Carbocation-polyol systems as efficient organic catalysts for the preparation of cyclic organic carbonates

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**Abstract:** Carbocation-polyol systems are shown to be highly efficient catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide at 50 oC and 5 MPa CO2 pressure. The best activity was shown by the combination of crystal violet and BINOL and this system could be recycled five times with no loss of activity. The presence of specific interactions between the amino groups of the carbocation and hydroxyl protons was confirmed by NMR experiments. Job’s plots for the crystal violet iodide / BINOL and brilliant green iodide / BINOL were constructed and showed that the catalytic system consists of one molecule of carbocation and one molecule of BINOL. Mechanistic studies using a deuterated epoxide indicated that there is some loss of epoxide stereochemistry during the reaction, but that predominant retention of stereochemistry is observed. On this basis a catalytic cycle is proposed.

Introduction

The search for valorization technologies for emitted carbon dioxide (CO2) is one of the most rapidly burgeoning fields of chemical exploration.[1] The coupling of CO2 with epoxides is a highly atom economical process, leading to the production of cyclic carbonates (Scheme 1) which are an important class of industrial intermediates and solvents.[1-4] This methodology is highly sustainable, already utilized in industry and the volume of cyclic carbonate production is expected to grow substantially in the near future due to their use as electrolytes in lithium ion batteries. The best catalysts for cyclic carbonate synthesis are based on a two-component metal complex / nucleophile catalyst combination.[2,3] Recently, purely organic catalysts have become a focus of studies[4] because their use can be more cost-effective, the catalysts are commercially available, and usually more sustainable and less toxic than metal complexes. In particular, quaternary ammonium and phosphonium salts are widely utilized as catalysts.[4-8] There are also examples of the use of imidazolium salts[9-15] and imidazolium-based ionic liquids[16] as catalysts for cyclic carbonate synthesis. In addition, two-component systems comprising an alcohol (or phenol) and a quaternary ammonium salt have been successfully tested.[17,18] This system represents a promising class of organic catalysts with the potential for further improvement.[4] Unfortunately, up to now the efficiency of the organic catalysts is no match for metal based catalysts.[4] This justifies the search for novel classes of organic catalysts.



**Scheme 1.** Synthesis of cyclic carbonates.

We have previously developed several catalytic systems for the synthesis of cyclic carbonates by coupling of CO2 and epoxides. These included highly efficient and robust aluminium(salen) complexes,[19,20] and stereochemically inert Co(III) complexes which function as “Brønsted acids in disguise” with the central metal ion only serving as an activator of the catalytically active Brønsted acidic NH groups.[21]

Herein, we describe the use of well known, commercially available stable carbocations in the form of triarylmethane dyes (Figure 1) as catalysts for cyclic carbonate synthesis. For this purpose we tested the iodide salt form of malachite green (MGI), brilliant green (BGI), and crystal violet (CVI) as bifunctional catalysts, the activities of which were augmented by the addition of Brønsted acids.



**Figure 1.** Carbocation dyes used as catalysts for cyclic carbonate synthesis.

Results and Discussion

Although rare, use of triarylmethylium (trityl) carbocations as catalysts for organic transformations, such as Diels-Alder and Michael reactions has been disclosed.[22] However, the use of triarylmethane dyes as organic catalysts, has to the best of our knowledge, not been previously reported. The reason for this seems to be connected to the fact that the activity of a carbocation is inversely related to its stability.[22-25] However, the carbocations exist as halide salts and thus are bifunctional systems involving a Lewis acidic center and a nucleophilic counterion. As such, they have similarity with ammonium salts which are a well-known class of catalysts for cyclic carbonate synthesis.[4-8] In addition, the amino substituents of triarylmethane dyes could interact with a Brønsted acid catalyst component. The resulting hydrogen bond formation would increase the Lewis acidities of the dyes.

Based on the accepted mechanism of bifunctional Lewis acid / halide ion catalysis, a potential mechanism of CO2 addition to epoxides promoted by the dyes is shown in Scheme 2. The Lewis acidic carbocation could activate the epoxide towards nucleophilic attack by the iodide anion. Subsequent addition of CO­2 and the elimination of iodide, bring the reaction to completion and regenerate the catalyst.



**Scheme 2.** Proposed mechanism of cyclic carbonate synthesis promoted by triarylmethane dyes.



**Figure 2.** Shifts of the signals of CVI’s central carbon on the addition of increasing concentrations of PO in CD2Cl2. a) just CVI (0.33 M), b) CVI:PO = 2:1, c) CVI:PO = 1:1, d) CVI:PO = 1:2, e) CVI:PO = 1:3, f) CVI:PO = 1:10. The splitting of the 13C signal in spectra e) and f) suggests that at high PO to CVI ratios, two PO molecules may interact with each CVI.

To demonstrate a Lewis acidic interaction of the carbocations with epoxides, NMR experiments on mixtures of CVI and propylene oxide (PO) were carried out in CD2Cl2. Both 1H and 13C NMR spectra revealed significant shifts of the signals of the dimethylamino groups of CVI and the epoxide’s methyl group to higher fields as the PO concentration increased (see the Supporting information). Moreover, the 13C NMR spectra showed a shift of the carbocation’s carbon signal (178.02 ppm) to higher field, correlated with increasing epoxide concentration (Figure 2). Thus the spectra indicate that the epoxide did coordinate with the carbocation of CVI.

The addition of CO2 to neat styrene oxide (SO) was selected as a benchmark reaction to test the activities of the dyes. As the dyes were commercially available in their chloride form, both MG and CV were tested in their original (Table 1, entries 1,2) and iodide forms (Table 1, entries 3,5). The chloride to iodide exchange was easily brought about, in a two phase CH2Cl2-H2O system, using a twentyfold excess of potassium iodide. As expected, the iodide form was much more active, so for all the dyes it was their iodide form that was tested further.

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| **Table 1.** Comparison of the catalytic activities of MGI, BGI, CVI and TBAI.[a] |
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| **Entry** | **Catalyst** | **Conversion% (selectivity%)[b]** |
| 1[c] | MG | <1 (not determined) |
| 2[c] | CV | <1 (not determined) |
| 3 | MGI | 8 (>99) |
| 4 | BGI |  28 (>99)  |
| 5 | CVI |  45 (>99) |
| 6[d] | CVI |  32 (>99) |
| 7 | Bu4NI |  41 (>99) |
| [a] Reaction conditions: 2 mol% catalyst unless specified otherwise, neat SO. [b] Conversions were determined by 1H NMR using the catalyst signals as internal standard. [c] The dyes were used in their chloride forms. [d] The catalyst loading was 1% mol. |

Among the dyes, CVI was the most active and its catalytic activity was similar to that of tetrabutylammonium iodide (TBAI) (Table 1, entries 5 and 7). Both MGI and BGI were much inferior to CVI and TBAI (Table 1, runs 3,4 and 5,7). The relative order of activity of the dyes was unexpected. Had the Lewis acidity of the cations been the most important factor, the opposite trend would have been expected since the pKR+ values for MGI and CVI are 6.9 and 9.4 respectively.[22] This suggests that there was a compensating effect influencing the catalytic activity of the dye / iodide ion bifunctional catalyst. Most likely, the tighter the ion pair, the less active is the catalyst and the expected activity trend in the series of dyes would then be MGI < BGI < CVI as observed. The dissociation of the ion pairs should lead to better catalytic performance which was supported by experiments. Thus, halving the CVI concentration led to a relatively small change in the conversion of SO (Table 1, entries 4 and 6), consistent with greater ion pair dissociation, accompanying the CVI dilution.

The introduction of anion complexing agents should lead to better catalytic performance by separating the ion pairs into Lewis acidic and nucleophilic parts and, thus, revealing the hidden potential of their activity. For this purpose several polyalcohols and carboxylic acids (Figure 3) were investigated. These can complex iodide whilst simultaneously forming hydrogen bonds with the amino groups of the dyes and coordinating an alcoholic oxygen to the cationic center of the dye.



**Figure 3.** Compounds used as Brønsted acid additives and an example of their postulated mode of action.

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| **Table 2.** Activity of polyol additives in the reaction of styrene oxide with CO2. [a] |
| **Entry** | **Polyol** | **Catalyst** | **Conversion%[b]** |
| 1 | TADDOL | Bu4NI | 70 |
| 2 | *Meta-bis-*TADDOL | Bu4NI | 71 |
| 3 | CH2*-bis-*TADDOL | Bu4NI | 76 |
| 4 | TADDOL | BGI | 41 |
| 5 | *Meta-bis-*TADDOL | BGI | 55 |
| 6 | CH2*-bis-*TADDOL | BGI | 64 |
| [a] Reaction conditions: 1.25 mol% of *bis*-TADDOLs (or 2.5 mol% TADDOL), 2.5 mol% of TBAI (or BGI), neat SO, 50oC, 5 MPa CO2, 24 h. [b] Conversions were determined using 1H NMR spectroscopy. |

Initially, TADDOL additives were tested with TBAI and BGI to investigate any cooperative interactions between the two catalyst partners. In these experiments, twice as much TADDOL as *bis*-TADDOL was used so that the total number of available hydroxyl groups would be kept constant. The results are shown at Table 2. In the case of TBAI no significant difference in catalytic activities of the TADDOLs was detected (Table 2, entries 1–3). However, in the case of BGI, the TADDOLs were found to have markedly different activities (Table 2, entries 4–6). The best activator was found to be CH2-*bis*-TADDOL which has the greatest distance between its two pairs of hydroxyl groups (Table 2, entry 6). This observation supports the hypothesis that there would be activating interactions between the carbocation’s amino groups and hydroxyl protons of the polyols

Table 3 summarizes the activities of the dyes relative to TBAI with the other types of polyol additives. The polyols themselves were not catalytically active (Table 3, entry 1). The activity of TBAI was increased by use of polyols in the order BIMBOL<TADDOL<H8-BINOL<BINOL (Table 1, entry 7; Table 2, entries 1-3 and Table 3, entries 2-5). The addition of BINOL also led to an increase in the activities of the carbocation dyes, even of the least reactive MGI (Table 1, entry 3, Table 3, entry 6). The effect was even more pronounced in the case of BGI (Table 1, entry 4, Table 2 entries 4-6 and Table 3, entries 7-10). The order of efficiency of the additives was TADDOL<BIMBOL<H8-BINOL<BINOL. At higher concentrations, the catalyst system of BGI/BINOL became more active than that of TBAI/BINOL (Table 3, entries 4,5 and 9,10). Finally, the most efficient catalyst was CVI/BINOL (Table 1, entries 5,6 and Table 3, entries 12-14). The order of the efficiency was TADDOL<BIMBOL<BINOL. It is notable that the inexpensive diol BINOL was more active than the TADDOL derivatives. The greater acidity of BINOL (pKa = 13.2, DMSO26) and its lower steric bulk compared to TADDOL (pKa = 19.2, DMSO26) may explanation this. Use of terephthalic acid with BGI (Table 3, run 11) resulted in complete inhibition of the activity of BGI.

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| **Table 3.** Catalytic activity of TBAI, MGI, BGI and CVI in the presence of additives.[a] |
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| **Entry** | **Catalyst (mol%)** | **Additive (mol%)** | **Conversion %[b]** | **Selectivity %** |
| 1 |  | BINOL, BIMBOL, H8-BINOL, TADDOL (1.0) | <1 |  |
| 2 | Bu4NI (2.5) | BIMBOL (1.25) | 53 | >99 |
| 3 | Bu4NI (2.5) | H8-BINOL (2.5) | 82 | >99 |
| 4 | Bu4NI (2.5) | BINOL (2.5) | 88 | >99 |
| 5 | Bu4NI (1.0) | BINOL (2.5) | 69 | >99 |
| 6 | MGI (1.0) | BINOL (1.0) | 12 | >99 |
| 7 | BGI (2.5) | BIMBOL (1.25) | 58 | >99 |
| 8 | BGI (2.5) | H8-BINOL (2.5) | 82 | >99 |
| 9 | BGI (1.0) | BINOL (1.0) | 49 | >99 |
| 10 | BGI (2.5) | BINOL (2.5) | 100 | >99 |
| 11 | BGI (2.5) | Terephthalic acid (2.5) | 0 |  |
| 12 | CVI (1.0) | TADDOL (1.0) | 48 | >99 |
| 13 | CVI (1.0) | BIMBOL (0.5) | 57 | >99 |
| 14 | CVI (1.0) | BINOL (1.0) | 82 | >99 |
| [a] Reaction conditions: neat SO, 50oC, 5 MPa CO2, 24 h. [b] Conversions were determined by 1H NMR using the catalyst signals as internal standard. |

In order to explore the nature of the interactions between BINOL and a dye molecule, 1H and 13C NMR spectra of mixtures of BGI and different concentrations of BINOL were recorded (Figure 4). Significant shifts to lower fields of the hydroxyl protons of BINOL were the most conspicuous change in the spectra of BINOL within the mixture (Figure 4, b–e). Some upfield shifts of CH2 protons within the BGI amino groups and of the BGI aromatic protons (*ortho* to the amino groups) with increasing BINOL concentration were also observed (Figure 4, a–d). In addition, 0.2 ppm shifts of the carbocation’s 13C NMR signal to higher fields in spectra at a 1:3 ratio of BGI/BINOL was detected (see Supporting Information). These spectra indicate that the Lewis acidic central carbon atom of BGI interacted with BINOL through a lone pair of an OH group in a similar way to its interaction with PO (Figure 2). Such interaction should lead to greater acidity of the hydroxyl group and to the shifts of the proton resonance to a lower field.





**Figure 4.** 1H NMR spectra of different ratios of BGI:BINOL in CD2Cl2. a) BGI only; b) BINOL:BGI = 1:1; c) BINOL:BGI = 2:1; d) BINOL:BGI = 3:1; e) BINOL only.



**Figure 5.** Job’s plot for the BGI:BINOL and CVI:BINOL systems in the synthesis of styrene carbonate from SO and CO2. Reaction conditions: neat SO, 2 mol% BINOL+carbocation, 50oC, 5MPa CO2, 24 h.

In order to determine the optimal ratio between the dyes and BINOL, Job’s plots of the activity of BGI or CVI / BINOL were constructed (Figure 5). The total loading of the BINOL-carbocation system was kept constant at 2 mol%. As shown by Figure 5, for BGI the highest yields of styrene carbonate were achieved in the range BGI/BINOL = 2:1 to BGI/BINOL = 1:1. For CVI, a similar dependence was observed with the best ratio CVI/BINOL being 1:1.

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| **Table 4.** CVI/BINOL catalysed synthesis of cyclic carbonates |
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| **Entry** | **Cyclic carbonate** | **CVI+BINOL mol%** | **Yield %[a]** **(Conversion%)[b]** | **Selectivity %** |
| 1 | **2a** | 1+1 | 72 (82) | >99 |
| 2 | **2b** | 1+1 | 48 (54) | >99 |
| 3 | **2b** | 2+2 | 54 (100) | >99 |
| 4 | **2c** | 1+1 | (76) | >99 |
| 5 | **2c** | 2+2 | 70 100) | >99 |
| 6 | **2d** | 1+1 | 70 (100) | >99 |
| 7 | **2e** | 1+1 | 65 (100) | >99 |
| 8 | **2f** | 1+1 | (37) | >99 |
| 9 | **2f** | 2+2 | 60 (78) | >99 |
| 10 | **2g** | 2+2 |  56 (100) | >99 |
| 11 | **2h** | 2+2 |  79 (100) | >99 |
| 12 | **2i** | 2+2 |  71 (100) | >99 |
| 13 | **2j** | 2+2 |  61 (100) | >99 |
| 14 | **2k** | 1+1 | 0 |  |
| 15 | **2k** | 5+5 | 10 (20) | >99 |
| 16 | **2l** | 5+5 | 31 (70) | >99 |
| [a] The cyclic carbonates were isolated by flash chromatography on silica. [b] Conversions were determined by 1H NMR using the catalyst signals as internal standard. |

The 1:1 CVI-BINOL system was used for synthesis of ten cyclic carbonates **2a-j** from terminal epoxides **1a-j** (Table 4, entries 1-13). For the more reactive epoxides **1a,d,e**, good conversions were obtained using just 1 mol% of each catalyst component (Table 4, entries 1,6,7). However, other aromatic and aliphatic epoxides **1b,c,f** gave rather low conversions when 1 mol% of each catalyst component was used, but much better results when 2 mol% of each component was used (Table 4, entries 2-5,8,9). Therefore, 2 mol% of each catalyst component was used with the remaining substrates. Under these conditions, high conversions were obtained with substrates possessing long alkyl chains, ethers and alcohols in their sidechains (Table 4, entries 7-11). These results show that the CVI-BINOL system has general applicability and tolerates functional groups within the epoxide substrate. Cyclic disubstituted epoxides **1k,l** were also investigated as substrates. With a catalyst loading of 1 mol% of each component, cyclohexene oxide **1k** failed to react (Table 4, entry 14). Increasing the catalyst loading to 5 mol% of each component resulted in formation of *cis*-cyclohexene carbonate in just 10% yield (Table 4, entry 15). No polycarbonate was formed in these reactions. Cyclopentene oxide **1l** was a slightly more successful substrate, giving cyclopentene carbonate **2l** in 31% yield when 5 mol% of each catalyst component was used.

The stability of the CVI/BINOL catalytic system was investigated by catalyst reuse experiments using PO at 50 oC and 50 bar CO2 pressure with a reaction time of 24 h. After the first 24 h period, the yield of cyclic carbonate **2d** was determined by 1H NMR spectroscopy, then another portion of propylene oxide was added to the reaction mixture. The results are shown at Table 5. The system could be recharged five times with no loss of activity.

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| **Table 5.** Reusability of the CVI-BINOL catalytic system.[a] |
| **Entry** | **Cycle** | **Catalyst system concentration, mol%** | **Conversion %[b]** |
| 1 | 1 | 2 | 100 |
| 2 | 2 | 1 | 100 |
| 3 | 3 | 0.67 | 95 |
| 4 | 4 | 0.5 | 74 |
| 5[c] | 5 | 2 | 100 |
| [a] Reaction conditions: 1 mol% BINOL, 1 mol% CVI, neat PO (50 mg, 0.06 mL, 0.86 mmol), 50oC, 5 MPa CO2, 24 h. The second and subsequent cycles included the addition of a fresh 50 mg portion of epoxide **1d** to the reaction mixture after each 24 h reaction period. [b] Conversions were determined using 1H NMR spectroscopy. [c] Reaction conditions: 1 mol% BINOL, 1 mol% CVI, both recovered from the experiment of entry 4 following distillation of **2d**, neat PO (50 mg, 0.06 mL, 0.86 mmol), 50oC, 5 MPa CO2, 24 h. |

To investigate the mechanism of the reaction, deuterated epoxides **3a,b**[26] were used to study the stereochemistry of the reaction (Scheme 3). In both cases, deuterated cyclic carbonates **4a,b** were formed with predominant retention of epoxide stereochemistry, but with some epimerization, the amount of which depended on the amount of catalyst used as shown in Table 6. A control experiment in which epoxide **3b** was heated to 50 oC under nitrogen in the presence of 2 mol% of both CVI and BINOL showed that it did not epimerize under these conditions.



**Scheme 3.** Use of deuterated epoxides **3a,b** to study the stereochemistry of cyclic carbonate synthesis.

On the basis of the spectroscopic and stereochemical studies, a possible mechanism for the reaction is proposed in Scheme 4. The carbocation acts as a Lewis acid, activating the BINOL to become a stronger Brønsted acid. The increase in the acidity of the BINOL OH group allows it to form a stronger hydrogen bond with the epoxide and triggers the epoxide ring opening by the iodide ion to give intermediate **5**. The iodide ion itself may be positioned in space by the second OH group of BINOL. The remaining OH group in intermediate **5** could coordinate to CO2, both activating and organizing it towards intramolecular carbonate formation to give intermediate **6** which can then cyclise to form the cyclic carbonate product and regenerate the catalyst components.

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| **Table 6.** Synthesis of deuterated cyclic carbonates **4a,b**.[a] |
| **Entry** | **Epoxide** | **Catalyst system concentration, mol%** | **4a:4b** |
| 1 | **3b** | 2 | 11:89 |
| 2 | **3b** | 6 | 22:78 |
| 3 | **3a** | 6 | 73:27 |
| [a] Reaction conditions: 2-6 mol% BINOL, 2-6 mol% CVI, neat epoxide **3a** or **3b**, 50oC, 5 MPa CO2, 24 h. |



**Scheme 4.** A possible mechanism rationalizing the synergistic effect of BIMBOL on the activity of the dyes in synthesis of cyclic carbonates.

Intermediates **5** and **6** could also undergo a non-productive SN2 reaction of the alkyl iodide with external iodide. This reaction would only be visible (as loss of stereochemical purity) in deuterated epoxides such as **3a,b** and the relative rate of reaction with iodide to intramolecular cyclization of the carbonate would be expected to increase as the concentration of iodide in the reaction increases, ie as the catalyst loading increased, thus accounting for the results presented in Table 6.

Experimental

**Materials**

Commercial reagents were used as received unless stated otherwise. Column chromatography was performed using Silica Gel Kieselgel 60 (Merck).

**Instrumentation**

1H and 13C NMR spectra were recorded on Bruker Avance 300 and Bruker Avance III–400 spectrometers (operating at 300 and 400 MHz for protons, respectively). Melting points were determined in open capillary tubes and are uncorrected. Elemental analysis was performed at the elemental analysis laboratory of the Nesmeyanov’s Institute of OrganoelementCompounds of Russian Academy of Sciences (INEOS RAS). All solvents were purified according to standard procedures.

**Synthesis of carbocations**

**Malachite green iodide.** Malachite green chloride (1.0 g, 2.7 mmol) dissolved in CH2Cl2 (10 ml) was added to a solution of KI (7.0 g, 42 mmol) in water (10 ml). The resulting suspension was stirred at room temperature for 4 h, then the organic layer was separated, dried over MgSO4 and evaporated under reduced pressure to give malachite green iodide (0.95g, 94%) as green crystals. Mp 100–102 °C; max(KBr) 2920, 2851, 1583, 1363 and 1167 cm-1; 1H NMR (400 MHz, CDCl3) δ 7.73–7.68 (m, 1H), 7.56 (t *J* 7.6 Hz, 2H), 7.41 (d *J* 8.8 Hz, 4H), 7.34 (d *J* 7.6 Hz, 2H), 7.00 (d *J* 8.9 Hz, 4H), 3.40 (s, 12H); 13C NMR (101 MHz, CDCl3) δ 177.68, 156.98, 141.00, 139.50, 134.73, 133.13, 128.61, 127.38, 113.98, 41.43. X-ray fluorescence data: no Cl was detected.

**Brilliant green iodide.** Brilliant green mono-oxalate (1.0 g, 2.0 mmol) dissolved in CH2Cl2 (10 ml) was added to a solution of KI (7.0 g, 42 mmol) in water (10 ml). The resulting suspension was stirred at room temperature for 4 h, then was neutralized by the addition of aqueous NaOH. The organic layer was separated, dried over MgSO4 and evaporated under reduced pressure to give brilliant green iodide (0.92 g, 90%) as green crystals. Mp 186–189 °C; max(KBr) 3060, 2972, 2928, 1580, 1341 and 1186 cm-1; 1H NMR (400 MHz, CDCl3) δ 7.73–7.68 (m, 1H), 7.56 (t *J* 7.6 Hz, 2H), 7.41 (d *J* 8.8 Hz, 4H), 7.34 (d *J* 7.6 Hz, 2H), 7.00 (d *J* 8.9 Hz, 4H), 3.40 (s, 12H); 13C NMR (101 MHz, CDCl3) δ 177.68, 156.98, 141.00, 139.50, 134.73, 133.13, 128.61, 127.38, 113.98, 41.43. X-ray fluorescence data: no Cl was detected.

**Crystal violet iodide.** Crystal violet chloride (1.0 g, 2.4 mmol) dissolved in CH2Cl2 (10 ml) was added to a solution of KI (7.0 g, 42 mmol) in water (10 ml). The resulting suspension was stirred at room temperature for 4 h, then the organic layer was separated, dried over MgSO4 and evaporated under reduced pressure to give crystal violet iodide (0.94g, 92%) as green crystals. Mp 192–194 °C; max(KBr) 3087, 2913, 2852, 2808, 1581, 1358 and 1171 cm-1; 1H NMR (400 MHz, CDCl3) δ 7.03 (d *J* 9.0 Hz, 6H), 6.60 (d *J* 9.0 Hz, 6H), 3.03 (s, 18H); 13C NMR (101 MHz, CDCl3) δ 177.57, 155.32, 139.44, 126.25, 112.32, 40.76. X-ray fluorescence data: no Cl was detected. Calculated for C25H30IN3.H2O: C, 58.03; H, 6.23; N, 8.12. Found: C, 57.95; H, 6.19; N, 7.99.

Synthesis of cyclic carbonates

All cyclic carbonate syntheses were carried out in autoclaves with 50 bar carbon dioxide starting pressure. The reactions were heated to 50 oC and magnetically stirred. After completion of the experiment, the autoclave was cooled to room temperature before the pressure was released. The reaction mixture was analysed by 1H NMR spectroscopy and passed through a pad of silica to separate the catalyst. Column chromatography (SiO2, EtOAc/hexane, 1:3) was then used to purify the cyclic carbonates.

**Styrene carbonate 2a:** Mp 50–52 °C; max(ATR) 3037, 2921, 1782, 1160 and 1050 cm-1; 1H NMR (400 MHz, CDCl3) δ 7.44–7.32 (m, 5H), 5.66 (t *J* 8.0 Hz, 1H), 4.82–4.73 (m, 1H), 4.37–4.26 (m, 1H); 13C NMR (101 MHz, CDCl3) δ 155.00, 135.88, 129.80, 129.31, 126.00, 78.11, 71.28.

**4-Chlorostyrene carbonate 2b:** Mp 67–70 °C; max(ATR) 3087, 2964, 2912, 1789, 1162 and 1048 cm-1; 1H NMR (400 MHz, CDCl3) δ 7.48–7.25 (m, 4H), 5.65 (t *J* 8.0 Hz, 1H), 4.79 (t *J* 8.2 Hz, 1H), 4.29 (dd *J* 8.6, 7.9 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 154.65, 135.85, 134.35, 129.59, 127.37, 77.34, 71.10.

**4-Bromostyrene carbonate 2c:** Mp 70–72 °C; max(ATR) 2951, 2522, 2161, 2017, 1981, 1801 and 1771 cm-1; 1H NMR (400 MHz, CDCl3) δ7.59 (d *J* 8.0 Hz, 2H), 7.25 d, *J* 8.0 Hz2H), 5.64 (t *J* 8.0 Hz, 1H), 4.80 (t *J* 8.0 Hz, 1H), 4.30 (t *J* 8.0 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ154.5, 134.8, 132.5, 127.4, 123.9, 77.2, 70.9.

**3-Chloropropylene carbonate 2d:** max(ATR) 2967, 1779, 1159 and 1055 cm-1; 1H NMR (400 MHz, CDCl3) δ 5.02–4.93 (m, 1H), 4.60–4.53 (m, 1H), 4.37 (dd *J* 8.9, 5.7 Hz, 1H), 3.82–3.67 (m, 2H); 13C NMR (101 MHz, CDCl3) δ 154.49, 74.48, 67.06, 44.03.

**Propylene carbonate 2e:** max(ATR) 2988, 2924, 1781, 1174 and 1044 cm-1; 1H NMR (400 MHz, CDCl3) δ 4.92–4.67 (m, 1H), 4.64–4.38 (m, 1H), 4.07–3.89 (m, 1H), 1.43 (d, *J* = 6.3 Hz, 3H); 13C NMR (101 MHz, CDCl3) δ 155.22, 73.74, 70.78, 19.45.

**1,2-Decylene carbonate 2f:** max(ATR) 2931, 2835 and 1796 cm-1; 1H NMR (400 MHz, CDCl3) δ4.71–4.68(m, 1H), 4.52 (t *J* 8.0 Hz, 1H), 4.06 (t *J* 8.0 Hz, 1H), 1.83–1.63 (m, 2H), 1.47–1.26 (m, 12H), 0.87 (t *J* 8.0 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ155.1, 77.0, 69.4, 33.9, 31.8, 29.3, 29.1, 29.0, 24.3, 22.6, 14.1.

**1,2-Hexylene carbonate 2g:** max(ATR) 2941, 2922, 2899 and 1796 cm-1; 1H NMR (400 MHz, CDCl3) δ4.73–4.66(m, 1H, OCH), 4.52 (t *J* 8.0 Hz, 1H), 4.06 (t *J* 8.0 Hz, 1H), 1.86–1.65 (m, 2H), 1.49–1.35 (m, 4H), 0.92 (t *J* 8.0 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ155.1, 76.8, 69.4, 33.5, 26.4, 22.2, 13.8.

**1,2-Dodecylene carbonate 2h:** max(ATR) 2931, 2832 and 1798 cm-1; 1H NMR (400 MHz, CDCl3) δ4.73–4.66(m, 1H), 4.52 (t *J* 8.0 Hz, 1H), 4.06 (t *J* 8.0 Hz, 1H), 1.84–1.70 (m, 2H), 1.63–1.26 (m, 16H), 0.88 (t *J* 8.0 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ155.1, 77.1, 69.4, 33.9, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 24.3, 22.6, 14.1.

**3-Phenoxypropylene carbonate 2i:** Mp 94–96 °C;max(ATR) 3429, 3061, 2989, 2924, 2328 and 1791 cm-1; 1H NMR (400 MHz, CDCl3) δ7.30 (t *J* 8.0 Hz, 2H), 7.02 (t *J* 8.0 Hz, 1H), 6.91 (d *J* 8.0 Hz, 2H), 5.06–5.01 (m, 1H), 4.62–4.55 (m, 2H), 4.24 (dd *J* 11.0, 4.0 Hz, 1H), 4.16 (dd *J* 11.0, 4.0 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ157.7, 154.6, 129.7, 122.0, 114.6, 74.0, 66.8, 66.2.

**Glycerol carbonate 2j:** .max(ATR) 3382, 2901 and 1799 cm-1; 1H NMR (400 MHz, CDCl3) δ4.84–4.78 (m, 1H), 4.52 (t *J* 8.0 Hz, 1H), 4.44 (dd *J* 8.0, 4.0 Hz, 1H), 3.96 (d *J* 16.0, 4.0 Hz, 1H), 3.68 (d *J* 16.0, 4.0 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ155.4, 76.6, 65.8, 61.6.

***Cis*-Cyclohexene carbonate 2k:** Mp 35−37 °C;max(ATR) 2933, 2861 and 1784 cm-1; 1H NMR (400 MHz, CDCl3) δ4.70–4.65(m, 2H), 1.91–1.87 (m, 4H), 1.66–1.57 (m, 2H), 1.46–1.36 (m, 2H); 13C NMR (100 MHz, CDCl3) δ155.4, 75.7, 26.8, 19.2.

**Cyclopentene carbonate 2l:** Mp 30−33 °C;max(ATR) 2967, 2871 and 1789 cm-1; 1H NMR (400 MHz, CDCl3) δ5.11­–5.10(m, 2H), 2.19–2.14 (m, 2H), 1.83–1.63 (m, 4H); 13C NMR (100 MHz, CDCl3) δ155.4, 81.8, 33.1, 21.5.

Conclusions

Catalytic systems consisting of commercially available carbocations and polyols were found to be active as catalysts for cyclic carbonate synthesis. Carbocations in these systems act as activators of polyol hydroxyl groups, increasing their Brønsted acidity. Malachite green, brilliant green, and crystal violet have been used as antiseptic, antibacterial and fungicidal agents to treat both humans and animals.[27] As such they can be considered as greener and safer catalysts than those based on complexes of toxic metals such as cobalt, chromium and aluminium. The catalytic activity of the dye based catalysts is comparable to that often reported for metal-based catalysts,[2,3] though not with the very best metal based systems[20] which have been highly developed over more than a decade.

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