very little energy input is required, hence processes at mild temperatures (< 100 °C) and atmospheric pressures should be targeted.

The insertion of carbon dioxide into epoxides to afford either five-membered ring cyclic carbonates or the corresponding polycarbonate has attracted considerable attention due to the industrial application of the products arising from these reactions. For example, North and co-workers have employed bimetallic aluminium salen complexes incorporating an ammonium bromide co-catalyst to prepare cyclic carbonates in good yield from not only highly purified carbon dioxide but also directly from a fossil fuel power station stack by use of a supported salen catalyst and flow reactor.[4] These reactions take place at mild temperatures and atmospheric pressures. Interestingly, structurally related salen-based catalysts have been successful in the corresponding polycarbonate process, for example Darenbourg and co-workers[5] have reported several studies employing a chromium-based salen complex to afford a range of polycarbonates; as have Lee and co-workers who have employed salen–cobalt catalysts.[6] Other catalytic systems have also been successfully employed by both Coates[7] and more recently Williams,[8] who has developed a series of highly active bimetallic catalysts that are able to perform the polymerisation reactions with atmospheric pressure carbon dioxide. Decortes and Kleij have also reported atmospheric pressure CO₂ insertion to form five-membered ring carbonates using zinc–salophen catalysts.[9]

Far less exposure has been given to carbon dioxide insertion into other heterocyclic ring systems, mainly due to the requirement for a high-energy substrate such as an epoxide for the insertion to be favourable. One possible product from carbon dioxide insertion into the challenging four-membered ring analogue of epoxides, oxetanes, would be the synthesis of six-membered ring cyclic carbonates or polycarbonates. Trimethylene carbonate (TMC) is a useful monomer for ring-opening polymerization, as complete retention of carbon dioxide is observed when polymerized to using a metal or non-metal catalyst (Scheme 1).[10] These polymers are of significant value since they are biodegradable and can be used in a range of medical devices.[11]

Traditionally TMC has been prepared from 1,3-propanediol and the highly poisonous phosgene gas, however, more recently several greener alternatives have arisen, for
We have recently shown that electrosynthesis can be a powerful tool for a range of important reactions and can be employed in the catalyst-free synthesis of five-membered ring cyclic carbonates under atmospheric pressure carbon dioxide and mild temperatures. The importance of six-membered cyclic carbonates and their inherent thermodynamic instability prompted us to investigate this important carbon dioxide insertion reaction. We believed that it should be possible to develop an electrochemical system that is easy to set up, cheap, reliable, requires no expensive catalysts, runs under atmospheric CO₂ pressures and at ambient temperatures. Importantly, employing an electrosynthetic system is cost neutral in terms of energy consumption if combined with a suitable renewable energy source, for example, solar.

Results and Discussion

We started our investigation by applying our previously reported optimized conditions for the synthesis of five-membered ring cyclic carbonates from carbon dioxide and epoxides. Gratifyingly, this resulted in the selective synthesis of TMC from trimethylene oxide 3, and under these reaction conditions we did not observe the thermodynamically more stable co-polymer 2. However, compound 1 was only formed in a disappointing 40% yield (Table 1, Entry 12), a range of electrode materials were then screened in an attempt to enhance the isolated yield observed but this process proved fruitless.

Table 1. Optimization studies for the production of TMC 1 from trimethylene oxide 3.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Supporting Electrolyte</th>
<th>Temp. [°C]</th>
<th>Current [mA]</th>
<th>Ratio [1/2]</th>
<th>Yield [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Bu₄NBr</td>
<td>25</td>
<td>60</td>
<td>&gt;99:1</td>
<td>25</td>
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<td>2</td>
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<td>25</td>
<td>60</td>
<td>&gt;99:1</td>
<td>50</td>
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<td>3</td>
<td>Bu₄NCl</td>
<td>25</td>
<td>60</td>
<td>&lt;5</td>
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<tr>
<td>4</td>
<td>Bu₄NPF₆</td>
<td>25</td>
<td>60</td>
<td>&gt;99:1</td>
<td>&lt;5</td>
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<tr>
<td>5</td>
<td>Bu₄NI</td>
<td>25</td>
<td>60</td>
<td>&gt;99:1</td>
<td>50⁴</td>
</tr>
<tr>
<td>6</td>
<td>Bu₄NI</td>
<td>25</td>
<td>60</td>
<td>&gt;99:1</td>
<td>15</td>
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<td>7</td>
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<td>25</td>
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<td>&gt;99:1</td>
<td>16⁴</td>
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<tr>
<td>8</td>
<td>Bu₄NI</td>
<td>25</td>
<td>30</td>
<td>&gt;99:1</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>Bu₄NI</td>
<td>25</td>
<td>30</td>
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<td>60</td>
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<td>10</td>
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<td>120</td>
<td>&gt;99:1</td>
<td>30</td>
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<td>11</td>
<td>Bu₄NI</td>
<td>50</td>
<td>60</td>
<td>86:14</td>
<td>51</td>
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<td>12</td>
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<td>50</td>
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<tr>
<td>13</td>
<td>Bu₄NBr</td>
<td>75</td>
<td>0</td>
<td>&lt;5</td>
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<tr>
<td>14</td>
<td>Bu₄NI</td>
<td>75</td>
<td>0</td>
<td>&lt;5</td>
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<td>75</td>
<td>60</td>
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<tr>
<td>16</td>
<td>Bu₄NBr</td>
<td>75</td>
<td>60</td>
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<tr>
<td>17</td>
<td>Bu₄NI</td>
<td>75</td>
<td>30</td>
<td>58:42</td>
<td>59</td>
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<tr>
<td>18</td>
<td>Bu₄NI</td>
<td>75</td>
<td>90</td>
<td>96:4</td>
<td>96</td>
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</tbody>
</table>

[a] General conditions: Cu cathode, Mg anode, CO₂ (1 atm, balloon), supporting electrolyte (1.0 equiv.), MeCN, single compartment cell, 60 mA, 6 h. [b] Ratio calculated from the crude reaction ¹H NMR spectrum by integration of cyclic carbonate vs. co-polymer signals. [c] Isolated yield of TMC 1 after chromatography. [d] 0.25 equiv. Bu₄NI employed. [e] 0.50 equiv. Bu₄NI employed. [f] 0.75 equiv. Bu₄NI employed.

We then turned our attention to the supporting electrolyte and a screen employing tetrabutylammonium chloride, bromide, iodide and hexafluorophosphate identified the iodide as the most promising candidate, with 50% yield of TMC 1 being formed at 25 °C with >99:1 selectivity for the monomer (Table 1, Entry 2). Further studies showed that 0.75 equiv. of the supporting electrolyte was required for good yield to be achieved (50%, Table 1, Entry 7) and...
an increase in yield to 60% could be achieved through a slight increase in the applied current (60 to 90 mA, Table 1, Entry 9). [20]

A series of experiments to look at the effect of temperature on the reaction were also carried out and finally we were able to obtain TMC 1 in 96% yield, although the reaction was not quite 100% selective for the monomer (Table 1, Entry 18).

Kleij and co-workers recently reported the synthesis of five-membered cyclic carbonates in excellent yield with either an iron- or aluminium-based catalyst at 10–2 atm CO2. [21] They also reported high yields and selectivity of oxetane to TMC 1 with the same systems but observed that addition of steric bulk to the oxetane substrate at the 3,3-position (two methyl groups, 4) dramatically decreased the yield and selectivity of the CO2 incorporation reaction (typically 9–28% yield, Table 2 Entries 1 and 2). Darenbourg has also reported that 3,3-substituted oxetanes are slow substrates for CO2 insertion at 35 atm but has not yet disclosed the yields when employing his vanadium-catalysed conditions (Table 2, Entry 3). [15] When employing (salen)Cr[III] chloride complexes, Darenbourg has reported a product distribution of 88% in favour of copolymer 6, when exploring the equilibrium distribution of a range of oxetanes. [22]

Under our conditions the formation of 5,5-dimethyl-1,3-dioxan-2-one 5 proceeded relatively smoothly with an unoptimised 70% yield being obtained at 50 °C when employing tetrabutylammonium iodide and 60 mA (Table 2, Entry 4).

<table>
<thead>
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</thead>
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<tr>
<td>1[a]</td>
<td>10–2</td>
<td>85 (18 h)</td>
<td>NR</td>
<td>9</td>
<td>[21a]</td>
</tr>
<tr>
<td>2[b]</td>
<td>10–2</td>
<td>70 (18 h)</td>
<td>54:46</td>
<td>26</td>
<td>[21b]</td>
</tr>
<tr>
<td>3[c]</td>
<td>35</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>[15]</td>
</tr>
<tr>
<td>4[d]</td>
<td>35</td>
<td>110 (50 h)</td>
<td>88:12</td>
<td>NR</td>
<td>[22]</td>
</tr>
<tr>
<td>5[e]</td>
<td>1</td>
<td>50 (6 h)</td>
<td>&gt;99:1</td>
<td>70</td>
<td>this work</td>
</tr>
</tbody>
</table>

[a] Conditions: [Fe(TPhOA)]2 (0.5 mol-%), Bu4NI (5 mol-%), MEK, CO2 (10–2 atm), 85 °C. [b] Conditions: Al triphenolate catalyst (0.5 mol-%), Bu4NI (2.5 mol-%), CO2 (10–2 atm), 70 °C. [c] VO(acac)2 (5 mol-%). BuNBr (5 mol-%), 60 °C. CO2 (35 atm). [d] (salen)Cr[III] chloride complex, Bu4NN3 (2 equiv.), CO2 (35 atm), toluene, 110 °C. [e] Conditions: Cu cathode, Mg anode, CO2 (1 atm, balloon), Bu4NI (1.0 equiv.), MeCN, single compartment cell, 90 mA, 50 °C. [f] NR = not reported.

A proposed mechanism is described in Scheme 3 in which magnesium iodide is prepared in situ, following the reports of North and co-workers tributylamine is released under the reaction conditions [4g] and also activates CO2 towards eventual incorporation to TMC, with magnesium iodide regeneration.
Conclusions

We have developed, to the best of our knowledge, the first selective procedure for the formation of the TMC monomer 1 at atmospheric pressure carbon dioxide from oxetane.[23] This process is one of only a handful of approaches that allow the conversion of oxetane to the cyclic carbonate rather than the thermodynamically more stable polymer 2. The yields obtained are comparable or better than those already reported in the area. The equipment required to perform this CO₂ incorporation reaction is cheap and should be readily available in any undergraduate teaching facility, that is, copper wire, magnesium ribbon and a power supply. The protocol described affords the highest reported yield for the 3,3-dimethyl-substituted oxetane and we are currently exploring the CO₂ insertion into these challenging substituted oxetanes, for which there are currently very few commercially available.

Experimental Section

Representative Procedure for the Formation of Cyclic Carbonates: Trimethylene Carbonate (TMC) (2)[15,24] Tetrabutylammonium iodide (0.74 g, 2.0 mmol) was dissolved in acetonitrile (145 mL), the resulting solution was flushed with CO₂ for 1 h at room temperature and trimethylene oxide (0.12 g, 2.0 mmol) added as a solution in acetonitrile (5 mL). The reactor was heated to 75 °C and potential was then applied to the system (constant current: 90 mA) for 6 h (96 %). M.p. 45–47 °C (lit.[21] 45–47 °C). 1H NMR (400 MHz, CDCl₃, Me₄Si): δ = 2.12–2.18 (m, 2 H), 4.45–4.48 (m, 4 H) ppm. 13C NMR (100 MHz, CDCl₃, Me₄Si): δ = 21.8, 68.0, 148.5 ppm. IR (CH₂Cl₂): v ≈ 1252 (C=O), 1740 (C=O) cm⁻¹.

Acknowledgments

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References


See ref.[19] for optimized conditions.

See Table S1 in the Supporting Information for full details.


[23] A low pressure CO$_2$ route from 3-chloropropan-1-ol has been reported: M. R. Reithofer, Y. N. Sum, Y. Zhang, *Green Chem.* 2013, 15, 2086.


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