Highly Efficient Organocatalyzed Conversion of Oxiranes and CO_2 into Organic Carbonates

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

Introduction

Current (catalytic) research centered on the use of carbon dioxide (CO_2) as a cheap and renewable source of carbon focuses on the incorporation into other organic scaffolds as to be able to partially replace fossil fuel based chemistries.[1-9] Considerable progress in this area has been achieved leading to a wide variety of organic structures one may obtain using CO_2 as a molecular synthon.[10-14] Among these organic products, organic carbonates[7,8,15-17] have conquered a prominent position being useful in a number of applications including their use as fuel additives, as non-protic solvents and as monomer intermediates for polymeric structures.[18] In the last decade, highly efficient catalytic methods for their preparation have emerged with those incorporating Lewis acidic metal ions probably among the most active reported to date.[15,19-22] Notwithstanding, the use of metal-based catalysts in industrial settings is not always desired and the presence of trace amounts of (toxic) metals in final products is subject of 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 Brøndstedt acids,[26-31] (supported) phosphonium, ammonium or imidazolium salts and 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 is still posing a major challenge to be able to compete with metal-based catalysts eventually providing more

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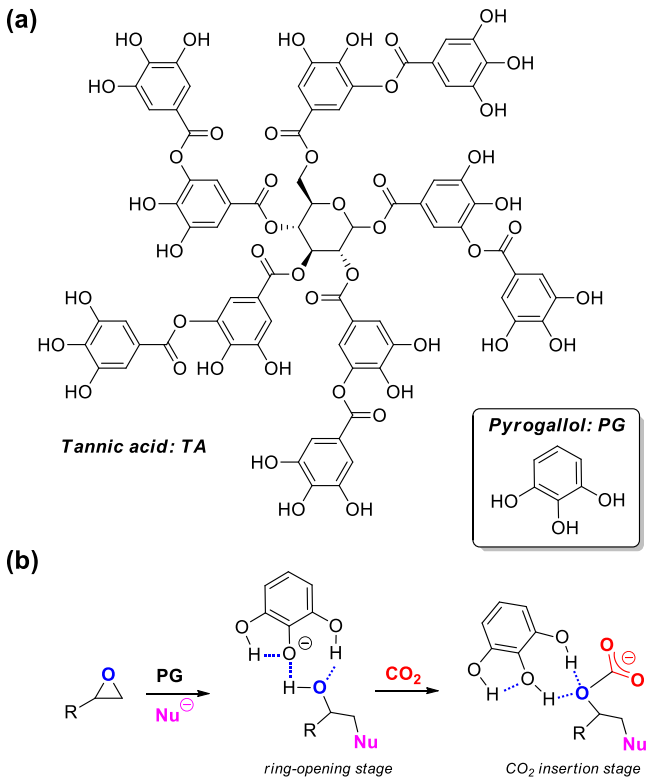
sustainable catalysis solutions.



Scheme 1. (a) Chemical structure of tannic acid (**TA**) and pyrogallol (**PG**). (b) Stabilization of intermediates in organic carbonate synthesis through H–bonding using **PG**.

In the course of our studies devoted to the development of new and more efficient organocatalytic methodology for organic carbonate formation, we and others have shown that activation of oxiranes through hydrogen-bonding using 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 able to mediate the coupling between terminal epoxides and CO_2 under extremely mild reaction conditions (25–45ºC, 2–10 bar CO_2 pressure, 2 mol% catalyst). Of particular importance is the cooperative nature of the adjacent phenol groups that allows for an extended hydrogen-bond network upon activation of the oxirane thereby lowering the activation barrier for its ring-opening by an external nucleophile (Scheme 1b, below) and beyond.[31,42] We thought that an even higher local concentration of phenolic sites would be beneficial for catalytic turnover and therefore considered tannic acid (*i.e.* **TA**, Scheme 1a) as catalyst additive being a naturally occurring plant phenol that is commercially available and cheap. The presence of multiple phenol fragments in tannic acid should facilitate highly efficient activation of oxiranes through similar synergistic effects as noted for **PG**.

Herein we report on the use of binary catalyst systems derived from tannic acid 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] with appreciable turnover frequencies able to compete with those reported for many known metal-based catalysts. The observation of synergistic effects for improved catalyst stability and lifetime creates new potential for new organocatalyst design in this area of CO_2 catalysis.

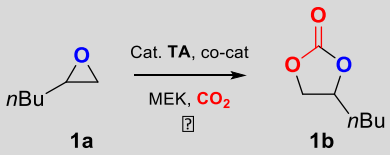
Results and Discussion

First we combined tannic acid **TA** with NBu_4I to obtain a binary catalyst system capable of mediating the coupling between 1,2-epoxyhexane **1a** (a benchmark substrate) and CO_2. Our previous result using pyrogallol/NBu_4I as binary catalyst system (5 mol% each with respect to the same substrate, MEK as solvent, MEK = 2-butanone)[49] gave a yield of 100% (93% isolated) at 45ºC after 18 h. Thus, we first attempted to use similar conditions (Table 1, entry 1) with a slightly lower amount of hydrogen-bond donor, *i.e.* **TA** (0.50 mol%). However, we observed that under these conditions, the tannic acid was not fully soluble therefore complicating epoxide turnover. We were pleased to find that an increase of the reaction temperature to 80ºC gave a homogeneous catalyst solution when the catalyst loading was kept low enough, *i.e.* at 0.05 mol% of **TA** (entry 3) leading to quantitative formation of the cyclic carbonate **1b** in high selectivity (>99%). The use of the nucleophilic reagent alone (see entries 4 and 5) led to a much lower yield in cyclic carbonate **1b**, emphasizing the imperative role of the tannic acid to mediate this

conversion. In the presence of tannic acid **TA** and absence of co-catalyst (NBu_4I) no conversion was noted (entry 6).

We then varied the co-catalyst loading (entries 7-11) while keeping [**TA**] at 0.05 mol%, and observed that quantitative conversion of **1a** into **1b** could still be achieved at an NBu_4I loading of 2 mol%. Interestingly, the initial TOF under these conditions was quite high (236 h^{-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 around 0.03 mol% (entry 12) to give substantially higher conversion of **1a** compared to the turnover facilitated by the co-catalyst NBu_4I alone (*cf.*, entry 5). The reaction temperature had a significant effect on the conversion rate (see entries 14 and 15 versus 3) and 80ºC seems to be rather optimal for this catalyst system.

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



Entry	**TA** [mol%]	NBu_4**X** [mol%]	Solvent	T [ºC]	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), $p(CO_2)^0$ = 10 bar, co-catalyst NBu_4**X** (amount indicated), 18 h, 30 mL autoclave as reactor. MEK = 2-butanone and ACE = acetone (5 mL). [b] Yield determined by ^{1}H NMR ($CDCl_3$) using mesitylene as an internal standard. Selectivity for the cyclic carbonate was >99%. [c] Not fully homogeneous. [d] Isolated yield 99%. [e] Using 2.5 mL of MEK, t = 2 h; TON = 472, TOF = 236 h^{-1}; the reaction in absence of **TA** afforded only 8% of **1b**. [f] $p(CO_2)^0$ = 6 bar. [g] Using only 2.5 mL of solvent. [h] Using pyrogallol as catalyst. [i] Reaction time 6 h. [j] Average TOF/h/**TA** = 195 h^{-1}.

When the initial pressure was lowered to 6 bar, the yield of **1b** remained quantitative (entry 16). Upon changing the nature of the nucleophile (entries 17 and

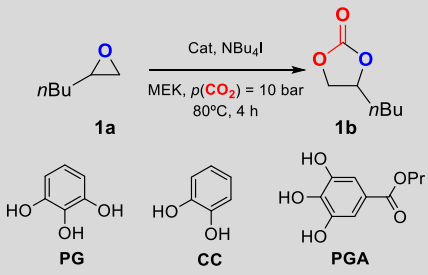
18), a lower yield of **1b** was apparent when chloride was used, whereas the bromide based binary catalyst gave a similar result, *i.e.* quantitative conversion of epoxide **1a** could be attained (cf., entry 9).[50] The use of an alternative solvent (acetone; entry 19) also gave productive catalysis in line with our previous results on Zn-catalyzed carbonate formation.[51] Further lowering the tannic acid **TA** loading to 0.025 mol% and performing the catalysis in only 2.5 mL of MEK still gave quantitative conversion (entry 20).[52]

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

For the comparative studies we used a high-throughput experimentation platform (AMTEC reactor, see Supporting Information) and estimated the reactivity of the polyphenols under similar reaction conditions (entries 1-11; reaction time 4 h). Moreover, for completion, the conversion obtained in the absence of the polyphenol additive was also examined (entry 12). In the latter case very low conversion was noted (8%) and the production of carbonate **1b** noted under these conditions is thus the effect of using the binary catalysts comprising of the polyphenol structures. Comparisons were made between the conversion/activity of the **TA** based catalyst (entry 1) and those consisting of 1, 5 or 10 equiv of polyphenols **PG**, **CC** or **PGA** (entries 3–11).

From the data noted in Table 2 it is clear that the TA based systems show favorable comparative reactivity behavior with high molecular 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, the **TA** structure contains a significant amount of water (12% weight loss upon drying)[53] and reported TON/TOF values in Table 2 are uncorrected. The reactive polyphenol units within **TA** are non-randomly distributed compared to the other investigated catalyst systems during catalysis which likely reduces their accessibility. We hypothesize that intramolecular H-bonding is in fact controlling the accessibility of the polyphenol units, a phenomenon which cannot be (fully) counterbalanced by the use of a moderately polar solvent such as MEK. Since the reactions in MEK needed an increased reaction temperature (80ºC) for full dissolution of both catalyst components, it seems plausible to assume that this solvent indeed is not able to break up intra/intermolecular H-bonding between the separate polyphenol units at lower temperatures. Despite these features, at very low loading of **TA** (0.03 mol%) the relative reactivity seems to indicate that the high local concentration of phenol groups provides some degree of synergy leading to efficient catalysis behavior. Thus, the overall catalytic effect should be taken into account rather than trying to quantitatively correlate the findings in Table 2.

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



Entry	Phenol	Amount [mol%]	Conv. [%]	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), $p(CO_2)^0$ = 10 bar, NBu_4I (2.0 mol%), 4 h, 80ºC, MEK (2.5 mL), AMTEC reactor. [b] Yield determined by ^1H NMR ($CDCl_3$) using mesitylene as an internal standard. Selectivity for the cyclic carbonate was >99%. [c] Total turnover number per molecule of catalyst based on reported yields. [d] Average turnover frequency per molecule of catalyst based on reported yields. [e] Only 2.0 mol% NBu_4I used.

Remarkably, upon comparing the reactivity of **PG**, **CC** and **PGA** as catalyst additives (cf., entries 3-11), one can note the lower efficiency of **PG** among the polyphenols studied. This result contrasts our previous findings[45] where the catalytic efficiency of **PG** proved to be markedly better than that observed for **CC** at 45ºC. 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 1,2-epoxyhexane **1a** into carbonate **1b** at 80ºC 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 level after 4 h at this catalyst loading, whereas the tannic acid **TA** and catechol **CC** still retain good activity. These results seem to indicate some catalyst degradation for both **PG** and **PGA** based binary catalysts under the operative conditions.

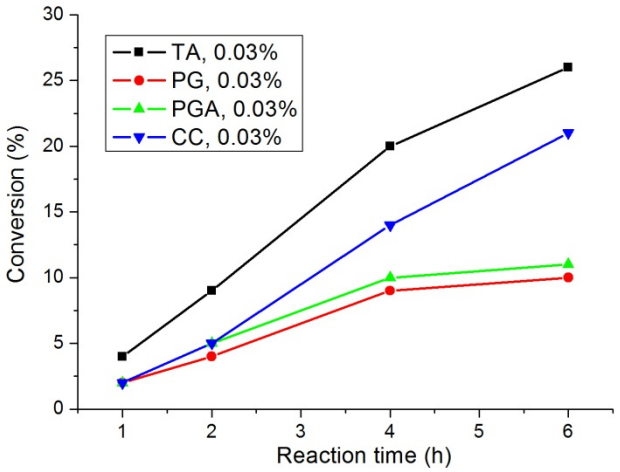


Figure 1. Comparison of the catalytic performance of polyphenol based binary catalysts in the conversion of **1a** into **1b**. For reactions conditions: see Table 2.

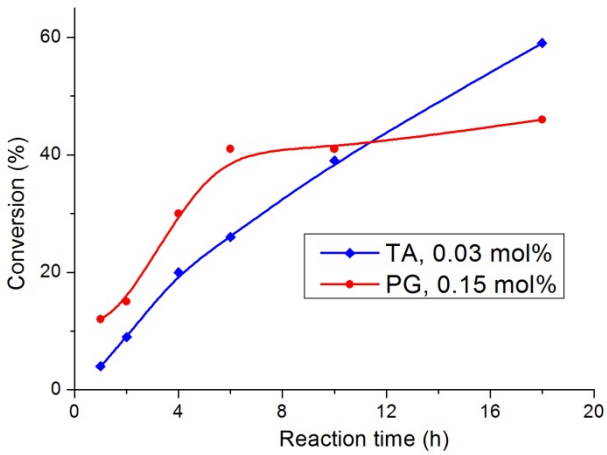
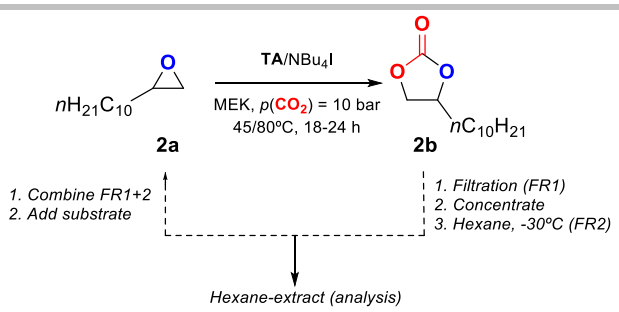


Figure 2. Comparison of the catalytic performance of **TA** (0.03 mol%) and **CC** (0.15 mol%) based binary catalysts in the conversion of **1a** into **1b**. For reactions conditions: see Table 2.

In order to make the comparison more realistic we also followed the performance of 0.03 mol% of **TA** and 0.15 mol% of **PG** during 18 h (Figure 2). As can be noted, after about 5 h the reactivity of the **PG**-based binary catalyst is drastically reduced while the **TA**-based system still shows appreciable activity. This further supports the view that the **TA** is a more stable catalyst under these conditions and has a longer life-time compared to **PG**. The more effective catalytic behavior of **TA** is probably the result of a higher local concentration of phenol groups present in the catalyst structure which likely does not induce strong intermolecular effects. As previously reported by us,[45] in the pyrogallol case (Scheme 1**b**) potential catalyst degradation may occur via irreversible proton transfer of the phenol to the substrate with the nucleophilic additive also being 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 quickly lead to unproductive catalysis behavior and incomplete substrate conversion. It therefore seems that tannic acid **TA** holds promise as a catalytic additive under dilute conditions, whereas for the other polyphenols much higher concentrations are required to maintain similar effective turnover. To probe the hypothesis that indeed the disappearance of phenol sites may be responsible for losing catalytic activity, we decided to investigate the recyclability of the binary catalyst **TA**/NBu_4I in the conversion of 1,2-epoxy-dodecane **2a** (Scheme 2) into carbonate **2b** at two different reaction temperatures (45 and 80ºC).



Scheme 2. Recycling studies using 1,2-epoxy-dodecane **2a** (6 mmol) as substrate and **TA**/NBu_4I (0.25-0.50 and 2.5–5.0 mol%, respectively) in MEK (15 mL) at $p(CO_2)$ = 10 bar.

At both reaction temperatures (see Supporting Information for details), the catalyst was easily separated 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 were reused in a second catalyst cycle. The catalyst recycled at 80ºC showed a significant drop in conversion (89→27%) whereas at 45ºC a similar though slightly reduced conversion drop (54→24%) was noted. The catalyst structure after the second cycle was separated from the product/substrate phase and subjected to ^{1}H NMR, IR and TGA (thermo-gravimetric) analysis. The combined analytic data clearly showed a loss of reactive phenol units likely caused by competing reactions between the polyphenol and the substrate/nucleophile (see for analytical data the Supporting Information), giving halohydrin and NBu_4-based **TA** salt byproducts which were identified by ^{1}H NMR as also previously reported for the degradation of PG under forcing conditions.[46] The regeneration of the **TA** structure was probed by treatment of the isolated solid fraction from the recycling experiments under acidic conditions. Treatment of the recycled material with concentrated HCl (37%) regenerated the **TA** species as evidenced by ^{1}H NMR and IR analysis showing very high similarity to the spectroscopic footprint of the commercial product. Thus, the acid treatment indicates the possibility of catalyst regeneration (see the Supporting Information). When

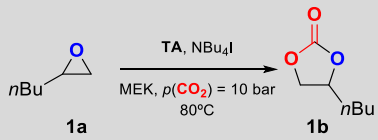
the recycled binary catalyst was reused in the synthesis of cyclic carbonate **2b** (Scheme 2), an improved yield of 51% (versus 24% for the untreated recovered **TA**) was determined at 80ºC.

The mass balance for both **TA** (FR1, Scheme 2) and NBu_4I (FR2, Scheme 2) was then carefully checked. Whereas for FR1 a virtually complete isolation of the original **TA** amount (24.6 versus 25.7 mg; 96%) was noted, a clear loss of the co-catalytic NBu_4I (FR2, 35.2 versus 56.8 mg; 62%) was apparent. Finally, we then checked separately the activity of a regenerated **TA** sample with a fresh amount of NBu_4I in the synthesis of cyclic carbonate **1b** and compared the conversion with the original data using 0.03 mol% of TA at 80ºC for 18 h (79% conversion; see entry 12 Table 1). Fortunately, we found a comparable conversion (75%) for the regenerated **TA** catalyst supporting the view that it can be easily recycled upon acid treatment.

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), $p(CO_2)^0$ = 10 bar, 80ºC, MEK (5 mL), AMTEC reactor. [b] Yield determined by ^1H NMR ($CDCl_3$) using mesitylene as an internal standard. Selectivity for the cyclic carbonate was >99%. [c] Total turnover number per **TA** equivalent based on reported yields. [d] Average turnover frequency per **TA** equivalent based on reported yields.

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



Entry	**TA** [mol%]	NBu_4I [mol%]	t [h]	Conv. [%]	Yield [%][b]	TON[c]	TOF[d]
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	–	–

We then further investigated the application of the binary **TA**/NBu_4I catalyst couple in the synthesis of carbonate **1b** using relatively low amounts of **TA** (Table 3, 0.01–0.05 mol%) combined with 10 molar equiv of NBu_4I (with respect to **TA**) as nucleophile. At 0.05 mol% of **TA** (entry 1), carbonate **1b** was produced in 86% yield after 24 h with a high TON of 1721 and an average TOF/h of 72. Notably, in the absence of TA (entry 2) carbonate **1b** is produced only in 32% yield. Increasing the total reaction time to 66 h (entries 3 and 4) reduces this difference as expected which may also be an effect of partial catalyst degradation. When the **TA** loading was further reduced to 0.01 mol% (entries 5 and 7) the difference between the binary couple and the catalyst system comprising of the iodide nucleophile alone becomes less significant, despite the higher and valuable TONs observed (2220 after 24 h, 4458 after 66 h). Obviously the long-term stability plays a key role to attain high average activity.

Next the substrate scope was investigated (see Figure 3) using conditions that would allow for high conversion of the epoxide substrates **1a–16a** at the

reported temperature (80ºC) and pressure (10 bar). All carbonate products **1b–16b** were produced in a high-throughput reactor system at a 2 mmol substrate scale. Most of the substrates were converted in high conversion/selectivity with good to excellent isolated yields of up to 94% (except for **6b**; 57%). Note that under these reaction conditions the synthesis of **1b** was also probed in the absence of tannic acid **TA** providing only a low yield of 22%. The binary catalyst **TA**/NBu_4I tolerates a number of functional groups including alcohol, alkyl halide, heterocyclic ring systems, carbamate, ether, alkene and alkyne groups. Of further note is that the sterically more hindered substrate **9a** could also be converted (69%) with 40% isolated yield of carbonate **9b**, whereas the internal epoxide **10a** gave, as expected, much poorer results in line with the more challenging nature of this conversion for organocatalytic catalyst systems.[43]

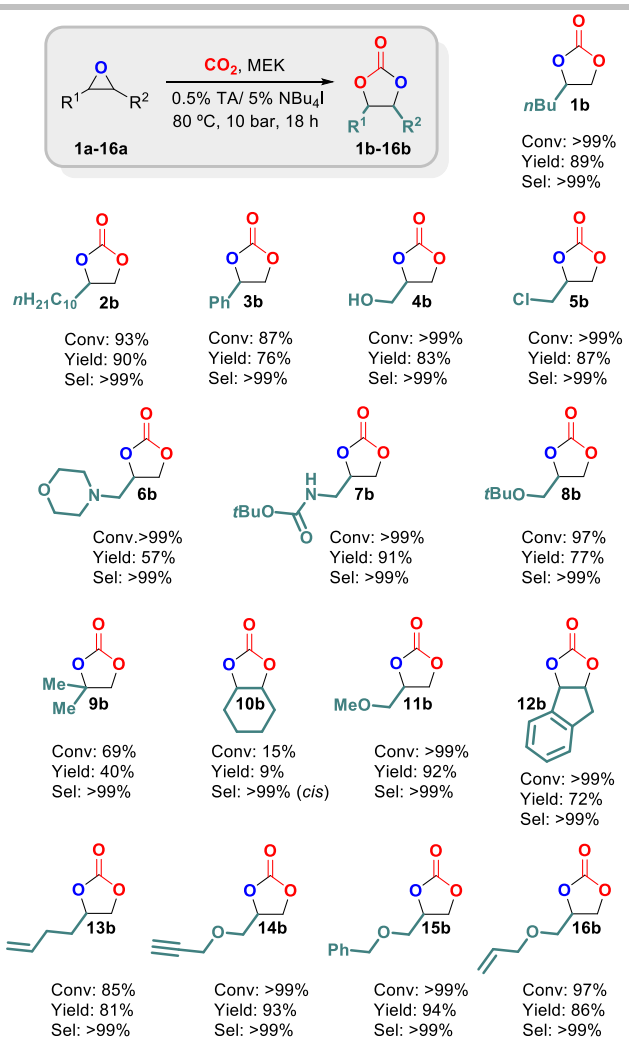


Figure 3. Substrate scope for the **TA**-mediated synthesis of organic carbonates **1b-16b**. General conditions: 2 mmol of epoxide, 0.5 mol% **TA**, 5 mol% NBu_4I, 80ºC, $p(CO_2)$º = 10 bar, 18 h, MEK (5 mL), AMTEC reactor. Note that under these conditions, the yield obtained for **1b** was only 22% in the absence of **TA**.

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

Conclusions

In summary, we here present a novel binary catalyst system based on a naturally occurring and fairly cheap polyphenol, *i.e*. tannic acid, which shows excellent catalytic reactivity at exceptionally low loadings being thus an attractive and sustainable organocatalytic alternative. Comparative catalysis studies have indicated that some degree of synergy between the various poly(phenol) units within the **TA** structure may help to increase catalyst lifetime, providing conceptually an interesting approach to further improve the potential of polyphenol-based organocatalysis in the area of CO_2 conversion. Our future work will be focusing on merging these concepts with the design of organocatalyst systems with improved reactivity and stability for similar type of CO_2 conversions, with a preferable use of hydrogen-bonding as a substrate activation strategy.

Experimental Section

General

Methylethyl ketone (MEK) and carbon dioxide (purchased from PRAXAIR) were used as received without further purification or drying prior to use. All phenolic compounds were commercially purchased from Sigma Aldrich and used without any further purification; the tannic acid **TA** was reagent grade, see also footnote 46. NMR spectra were recorded on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. FT-IR measurements were carried out on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, 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 tannic acid **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 (with $p(CO_2)$ = 5 bar) were carried out before finally stabilizing the pressure at 10 bar. The reactor was then heated to the required temperature and left stirring for a further 18 hours. Then the reactor was cooled down, 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, selectivity for the cyclic carbonate products was determined to be >99%.

Substrate scope experiments

All reactions were performed in an SPR16 Slurry Phase Reactor (Amtec GmbH). First, tannic acid **TA** (0.500 mol%, 17.0 mg) and NBu_4I (5.00 mol%, 36.9 mg) were put into reactors. Then, the AMTEC reaction vessels were tested for leaks charging with 1.5 MPa of N_2 to finally reduce the pressure to 0.2 MPa. After injecting into the reactors the chosen epoxide (example: 2.00 mmol, 200 mg in the case of 1,2-epoxyhexane) in MEK (5 mL) and using mesitylene (10.0 mol%, 24.0 mg) as internal standard (IS), the vessels were heated to the desired reaction temperature (T = 80 ºC). Once reaching the operating temperature, the CO_2 pressure was raised to 1 MPa and the reaction mixture was stirred at the appropriate temperature for 18 h. At the end of the reaction analysis of the crude product was done as reported above in the screening phase. Isolated yields and $^1H/^{13}C$ NMR spectra and IR spectra of all products prepared this way (cf., carbonates **1b-16b**) were obtained by removing the solvent and unreacted substrate under vacuum (at 0.5 mbar). The residue was then dissolved in DCM (except for the conversion of substrate **4a** whose solvent was ethyl acetate) and filtered through a path of silica; after removal of the solvent, the pure cyclic carbonate products were then 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 reported in the Supporting Information.

Recycling experiments

All reactions were performed in a 45 ml stainless steel reactor. In a typical experiment, a solution of tannic acid **TA** (0.250 mol%, 25.5 mg), nBu$_4$NI (2.50 mol%, 55.4 mg) and 1,2-epoxy-dodecane (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 (with $p(CO_2)$ = 0.5 MPa) were carried out before finally stabilizing the pressure at 1 MPa. The reactor was then heated to the required temperature and left stirring for an additional 18 h. Then the reactor was cooled down, 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 -30ºC. After 3 h, the flask was then warmed up to room temperature and the solution was then filtered and the collected precipitate (Solid 2; **FR2**) was washed with hexane (80 mL). The combined organic phases were then concentrated under vacuum to get 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 moved to the same reactor. Then a new portion of 1,2-epoxydodecane (6.00 mmol, 1.25 g) was added. Finally, the procedure continues as indicated above. To regenerate the catalyst, FR1 was treated with concentrated HCl for 18 hours. 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. Then 1,2-epoxydodecane (6.0 mmol, 1.25 g) was added. Finally the procedure continues as described above.

Acknowledgements

C.M. gratefully thanks the Marie Curie COFUND Action from the European Commission for co-financing 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 • hydrogen bonding • organic carbonates • synergy • tannic acid • organocatalysis

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[52] Possible product inhibition was also probed using a 1:1 mixture of the cyclic carbonate **1b** and its precursor **1a** 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 indicating no (significant) product inhibition (Supporting Information for details).

[53] Commercially available tannic acid is usually a combination of polygalloyl glucoses or polygalloyl quinic acid esters with the number of galloyl moieties per molecule varying depending on the plant source. Here we have used the commercial product from Aldrich (ACS reagent, 500 g = 77.50 Euro) which contains about 12% of weight loss upon drying. Further to this, considering the general structure of tannic acid that contains five *pseudo* pyrogallol units, we have thus compared the catalytic performance of tannic acid (0.03 mol%; 1 equiv) with that of pyrogallol (0.15 mol%; 5 equiv).

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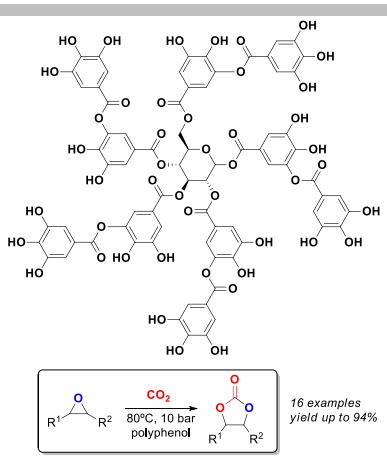
FULL PAPER

A highly efficient binary catalyst system is reported consisting of naturally occurring polyphenol, tannic acid, and a suitable nucleophile additive. This two component catalyst is highly active towards the formation of organic carbonates at very low loadings of the polyphenol with maximum TOFs exceeding 200 h^{-1}. The high reactivity of the tannic acid is ascribed to the



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