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PAPER

Organocatalytic promoted coupling of carbon dioxide with epoxides: a rational investigation of the cocatalytic activity of various hydrogen bond donors

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A catalytic platform based on an onium salt used in combination with organic cocatalysts of various structures was developed for the efficient CO_2/epoxide coupling under mild conditions. Through detailed kinetic studies by *in-situ* FT-IR spectroscopy, a rational investigation of the efficiency of a series of commercially available hydrogen bond donors co-catalysts was realized and the influence of different parameters such as the pressure, the temperature, the catalyst loading, and the nature of the epoxide on the reaction kinetics was evaluated. Fluorinated alcohols were found to be more efficient than other hydrogen bond donor activators proposed previously in the literature under similar conditions.

Introduction

The catalytic synthesis of five-membered cyclic carbonates *via* the coupling of an epoxide with CO_2 is a very promising method to convert CO_2 into valuable organic compounds and is currently the subject of numerous studies. [1-7] Although few catalysts gave satisfactory results under atmospheric pressure and ambient temperature,[3, 8] there is still place for identifying new catalytic platforms to promote an effective cycloaddition under mild conditions while respecting environmental standards. Metallic catalysts have proven to be efficient but their use generally suffers from some drawbacks in particular when metal residues are undesirable in the final product. In this context, organocatalysts have been proposed such as halide salts[9-12] and more recently (functionalized) ionic liquids [13-28] or quaternized glycine [29] and cholinium [30, 31] based ionic liquids were developed. However, halide salts and ionic liquids are generally only efficient at high temperature and pressure that favour their degradation[4, 32-35]. Their activities were enhanced by the addition of suitable hydrogen bond donors (HBDs) such as phenolic derivatives [36-38], (amino)alcohols [39-41], carboxylic acids [42-44], lecithin [45], cellulose [46, 47], chitosan [48-51], graphene oxide.[52], These HBDs interact with the O-donor group of the epoxide, therefore facilitating its ring opening by nucleophilic attack of the halide anion, and they stabilize by hydrogen bonding the oxyanion formed after epoxy-ring. opening. [38, 53, 54] For example, Kleij et al. proposed a very efficient (multi)phenolic compound/ammonium iodide organocatalytic system that fastened the coupling of CO_2 with epoxides at low temperature (25-45°C) and pressure (1 MPa).[38] Very recently, Mattson et al. reported on the use of silanols as a new class of HBDs allowing the synthesis of cyclic carbonates at 0.1 MPa and 25°C. Nevertheless, the conversion of epoxides into cyclic carbonates was very slow (18h) despite the use of a very high catalyst (TBAI) and co-catalyst (silanol) loading (10 mol%).[55] By the way, we recently proposed a novel combination of onium salts with catalytic amount of fluorinated HBDs for the fast synthesis of cyclic carbonates within a few minutes by reaction of CO_2 with epoxides under solvent free and mild experimental conditions.[56] To date, if many HBDs were claimed to exhibit high cocatalytic activity, choosing the most efficient additives to fasten the CO_2/epoxide coupling still remains a challenge as none of the studies reported in the literature were conducted in similar experimental conditions. Herein, we report for the first time a rational investigation of the cocatalytic activity of a series of commercially available HBDs (Figure 1) for the synthesis of cyclic carbonates from CO_2 and epoxides under mild conditions. Comparative kinetic studies were performed by online FTIR spectroscopy under pressure. Additionally, the influence of the pressure, the temperature, the catalyst loading and the nature of the epoxide on the kinetics and reaction has been evaluated for the most effective HBDs.

Experimental

Materials

Propylene oxide (PO) (purity ≥ 99%), styrene oxide (SO, purity ≥ 97%), cyclohexene oxide (CO, purity ≥ 98%), glycidol (GDO, purity ≥ 96%) and tetrabutylammonium bromide (TBABr, purity > 99%) were purchased from Aldrich. Carbon dioxide N45 was supplied by Air Liquide. Phenol, pyrocatechol,

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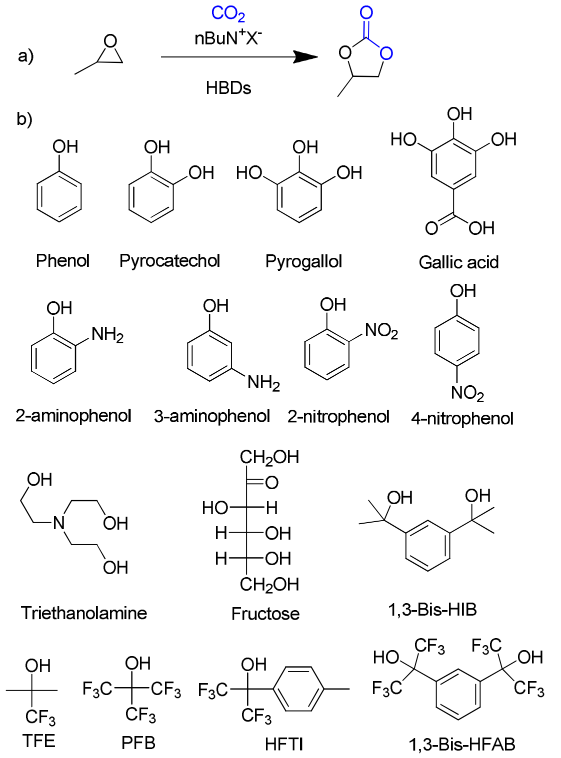

Figure 1 a) CO_2/epoxide coupling reaction b) Chemical structures of Hydrogen Bond Activators used in this work and their designations

pyrogallol, gallic acid, 2- and 3-aminophenol, 2- and 4-nitrophenol and triethanolamine were purchased from Sigma-Aldrich. α,α-(dihydroxy-1,3-diisopropyl)benzene (1,3-bis-HIB), 2,2,2-trifluoro-*tert*-butanol (TFB) and hexafluoro-(p-tolyl)-isopropanol (HFTI) were supplied by ABCR. Perfluoro-*tert*-butanol (PFB) and 1,3-bis(2-hydroxyhexafluoroisopropyl)-benzene (1,3-bis-HFAB) were purchased from Fluorochem. All reactants were used as received without any further purification.

Infrared set-up. The synthesis of cyclic carbonates from model epoxides and CO_2 was followed *in-situ* using a FTIR microscope (Perkin Elmer Spotlight400) working in transflection coupled with a home-made high pressure reflection cell. Infrared spectra of the liquid and the gas phases can be successively recorded. For our purpose, the cell was fitted with a sapphire window and a polyethylene spacer of 1.1 mm thickness which could contain a liquid volume of approximately 100µL. Single beam spectra of the liquid phase recorded with a 2 cm^{-1} resolution were obtained after the Fourier transformation of 300 accumulated interferograms. Spectra were recorded continuously every five minutes during 311 minutes. In the liquid phase, the strong absorption of PO and propylene carbonate in the mid infrared region between 400 and 4000 cm^{-1} requires the use of a very small pathlength (below 20 µm) that might lead to bad equilibration of the mixture. Therefore, in order to follow the apparition of the carbonate, we have chosen to look at overtones and combinations modes of PO and propylene carbonate in the near infrared region between 4000 and 6000 cm^{-1} where a good signal to noise ratio is obtained using a pathlength of about 2 mm. The reflection cell was heated using cartridge heaters disposed in the periphery of its body. A thermocouple located close to a cartridge heater was used to control the temperature with an accuracy of about ±1°C. The cell was connected to the CO_2 tank allowing the pressure to be raised up to 5 MPa.

Experimental procedure

An epoxide/catalyst mixture was introduced in the high pressure cell (100µL) at ambient temperature and the cell was heated up to the desired temperature before addition of CO_2. Experiments were conducted under mild conditions of temperature (25-100°C) and pressure (0.3-3 MPa) in neat epoxide. To follow kinetics, the infrared beam was focused in the epoxide-rich phase. At the end of the reaction, in order to determine the yield, the near IR (NIR) spectrum of the reaction mixture was compared with the corresponding spectrum of the neat carbonate. The absorbance of the peak associated to the ν(C=O) + ν(C-H) combination mode at 4800 cm^{-1} of propylene carbonate was normalized using the peak corresponding to 2 ν(C-H) stretching mode at 5785 cm^{-1} which doesn't evolve during the reaction. The yield for the entire kinetic was deduced by proportionality using the Beer-Lambert law according to Equation 1.

$$Yield\ (\%) = \frac{\left[\frac{A_{C=O}}{A_{C-H}}\right]_{Reaction\ mixture}}{\left[\frac{A_{C=O}}{A_{C-H}}\right]_{Neat\ carbonate}} \qquad [1]$$

All these experiments were conducted at least twice in order to check for their reproducibility.

Results and discussion

Cyclic carbonates from PO and CO_2.

A- Without hydrogen bond donors.

The organocatalysed synthesis of propylene carbonate (PC) by coupling of PO with CO_2 in the presence of 3 mol% of TBABr at 60 °C and 2 MPa was monitored by *in-situ* FTIR spectroscopy. Under these conditions, the system is biphasic with an epoxide rich phase that is "swollen" by a significant amount of CO_2 (χ_{CO2}= 0.2). [57] Moreover, knowing that TBABr (and the HBD) is soluble in this phase and insoluble in the gaseous CO_2 rich phase, the epoxide/CO_2 coupling only takes place in the epoxide rich phase. Kinetics studies were realized by monitoring the appearance of the peak associated to the ν(C=O) + ν(C-H) combination mode at 4800 cm^{-1} of propylene carbonate (Figure 2). It is worth noting that the consumption of PO can also be monitored thanks to the decrease of the peak at 6050 cm^{-1} (2 ν(C-H) mode of the epoxide ring). In addition, we also observe two peaks centred at 4950 and 5100 cm^{-1} (respectively associated to the combination bands $\nu_1+2\nu_2+\nu_3$ and $2\nu_1+\nu_3$ of CO_2) that attest for the presence of CO_2 in the mixture. Figure 3a shows the typical time dependence of the reaction yield measured from the height of

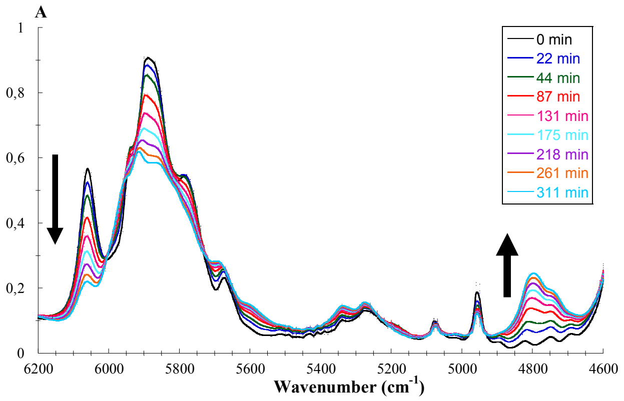

Figure 2 Evolution as a function of time of the Near Infrared spectra of the PO/CO$_2$/catalyst mixture at T = 60 °C and P = 2 MPa

the peak at 4800 cm^{-1} reflecting an increase of the PC concentration in the PO/CO$_2$ mixture. Figure 3b represents the consumption of PO by the decrease of the absorbance at 6050 cm^{-1}. As CO$_2$ is used in excess, the CO$_2$/PO coupling answers a pseudo-first order reaction and kinetic profiles were fitted according to the following equation: $[x]_t = C_0(1 - e^{-k't})$. In such experimental conditions, the kinetic constant k' was estimated to 0.38 h^{-1} and the reaction yield reached 42% after 100 minutes (Figures 3 and 4). Such fitting was applied for all the TBABr/HBD bicomponent organocatalysts investigated below.

B- Cocatalyst screening

The cocatalytic activity of commercial HBDs was then studied for the same model reaction between PO and CO$_2$ carried out in the presence of TBABr (3 mol%) at 60°C and 2 MPa. Equimolar amounts of HBDs (relative to TBABr) were used for the reaction.

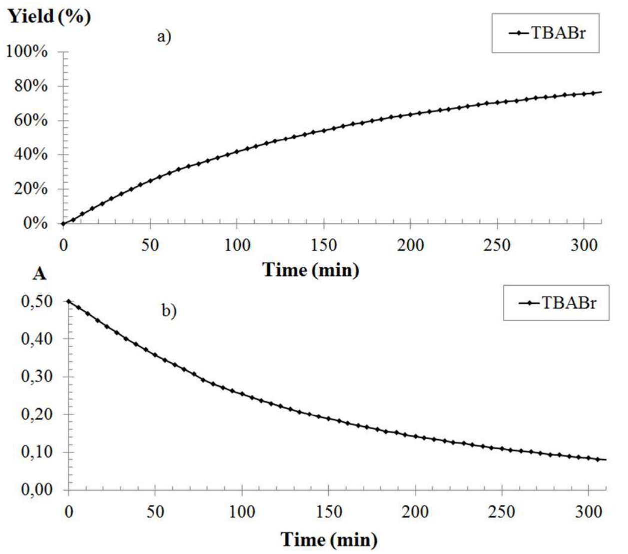

Figure 3 Kinetic study of the TBABr promoted coupling of CO$_2$ with PO: a) evolution of the reaction yield with time and b) evolution of the absorbance of the PO peak at 6500 cm^{-1} with time. Experimental conditions: T = 60°C, P = 2 MPa, TBABr = 3 mol%

(Multi)phenolic derivatives.

In line with the work of Kleij et al.,[38] pyrogallol was identified as an efficient HBD that allowed a 2.5-fold increase of the rate constant (k' = 0.97 h^{-1}) and enabled the full conversion of PO into propylene carbonate in 200 min (Figure 4). Pyrocatechol displayed a similar cocatalytic activity (k' = 0.93 h^{-1}) while phenol was less efficient with a k' = 0.52 h^{-1} (Figure 4). Those results are in close qualitative agreement with data reported in the literature at lower temperature (between 25 and 40°C) and with a different halide anion (iodide instead of bromide).[38] The difference of activity between these three (multi)phenolic compounds was confirmed by the reaction yields determined after 100 min of reaction (Figure 5). Gallic acid, a pyrogallol analogue displaying an additional carboxylic acid function, was also found to be a very efficient activator at only 1 mol% loading as evidenced by a high conversion (70%) after 100 min. The reaction was not tested for higher gallic acid contents because this compound was insoluble in PO at higher loading. The positive influence of the acidic function was further confirmed by comparing the cocatalytic activity of pyrogallol and gallic acid at 1 mol% loading. The coupling of CO$_2$ with PO was nearly complete within 250 min (conversion close to 95%) in the presence of gallic acid but only reached 82% with pyrogallol.

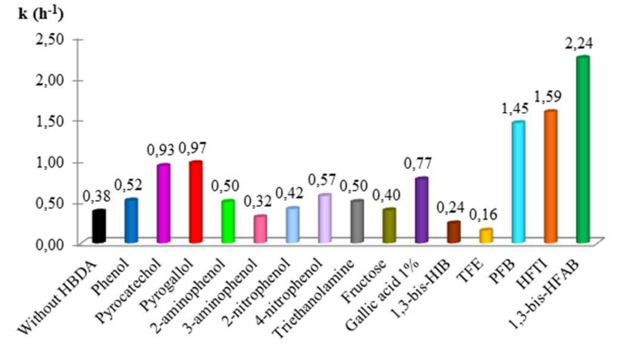

Figure 4 Kinetic rate constant determined for the coupling of CO$_2$ with PO promoted by TBABr/HBD bicomponent organocatalysts. Experimental conditions: T = 60°C, P = 2 MPa, TBABr = 3 mol%, [TBABr]/[HBD] = 1

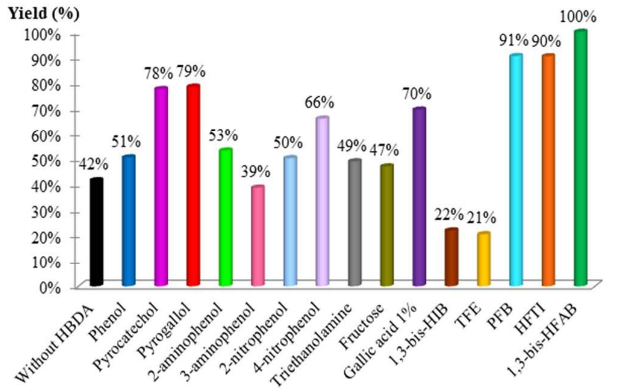

Figure 5 Coupling of CO$_2$ with PO promoted by TBABr/HBD bicomponent organocatalysts: reaction yields determined after 100 min. Experimental conditions: T = 60°C, P = 2 MPa, TBABr = 3 mol%, [TBABr]/[HBD] = 1

This result is consistent with those reported in the literature that showed that HBDs with carboxylic acid groups were more efficient than those bearing hydroxyl functions[26, 27, 44] as the proton of the acid moieties also interacted by hydrogen-bonding with the oxygen atom of the epoxides. However, the use of carboxylic acid-functionalized phenol derivative as potential HBD was restricted by its low solubility in the epoxide rich-phase. To highlight the crucial role of vicinal hydroxyl groups on the epoxide activation by phenolic HBDs, one OH group of pyrocatechol was replaced by a NH_2 function (Figure 1b, second line) and its cocatalytic activity was compared with the one of 3-aminophenol. Kinetics studies demonstrated that 2-aminophenol (k' = 0.50 h^{-1}, conv. = 53%) displayed a catalytic activity close to phenol (k' = 0.52 h^{-1}, conv. = 51%) whereas 3-aminophenol had no activity as evidenced by a conversion of 39% and a k' value of 0.32 h^{-1} comparable to the one obtained when using TBABr as sole catalyst (Figures 4 and 5). This result confirms an initial study reported in the literature suggesting that the proximity between the amine functional group and the hydroxyl group is a key parameter that affects the activity of HBDs.[38] However, the amine functional group is a weaker HBD than alcohol as the activity of pyrocatechol was two times higher than the one of 2-aminophenol. Finally, the substitution of an OH group of pyrocatechol by an electron withdrawing NO_2 group that increases the acidity of the phenol derivative and favours the formation of hydrogen bond between the O-donor group of PO and the OH group of the HBD was investigated. If 2-nitrophenol displayed the same activity than phenol, 4-nitrophenol was slightly more efficient (Figures 4 and 5) with a conversion of 66% which corresponds to a 1.5-fold increase of the reaction yield compared to the reference reaction without HBD. Indeed, the resonance stabilization of 4-nitrophenolate anion is higher than for 2-nitrophenol increasing the proton transfer probability. Moreover, the hydroxyl function of 2-nitrophenol is sterically hindered and could interact with the nitro function. Conclusively, the crucial role of vicinal hydroxyl groups was pointed out and the catalytic activity of phenol could be improved by substitution of the aromatic group by electron attractive substituents (nitro- or carboxylic acid groups).

Alcohol and sugar.

The co-catalytic efficiency of a variety of alcohols was also evaluated (Figure 1b, third line). First, triethanolamine, reported recently to fasten the KI promoted coupling of CO_2 with PO, was tested as potential HBD. When it was used in combination with TBABr, the aminoalcohol showed a low cocatalytic activity (k' = 0.50 h^{-1}; Figure 3) with a conversion of the epoxide into cyclocarbonate of 49% after 100 min of reaction, similar to that of phenol and 2-aminophenol (Figure 5). This result is quite surprising in view of Cheng et al. [58] and Werner et al. [41] results who claimed that triethanolamine associated with KI had a strong activating role. These results might be explained by the higher temperature at which the coupling of CO_2 with PO was realized in their studies and by the nature of the catalyst used (KI instead of TBABr). Fructose, a sugar exhibiting five hydroxyl groups, was also tested as potential cocatalyst. Unfortunately, fructose had a limited cocatalytic activity as the k' value (0.40 h^{-1}) and the reaction yield (47% after 100 min) were close to values observed for the reaction carried out without HBD (k' = 0.38 h^{-1}, conv. = 42%). Finally, α,α,α,-dihydroxy-1,3-disopropylbenzene (1,3-bis-HIB) inhibited the coupling of CO_2 with PO as the propylene carbonate yield and the k' value are 2 times lower than the one estimated for the reference reaction (Figure 3 and 4).

Fluorinated alcohols.

Recently, a new class of single and double HBD activators derived from fluorinated alcohols were identified to fasten the epoxide/CO_2 coupling under relatively mild conditions (Figure 1b, last line).[56] At 60°C and 2 MPa, hexafluoro-(p-tolyl)-isopropanol (HFTI) and perfluoro-*tert*-butanol (PFB), used in equimolar amounts compared to TBABr (3 mol%), were able to convert about 90% of PO into the corresponding cyclic carbonate after 100 min of reaction. The rate constant was 1.45 and 1.59 h^{-1} for PFB and HFTI, respectively, thus representing about 50% rate constant increase compared to the best HBD (pyrogallol; k' = 0.97 h^{-1}). In contrast, 2,2,2-trifluoro-*tert*-butanol (TFB) had a detrimental effect on the reaction since the rate constant was lower than without HBD (0.16 h^{-1} *vs* 0.38 h^{-1}). As reported elsewhere, the acidity and the hydrogen bonding capability of the tertiary alcohol that are both increased with the number of electron-withdrawing CF_3-substituents are important factors affecting the activating efficiency of fluorinated alcohols.[59] Thus, double HBD, 1,3-bis-(hydroxyhexafluoroisopropyl)benzene (1,3-bis-HFAB), combined to TBABr, presented an impressive activity as evidenced by a 6- or 2.3-fold increase of k' value compared to the system without HBD or with pyrogallol as HBD, respectively (Figure 4). PO/CO_2 coupling is quantitative in less than 100 min in the presence of 1,3-bis-HFAB, whereas the non-fluorinated analogue displayed no cocatalytic activity (1,3-Bis-HIB) (Figure 5). These results highlight the positive impact of substituting methyl groups of alcohols by -CF_3. Although these fluorinated alcohols are strong activators, they are not organocatalysts by themselves as only traces of propylene carbonate were detected during the cycloaddition of CO_2 onto PO using 3 mol% of fluorinated alcohol without any TBABr.

C- Influence of experimental parameters

Influence of the reaction temperature

The impact of the temperature on the PO/CO_2 coupling promoted by the TBABr/HFTI binary catalyst (catalyst loading = 3 mol%, [TBABr]/[HBD] =1) was investigated at a fixed CO_2 pressure of 2 MPa while varying the temperature from 25 to 100°C (Figure 6a). As expected, the reaction rate was fast at 100°C with a complete conversion of PO into PC within 50 minutes whereas at 60°C, the reaction was 3 times slower.

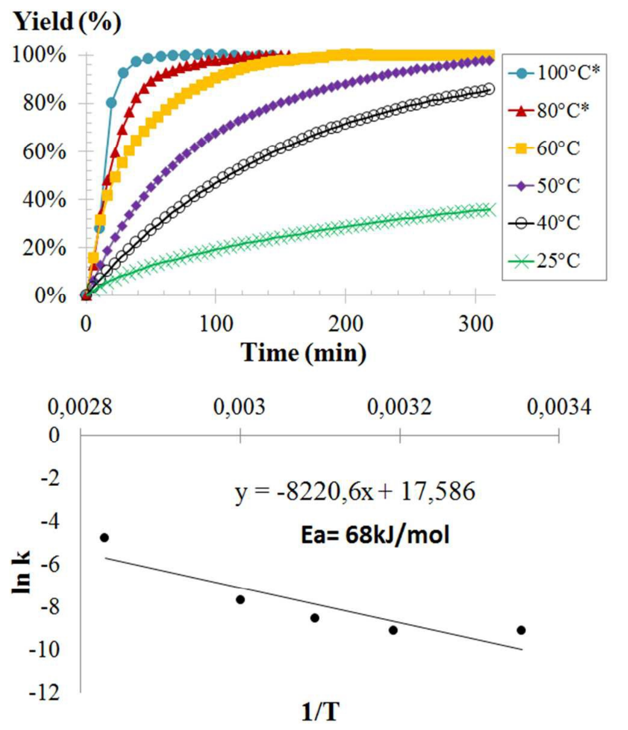

Figure 6 a) Effect of the temperature on the PO/CO_2 coupling promoted by the TBABr/HFTI bicomponent catalyst (*TBABr/PFTB). b) Determination of the activation energy E_a using the linear form of the Arrhenius equation ($\ln(k) = -E_a/RT + \ln(A)$). Experimental conditions: [TBABr] = 3 mol%, [TBABr]/[HFTI] = 1, P = 2 MPa.

At 25°C, the reaction was very slow and only reached about 35% conversion after 300 min. Using the Arrhenius equation, the activation energy of the reaction was estimated to 68 kJ/mol (Figure 6b).

Influence of the CO_2 pressure

One of the main challenges associated to the use CO_2 as a C1 feedstock relies on the development of processes that are efficient at low pressure. The impact of the pressure on the PO/CO_2 coupling was therefore studied at 60°C using the TBABr/1,3-bis-HFAB bicomponent organocatalyst ([TBABr] = 3 mol%, [TBABr]/[1,3-bis-HFAB] = 1) in a pressure range from 0.2 to 3 MPa. Figure 7 depicts the kinetic profiles of the PO/CO_2 pressures as low as 0.2 and 0.5 MPa, the reaction rate still remained acceptable with k' values of respectively 1.08 and 1.47 h^{-1}, rendering the reaction quantitative in 200 and 250 min respectively.

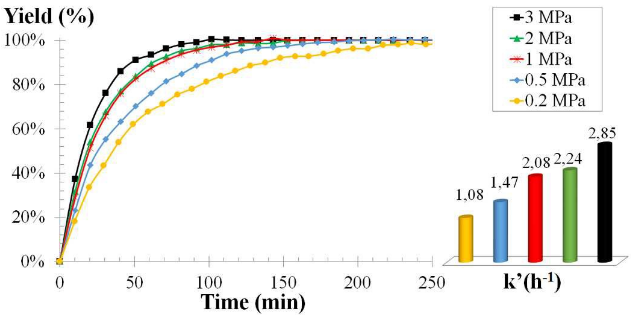

Figure 7 Effect of the pressure on the PO/CO_2 coupling promoted by the TBABr/1,3-bis-HFAB bicomponent catalyst. Experimental conditions: [TBABr] = 3 mol%, [TBABr]/[1,3-bis-HFAB] = 1, T = 60°C.

Influence of the HBD loading

The influence of the HBD concentration on the catalytic platform efficiency was investigated for the model reaction at 60°C and 2 MPa using 3 mol% TBABr and increasing amount of HFTI (from 0 to 5 mol%). The catalytic performances increased when the HFTI loading increased from 0 to 3 mol% (Figure 8). Importantly, the reaction slowed down at higher HFTI concentration (5 mol%), which is explained by the protonation of the bromine counter-ion by the fluorinated alcohol. This assumption was further supported by previous works that showed that the use of fluorinated alcohols as solvents, thus in large amount, had a detrimental effect on the CO_2/epoxide coupling.[60] The optimal composition (3 mol% TBABr and 3 mol% HFTI) provided a quantitative conversion of PO into PC in 150 minutes (Figure 9). The reaction slowed down when the total amount of TBABr and HFTI was decreased for an equimolar composition ([TBABr]/[HFTI]=1).

Influence of the nature of the epoxide

The coupling of CO_2 with a series of model epoxides such as cyclohexene oxide (CO), glycidol (GO) or styrene oxide (SO)

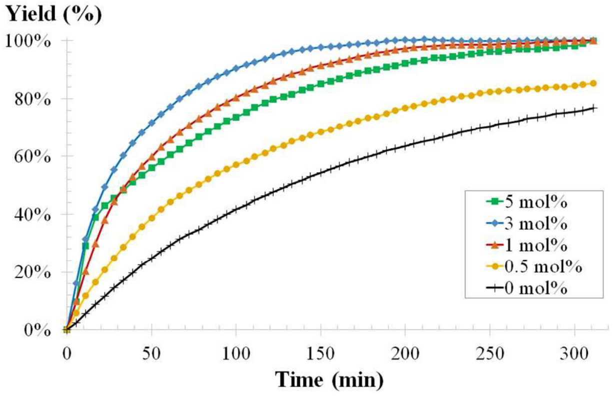

Figure 8 Coupling of PO and CO_2 using the TBABr/HFTI bicomponent catalyst: effect of the cocatalyst loading determined after 100 minutes Experimental conditions: [TBABr] = 3 mol%, T = 60°C, P = 2 MPa

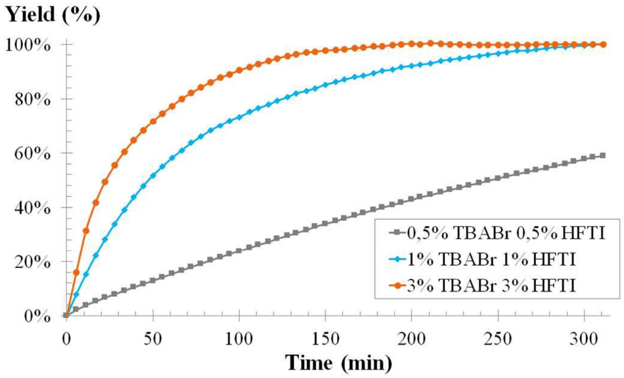

Figure 9 Change as a function of the time of the absorbance of the propylene carbonate during the cycloaddition of CO_2 onto propylene oxide (60°C, 2 Mpa) with various loading of TBABr and HFTI as catalysts and [TBABr]/[HFTI]=1.

was finally studied using TBABr as catalyst and HFTI as representative efficient HBD. In the absence of HBD, the synthesis of cyclohexene carbonate from CO and CO_2 was very slow at T = 60°C and P = 2 MPa and the conversion only reached 11% after 300 min (Table 1). Addition of 1 equivalent conversion of HFTI compared to TBABr fastened the reaction with a 2-fold increase of the conversion after the same period of time. Compared to the CO_2/PO coupling that was quantitative under these experimental conditions, the same reaction performed on CO was much slower as the result of a lower reactivity of di-substituted epoxides due to steric hindrances and charge delocalisation effects. Moreover, for a given temperature and pressure, the solubility of CO_2 in cyclohexene oxide is lower than in propylene oxide.[57] Finally, by increasing the temperature to 100°C, the CO_2/CO coupling yield was 3.5 times higher (73%) than the same reaction performed at 60°C. The booster effect of HFTI was also highlighted for the coupling of glycidol with CO_2. Indeed, only traces of glycerol carbonate were observed in the absence of HFTI after 300 min of reaction, while a conversion of 30% was noted in its presence. The effect of HFTI was confirmed for the conversion of SO into the corresponding cyclic carbonate. Thus, whatever the epoxide structure, kinetics studies highlight that the use of HFTI in combination with TBABr systematically enhanced the activity of TBABr without the formation of by-products.

Table 1 Coupling of different epoxide and CO_2 using the TBABr/HFTI bicomponent catalyst. Experimental conditions: [TBABr] = 3 mol%, [TBABr]/[HFTI] = 1, T = 60°C, P = 2 MPa, t = 300 min

Entry	Epoxide	Catalyst	HBD	T (°C)	P (MPa)	Conv (%)
1	Propylene oxide	TBABr	-	60	2	76%
2		TBABr	HFTI	60	2	100%*
3	Glycidol	TBABr	-	60	2	2%
4		TBABr	HFTI	60	2	30%
5	Styrene oxide	TBABr	-	60	2	43%
6		TBABr	HFTI	60	2	50%
7	Cyclohexene oxide	TBABr	-	60	2	11%
8		TBABr	HFTI	60	2	22%
9		TBABr	HFTI	100	2	73%

* Quantitative conversion after 150 minutes

Conclusions

We report for the first time a rational investigation of the cocatalytic activity of a series of commercially available hydrogen bond donors (HBDs) for the synthesis of cyclic carbonates from CO_2 and epoxides under mild conditions. Through detailed kinetic studies by online IR spectroscopy under pressure, pyrogallol, pyrocatechol, gallic acid, perfluoro-*tert*-butanol, hexafluoro-(p-tolyl)-isopropanol and 1,3-bis(2-hydroxyhexafluoroisopropyl)-benzene (1,3-bis-HFAB) were identified as the most efficient commercially available cocatalysts, even if the booster effect of Fluorinated Hydrogen Bond Donors (FHBD) was significantly higher. Then, we have investigated the influence of the temperature, the pressure, the nature of the epoxide and the FHBD loading on the kinetic and yield of the epoxide/CO_2 coupling reaction using the TBABr/FHBD bicomponent catalyst. As expected, increasing the temperature fastens significantly the rate of the reaction. Interestingly, the TBABr/FHBD bicomponent catalyst is active at low CO_2 pressure as quantitative transformation of PO is obtained at 60°C and 0.2 MPa in less than 5h. Additionally, whatever the nature of the epoxide, the use of FHBD in combination with TBABr systematically enhanced the activity of TBABr without formation of by-products. Therefore, the use of suitable hydrogen bond donor activators, more particularly alcohols with hexafluoroisopropanol functionalities, will expand the scope of the metal-free synthesis of cyclic carbonates under mild conditions, especially when considering the cycloaddition of CO_2 onto epoxidized vegetable oils which are expected to be less reactive than model epoxides.[61] This rational investigation is also expected to help researchers to identify suitable organocatalysts that offer the best compromise in terms of activity and cost as a less efficient hydrogen bond activator could remain competitive when its cost is more favourable in regard of the most active and expensive ones.

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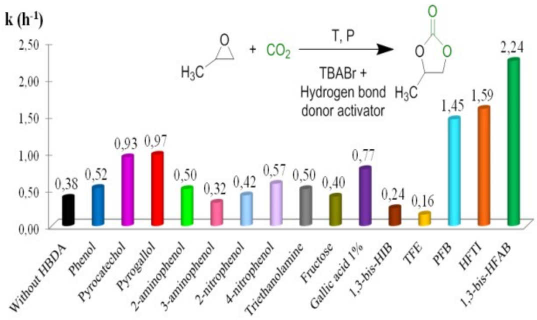

A rational investigation of the cocatalytic activity of a series of commercially available hydrogen bond donors (HBDs) for the synthesis of cyclic carbonates from CO_2 and epoxides under mild conditions.