

Tetrabutyl ammonium salts: cheap catalysts for the facile and selective synthesis of α -alkylidene cyclic carbonates from CO₂ and alkynol

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Dedication ((optional))

Abstract: n-tetrabutyl ammonium organic salts are used for the first time as catalysts for the coupling of CO_2 with 2-methyl-3-butyn-2-ol to form α -methylene cyclic carbonate. The final yields could reach 98% in less than 10 hours at 353K and 3MPa under solvent free conditions. A particular synergistic effect between the cation and the anion of the organocatalyst is demonstrated through catalyst screening. Online kinetic studies by ATR-IR spectroscopy correlated to DFT calculations reveal a compelling evolution of the solvation of the catalyst during the reaction that provide an understanding of the underlying reason for the observed unique kinetics and selectivity. Such in-depth fundamental mechanistic and kinetic studies enable determining and comprehending the key parameters favouring the design of novel highly active and selective catalysts for the valorisation of CO_2 as a chemical feedstock.

Carbon dioxide is a cheap, renewable and easily accessible source of carbon for producing high-value fine chemicals and monomers.^[1] In the last years, many academic and industrial researches have been devoted to the development of novel and sustainable synthetic pathways to convert CO₂ into cyclic carbonates finding wide applications as intermediates in the preparation of pharmaceuticals and agrochemicals products^[2]. Thus, five and six-membered cyclic carbonates are obtained from the catalytic coupling of CO₂ with different substrates such as epoxides ^[3], oxetanes ^[4], propargylic alcohols ^[5] and diols ^[6] using appropriate organic or transition metal catalysts. In particular, α-alkylidene cyclic carbonates, that are intermediates of great interest in organic^[7] and polymer^[8] synthesis, are synthesized by coupling CO₂ with propargylic alcohols. Until now, much work has focused on the use of metallic catalysts as recently reviewed by Song et al. [5a] and Kleij et al. [5b] In particular, silver based catalyst systems such as AgOAc/(DBU),^[9] Ag₂WO₄/Ph₃P,^[10] [(PPh₃)₂Ag]₂CO₃,^[11] AgOAc/ [P66614][DEIm]^[12] and more recently ZnBr₂/Et₃N based catalytic systems^[13] have proven to be efficient for the transformation of

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CO₂ into α-alkylidene cyclic carbonates at low temperature and pressure. Beside metal complexes that generally require a strict avoidance of moisture/air, organocatalysts such as tertiary phosphine ^[14], bicyclic amidines, guanidines ^[15] and ionic liquids (used as a solvent) ^[16] have been used to promote the coupling of CO2 with propargylic alcohols. In order to improve the selectivity and the efficiency, more sophisticated organocatalysts such as N-heterocyclic carbene (NHC)^[17], N-heterocyclic olefin^[18], and alkoxide-functionalized imidazolium betaine^[19] have also been developed for the selective preparation of α alkylidene cyclic carbonates. However, the low stability and/or moisture sensitivity of these catalysts might hamper their use for industrial applications. In this context, efforts are still needed to identify stable, cheaper and less/non-toxic organic catalysts that promote the selective carboxylative coupling of CO2 with propargylic alcohols.

In this communication, we report the first use of n-tetrabutyl ammonium (TBA) salts for the efficient and selective synthesis of α -alkylidene cyclic carbonates from CO₂ and a propargylic alcohol under solvent free conditions (Scheme 1). Through catalyst screening, kinetic studies and DFT calculations, we demonstrate a synergistic effect between the cation and the anion of the organocatalyst and hydrogen bonding solvation effects on the anion that are responsible for the efficiency of the system and an unexpected kinetic behaviour.



Anions: I⁻, Br⁻, Cl⁻, PF₆⁻, I₃⁻, Br₃⁻, N₃⁻, CN⁻, NCO⁻, SCN⁻, OAc⁻, MDA⁻ **Cations**: TBA⁺, TOA⁺, TMA⁺, NH₄⁺, Cu⁺, Na⁺, K⁺

Scheme 1. a) $CO_2/2$ -methyl-3-butyn-2-ol coupling; b) Structures of the organocatalysts investigated for the chemical fixation of CO_2 into α -methylene carbonate.

The influence of the counter-anion (I[°], Br[°], CI[°], Br₃[°], I₃[°], PF₆[°], N₃[°], NCO[°], CN[°], SCN[°], MDA[°] (Malondialdehyde), OAc[°]) of n-tetrabutyl ammonium (TBA⁺) was investigated for the reaction between CO₂ and 2-methyl-3-butyn-2-ol under solvent-free conditions (Table 1, entries 2-13). At 3 MPa and 353 K, only traces of product were observed without catalyst as highlighted by a conversion of only 3% after 70h (Table 1, entry 1). Halide anions

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either under their X⁻ or X₃⁻ form were found to be ineffective under the given conditions (Table 1, entries 2 - 6). The same conclusion is drawn for PF_6^- (entry 7).

Table 1. Coupling reaction of CO₂ with 2-methyl-3-butyn-2-ol catalyzed by various organic and inorganic salts. Reaction conditions: alcohol = 500 μ l, catalyst loading = 5 mol%, T=353K, P=3 MPa.



Entry	Catalyst	Time (h)	Conversion	Selectivity
			(%)	1:2
1	/	70	3	nd ^[a]
2	TBAI	6	0	-
3	TBABr	6	0	-
4	TBACI	6	<3	nd ^[a]
5	TBABr ₃	6	0	-
6	TBAI ₃	6	0	-
7	TBAPF ₆	6	0	-
8	TBAN ₃	6	51	99:1
9	TBANCO	6	93	95:5
10	TBACN	6	97	87:13
11	TBASCN	6	<3	nd ^[a]
12	TBAMDA	6	25	99:1
13	TBAOAc	6	60	99:1
14	NH₄OAc	6	0	-
15	TMAOAc	6	30	92:8
16	TOAOAc	6	4	99:1
17	TBD	6	87	15:85
18	MTBD	6	91	50:50

[a] nd: not determined

Interestingly, TBA⁺ with N₃⁻ as counter-anion displays a significant efficiency with a conversion of 51% after 6h of reaction and a high selectivity (99%) towards the formation of the cyclic carbonate 1 (entry 8) with negligible side product 2 formation that results from the addition of 2-methyl-3-butyn-2-ol to 1. Other nitrogen-containing anions such as NCO⁻ and CN⁻, are found to drastically boost the catalyst activity with a conversion of 93% and 97%, respectively, but at the expense of the selectivity towards the formation of 1 (entry 9-10) that respectively falls to 95% and 87%. SCN is however found to be ineffective (entry 11). A high selectivity of 99% is obtained with TBA⁺ with MDA⁻ or OAc⁻ counter-anion with a conversion of 25% or 60% (entry 12-13). As TBAOAc displays the best compromise between catalytic activity and selectivity, we have then screened a series of acetate based salts with different cations. Inorganic cations based acetate salts, namely CuOAc, NaOAc and KOAc, were found totally ineffective for the coupling reaction. Although NH₄OAc has no catalytic activity (entry 14), tetramethyl acetate (TMAOAc) and tetraoctyl acetate (TOAOAc) display some catalytic activity with a conversion of 30% and 4%, respectively, and a selectivity towards the formation of 1 of 92% and 99%, respectively (entry 15-16). Therefore, the efficiency of acetate based salts may result from a synergism between the anion and the cation of these ammonium salts. Indeed, we expect that with a bulkier cation, the electrostatic interaction between the cation and the anion should be weaker and the anion may display a higher Lewis basicity. Nevertheless, the high bulkiness of (TOAOAc) brings steric hindrance, thereby impeding on coupling reaction. Thus, it appears that (TBAOAc) displays an optimum alkyl chain length as it displays the highest catalytic activity in comparison with the shorter (TMAOAc) and longer (TOAOAc) ammonium salts. Finally, although other conventional organocatalysts such as TBD and MTBD displays a good efficiency, the selectivity towards the formation of **1** respectively falls to 15% and 50% (entry 17-18).^[15b]

To go further in the comprehension of the reaction mechanism, detailed kinetic investigations were performed by *in situ* Attenuated Total Reflectance (ATR)-Infrared (IR) spectroscopy by using the most active and selective catalysts (see Figure S1). These studies enable us to determine the kinetic profiles, the reaction yields, and the selectivity of the reaction that are affected by various parameters (anion type, pressure, temperature, catalyst loading). Figure 1 shows the time dependence of the yield of the synthesis of 1 and 2 catalyzed by various tetrabutyl ammonium salts (5 mol%) at 80°C and 3MPa.



Figure 1. Influence of the counter-anion of tetrabutyl ammonium on the formation of the α -methylene cyclic carbonate **1** (v = 1824 cm⁻¹) and acyclic carbonate side product **2** with time. Conditions: 2-methyl-3-butyn-2-ol (500µL), catalyst = TBA-Anion= 5 mol%, T = 353K, p CO₂ = 3MPa

As previously observed, the selectivity in **1** is excellent. A final yield of **1** of about 98% is obtained after about 10h for TBAOAc and TBAN₃ and after about 15h for TBAMDA. On the other hand, although TBACN and TBANCO display a faster kinetics, they are less selective as the final yield in **1** is about 85 and 90% respectively, in line with the screening results. Thus, it appears that slower kinetics is beneficial to the conversion and to the selectivity of the reaction. Regarding the kinetic profiles of the cyclic carbonate formation, they display a peculiar shape that does not fit a pseudo-first order kinetics as we would expect for such reaction when CO₂ is used in excess. Regarding the representative case of TBAOAc, the kinetic profile can be

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roughly divided in two parts: an almost linear evolution of the yields in **1** up to about 50-60% and then a speeding up of the reaction until the maximum yield is reached. Such observed unusual kinetic behaviour is roughly the same for all the other ammonium salts.

To shed light on this unusual phenomenon, the reaction catalyzed by $TBAN_3$ was further studied by in-depth in-situ ATR-IR kinetic measurements by following the intense band associated with the asymmetric vibration v_3 of the azide anion in the spectral range 1950-2050 cm⁻¹ (see Figure 2).



Figure 2. Evolution as a function of time of the ATR-IR spectra for 2-methyl-3butyn-2-ol (500 μ L) catalyzed by TBAN₃ (5 mol%) under 3 MPa of CO₂ and at 353 K. Insert: zoom on the azide anion contribution at t=0 (purple line), t=7h (red line) and t=14h (blue line)

On the spectrum corresponding to the initial solution at T=353 K and P=3 MPa, we detect the band associated to the azide anion at 2028 cm⁻¹. During the first 5.5 hours of the reaction, the position and intensity of this band do not evolve, whereas the intensity of bands associated to α-methylene carbonate, namely, the v(C=O) stretching mode at 1827 cm⁻¹ and the v(C=C) stretching mode at 1680 cm⁻¹, increases in line with the formation of 1. Importantly, after that period of time that corresponds to about 40% conversion of 2-methyl-3-butyn-2-ol into 1, the band associated to azide smoothly shifts towards lower frequencies, from 2028 cm⁻¹ after 5.5 h to 2012 cm⁻¹ after 7 h of reaction (70% conversion). In order to understand the origin of this shift of frequency during the reaction, Density Functional Theory (DFT) calculations of geometries, energies, and vibrational frequencies of different N3:2-methyl-3-butyn-2-ol complexes (1:1, 1:2, 1:3 and 1:4) were then carried out with the M062X functional using 6-311G(d,p) basis sets (see Supporting Information). The calculated wavenumbers for the v₃ stretching vibration of the different complexes are reported in Fig. S2. The experimental spectrum observed at about 2028 cm⁻¹ during the first 5.5 hours of reaction is well interpreted for a 1:4 complex. Then, the broad profile centered at 2012 \mbox{cm}^{-1} observed at an intermediate time of 5.5-7 hours is associated to smaller complexes, mainly 1:2 complex associated to a weak contribution of both 1:3 and 1:1 complexes. Finally, during the final part of the reaction, the band at 2000 cm⁻¹ can be assigned to free azide anions as reported previously by Darensbourg et al.^[20] Rationalization of experimental ATR-IR spectra data (Fig. 2) with theoretical ones (Fig. S2) suggests that the initial hydrogen bonding solvation shell stabilizing the charged azide anion limit its catalytic activity probably through a decrease of its $\ensuremath{\text{pKa}}$ value. $\ensuremath{^{[21]}}$ Thus, when 1 is formed during the first seven hours of the reaction, the hydrogen bonding solvation shell around the azide anion is progressively weakened as evidenced by the progressive shift of the azide anion peak from 2028 cm⁻¹ (1:4 complex) to 2012 cm⁻¹ (1:2 complex). Then, the peak at 2012 cm⁻¹ finally vanishes at the expense of the peak of the free azide anion N₃ that is the unique component observed at the end of the reaction. Thus, in the second part of the reaction, as more and more azide free molecules (with an expected higher pKa) are available to activate other 2-methyl-3-butyn-2-ol molecules, the kinetic of the reaction is speeded up with time. The observed unusual kinetic behaviour for this reaction is clearly due to an evolution during the reaction of the hydrogen bond solvation shell formed by 2-methyl-3-butyn-2-ol molecules around the azide anions. The same observation has been done on the the stretching vibration of the cyanate anion (NCO⁻) (see Supporting Information).

As TBAOAc was identified as one of the most selective catalyst, it was chosen as the model catalyst for further investigating the influence of temperature, pressure and catalyst loading (see supporting information). As a general rule, we observe that increasing the temperature and the catalyst loading fasten the reaction but has a detrimental effect on the selectivity. Interestingly, increasing the pressure speeds up the reaction and improves the selectivity. This can be explained by the higher CO₂ concentration dissolved in the alkynol phase at higher pressure that favors the reaction.^[22] Thus, in the pressure range investigated 1-5 MPa, the optimal conditions to maximize the yield of **1** under solvent free conditions are obtained at T=353K, P=5 MPa and 5 mol% of TBAOAc.

To give a detailed insight into the reaction mechanism, we have performed Density Functional Theory (DFT) calculations. The Gibbs energy profiles obtained at the M06-2X/6-311G(d,p) level for the uncatalysed and TBAOAc catalyzed (with one or two alkynol) reactions are depicted on Figure 3. The optimized structures of the corresponding intermediates and transition states are reported in the Supporting Information. Initial state (zero energy) corresponds to the sum of the Gibbs energy of each compound. As reported previously ^[15b, 18b], after the formation of a pre-reaction Van der Waals complex (VdW), the uncatalysed reaction is composed of two elementary steps, namely, the CO₂ electrophilic attack on the hydroxyl (TS1=50.7 kcal.mol⁻¹) and an intramolecular ring closure (TS2=68.6

kcal.mol⁻¹). The overall reaction is exothermic by 14.2 kcal.mol⁻¹ and the rate determining step is the second step of the reaction that represents the highest energy transition state of the reaction (68.6 kcal.mol⁻¹) explaining the very low conversion obtained without catalyst. The TBAOAc catalysed reaction has been modelled following a two-elementary process where the acetate anion activates the hydroxyl group of the alkynol. We have calculated the Gibbs energy profiles considering one or two alkynol molecules to explicitly account for solvation effects. We do not have considered the alternative pathway in which a CO₂ molecule can be activated by the nucleophilic acetate anion as it has been previously found that this pathway was not favourable.^[16] The initial step (TS1 at 3.9 kcal.mol⁻¹) corresponds to the deprotonation of the hydroxyl by the acetate anion with the simultaneous nucleophilic attack of the alkoxide anion onto the



Figure 3. Free energy profile for α -methylene carbonate formation without catalyst (yellow) and catalyzed by TBAOAc considering one alkynol (green) or two alkynol molecules (blue). The Lewis structures of the intermediates and transition states are displayed for the TBAOAc catalyzed reaction considering one alkynol molecule

carbon atom of CO2 to form a [TBA]+[carbonate]- ionic pair intermediate IR (-2.9 kcal.mol⁻¹) with the release of acetic acid. In the second step TS2 (19.8 kcal.mol⁻¹), the intramolecular nucleophilic addition from the carbonate anion to the C=C bond with the simultaneous pronation of the alkenyl anion by acetic acid leads to the formation of 1 and the regeneration of TBAOAc. The overall energy of the catalysed process is drastically lowered in comparison to that calculated without catalyst thus explaining the good experimental efficiency reported above for this catalyst. The same mechanism holds when two alkynol molecules are considered although the overall energy profile is lower in energy than that reported considering only one alkynol. This is due to the stabilization mechanism that involves additional intermolecular hydrogen bonds by the second alkynol molecule at each step of the process (see Supporting Information) that particularly impacts the initial van der Waals complex and the intermediate. As a result, the activation barriers are higher with two alkynol molecules (ΔG = 13.5 and 26.7 kcal/mol) than with only one (ΔG = 6.6 and 22.5 kcal/mol) in line

with the hydrogen bonding solvation effects and the kinetics observed experimentally.

In this communication, n-tetrabutyl ammonium organic salts are used as catalysts for the coupling of CO₂ with 2-methyl-3-butyn-2-ol to form α -methylene cyclic carbonate. In particular, TBAOAc and TBAN3 enable the selective and quantitative synthesis of α -alkylidene cyclic carbonates from CO₂ and an alkynol with 98% yields in less than 10 hours at 353K and 3 MPa under solvent free conditions. The unique kinetic profiles and frequency shifts of the anion peak evidenced by online ATR-IR spectroscopy and elucidated by DFT calculations are related to a remarkable evolution of the hydrogen bonding solvation of the catalyst during the reaction. This work should help pushing away the limitations of organocatalysts and clearly opens novel avenues to the design of stable, cheap and metal free catalyst able to promote the selective synthesis of α -alkylidene cyclic carbonates under mild and solvent free conditions.

Experimental Section

The Supporting Information contains details on experimental and computational methods.

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Keywords: ammonium salts • carbon dioxide • α-methylene carbonate • organocatalysis

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