ChemPubSoc Europe
DOI: 10.1002/cssc.201500710
CHEMSUSCHEM
Full Papers

Highly Efficient Organocatalyzed Conversion of Oxiranes and CO_2 into Organic Carbonates

Sergio Sopeña,[a] Giulia Fiorani,[a] Carmen Martín,[a] and Arjan W. Kleij*[a, b]

A binary catalyst system based on tannic acid/NBu_4X (X = Br, I) is presented as a highly efficient organocatalyst at very low catalyst loading for the coupling of carbon dioxide and functional oxiranes to afford organic carbonates in good yields. The presence of multiple polyphenol fragments within the tannic acid structure is considered to be beneficial for synergistic effects that lead to higher stabilization of the catalyst structure during catalysis. The observed turnover frequencies (TOFs) exceed 200 h^{-1} and are among the highest reported to date for organocatalysts in this area of CO_2 conversion. This organocatalyst system presents a useful, readily available, inexpensive, and, above all, reactive alternative for most of the metal-based catalyst systems reported to date.

Introduction

Current (catalytic) research centered on the use of CO_2 as an inexpensive and renewable source of carbon focuses on its incorporation into other organic scaffolds to enable the partial replacement of fossil-fuel-based chemistry.[1–9] Considerable progress in this area has led to a wide variety of organic structures from CO_2 as a molecular synthon.[10–14] Among these organic products, organic carbonates[7,8,15–17] have a prominent position as they are useful in a number of applications, including their use as fuel additives, aprotic solvents, and monomer intermediates for polymeric structures.[18] In the last decade, highly efficient catalytic methods for their preparation have emerged, and those incorporating Lewis acidic metal ions are among the most-active reported to date.[15,19–22] Nevertheless, the use of metal-based catalysts in industrial settings is not always desired, and the presence of trace amounts of (toxic) metals in the final products is subject to an increasingly lower limit accepted by end-users in commercial settings.

Therefore, from this viewpoint, one would ideally like to use organocatalysis for the formation of organic carbonates, and progress in this respect is characterized by the use of various types of catalysts based on ionic liquids;[23–25] (poly)alcohols and Brønsted acids;[26–31] (supported) phosphonium, ammonium, or imidazolium salts and their derivatives;[32–38] and others.[39–44] However, organocatalysts are usually much less effective in the activation of organic substrates and require longer reaction times, much higher reaction temperatures, and/or (much) higher loadings for effective turnover.[4] Thus, the generally observed lower reactivity of organocatalysts still poses a major challenge to their ability to compete with metal-based catalysts and eventually provide more-sustainable catalysis solutions.

In the course of our studies devoted to the development of a new and more efficient organocatalytic methodology for organic carbonate formation, we and others have shown that the activation of oxiranes through hydrogen bonding with polyphenolic compounds, fluorinated alcohols, and silanediols is very attractive.[45–48] In particular, pyrogallol (PG, i.e., 1,2,3-trihydroxybenzene) is an example of a highly efficient organocatalyst system that can mediate the coupling between terminal epoxides and CO_2 under extremely mild reaction conditions (25–45 °C, 0.2–1 MPa CO_2 pressure, 2 mol% catalyst). Of particular importance is the cooperative nature of the adjacent phenol groups that allows the formation of an extended hydrogen-bond network upon activation of the oxirane, which lowers the activation barrier for its ring-opening by an external nucleophile (Scheme 1 b).[31,42] We thought that an even higher local concentration of phenolic sites would be beneficial for catalytic turnover and, therefore, considered tannic acid (TA, Scheme 1 a) as a catalyst additive, as it is a naturally occurring plant polyphenol that is commercially available and inexpensive. The presence of multiple phenol fragments in TA should facilitate the highly efficient activation of oxiranes through similar synergistic effects to those noted for PG.

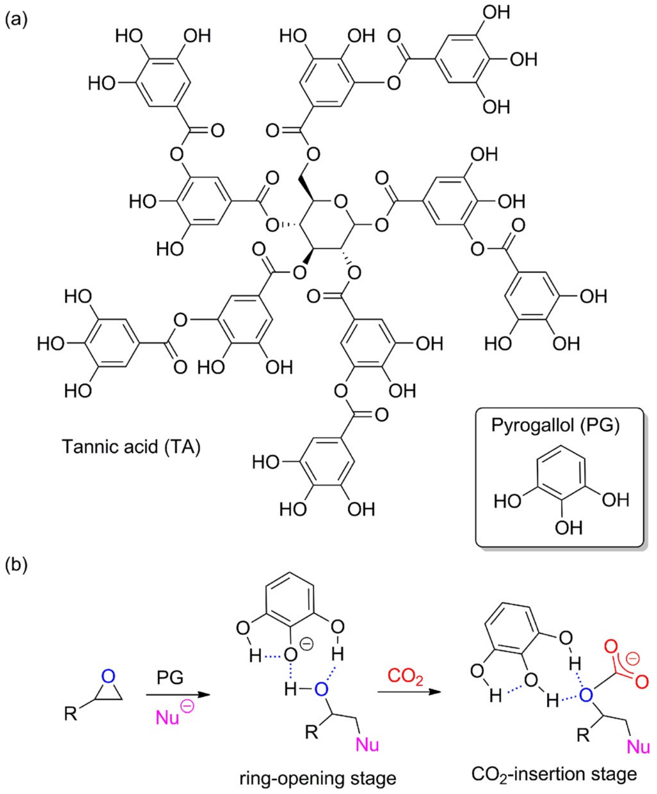
Herein, we report on the use of binary catalyst systems derived from TA and suitable nucleophiles for the coupling of CO_2 and various epoxides; these new catalyst systems are among the most active organocatalysts reported to date,[44] and their appreciable turnover frequencies (TOFs) compete with those reported for many known metal-based catalysts. The observation of synergistic effects for improved catalyst stability and lifetime creates the potential for new organocatalyst design in this area of CO_2 catalysis.

---

[a] S. Sopeña, Dr. G. Fiorani, Dr. C. Martín, Prof. Dr. A. W. Kleij
Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16, 43007 Tarragona (Spain)
E-mail: akleij@iciq.es

[b] Prof. Dr. A. W. Kleij
Catalan Institute for Research and Advanced Studies (ICREA)
Pg. Lluis Companys 23, 08010 Barcelona (Spain)

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201500710.



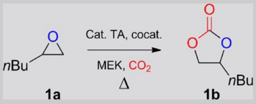
Scheme 1. (a) Chemical structures of TA and PG. (b) Stabilization of intermediates in organic carbonate synthesis through hydrogen bonding using PG.

Results and Discussion

First, we combined TA with NBu_4I to obtain a binary catalyst system capable of mediating the coupling of 1,2-epoxyhexane (**1a**, a benchmark substrate) and CO_2. Our previous study using PG/NBu_4I as a binary catalyst system [5 mol% of each with respect to the same substrate, 2-butanone (methyl ethyl ketone, MEK) as solvent][49] gave rise to a yield of 100% (93% isolated) after 18 h at 45 °C. Thus, we first attempted to use similar conditions (Table 1, entry 1) using a slightly lower amount of hydrogen-bond donor, that is, TA (0.50 mol%). However, under these conditions, we observed that the TA was not fully soluble; therefore, the epoxide turnover became more complicated. We found that an increase of the reaction temperature to 80 °C resulted in a homogeneous catalyst solution if the catalyst loading was kept low enough, that is, at 0.05 mol% of TA (Table 1, entry 3), and led to the quantitative formation of the cyclic carbonate **1b** with high selectivity (>99%). The use of the nucleophilic reagent alone (see Table 1, entries 4 and 5) led to a much lower yield of cyclic carbonate **1b**, which emphasizes the imperative role of the TA to mediate this conversion. In the presence of TA and absence of cocatalyst (NBu_4I), no conversion was noted (Table 1, entry 6).

We then varied the cocatalyst loading (Table 1, entries 7–11) and kept [TA] at 0.05 mol%; quantitative conversion of **1a** to **1b** could still be achieved at a NBu_4I loading of 2 mol%. Interestingly, the initial TOF under these conditions was relatively high (236 h^{-1}; Table 1, entry 10; t = 2 h); in the absence of TA, only an 8% yield of **1b** was noted after 2 h. The catalyst loading, [TA], could be further reduced to approximately 0.03 mol% (Table 1, entry 12) to yield a substantially higher conversion of **1a** compared to the turnover facilitated by the cocatalyst NBu_4I alone (cf., Table 1, entry 5). The reaction temperature had a significant effect on the conversion rate (see Table 1, entries 14 and 15 vs. 3), and 80 °C seems to be optimal for this catalytic system.

Table 1. Screening of conditions and (co)catalyst loadings using various nucleophiles, TA, and using 1,2-epoxyhexane (**1a**) as the substrate.[a]



Entry	Loading [mol%] TA	Loading [mol%] NBu_4X	Solvent	T [°C]	Yield[b] [%]
1	0.50[c]	I (5.0)	MEK	45	16
2	2.0[c]	I (5.0)	MEK	80	93
3	0.05	I (5.0)	MEK	80	>99[d]
4	0	I (5.0)	MEK	80	47
5	0	I (2.0)	MEK	80	41
6	0.05	0	MEK	80	0
7	0.05	I (4.0)	MEK	80	>99
8	0.05	I (3.0)	MEK	80	>99
9	0.05	I (2.0)	MEK	80	>99
10[e]	0.05	I (2.0)	MEK	80	24
11	0.05	I (1.0)	MEK	80	82
12	0.03	I (2.0)	MEK	80	79
13	0.01	I (2.0)	MEK	80	47
14	0.05	I (5.0)	MEK	70	76
15	0.05	I (5.0)	MEK	60	53
16[f]	0.05	I (5.0)	MEK	80	>99
17	0.05	Br (2.0)	MEK	80	>99
18	0.05	Cl (2.0)	MEK	80	70
19	0.05	I (2.0)	ACE	80	>99
20[g]	0.025	I (2.0)	MEK	80	>99
21[h]	0.15	I (2.0)	MEK	80	62
22[i,j]	0.03	I (2.0)	MEK	80	35
23[h,i]	0.15	I (2.0)	MEK	80	33
24[h,i]	0.30	I (2.0)	MEK	80	55

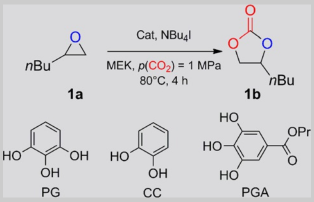
[a] General conditions: 1,2-epoxyhexane (8.3 mmol), $p_{CO_2}{}^0 = 1$ MPa, cocatalyst NBu_4X (amount indicated), 18 h, 30 mL autoclave as reactor; MEK or ACE (acetone; 5 mL). [b] Yield determined by ^1H NMR spectroscopy ($CDCl_3$) using mesitylene as an internal standard; selectivity for the cyclic carbonate was >99%. [c] Not fully homogeneous. [d] Isolated yield 99%. [e] Conditions: MEK (2.5 mL), $t = 2$ h; TON = 472, TOF = 236 h^{-1}; the reaction in the absence of TA afforded only 8% of **1b**. [f] $p_{CO_2}{}^0 = 0.6$ MPa. [g] Only 2.5 mL solvent. [h] PG as catalyst. [i] Reaction time 6 h. [j] Average TA TOF = 195 h^{-1}.

At a lower initial pressure of 0.6 MPa, the yield of **1b** remained quantitative (Table 1, entry 16). Upon changing the nature of the nucleophile (Table 1, entries 17 and 18), a lower yield of **1b** was apparent if the chloride was used whereas the bromide-based binary catalyst gave rise to a similar result, that is, quantitative conversion of epoxide **1a** could be attained (cf., Table 1, entry 9).[50] The use of an alternative solvent (acetone; Table 1, entry 19) also resulted in productive catalysis in line with our previous results on Zn-catalyzed carbonate formation.[51] A further decrease of the TA loading to 0.025 mol%

in only 2.5 mL of MEK still resulted in quantitative conversion (Table 1, entry 20).[52]

Finally, a comparison was made between the TA-based binary catalyst TA/NBu_4I and our previously reported binary couple PG/NBu_4I (Table 1, entries 21–24). As the TA structure contains five (substituted) PG units,[53] the comparison was made with the synthesis of carbonate **1 b** mediated by 5 equivalents of PG. After 18 h, a difference between the yields of **1 b** promoted by TA (Table 1, entry 12: 79 %) and PG (5 equiv., Table 1, entry 21: 62 %) was observed; for a reduced reaction time of 6 h, a much smaller difference in the yield of **1 b** was noted (cf., Table 1, entries 22 and 23; 35 vs. 32 % yield). Under these conditions, the TA-derived binary catalyst system (i.e., TA/NBu_4I) still displayed an appreciably high average TOF of 195 h^{-1}. Next, we decided to make a further comparison between TA and various polyphenol-based structures including PG, catechol (CC), and propyl gallate (PGA, see Table 2).

Table 2. Screening of various polyphenols in the synthesis of carbonate **1 b**.[a]



Entry	Phenol	Amount [mol %]	Conversion [%]	Yield [%][b]	TON[c]	TOF[d]
1	TA	0.03	21	20	634	159
2	TA	0.15	47	44	295	74
3	PG	0.03	10	9	303	76
4	PG	0.15	32	30	200	50
5	PG	0.30	43	41	138	34
6	CC	0.03	15	14	461	115
7	CC	0.15	42	41	272	68
8	CC	0.30	51	48	158	40
9	PGA	0.03	11	10	344	86
10	PGA	0.15	46	44	290	72
11	PGA	0.30	65	64	218	54
12[e]	–	0	8	7	–	–

[a] General conditions: 1,2-epoxyhexane (4.15 mmol), $p_{CO_2}{}^0 = 1$ MPa, NBu_4I (2.0 mol %), 4 h, 80 °C, MEK (2.5 mL), AMTEC reactor. [b] Yield determined by ^1H NMR spectroscopy ($CDCl_3$) using mesitylene as an internal standard; selectivity for the cyclic carbonate was > 99 %. [c] Total TON per molecule of catalyst based on reported yields. [d] Average TOF per molecule of catalyst based on reported yields. [e] Only 2.0 mol % NBu_4I used.

For the comparative studies, we used a high-throughput experimentation platform (AMTEC reactor, see the Supporting Information) and estimated the reactivity of the polyphenols under similar reaction conditions (Table 2, entries 1–11; reaction time 4 h). Moreover, for completion, the conversion obtained in the absence of the polyphenol additive was also examined (Table 2, entry 12). In the latter case, very low conversion was noted (8 %); thus, the production of carbonate **1 b** under these conditions is caused by the binary catalysts containing the polyphenols. Comparisons were made between the conversion and activity of the TA-based catalyst (Table 2, entry 1) and those consisting of 1, 5, or 10 equivalents of the polyphenols PG, CC, or PGA (Table 2, entries 3–11). According to the data in Table 2, the TA-based systems show favorable comparative reactivity behavior with high molecular turnover numbers (TONs) and TOFs. It should be mentioned that is difficult to use a correct reference system for TA as PG and CC are electronically different from the pseudo-PG units within the TA structure, and PGA probably represents a better electronic match. Furthermore, TA contains a significant amount of water (12 % weight loss upon drying),[53] and the reported TON and TOF values in Table 2 are uncorrected. The reactive polyphenol units within TA are nonrandomly distributed during catalysis, which likely reduces their accessibility relative to the other investigated catalyst systems. We hypothesize that intramolecular hydrogen bonding controls the accessibility of the polyphenol units, a phenomenon that cannot be (fully) counterbalanced by the use of a moderately polar solvent such as MEK. As the reactions in MEK needed an increased reaction temperature (80 °C) for the full dissolution of both catalyst components, it seems plausible to assume that this solvent is not able to break up intra- and intermolecular hydrogen bonding between the separate polyphenol units at lower temperatures. Despite these features, at very low TA loading (0.03 mol %) the relative reactivity seems to indicate that the high local concentration of phenol groups provides some degree of synergy that leads to efficient catalysis behavior. Thus, one should consider the overall catalytic effect rather than attempting to correlate quantitatively the findings in Table 2.

Remarkably, upon comparing the reactivity of PG, CC, and PGA as catalyst additives (cf., Table 2, entries 3–11), one can note the lower efficiency of PG among the polyphenols studied. This result contrasts with our previous findings in which the catalytic efficiency of PG was markedly better than that observed for CC at 45 °C.[45] Intrigued by this discrepancy, we decided to investigate the long-term temperature effect on the catalytic performance of the polyphenol additives in more detail by measuring the conversion of **1 a** to carbonate **1 b** at 80 °C at various time intervals (full data in the Supporting Information, Tables S1–S3). First, we compared the kinetic profiles of TA, PG, CC, and PGA during the first 6 h using equimolar amounts of polyphenol (0.03 mol %; see Figure 1). Interestingly, both triphenolic derivatives PG and PGA show inferior catalytic behavior as the conversion already seems to reach a plateau after 4 h at this catalyst loading whereas TA and CC retain good activity. These results seem to indicate some catalyst degradation for the PG- and PGA-based binary catalysts under the operating conditions.

To make the comparison more realistic, we also compared the catalytic performance of TA (0.03 mol %) and PG (0.15 mol %) over 18 h (Figure 2). After approximately 5 h, the reactivity of the PG-based binary catalyst decreased drastically whereas the TA-based system still showed appreciable activity. This further supports the view that TA is a more stable catalyst under these conditions and has a longer lifetime than the PG-based catalyst. The more effective catalytic behavior of TA is probably the result of a higher local concentration of phenol

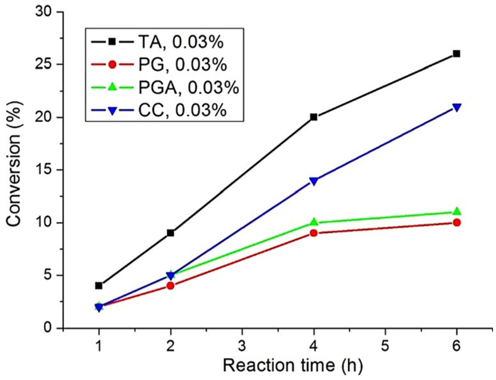


Figure 1. Comparison of the catalytic performance of polyphenol-based binary catalysts in the conversion of **1a** to **1b**. For reactions conditions, see Table 2.

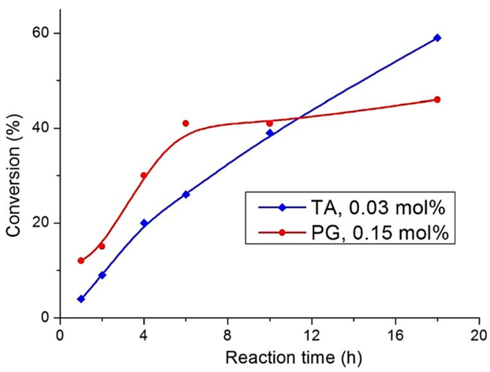
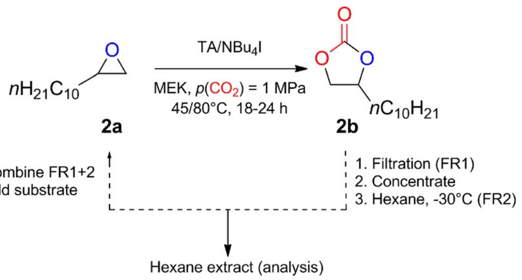


Figure 2. Comparison of the catalytic performance of TA- (0.03 mol%) and CC-based (0.15 mol%) binary catalysts in the conversion of **1a** to **1b**. For reactions conditions, see Table 2.

groups in the catalyst structure, which likely does not induce strong intermolecular effects. As we reported previously,[45] for PG (Scheme 1b), potential catalyst degradation may occur through irreversible proton transfer from PG to the substrate with the nucleophilic additive also involved. This eventually translates into lower catalytic efficiencies, and higher reaction temperatures in combination with very low catalyst loadings (0.03–0.15 mol%) may lead quickly to unproductive catalysis behavior and incomplete substrate conversion. Therefore, it seems that TA holds promise as a catalytic additive under dilute conditions whereas much higher concentrations are required to maintain similarly effective turnovers for the other polyphenols. To probe the hypothesis that the disappearance of phenol sites may be responsible for the loss of catalytic activity, we decided to investigate the recyclability of the binary catalyst TA/NBu$_4$I in the conversion of 1,2-epoxydodecane (**2a**, Scheme 2) into carbonate **2b** at two different reaction temperatures (45 and 80 °C).

At both reaction temperatures (see the Supporting Information for details), the catalyst was separated readily from the product-containing hexane phase. The hexane solution was then concentrated and showed virtually pure carbonate product **2b**, indicating that no significant catalyst components were extracted. Two solid catalyst fractions (FR1 and FR2, Scheme 2) could be separated and reused in a second catalyst cycle. The catalyst recycled at 80 °C showed a significant drop in conversion (89→27%), whereas a similar though slightly reduced conversion drop (54→24%) was noted at 45 °C. After the second cycle, the catalyst was separated from the product/substrate phase and subjected to ^{1}H NMR spectroscopy, IR spectroscopy, and thermogravimetric analysis (TGA). The combined analytic data showed a clear loss of reactive phenol units, likely caused by competing reactions between the polyphenol and the substrate/nucleophile (for analytical data see the Supporting Information). This afforded a halohydrin and NBu$_4$-based TA salt byproducts, which were identified by ^{1}H NMR spectroscopy, as also reported previously for the degradation of PG under forcing conditions.[46] The regeneration of the TA structure was probed by acid treatment of the isolated solid fraction from the recycling experiments. The treatment of the recycled material with concentrated HCl (37%) regenerated the TA species, as evidenced by ^{1}H NMR and IR spectroscopy analysis; the spectra showed very high similarity to the spectra of the commercial product. Thus, the acid treatment indicates the possibility of catalyst regeneration (see the Supporting Information). The recycled binary catalyst was reused in the synthesis of cyclic carbonate **2b** (Scheme 2), and an improved yield of 51% (vs. 24% for the untreated recovered TA) was determined at 80 °C.

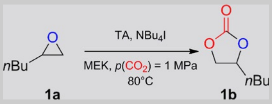


Scheme 2. Recycling studies with **2a** (6 mmol) as the substrate and TA/NBu$_4$I (0.25–0.50 and 2.5–5.0 mol%, respectively) in MEK (15 mL) at p_{CO_2} = 1 MPA.

The mass balance for both TA (FR1, Scheme 2) and NBu$_4$I (FR2, Scheme 2) was then checked carefully. Although a virtually complete isolation of the original TA amount (24.6 vs. 25.7 mg; 96%) was noted for FR1, a clear loss of the cocatalytic NBu$_4$I (FR2, 35.2 vs. 56.8 mg; 62%) was apparent. Finally, we checked separately the activity of a regenerated TA sample using a fresh amount of NBu$_4$I in the synthesis of cyclic carbonate **1b** and compared the conversion with the original data for 0.03 mol% TA at 80 °C for 18 h (79% conversion; see Table 1, entry 12). Fortunately, the comparable conversion (75%) found for the regenerated TA catalyst supports the view that it can be readily recycled upon acid treatment.

We then further investigated the application of the binary TA/NBu$_4$I catalyst in the synthesis of carbonate **1b** using relatively low amounts of TA (Table 3, 0.01–0.05 mol%) combined with 10 equivalents of NBu$_4$I (with respect to TA) as the nucleophile. At 0.05 mol% TA (Table 3, entry 1), carbonate **1b** was produced in 86% yield after 24 h with a high TON of 1721 and

Table 3. TA-mediated synthesis of carbonate **1 b** under various conditions.[a]



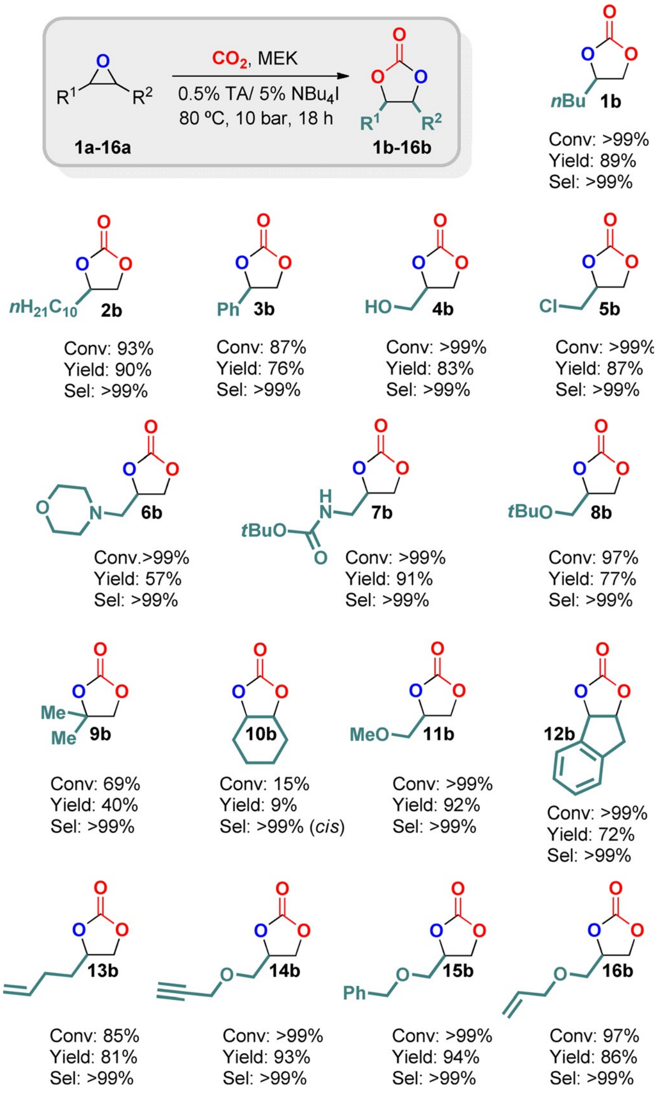
Entry	Loading [mol %]		t	Conversion	Yield[b]	TON[c]	TOF[d]
	TA	NBu_4I	[h]	[%]	[%]		
1	0.05	0.5	24	96	86	1721	72
2	–	0.5	24	36	32	–	–
3	0.05	0.5	66	100	100	1985	30
4	–	0.5	66	76	76	–	–
5	0.01	0.1	24	26	24	2220	92
6	–	0.1	24	18	16	–	–
7	0.01	0.1	66	53	45	4458	68
8	–	0.1	66	55	48	–	–

[a] General conditions: 1,2-epoxyhexane (10 mmol), $p_{CO_2}{}^0 = 1$ MPa, 80 °C, MEK (5 mL), AMTEC reactor. [b] Yield determined by ^1H NMR spectroscopy ($CDCl_3$) with mesitylene as an internal standard; selectivity for the cyclic carbonate was > 99 %. [c] Total TON per TA equivalent based on reported yields. [d] Average TOF per TA equivalent based on reported yields.

an average TOF of 72 h^{-1}. Notably, in the absence of TA (Table 3, entry 2), carbonate **1 b** was produced in only 32 % yield. An increased total reaction time of 66 h (Table 3, entries 3 and 4) reduced this difference as expected, which may also be an effect of partial catalyst degradation. When reducing the TA loading further to 0.01 mol % (Table 3, entries 5 and 7) the difference between the binary couple and the catalyst system comprising the iodide nucleophile alone became less significant despite the higher and valuable TONs observed (2220 after 24 h, 4458 after 66 h). Clearly, the long-term stability plays a key role in the attainment of high average activity.

Next, the substrate scope was investigated (see Scheme 3) under conditions that would enable high conversion of the epoxide substrates **1 a–16 a** at the reported temperature (80 °C) and pressure (1 MPa). All carbonate products **1 b–16 b** were produced in a high-throughput reactor system at a 2 mmol substrate scale. Most of the products were obtained at high conversion and selectivity with good-to-excellent isolated yields of up to 94 % (except for **6 b**; 57 %). Under these reaction conditions, the synthesis of **1 b** was also probed in the absence of TA and only a low yield of 22 % was achieved. The binary catalyst TA/NBu_4I tolerates several functional groups including alcohol, alkyl halide, heterocyclic ring systems, carbamate, ether, alkene, and alkyne groups. Furthermore, the sterically more hindered substrate **9 a** could also be converted (69 %) and provided 40 % isolated yield of carbonate **9 b** whereas the internal epoxide **10 a** resulted in much poorer results, as expected, in line with the more challenging nature of this conversion for organocatalytic catalyst systems.[43]

The conversion of internal epoxides was computed to be more energetically demanding (cf., higher kinetic barriers) than the conversion of terminal epoxides.[54] Nonetheless, the formation of all carbonates was mediated by only 0.5 mol % TA; this is an attractive feature within the context of providing a sustainable and reactive alternative for metal-based carbonate-formation reactions.



Scheme 3. Substrate scope for the TA-mediated synthesis of organic carbonates **1 b–16 b**. General conditions: epoxide (2 mmol), TA (0.5 mol %), NBu4I (5 mol %), 80 °C, $p_{CO2}0 = 1$ MPa, 18 h, MEK (5 mL), AMTEC reactor; under these conditions, the yield obtained for 1 b was only 22 % in the absence of TA.

Conclusions

We present here a new binary catalyst system based on a naturally occurring and fairly inexpensive polyphenol, that is, tannic acid (TA), which shows excellent catalytic reactivity at exceptionally low loadings. Therefore, this system is an attractive and sustainable organocatalytic alternative. Comparative catalysis studies have indicated that some degree of synergy between the various polyphenol units within the TA structure may help to increase the catalyst lifetime; this provides a conceptually interesting approach for the further improvement of polyphenol-based organocatalysis in the area of CO_2 conversion. Our future work will be focused on merging these concepts with the design of organocatalyst systems with improved reactivity and stability for similar CO_2 conversions and the preferable use of hydrogen-bonding as a substrate-activation strategy.

Experimental Section

General

Methyl ethyl ketone and carbon dioxide (purchased from PRAXAIR) were used as received without further purification or drying. All phenolic compounds were purchased from Sigma–Aldrich and used without further purification; the TA was reagent grade, see also Ref. [53]. The NMR spectra were recorded using Bruker AV-400 and AV-500 spectrometers and referenced to the residual deuterated solvent signals. The FTIR measurements were performed with a Bruker Optics FTIR Alpha spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and a KBr beam splitter at 4 cm^{-1} resolution.

Standard autoclave screening experiments

All reactions were performed in a 30 mL stainless-steel reactor. In a typical experiment, a solution of TA (0.050 mol %, 7.05 mg), NBu_4I (2.00 mol %, 61.3 mg), 1,2-epoxyhexane (8.30 mmol, 831 mg), and mesitylene (1.00 mL, 7.18 mmol) in MEK (5 mL) was added to a stainless-steel reactor. Three cycles of pressurization and depressurization of the reactor ($p_{CO_2} = 0.5$ MPa) were performed, and the pressure was stabilized at 1 MPa. The reactor was heated to the required temperature, and the mixture was stirred for a further 18 h. Then, the reactor was cooled and depressurized, and an aliquot of the solution was analyzed by means of ^1H NMR spectroscopy using $CDCl_3$ as the solvent. The yield was determined using mesitylene as the internal standard. In all cases, the selectivity for the cyclic carbonate product was determined to be >99 %.

Substrate scope experiments

All reactions were performed in an SPR16 Slurry Phase Reactor (Amtec GmbH). First, TA (0.500 mol %, 17.0 mg) and NBu_4I (5.00 mol %, 36.9 mg) were put into the reactors. Then, the reaction vessels were tested for leaks using N_2 (1.5 MPa) to a final reduced pressure of 0.2 MPa. After the injection into the reactors of the chosen epoxide (e.g., 2.00 mmol, 200 mg for 1,2-epoxyhexane) in MEK (5 mL) and mesitylene (10.0 mol %, 24.0 mg) as an internal standard (IS), the vessels were heated to the desired reaction temperature ($T = 80$ °C). Once the operating temperature was reached, the CO_2 pressure was increased to 1 MPa and the reaction mixture was stirred at the appropriate temperature for 18 h. At the end of the reaction, the analysis of the crude product was performed as reported above for the screening phase. The crude products were obtained by removing the solvent and unreacted substrate under vacuum (50 Pa). The residue was then dissolved in dichloromethane (DCM, except for the conversion of substrate **4a**, for which the solvent was ethyl acetate) and filtered through silica; after the removal of the solvent, the pure cyclic carbonate products were obtained. The identity of each of the carbonate products was confirmed by comparison to previously reported literature data, and full tabular data and copies of all spectra are provided in the Supporting Information.

Recycling experiments

All reactions were performed in a 45 mL stainless-steel reactor. In a typical experiment, a solution of TA (0.250 mol %, 25.5 mg), nBu_4NI (2.50 mol %, 55.4 mg), and 1,2-epoxydodecane (6.00 mmol, 1.25 g) in MEK (15 mL) was added to a stainless-steel reactor. Three cycles of pressurization and depressurization of the reactor ($p_{CO_2} =$ 0.5 MPa) were performed before final stabilization of the pressure at 1 MPa. The reactor was then heated to the required temperature, and the mixture was stirred for an additional 18 h. Then, the reactor was cooled and depressurized, and the reaction mixture was separated from the precipitate (Solid 1; FR1) and moved to a flask. The solvent was removed under vacuum, and hexane (80 mL) was added. Then, the hexane solution was cooled to -30 °C. After 3 h, the flask was warmed to room temperature, the solution was filtered, and the collected precipitate (Solid 2; FR2) was washed with hexane (80 mL). The combined organic phases were then concentrated under vacuum to afford the pure cyclic carbonate. For a new reaction cycle, Solid 1 (FR1) was put into a stainless-steel reactor, and Solid 2 (FR2) was dissolved in MEK (15 mL) and added to the same reactor. A new portion of 1,2-epoxydodecane (6.00 mmol, 1.25 g) was added. Finally, the procedure continued as described above. To regenerate the catalyst, FR1 was treated with concentrated HCl for 18 h. Then, the mixture was filtered and washed with diethyl ether and hexane. The obtained precipitate was then dried under vacuum and combined with FR2 in a new catalytic cycle in MEK (15 mL) and transferred to a pressure reactor, and 1,2-epoxydodecane (6.0 mmol, 1.25 g) was added. Finally, the procedure continued as described above.

Acknowledgements

C.M. gratefully thanks the Marie Curie COFUND Action from the European Commission for cofinancing a postdoctoral fellowship. G.F. kindly acknowledges financial support from the European Community through a Marie Curie Intra-European Fellowship (FP7-PEOPLE-2013-IEF, project RENOVACARB, Grant Agreement no. 622587). Further acknowledgements go to ICIQ, ICREA, and the Spanish Ministerio de Economía y Competitividad (MINECO) through project CTQ2014-60419-R, and support through Severo Ochoa Excellence Accreditation 2014–2018 (SEV-2013-0319). Dr. Marta Giménez and Cristina Rivero are thanked for their help regarding the high-pressure experiments.

Keywords: carbon dioxide · homogeneous catalysis · hydrogen bonding · oxygen heterocycles · ring expansion

[1] *Carbon Dioxide as Chemical Feedstock* (Ed.: M. Aresta), Wiley-VCH, Weinheim, **2010**.
[2] M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510; *Angew. Chem.* **2011**, *123*, 8662.
[3] M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, *ChemSusChem* **2011**, *4*, 1216.
[4] G. Fiorani, W. Guo, A. W. Kleij, *Green Chem.* **2015**, *17*, 1375.
[5] M. Mikkelsen, M. Jørgensen, F. C. Krebs, *Energy Environ. Sci.* **2010**, *3*, 43.
[6] D. R. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388.
[7] M. North, R. Pasquale, C. Young, *Green Chem.* **2010**, *12*, 1514.
[8] P. P. Pescarmona, M. Taherimehr, *Catal. Sci. Technol.* **2012**, *2*, 2169.
[9] N. Kielland, C. J. Whiteoak, A. W. Kleij, *Adv. Synth. Catal.* **2013**, *355*, 2115.
[10] O. Jacquet, X. Frogneux, C. Das Neves Gomes, T. Cantat, *Chem. Sci.* **2013**, *4*, 2127.
[11] H. Mizuno, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2011**, *133*, 1251.
[12] M. D. Greenhalgh, S. P. Thomas, *J. Am. Chem. Soc.* **2012**, *134*, 11900.
[13] T. León, A. Correa, R. Martin, *J. Am. Chem. Soc.* **2013**, *135*, 1221.
[14] Y. Li, I. Sorribes, T. Yan, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 12156; *Angew. Chem.* **2013**, *125*, 12378.
[15] C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353.
[16] B. Schäffner, F. Schäffner, S. P. Verevkin, A. Börner, *Chem. Rev.* **2010**, *110*, 4554.
[17] J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663.

[18] See, for example: D. J. Darensbourg, A. I. Moncada, W. Choi, J. H. Reibenspies, *J. Am. Chem. Soc.* **2008**, *130*, 6523.
[19] C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.* **2013**, *135*, 1228.
[20] T. Ema, Y. Miyazaki, S. Koyama, Y. Yano, T. Sakai, *Chem. Commun.* **2012**, *48*, 4489.
[21] J. Meléndez, M. North, P. Villuendas, *Chem. Commun.* **2009**, 2577.
[22] J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang, B. Han, *Green Chem.* **2009**, *11*, 1031.
[23] J. Sun, S. Zhang, W. Cheng, J. Ren, *Tetrahedron Lett.* **2008**, *49*, 3588.
[24] Z.-Z. Yang, Y.-N. Zhao, L.-N. He, J. Gao, Z.-S. Yin, *Green Chem.* **2012**, *14*, 519.
[25] Z. Z. Yang, L.-N. He, C.-X. Miao, S. Chanfreau, *Adv. Synth. Catal.* **2010**, *352*, 2233.
[26] J. L. Song, Z. F. Zhang, B. X. Han, S. Q. Hu, W. J. Li, Y. Xie, *Green Chem.* **2008**, *10*, 1337.
[27] S. G. Liang, H. Z. Liu, T. Jiang, J. L. Song, G. Y. Yang, B. X. Han, *Chem. Commun.* **2011**, *47*, 2131.
[28] C. Qi, J. Ye, W. Zeng, H. Jiang, *Adv. Synth. Catal.* **2010**, *352*, 1925.
[29] J. Sun, W. G. Cheng, Z. F. Yang, J. Q. Wang, T. T. Xu, J. Y. Xin, S. J. Zhang, *Green Chem.* **2014**, *16*, 3071.
[30] J. Sun, L. J. Han, W. G. Cheng, J. Q. Wang, X. P. Zhang, S. J. Zhang, *ChemSusChem* **2011**, *4*, 502.
[31] J. Q. Wang, J. Sun, W. G. Cheng, K. Dong, X. P. Zhang, S. J. Zhang, *Phys. Chem. Chem. Phys.* **2012**, *14*, 11021.
[32] J. Q. Wang, D. L. Kong, J. Y. Chen, F. Cai, L.-N. He, *J. Mol. Catal. A* **2006**, *249*, 143.
[33] Q.-W. Song, L.-N. He, J.-Q. Wang, H. Yasuda, T. Sakakura, *Green Chem.* **2013**, *15*, 110.
[34] M. H. Anthofer, M. E. Wilhelm, M. Cokoja, M. Drees, W. A. Herrmann, F. E. Kühn, *ChemCatChem* **2015**, *7*, 94.
[35] V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* **2002**, *4*, 2561.
[36] X. Chen, J. Sun, J. Q. Wang, W. G. Cheng, *Tetrahedron Lett.* **2012**, *53*, 2684.
[37] T. Werner, H. Buettner, *ChemSusChem* **2014**, *7*, 3268. See also: C. Kohrt, T. Werner, *ChemSusChem* **2015**, *8*, 2031.
[38] T. Werner, N. Tenhumberg, H. Buettner, *ChemCatChem* **2014**, *6*, 3493–3500.
[39] Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema, T. Sakai, *Org. Lett.* **2010**, *12*, 5728.
[40] R. A. Watile, K. M. Deshmukh, K. P. Dhake, B. M. Bhanage, *Catal. Sci. Technol.* **2012**, *2*, 1051.
[41] Y. M. Shen, W. L. Duan, M. Shi, *Adv. Synth. Catal.* **2003**, *345*, 337.
[42] B. Chatelet, L. Joucla, J.-P. Dutasta, A. Martinez, K. C. Szeto, V. Dufaud, *J. Am. Chem. Soc.* **2013**, *135*, 5348.
[43] B. Chatelet, L. Joucla, J.-P. Dutasta, A. Martinez, V. Dufaud, *Chem. Eur. J.* **2014**, *20*, 8571.
[44] M. E. Wilhelm, M. H. Anthofer, M. Cokoja, I. I. E. Markovits, W. A. Herrmann, F. E. Kühn, *ChemSusChem* **2014**, *7*, 1357.
[45] C. J. Whiteoak, A. Nova, F. Maseras, A. W. Kleij, *ChemSusChem* **2012**, *5*, 2032.
[46] C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij, M. A. Pericàs, *Green Chem.* **2014**, *16*, 1552.
[47] Quite recently, Mattson et al. reported interesting and highly active silanediol catalysts for organic carbonate formation, see: A. M. Hardman-Baldwin, A. E. Mattson, *ChemSusChem* **2014**, *7*, 3275.
[48] S. Gennen, M. Alves, R. Méreau, T. Tassaing, B. Gilbert, C. Detrembleur, C. Jerome, B. Grignard, *ChemSusChem* **2015**, *8*, 1845.
[49] MEK was previously used by us and others as it is a good medium for CO_2 dissolution: A. Decortes, M. Martínez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Chem. Commun.* **2010**, *46*, 4580.
[50] Compared with the reaction listed in Table 1, entry 5, the background reactions in the presence of 2 mol% of NBu_4Cl (44%) or 2 mol% NBu_4Br (60%) show similar or improved conversion rates. However, in the presence of TA, the chloride-based binary catalyst (cf., Table 1, entry 18) is somewhat less effective whereas the bromide- and iodide-based ones (Table 1, entries 9 and 17) give quantitative conversions. As our previous studies were performed using NBu_4I as the nucleophilic additive, we continued using this cocatalytic mediator for comparative reasons.
[51] A. Decortes, A. W. Kleij, *ChemCatChem* **2011**, *3*, 831.
[52] Possible product inhibition was also probed using a 1:1 mixture of the cyclic carbonate **1 b** and its precursor **1 a**, taking the reaction in the absence of the product as a reference. In both cases, a similar conversion was noted at the end of the reaction; therefore, no (significant) product inhibition occurs (see the Supporting Information for details).
[53] Commercially available TA is usually a combination of polygalloyl glucoses or polygalloyl quinic acid esters, with the number of galloyl moieties per molecule depending on the plant source. Here, we have used the commercial product from Aldrich (ACS reagent, 500 g = 77.50 €), which loses approximately 12% of its weight upon drying. Further, as the general structure of TA contains five pseudo-PG units, we have compared the catalytic performance of TA (0.03 mol%; 1 equiv.) with that of PG (0.15 mol%; 5 equiv.).
[54] F. Castro-Gómez, G. Salassa, A. W. Kleij, C. Bo, *Chem. Eur. J.* **2013**, *19*, 6289.

Received: May 26, 2015
Revised: July 20, 2015