Journal of Molecular Catalysis A: Chemical 365 (2012) 162–171

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Synthesis of 5-membered cyclic carbonates by oxidative carbonylation of 1,2-diols promoted by copper halides

Potenzo Giannoccaro[a,*], Michele Casiello[a], Antonella Milella[a], Antonio Monopoli[a], Pietro Cotugno[a], Angelo Nacci[a,b]

[a] Department of Chemistry, University of Bari "Aldo Moro", Via Orabona, 4, 70126 Bari, Italy
[b] CNR – ICCOM, Department of Chemistry, University of Bari "Aldo Moro", Via Orabona, 4, 70126 Bari, Italy

ARTICLE INFO

Article history:
Received 26 May 2012
Received in revised form 1 August 2012
Accepted 29 August 2012
Available online 7 September 2012

Keywords:
Oxidative carbonylation
Copper halides
5-Membered cyclic carbonates
1,2-Diols
Solvent free
Mechanistic study

ABSTRACT

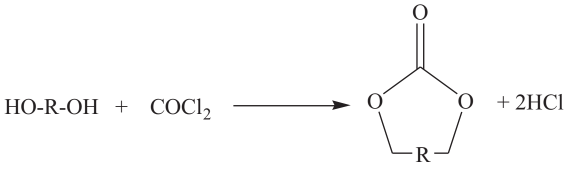
Copper halides, CuX_2 (X = Cl, Br), promote the oxidative carbonylation of vicinal diols [1,2-ethandiol (1,2-ED), 1,2-propanediol (1,2-PD), 1,2-butanediol (1,2-BD)] into the corresponding 5-membered cyclic carbonates, under CO/O_2 (Ptot = 3 MPa; $P_{(O2)}$ = 0.5 MPa), at 373 K, in CH_3CN and in the presence of a base as co-catalyst. Under these conditions, however, copper salts catalysts proved to be unstable (max turnover, 21.1 mol/mol), evolving into a pale green, insoluble and inactive material, by reaction with water, by-product of the carbonylation process. Contrarily, by carrying out reactions directly in diol, and using DMF as the base, catalytic systems showed to be stable and efficient. Under these conditions, when approximately 40% of the diol has been converted into carbonate, CO_2 begins to be formed, deriving from the CO oxidation promoted by H_2O that accumulates in the system. The extent of this side reaction, which lowers the yield of CO into cyclic carbonate, increases with the progress of carbonylation. After a diol conversion of 70%, the oxidation of CO to CO_2 becomes the main reaction and prevents the complete carbonylation of the diol. The most probable reaction mechanism is also reported and discussed.

© 2012 Elsevier B.V. All rights reserved.

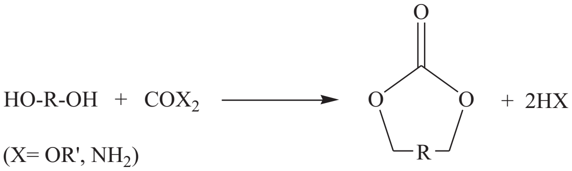
1. Introduction

Cyclic carbonates are non-toxic, easily biodegradable, high polar and high boiling liquids, that are used as raw materials for industry in a wide range of applications: solvents of degreasing, diluents of epoxy resins and polyurethanes [1,2], additives for fuels, chemical intermediates for the synthesis of polycarbonates and other polymeric substances [1,3] and for dimethyl carbonate synthesis (DMC) by a trans-esterification process with methanol [4].

The main synthetic methods of access to cyclic carbonates are based on carbonylation or carboxylation processes. The former are achieved by reacting diols with toxic phosgene (Eq. (1)) or with less toxic carbonyl derivates, like dialkyl carbonates or urea (Eq. (2)) [5].



(1)



(2)

Although the phosgene method is simple to be realized and requires mild temperature conditions, it has the disadvantage of using a highly toxic and hazardous reagent. In addition, this suffers from two other drawbacks: the low selectivity in the reaction products and the cost of disposing of HCl, that is formed in stoichiometric amounts. The other two procedures, while being more eco-friendly routes, show the problems of requiring stoichiometric amounts of organic carbonates or urea, which have a cost, the need for high temperatures ($T > 130\,^{\circ}C$) and for expensive catalysts based on metal oxides [6]. Moreover, since the synthetic reactions are reversible, the conversion is never complete, and tedious separation steps are necessary. In the case of reactions with urea, the recycling of ammonia, that is formed in stoichiometric amounts, is mandatory [7]. With regard to the carboxylation method, it is mostly accomplished by reacting CO_2 with olefins and oxygen, or directly CO_2 with epoxides or diols. Although these procedures are preferable to the phosgene route, as they have the advantage of using a greenhouse gas, they suffer from other problems, which still

---

* Corresponding author. Tel.: +39 060 5442093; fax: +39 080 5442129.
E-mail address: giannoccaro@chimica.uniba.it (P. Giannoccaro).

1381-1169/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2012.08.026

remain unsolved. In particular, procedures employing olefin and oxygen [8], have the disadvantage of requiring drastic reaction temperatures and efficient control systems, being the olefin/oxygen mixtures potentially explosive. Protocols with epoxides are interesting [9], because they occur under milder conditions, but require expensive starting materials. Finally, procedures based on CO_2 and diols are to be preferred from the economical point of view, but usually occur at high temperatures and proceed with lower conversions [10].

It is noteworthy that many valuable organic compounds, like linear organic carbonates [11], ureas and carbamates [12], and oxalates [11a], can be prepared conveniently by oxidative carbonylation processes, using dioxygen as an oxidant (Eq. (3)). These processes should be preferred to the methods described above, since they do not give by-products.

$$CO + 2HY + O_2 \rightarrow COY_2 + H_2O \quad (3)$$

$$(Y = OR, -NH_2, -NHR; -NR_2)$$

Recently, these procedures have been successfully applied to the carbonylation of bi-functional substrates, such as amino-alcohols and diamines, which have been converted into cyclic carbamates [13], N,N-bis(hydroxyalkyl)ureas [14], and cyclic ureas [15].

Little attention has been devoted to the oxidative carbonylation of diols, which could be conveniently converted into cyclic carbonates (Eq. (4)). In the middle of ‘80. Tam [16] reported that Pd(II) can promote this reaction, but the method appeared of little synthetic importance, due to both the requirement of stoichiometric amounts of copper, as an oxidant, and the very poor catalyst stability. The formation of ethylene carbonate by oxidative carbonylation of ethylene glycol, promoted by $Co(OAc)_2$, using O_2 as an oxidant, has also been reported in a patent [17]. The catalytic system, in this case, seems to be not efficient due to the very low values of both yields (2%) and turnover.

Only recently two different research groups have reported their preliminary results on some palladium-based catalytic systems, that are able of promoting efficiently the oxidative carbonylation of diols into cyclic carbonates under both homogeneous [18] and heterogeneous [19] conditions.

The oxidative carbonylation method has been also extended to glycerol, a triol, that has been converted into glycerol carbonate as described in a patent [20] and in a recent study [21,22a].

In this paper we describe the first copper-based catalytic systems, able to convert diols into the corresponding cyclic carbonates, using O_2 as an oxidant.

2. Experimental

Unless otherwise stated, all manipulations were carried out in air. Solvents, copper halides ($CuCl_2$, $CuBr_2$), diols [1,2-ethandiol (1,2-ED), 1,2-propanediol (1,2-PD), 1,2-butanediol (1,2-BD)], bases (Na_2CO_3, C_6H_5COONa, CH_3COONa, NEt_3, pyridine, N,N-dimethylformamide (DMF), ligands [triphenylphosphine (PPh_3), triphenylphosphine oxide ($OPPh_3$), 1,2-bis(diphenylphosphino)ethane (dppe) and 2,2′-bipyridine (bipy)] were Aldrich or Fluka products and were used as received. Products were identified by IR, GLC and GLC-MS and by comparison with the literature data. IR spectra were recorded on a Shimadzu IR-Prestige-21 spectrophotometer. GLC quantitative analyses and separations were performed by using a Varian Cromopack CP3800 GLC equipped with a CP Sil 8 CB capillary column (50 m, 0.53 mm ID), connected to a FID detector. GLC-MS analyses were carried out with a Shimadzu GLC 17-A linked to a Shimadzu GLC/MS QP5050A selective mass detector (capillary column: HP-5 MS, 30 m). Analyses of gas mixture: at the end of reaction, the residual gas mixture was collected at atmospheric pressure in a graduated cylinder connected to a gas burette and analyzed for CO_2. Analyses were carried out on a Porapak Q (3.5 m) column, using a Varian Cromopack CP3800 GLC equipped with a thermal conductivity detector.

Catalytic tests were carried out in a 55,6 mL stainless still autoclave mounted in an electrical oven having a magnetic stirrer on its base. Catalyst, co-catalyst, solvent and reagents were introduced in a glass vial (~12 mL) placed into the autoclave, in order to avoid any contact with metal walls. Under these conditions, the free volume for gaseous mixture is in the range 30–35 mL. Activity and selectivity were obtained by GLC, detecting the reacted diol and the formed carbonate using toluene or xylene as an external standard.

XPS analyses were carried out using a Thermo Fisher Theta Probe spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV) with a spot size of 400 μm, corresponding to a power of 100 W and at a take- off angle of 53°. Survey spectra (0–1300 eV) were acquired at a pass energy of 200 eV with a resolution of 1 eV. High resolution spectra for C1s, O1s, Cl2p and Cu2p were recorded at a pass energy of 100 eV with a resolution of 0.05 eV. Charge correction of the spectra was performed by taking the alkyl type carbon (C—C, C—H) component of the C1s spectrum as internal reference (binding energy, BE = 284.5 eV).

Atomic percentages were calculated from the high resolution spectra using the Scofield sensitivity factors set in the Thermo Avantage software (Thermo Fisher Corporation) and a nonlinear Shirley background subtraction algorithm. XPS analysis was repeated on three different spot of the sample.

2.1. *CO/O_2 ratio*

Although the CO/O_2 compressed mixtures are potentially explosive in a wide range (flammability range for CO in O_2 at room temperature is 16.7–93.5%) [23], many studies on oxidative carbonylation have been conducted and are still carried out with a 2:1 ratio ($CO:O_2$), without the occurrence of incidents [22]. As an example, DMC synthesis on industrial scale (the EniChem process) is carried out with this ratio [24]. However, when using mixtures in the flammability range, it is always advisable using suitable equipment and special care. In this work, we used autoclaves equipped with appropriate rupture discs (strength 10 MPa). Due to their small size (see above) and in the absence of a device able to carry the reactions at a constant pressure, we used 5:1 mixtures of CO/O_2. In any way, we found that the reactions take place even using mixture with 15:1 ratios. In these cases reactions are slower.

2.2. *Catalytic tests*

2.2.1. *Synthesis of 4-methyl-1,3-dioxolan-2-one*

In a typical experiment the glass vial was charged with solvent (CH_3CN, 9.0 mL), catalyst ($CuCl_2$, 0.60 mmol), co-catalyst (Na_2CO_3, 0.60 mmol) and 1,2-PD (10 mmol). The vial was introduced into the autoclave which was sealed and charged with O_2 (0.5 MPa) and CO up to a total pressure of 3 MPa. Under these conditions, also taking into account the free volume of the autoclave and the stoichiometry of the carbonylation process (Eq. (4)), the diol is the limiting reagent. The autoclave was heated at 100 °C and allowed to react for 3 h. After this time, it was cooled to room temperature and the residual gas mixture was analyzed for CO_2. The reaction mixture was analyzed by IR, GLC and GLC-MS for reactants and products. GLC analyses were performed by adding to the reaction mixture a weighed amount of toluene as external standard. The IR spectrum showed the presence of a strong absorptions around 1800 cm^{-1} assigned to cyclic carbonates *4-methyl-1,3-dioxolan-2-one* [25], whose presence was confirmed by means of GLC-MS analysis [*m*/*z* (in parenthesis, relative intensity): 102 (M^+, 2), 87

(10), 57 (64), 43 (73), 29 (100)] [11g]. The IR spectrum also showed the presence of a medium absorption at 2343 cm^{-1}, assigned to CO_2 and broad absorptions in the range 3600–3500 cm^{-1} and 1640–1610 cm^{-1}, assigned to H_2O, co-product of reaction and to OH group of unreacted diol. GLC quantitative analysis showed the disappearance of 7.9 mmol of 1,2-PD and the formation of 7.6 mmol of 4-methyl-1,3-dioxolan-2-one (see Table 2, entry 3).

The carbonylation of 1,2-PD under the other conditions discussed in the paper were carried out in the same way. Conversions and the selectivities are reported in Table 2.

2.2.2. Synthesis of 1,3-dioxolan-2-one

The reaction was carried out as described above using 1,2-ED (10 mmol) as diol. The IR spectrum showed the presence of two strong absorption at 1805 cm^{-1} (vs) and 1774 cm^{-1} (s), assigned to cyclic carbonate, 1,3-dioxolan-2-one [11g,26], whose presence was also confirmed by means of GLC–MS analysis. m/z: 88 (M^+, 47), 58 (5), 43 (65), 29 (100) [11g]. The spectrum also showed the presence of a medium absorption at 2343 cm^{-1}, assigned to CO_2 and broad absorptions in the range 3600–3500 cm^{-1} and 1640–1610 cm^{-1}, assigned to H_2O, and to OH group of unreacted diol. GLC quantitative analysis: reacted 1,2-ED, 8.0 mmol; ethylene carbonate, 7.5 mmol (see Table 2, entry 18).

2.2.3. Synthesis of 4-ethyl-1,3-dioxolan-2-one

The reaction was carried out as described above using 1,2-BD (10 mmol) as diol. The IR spectrum showed absorptions at 1801 cm^{-1} (s), assigned to *4-ethyl-1,3-dioxolan-2-one* [25], at 2343 cm^{-1}(m), assigned to CO_2, and in the range 3600–3500 cm^{-1} and 1640–1610 cm^{-1}, assigned to H_2O, and to OH group of unreacted diol. The presence of cyclic carbonate was also confirmed by GLC–MS analysis. m/z: 116 (M^+, 1), 87 (22), 71 (2), 44 (19), 43 (100), 42 (54), 29 (30). GLC quantitative analysis: reacted 1,2-BD, 6.5 mmol; butylene carbonate, 6.0 mmol (see Table 2, entry 19).

2.3. Catalyst stability

2.3.1. Reactions in acetonitrile

In a typical experiment the glass vial was charged with solvent (CH_3CN, 9.0 mL), catalyst ($CuCl_2$, 0.60 mmol), co-catalyst (Na_2CO_3, 0.60 mmol), and 1,2-PD (20 mmol). The vial was introduced into the autoclave which was sealed and charged with O_2 (0.5 MPa) and CO up to a total pressure of 3.0 MPa (PO_2, 0.5). Under these conditions, O_2 is the limiting reagent. The autoclave was heated at 100 °C and allowed to react for 3 h. After this time, it was cooled to room temperature and the residual gas mixture was evacuated and optionally analyzed for CO_2 content. A small aliquot (0.1 mL) of the reaction mixture was withdrawn and analyzed for diol reacted and carbonate formed. Then, the autoclave was recharged with a fresh mixture of CO/O_2 under the same conditions of pressure and allowed to react for further 3 h. After reaction, the gas mixture and the reaction solution were analyzed as above. The recharging of autoclave and analysis of its contents were repeated every 3 h until the conversion of the starting diol remained constant, indicative of the deactivation of the catalyst. Times are reported in Table 3, column 4. For a better quantification of diol and carbonate, catalyses were repeated using the same procedures, but GLC analyses were made on the entire reaction mixture after the deactivation time. Considering catalysis in entry 1, Table 3, the GLC analysis carried out after the addition of 0.875 g of toluene as a standard, showed the disappearance of 10.6 mmol of 1,2-PD and the formation of 10.2 mmol of carbonate (96% of selectivity). Data in Table 3, are reported as turnover number and conversion%. Analyses under different conditions were carried out in the same way. Selectivities in all cases were ≥96%. Results are reported in Table 3. Catalyst stability under different conditions (base and ligand) was obtained in the same way, data are report in Table 3. The CO_2 content in the gas mixture was low during all cycles.

2.3.2. Solvent free reactions

In a typical experiment the glass vial was charged with ~5 mL of diol (89.5 mmol for 1,2-ED, 68.1 mmol for 1,2-PD and 56.5 mmol for 1,2-BD), 0.5 mL of DMF and 0.60 mmol of $CuCl_2$. The vial was introduced into the autoclave which was sealed and charged with O_2 (0.5 MPa) and CO up to a total pressure of 3.0 MPa. The autoclave was heated at 100 °C for 2 h. After this time, reactor was cooled to room temperature, evacuated from the residual gas mixture and recharged with a fresh mixture of CO/O_2 at the starting pressure. Then, the mixture was allowed to react at 100 °C for other 2 h. These reaction cycles were repeated every 2 h for a total of 4 times per day and for 5 consecutive days. At the end of each day, both gas and liquid reaction mixtures were analyzed respectively for CO_2, diol reacted and carbonate formed. Analyses of the liquid mixture were carried out on a small aliquot, which was appropriately diluted with acetonitrile. Below, analysis after the first day of reaction is reported. Analysis was carried out by adding to 0.103 g of reaction solution 5 mL of CH_3CN and 0.0312 g of xylene as standard. The amount of diol and carbonate detected in the analyzed sample was related to total mass (5.73 g). The data showed that there had been the disappearance of 15.9 mmol of 1,2-PD and the formation of 15.3 mmol of carbonate (96% of selectivity). The total amount of diol reacted at the end of each daily cycle is reported in Table 4 and plotted in Fig. 3. Selectivities were found to be ≥96%.

Analysis of gas mixture: CO_2 began to form at the end of the second day. Regarding the carbonylation of 1,2-PD, the amount (mmol) found at the end of the second, third, fourth and fifth day was 0.6, 1.3, 1.9, 2.4, respectively. The reaction liquid mixture was distilled under reduced pressure: three fractions were obtained containing respectively, H_2O and DMF, 1,2-PD (0.52 g) and propylene carbonate (2.42 g). The solid obtained after distillation was treated with 3 mL of water and 2 mL of an 1 M HCl solution. The resulting solution was evaporated to dryness and the solid residue, consisting of $CuCl_2$ was active in catalysis.

2.4. Carbonylation mechanism: reductive step

A glass vial was charged with CH_3CN (10 mL) and equimolar amount of 1,2-PD (0.28 g, 3.7 mmol), $CuCl_2$ (0.5 g, 3.7 mmol) and Na_2CO_3 (0.39 g, 3.7 mmol). The vial was introduced into the autoclave, which was sealed, charged with CO up to a total pressure of 2.5 MPa and allowed to react at 100 °C for 3 h. After this time, the autoclave was cooled to room temperature and the reaction mixture was analysed by IR and GLC. IR spectrum showed the presence a strong absorption at 1800 cm^{-1} assigned to propylene carbonate and a medium absorption at 2343 cm^{-1}, assigned to CO_2. From GLC analyses 1.8 mmol of unreacted diol and 1.8 mmol of propylene carbonate were detected.

2.5. XPS characterization of deactivated catalyst

XPS analyses were carried out on the solid sample recovered from the reaction mixture after deactivation (Table 3, entry 1).

In the survey spectrum, signals attributed to C, O, Cl and Cu were identified. Atomic percentages were then obtained from the high resolution spectra and results are reported in Table 1.

Processing of the $Cu2p_{3/2}$ spectral region was performed starting from a linear background subtraction instead of a non-linear routine in order to avoid truncation of the shake-up signals at higher BE [27]. A deeper inspection of the high resolution Cu2p spectrum, reported in Fig. 1, allowed to gain further information. The spectrum reveals the presence of shake-up signals (s) characteristic of Cu(II) compounds. The shake-up signals shape and relative

Table 1
XPS atomic percentages.

	XPS atomic percentage (%)
Cu	19.1 ± 0.3
O	35.8 ± 0.1
Cl	12.1 ± 0.7
C	33.0 ± 0.9

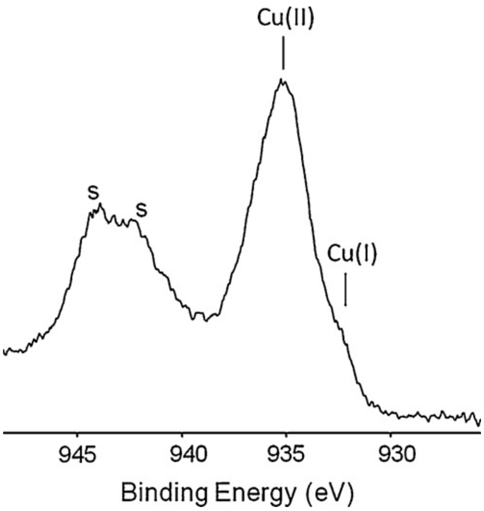


Fig. 1. XPS Cu2p photoelectron spectrum showing that Cu is mainly in the form of Cu(II), as also evident from the presence of the shake-up signals (s). The shoulder at lower BE is indicative of traces of Cu (I).

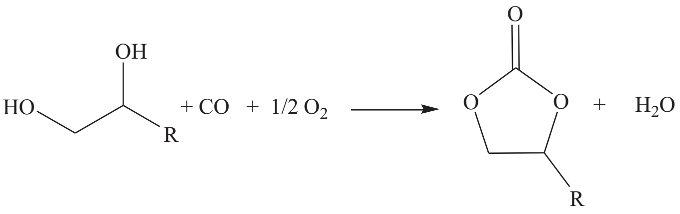
intensity along with the Cu2p$_{3/2}$ peak position can be of help to identify the kind of Cu(II) compound prevailing in the sample. Comparing the spectrum of Fig. 1 with those reported in literature for Cu_2O, CuO, $Cu(OH)_2$ [28–30], $CuCl_2$ [31] standard reference materials, it appears quite straightforward that copper is mainly present in the sample as hydroxylated copper(II). This outcome is also confirmed by the position of the main Cu2p$_{3/2}$ peak at 935.1 eV [32]. In the Cu2p$_{3/2}$ spectrum, a shoulder at 932.3 eV can be also distinguished which indicates traces of Cu(I) compounds, like CuCl (BE = 932.4 eV) or Cu_2O [32]. Due to the very low peak separation, an unambiguous assignment between these two components is difficult to achieve, however a curve-fitting procedure of the Cu2p$_{3/2}$ component allowed to estimate the Cu(I) amount, which was found to be 2% of the Cu percentage. It should be pointed that the traces of Cu(I) detected could be due to the XPS analysis itself, since the reduction of Cu(II) to Cu(I) under X-ray exposure has been deeply documented in literature [33].

The quantitative analysis reported in Table 1 shows that chlorine is also present in the sample and its BE value of 198.2 eV is indicative of a Cu(II)—Cl bond [33]. These results suggest that the deactivated catalyst is a chloro-hydroxo copper compound of formula $CuCl_x(OH)_y$ (see also Section 3.2). To determine the exact composition, we calculated the oxygen amount directly bound to copper by subtracting to the overall oxygen percentage (35.8%) the one bonded to carbon. The latter was estimated by the curve-fitting of the C1s high resolution spectrum (Fig. 2), which consists of four components, whose assignments and atomic percents are reported in Fig. 2 [34], and was found to be 14.8%. As a consequence, the percent of O bonded to Cu resulted was equal to 21.0%. Taking into account that the Cu(II) atomic percent is equal to 17.1%, the composition of the deactivated compound resulted to be $Cu_{17.1}Cl_{12.1}(OH)_{21.0}$, which corresponded to the minimal formula $CuCl_{0.7}(OH)_{1.2}$.

3. Results and discussion

3.1. General

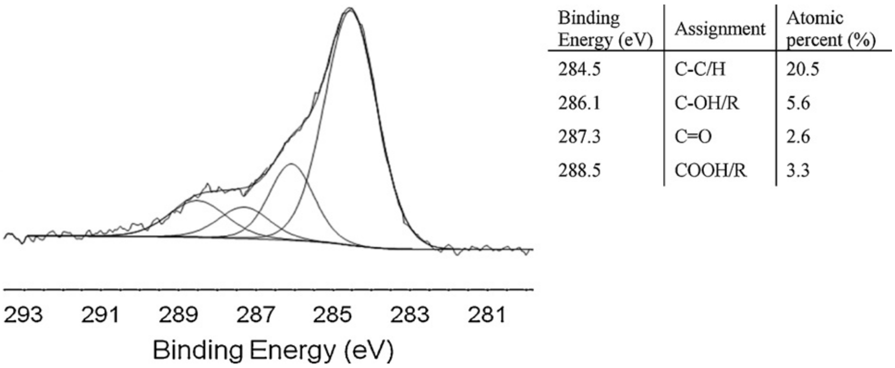
Copper halides, CuX_2 (X = Cl, Br), promoted the oxidative carbonylation of vicinal diols into their relevant cyclic carbonates, according to the stoichiometry of Eq. (4):



(4)

Catalytic efficiency (activity and stability) proved to be influenced by the nature of the solvent, the presence of bases and ligands.

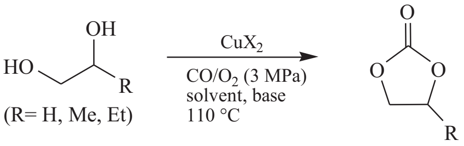
Table 2 summarizes the most significant results of reactions carried out in CH_3CN, which was found to be the best solvent, at 373 K in the presence of a 5:1 mixture of CO/O_2 ($P_{(O2)}$ = 0.5 MPa; Ptot = 3.0 MPa). Catalysis was efficient only when reactions were carried out in the presence of catalytic amounts of a base like sodium carbonate, acetate or benzoate (entries 1–11). Under these conditions, both $CuCl_2$ and $CuBr_2$ converted 1,2-PD into the corresponding 5-membered cyclic carbonates, but copper chloride was always more active than the corresponding bromide (entries 3–5 versus 6–8).



Binding Energy (eV)	Assignment	Atomic percent (%)
284.5	C-C/H	20.5
286.1	C-OH/R	5.6
287.3	C=O	2.6
288.5	COOH/R	3.3

Fig. 2. Curve-fitting of the C1s spectrum.

Table 2
Oxidative carbonylation of 1,2-diols with copper catalysts.[a]



Entry	Catalyst	Base	B/Cu (molar ratio)	Ligand	Diol	Conv.%	Selectivity. (%)
1	$CuCl_2$	–	0	–	1,2-PD	0	–
2	$CuBr_2$	–	0	–	1,2-PD	0	–
3	$CuCl_2$	Na_2CO_3	1	–	1,2-PD	79	96
4	$CuCl_2$	Na_2CO_3	2	–	1,2-PD	82	96
5	$CuCl_2$	Na_2CO_3	4	–	1,2-PD	74	97
6	$CuBr_2$	Na_2CO_3	1	–	1,2-PD	42	95
7	$CuBr_2$	Na_2CO_3	2	–	1,2-PD	50	96
8	$CuBr_2$	Na_2CO_3	4	–	1,2-PD	65	94
9	$CuCl_2$	CH_3COONa	1	–	1,2-PD	76	94
10	$CuCl_2$	C_6H_5COONa	1	–	1,2-PD	75	94
11	$CuCl_2$	Na_2CO_3[b]	1	–	1,2-PD	89	73
12	$CuCl_2$	NaOH[c]	1	–	1,2-PD	66	89
13	$CuCl_2$	NaOH[d]	1	–	1,2-PD	35	88
14	$CuCl_2$	Pyridine	–[e]	–	1,2-PD	0	–
15	$CuCl_2$	DMF	–[f]	–	1,2-PD	0	–
16	$CuCl_2$	DMF	–[g]	–	1,2-PD	90	96
17	$CuCl_2$	NEt_3	–[h]	–	1,2-PD	79	81
18	$CuCl_2$	Na_2CO_3	1	–	1-2-ED	80	94
19	$CuCl_2$	Na_2CO_3	1	–	1,2-BD	65	92
20	$CuBr_2$	Na_2CO_3	1	–	1-2-ED	49	93
21	$CuBr_2$	Na_2CO_3	1	–	1,2-BD	42	93
22	$CuCl_2$	Na_2CO_3	1	PPh_3 L/Cu = 1	1,2-PD	65	91
23	$CuCl_2$	Na_2CO_3	1	PPh_3 L/Cu = 2	1,2-PD	60	92
24	$CuCl_2$	Na_2CO_3	1	$OPPh_3$	1,2-PD	68	92
25	$CuCl_2$	Na_2CO_3	1	Dppe	1,2-PD	63	93
26	$CuCl_2$	Na_2CO_3	1	Bipy	1,2-PD	60	91
27	CuCl	Na_2CO_3	1	–	1,2-PD	75	93

[a] Unless otherwise stated, all the reactions were carried out by dissolving in CH_3CN (9 mL), CuX_2 (0.60 mmol), base (0.60 mmol or an amount according to molar ratio), diol (10 mmol), $T = 100\,^\circ C$, CO/O_2 ($PO_2 = 0.5$ MPa; Pt = 3 MPa), for 3 h (see Section 2.2).

[b] Reaction was carried out at 120 °C.

[c] Solid NaOH was used.

[d] 1 mL of an aqueous solution 0.6 N was added.

[e] Reaction was carried out in CH_3CN/Py (v/v = 9/0.5).

[f] Reaction was carried out in DMF as the solvent.

[g] Reaction was carried out in CH_3CN/DMF (v/v = 9/1) for 10 h.

[h] Reaction was carried out in CH_3CN/NEt_3 (v/v = 9/1).

It was found that the activity depended on the base/Cu(II) molar ratio. In the case of $CuCl_2$, best results were found with 1:1 or 1:2 ratios (Table 2, entries 3–5), while a different trend was observed with $CuBr_2$ (entries 6–8). All the reactions were carried out at 100 °C, an increase of temperature promoted the oxidation of diol at the expense of the selectivity of process (Table 2, Entry 11).

It was also investigated the influence of other bases, such as NaOH, pyridine, N,N-dimethyl formamide (DMF) and NEt_3. This latter exhibited comparable performance with that of Na_2CO_3, but showed the drawback of promoting the formation of undesired side-products such as N,N′-tetraethylurea and N,N-diethylpropionamide (Table 2, entry 17) [35].

On the contrary, NaOH was less efficient and in this case catalyst activity decreased further by using aqueous solutions in place of the pure base (Table 2, entries 12 and 13). This trend was most likely due to the inhibitory effect of water on catalyst stability (see Section 3.3). Moreover, carbonylation was totally inhibited by pyridine and DMF (entries 14 and 15), even if in the latter case catalyst activity steadily increased by adding acetonitrile until to reach a DMF:CH_3CN ratio of 1:9 (v/v) (Table 2, entry 16)

The CuX_2/Na_2CO_3 catalytic system (X = Cl, Br, molar ratio = 1) was also applied to the carbonylation of 1,2-ethanediol and 1,2-butanediol, that were successfully converted into the corresponding cyclic carbonates. Data in Table 2 show that even with these substrates $CuCl_2$ was more active than $CuBr_2$ (entries 18 and 21).

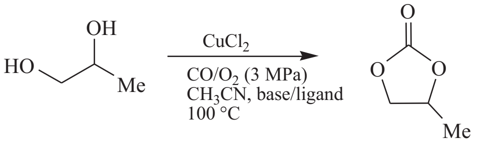
3.2. Catalyst stability

To evaluate the catalyst stability, carbonylations were carried out with excess amounts of diol and monitored until conversions remained constant over the time (see Section 2.3). Data reported in Table 3 show that in CH_3CN, the $CuCl_2/Na_2CO_3$/1,2-PD system (0.6 mmol, 0.6 mmol, 20 mmol), exhibited a lifetime of 9 h with a turnover number of 17.5 (expressed as mole of substrate reacted per mole of catalyst, Table 3, entry 1). The turnover values decreased in the order when sodium acetate (TN = 15.6) or benzoate (TN = 15.3) was used as a base (Table 3, entries 2 and 3). The deactivated systems revealed the presence of a copper-based pale green solid, with a supernatant colourless solution. The solid proved to be inactive in catalysis and its XPS analysis showed the copper(II) hydroxyl chloride as the predominant species with a minimal formula of $CuCl_{0.7}(OH)_{1.2}$ (see Section 2.5).

It was reported that copper halides used as catalysts in DMC synthesis, evolved under working condition to less active compounds. Pacheco and Marshall [36] reported the formation of a product of formula $CuCl_x(OH)_y$. Fleet [37] described the formation of two main phases, $Cu(OH)Cl$ and $Cu_2(OH)_3Cl$, along with small amounts of CuO.

On these bases, deactivation of our systems must be attributed to the formation of these phases promoted by water, co-product of oxidative carbonylation of diols (Eq (4)).

Table 3
Oxidative carbonylation of 1,2-PD. Stability of catalyst.[a]



Entry	Base	Ligand	Time (h)	Turnover[b] Number	Conversion[c] (%)
1	Na_2CO_3	–	9	17.5	53
2	CH_3COONa	–	9	15.6	47
3	C_6H_5COONa	–	9	15.3	46
4[d]	Na_2CO_3	–	3	8.3	25
5[e]	Na_2CO_3	–	9	18.2	55
6	Na_2CO_3	PPh_3 L/Cu = 1	15	20.3	61
7	Na_2CO_3	$OPPh_3$	15	21.0	63
8	Na_2CO_3	Dppe	15	21.1	63
9	Na_2CO_3	Bipy	15	20.0	60

[a] All the reaction were carried out at 100 °C in CH_3CN (9 mL), using, $CuCl_2$ (0.60 mmol), base (0.60 mmol), ligand (0.60 mmol or an amount according to molar ratio), 1,2-PD (20 mmol) (see for details Section 2.3.1).
[b] Expressed as mole of 1,2-PD reacted per mole of $CuCl_2$.
[c] Selectivities were ≥96%.
[d] 0.5 mL of water were added to initial mixture.
[e] After 3 h of reaction, Na_2SO_4 (1.0 g) was added.

Eqs. (5) and (6) show the reaction stoichiometry leading to the formation of the copper (II) hydrolysis by-products $CuCl_xOH_y$ in the presence of a generic base B and Na_2CO_3 respectively.

$$CuCl_2 + yH_2O + yB \rightarrow CuCl_{(2-y)}OH_y + yBHCl \tag{5}$$

$$CuCl_2 + y/2H_2O + y/2Na_2CO_3 \rightarrow CuCl_{(2-y)}OH_y + y/2CO_2 + yNaCl \tag{6}$$

Most likely, hydrolysis would be suppressed in the absence of bases and catalyst would be more stable. Unfortunately, under these conditions carbonylation does not occur, being the base essential for the formation of the key intermediate of catalytic process (see Section 3).

Blank tests showed that the addition of water to a CH_3CN solution containing equimolecular amounts of $CuCl_2$ and Na_2CO_3, promoted the reaction (7).

$$CuCl_2 + Na_2CO_3 + H_2O \rightarrow Cu(OH)_2 + 2NaCl + CO_2 \tag{7}$$

Noteworthy, reaction mixture of the blank undergoes the same colour change of the catalytic solutions. Their initial deep yellow–brown colour clears up with the progress of reaction until to completely disappear. The final solutions were colourless, with the presence of a light green solid, inactive in catalysis. We found that the solid formed in both catalysis and blank, could be converted into the active $CuCl_2$, by reaction with aqueous HCl and successive vacuum drying of the resulting solution.

The negative effect of water on the catalyst lifetime was confirmed in two separate experiments. (i) the addition of small amounts of H_2O to the reagents at the beginning of reaction that reduced lifetime to only 3 h (Table 3, entry 4); and (ii) the addition of dehydrating agent that, conversely, increased that catalyst performance (Table 3, entry 5). The decrease of activity observed in reaction with aqueous NaOH (Table 2, entry 13) could be inferred to inhibitory effect of H_2O.

In an attempt to prepare more stable catalysts, we studied activity of $CuCl_2$ in the presence of ligands, as the coordination should inhibit the hydrolysis process. Data in Tables 1 and 2 confirmed this assumption, showing that the addition of ligands prolonged the catalyst lifetime and consequently the total turnover number (Table 3, entries 6–9).

Table 4
Oxidative carbonylation under solventless conditions.[a]

Diol	mmol reacted				
	1st day	2nd day	3rd day	4th day	5th day
1,2-PD	15.9	28,9	40	47.1	47.3
1,2-ED	23.1	42.1	57.9	63.7	63.8
1,2-BD	12.9	22.3	32.1	38.4	38.9

[a] In a typical experiment: 5 mL of diol, 0.5 mL of DMF and 0.60 mmol of $CuCl_2$ under O_2 (0.5 MPa) and CO up to a total pressure of 3.0 MPa, at 100 °C. Selectivities were found to be higher than 96% in all cases (see Section 2.3.2).

However, in all of these cases, the increase of the catalyst stability was accompanied by a decrement of the reaction rates (see the minor conversions at 3 h in Table 2, entries 22–26). This opposite effect of ligands can be justified taking into account that coordination inhibits the $CuCl_2$ hydrolysis, prolonging the catalyst lifetime (Eqs. (5) and (6)), but also slows down formation of the key intermediate, decelerating the entire diol carbonylation process.

3.3. *Solvent free catalysis*

We found that the inhibitory effect of water on catalyst stability can be limited by carrying out reactions directly in diols in the presence of DMF as the base (see Section 2.3.2).

Thus, the systems realized by adding to diol (5 mL, 1,2-ED, 1,2-PD, 1,2-BD), 0.5 mL of DMF and 0.60 mmol of $CuCl_2$, proved to be very effective for the synthesis of cyclic carbonates.

Table 4 and Fig. 3 report mmol of diol reacted and conversion percentages over the time, respectively. As can be seen, under these conditions catalyst was still active after 5 days and carbonylation reached the maximum value of ~70% for all the diols (for details, see Section 2).

The increased stability, under these conditions, could be justified assuming that diols, owing to their high concentration, interact with active sites of Cu (II), preventing the deleterious effect of water (Eqs. (5) and (6)).

We ascertained that the incomplete diol carbonylation is imputable to the side oxidation reaction of CO to CO_2, promoted water, coproduct of reaction. This reaction begins to appear after about 45% of the diol reacted (~two days) and continuously increases with the progress of the reaction becoming dominant when conversion reaches 70%. Under these conditions, as water

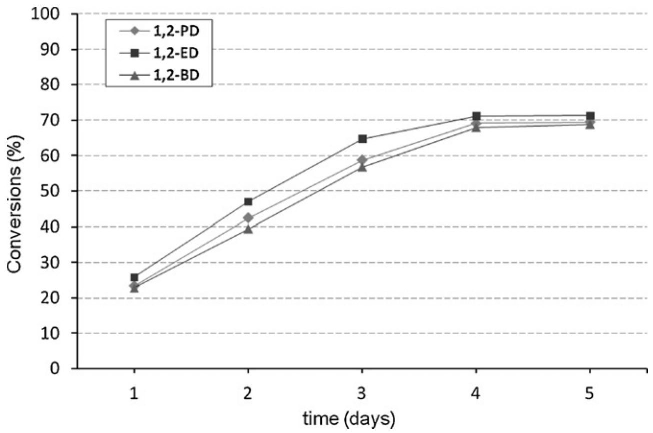


Fig. 3. Carbonylation of 1,2-ED, 1,2-PD and 1,2-BD under solventless conditions.

prevents further carbonylation of the diol and degrades the catalyst promoting the formation of the green inactive solid, it is convenient to stop the reaction and proceed with the separation of the reaction mixture components. After separation, the remaining solid residue was treated with aqueous HCl and the resulting solution was evaporated to dryness. It was obtained a brown solid, consisting of $CuCl_2$, that is active for a new catalysis cycle.

The direct oxidation of CO to CO_2 is a well known side-reaction in the oxidative carbonylation processes catalyzed by transition metals [38]. The process is promoted by H_2O which interacts with CO coordinated to active sites of copper. Consequently, $CuCl_2$ instead of reacting with diol to form the alkoxy carbonyl, ClCuCO—OROH, key intermediate of process (see next section), gives rise through the same mechanism to an hydroxyl carbonyl species (ClCuCOOH), which then decomposes into CO_2 and Cu(0). The latter, by reaction with O_2, reforms Cu(II) that can continue the oxidation of CO (see Scheme 3, pathways 6–8).

Since the oxidation of CO can not be suppressed, the industrial applications based on these processes make use of suitable precautions to limit its effect. For example, in the EniChem process for the synthesis of DMC [4a,39], the need for the water extraction from the system, plays a fundamental role in reactor design.

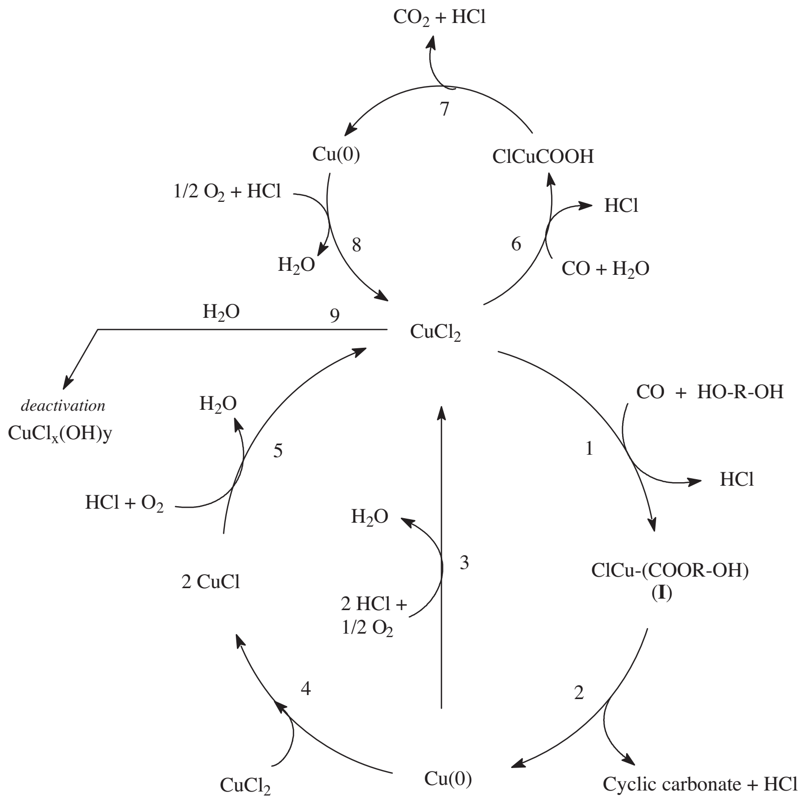
4. Reaction mechanism

It is well known that oxidative carbonylation processes catalyzed by transition metals proceed through two main steps, the first one reductive and the second one oxidative. Their sequence depends on both the metal catalyst and its oxidation state. Concerning the oxidative carbonylation of alcohols, in particular of methanol, Pd and Cu were found to be the most active metals.

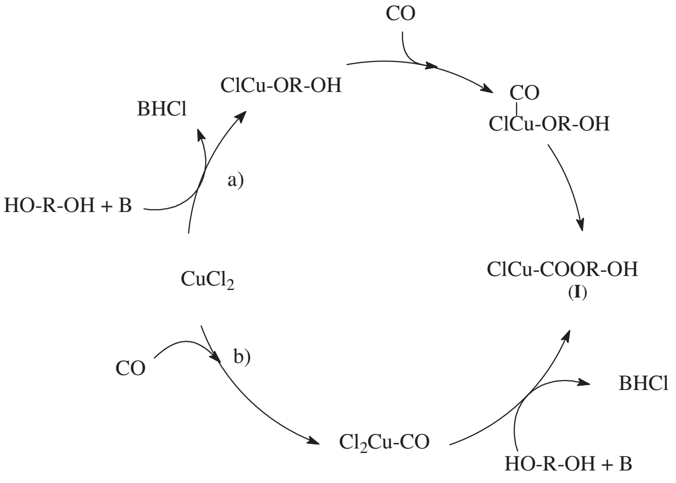
Processes promoted by Pd(II) start with a reductive step, in which the formation of carbonate occurs, followed by the oxidative step, that restores the catalytically active species [38].

The sequence of steps in systems making use of copper depends on the oxidation state of initial species. For example, in DMC synthesis promoted by CuCl [4a,39], the first step consists of the oxidation of cuprous chloride into copper methoxychloride $CuCl(OCH_3)$. The latter by reaction with CO gives rise to the reductive step producing DMC and restoring the catalytic species CuCl. DMC synthesis has also been realized with several $CuCl_2$-based systems, operating under both homogeneous and heterogeneous conditions [41]. In these cases, $CuCl_2$ reacts with methanol affording a methoxychloride specie, which begins the catalytic cycle with the reductive step.

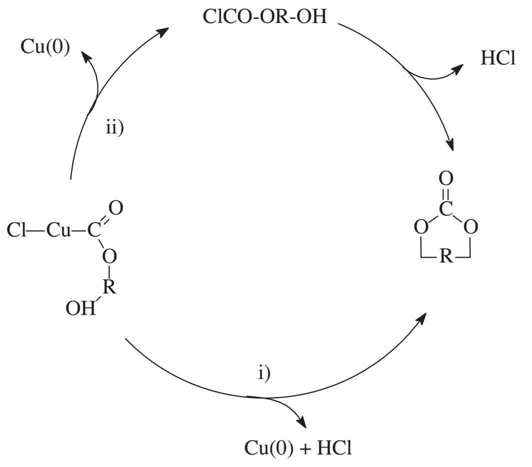
It should be emphasized that the sequence of the two steps should be not dependent on the oxidation state of initial copper



Scheme 1. The plausible reaction mechanism.



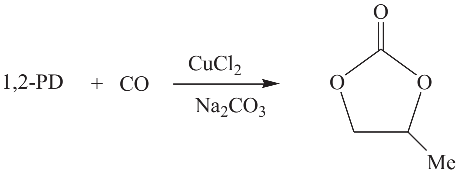
Scheme 2. Proposed pathways to the formation of ClCu—COOR—OH.



Scheme 3. Proposed mechanism for decomposition of ClCu—COOR—OH to cyclic carbonate.

species, since under reaction condition (CO/O_2), copper would be present in both Cu(II) and Cu(I) forms.

In an attempt to determine the mechanism of formation of cyclic carbonates, by oxidative carbonylation of diols, we reacted stoichiometric amounts of $CuCl_2$ or CuCl and 1,2-PD, with either CO or O_2. We found that $CuCl_2$ was able to convert 1,2-PD, into propylene carbonate in the presence of Na_2CO_3, when it is allowed to react with sole CO (P_{CO} = 2–3 MPa, Eq (8).).



(8)

In contrast, CuCl did not afford the cyclic carbonate when the reaction was carried out with sole CO, as well as only trace amounts of the carbonylation product were detected by performing reaction first with O_2 (PO_2 = 0.5–0.8 MPa) at 70 °C and then with CO at 100 °C. In the latter case, we established that, Cu(II), produced by oxidation of the Cu(I) in the absence of CO, oxidizes directly the 1,2-PD.

To confirm this, we found that: (i) $CuCl_2$ oxidizes 1,2-PD and reduces to Cu (I), when reacted under N_2 at 70 °C; (ii) CuCl under a mixture of CO/O_2, which are catalysis condition, is active to promote the carbonylation of 1,2-PD (Table 2, entry 27). These results suggest that catalysis is initiated from Cu(II) by a reductive step.

The most probable catalytic cycle is reported in Scheme 1. Similarly to that found for the Pd(II) catalyzed carbonylation of mono alcohols [40], and recently also for diols [11g], it can be assumed that diol conversion into carbonates proceeds through the formation of the copper alkoxy carbonyl intermediate ClCu—(COOR—OH) (**I**) (Scheme 1, pathway 1).

Alkoxy carbonyl complexes of diols, stabilized by Cu(II) are not known. Recently, some of us [11g] were able to isolate a series of their analogous with Pd(II). All of them decompose to give cyclic carbonates.

On the basis of data reported in the literature concerning the formation of alkoxy carbonyl complexes of mono-alcohols [40,42], the intermediate **I** could be formed according to one of pathways suggested in Scheme 2. Following pathway (a), $CuCl_2$ gives rise, in the presence of a base, to an alkoxy complex, that evolves into the corresponding alkoxy carbonyl derivative by coordination of CO followed by its insertion into the Cu–alkoxy bond.

Following pathway (b), $CuCl_2$ should first coordinate CO and then undergo a base assisted nucleophilic attack by diol, affording the alkoxy carbonyl species **I**. All Attempts to isolate this latter complex were unsuccessfully.

With regard to the evolution of the intermediate **I** into cyclic carbonate, unlike what has been proposed for DMC synthesis, in which an interaction between the two molecules, ClCu—$COOCH_3$ and ClCu—OCH_3, should occur [4a], we propose the two plausible pathways depicted in Scheme 3: (i) an intramolecular attack of OH group to the carbonyl moiety or ii) the decomposition of **I** to chloroformate with subsequent base-assisted cyclization. The evolution of alkoxycarbonyl or amino carbonyl complexes into chlorofomate or chloroformamide, has been well documented by some of us [11g,8d,13a,36].

The restore of the initial active species of Cu(II), could occur either by direct reoxidation of Cu(0) with O_2 (Eq. (9) and Scheme 1, pathway 3) or by reaction of Cu(0) with Cu(II) and subsequent oxidation of the resulting Cu(I) (Eq. (10) and Scheme 1, pathways 4 and 5).

$$\mathrm{Cu(0)} + ½\mathrm{O_2} + 2\mathrm{H^+} \rightarrow \mathrm{Cu(II)} + \mathrm{H_2O} \tag{9}$$

$$\mathrm{Cu(0)} + \mathrm{Cu(II)} \rightarrow 2\mathrm{Cu(I)} \tag{10}$$

5. Conclusions

We have found, for the first time that copper halides, widely used for the oxidative carbonylation of methanol into DMC, can also be used for converting vicinal diols into the corresponding 5-membered cyclic carbonates.

For the synthesis of moderate amounts of carbonate, is preferable to carry out reactions in acetonitrile. Under these conditions, even if the catalyst is poor stable, it is possible to convert selectively in carbonate 17 mol of diol per mol of $CuCl_2$. For larger amounts, it is more convenient to perform carbonylation directly in the diol. In this case, the process must be stopped when 70% of the diol has been reacted, since water, which is formed as a co-product, prevents further carbonylation.

Scheme 1 summarizes the overall behavior of the catalytic system. In the absence or with low water amounts, catalyst $CuCl_2$ operates according to the pathways 1–5 and converts the diol into cyclic carbonate. With the reaction progress, part of catalyst is engaged in the oxidation process of CO to CO_2 (pathways 6–8), which is promoted by the increasing of water concentration in the reaction mixture. When this latter reaches a critical value, and this, under solventless conditions, occurs when ca. 70% of diol has been carbonylated, CO oxidation becomes the predominant process. Under these conditions, water also promoted the catalyst deactivation affording an insoluble and poorly active chloro-hydroxo compound, $CuCl_x(OH)_y$ (pathway 9).

Acknowledgements

Partial financial support of this work by the Ministry of University and Scientific Research of Italy (MIUR) and by University of Bari is gratefully acknowledged.

References

[1] J.H. Clements, Ind. Eng. Chem. Res. 42 (2003) 663–674.

[2] P.T. Anastas, R.L. Lankey, Green Chem. 2 (2000) 289–295.

[3] J.P. Parrish, R.N. Salvatore, K.W. Jung, Tetrahedron 56 (2000) 8207–8237.

[4] (a) D. Delledonne, F. Rivetti, U. Romano, Appl. Catal. A 221 (1–2) (2001) 241–251;
(b) H. Wang, M. Wang, N. Zhao, W. Wei, Y. Sun, Catal. Lett. 105 (3–4) (2005) 253–257;
(c) C.H. Yang, W.B. Li, J.Q. Liu, S.J. Tan, Y.Z. Han, J. Fuel Chem. Technol. 30 (2002) 551–554;
(d) Y.H. Chang, C.H. Yang, W.B. Li, L. Bai, Y.Z. Han, X.K. Wang, J. Fuel Chem. Technol. 29 (2001) 566–569;
(e) M. Sankar, S. Satav, P. Manikandan, ChemSusChem 3 (2010) 575–578;
(f) R.A. Grey, US Patent No 5091543 (1992);
(g) J.H. Clements, H.P. Klein, E.T. Marquis, PCT Int. Appl. (2003), WO 2003089424 A1 20031030.

[5] (a) Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 18, Wiley, New York, 1985, p. 651;
(b) M. Aresta, E. Quaranta, Chem. Tech. 27 (1997) 32;
(c) P.E. Strege, J.M. Renga, US Patent No 53448811 (1982);
(d) A.A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951–976;
(e) J. Sun, S. Fujita, M. Arai, J. Organomet. Chem. 690 (2005) 3490–3497;
(f) D.J. Darensbourg, Chem. Rev. 107 (2007) 2388–2410;
(g) T. Sakakura, K. Kohno, Chem. Commun. (2009) 1312–1330.

[6] (a) K.R. Muller, B. Buchholz, J. Hess, US Patent No 5212321 (1993);
(b) H. Komura, T. Yoshino, Y. Ishido, Bull. Chem. Soc. Jpn. 46 (1973) 550–553;
(c) Y.K. Iwakuni, Y.M. Kuga, M.I. Ohtake, US Patent No 4880942 (1989).

[7] Q.B. Li, W.Y. Zhang, N. Zhao, W. Wei, Y.H. Sun, Catalyst Today 115 (2006) 111–116.

[8] (a) C. Fumagalli, G. Caprare, P. Roffia, US Patent No 4009183 (1977);
(b) M. Aresta, A. Dibenedetto, I. Tommasi, Appl. Organometal. Chem. 14 (2000) 799–802;
(c) J.A. Verdol, US Patent No 3205305 (1962).

[9] (a) V. Calò, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561–2563;
(b) D.J. Darensourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155–174;
(c) R. Srivastava, D. Srinivas, P. Ratnasamy, J. Catal. 233 (2005) 1–15;
(d) H. Yasuda, L.-N. He, T. Sakakura, J. Catal. 209 (2002) 547–550;
(e) D. Srinivas, R. Srivastava, P. Ratnasamy, US Patent Appl. 20060094893 (2006).

[10] (a) H. Chen, X. Zhao, Y. Wang, Petrochem. Technol. 11 (2005) 1037–1040;
(b) S.-Y. Huang, S.-G. Liu, J.-P. Liu, N. Zhao, W. Wei, Y.-H. Sun, J. Fuel Chem. Technol. 35 (2007) 701–705.

[11] (a) F. Rivetti, U. Romano, J. Organomet. Chem. 174 (1979) 221–226;
(b) D.M. Fenton, P.J. Steinwand, J. Org. Chem. 39 (1974) 701–704;
(c) M. Graziani, P. Uguagliati, G. Carturan, J. Organomet. Chem. 27 (1971) 275–278;
(d) G. Cavinato, L. Toniolo, J. Organomet. Chem. 444 (1993) C65–C66;
(e) P. Brechot, Y. Chauvin, D. Commereuc, L. Saussine, Organometallics 9 (1990) 26–30;
(f) P. Giannoccaro, C.F. Nobile, M. Latronico, Inorg. Chim. Acta 175 (1990) 133–139;
(g) P. Giannoccaro, D. Cornacchia, S. Doronzo, E. Mesto, E. Quaranta, M. Aresta, Organometallics 25 (2006) 2872–2879.

[12] (a) S. Fukuoka, M. Chono, M. Kohno, J. Org. Chem. 49 (1984) 1458–1460, and J. Chem. Soc., Chem. Commun. (1984) 399–400.;
S. Fukuoka, M. Chono, M. Kohno, J. Chem. Soc., Chem. Commun. (1984) 399–400;
(b) H. Alper, F.W. Harstock, J. Chem. Soc., Chem. Commun. (1985) 1141–1142;
(c) H. Alper, G. Vasapollo, F.W. Harstock, M. Mlekuz, D.J.H. Smith, G.E. Morris, Organometallics 6 (1987) 2391–2393;
(d) P. Giannoccaro, J. Organomet. Chem. 336 (1987) 271–278;
(e) P. Giannoccaro, C.F. Nobile, G. Moro, A. La Ginestra, C. Ferragina, M.A. Massucci, P. Patrono, J. Mol. Catal. 53 (1989) 349–357;
(f) B. Gabriele, R. Mancuso, G. Salerno, M. Costa, Chem. Commun. (2003) 486–487;
(g) B. Gabriele, G. Salerno, R. Mancuso, M. Costa, J. Org. Chem. 69 (2004) 4741–4750;
(h) P. Giannoccaro, S. Doronzo, C. Farragina, in: H.U. Blaser, A. Baiker, R. Prins (Eds.), Heterogeneous Catalysis and Fine Chemicals IV, 1977, pp. 633–640;
(i) J.E. McCusker, F. Qian, L. McElwee-White, J. Mol. Catal. A: Chem. 159 (2000) 11–17;
(l) A. Kelkar, D.S. Kolhe, S. Kanagasabapathy, R.V. Chaudhary, Ind. Eng. Chem. Res. 31 (1992) 172–176;
(m) S. Kanagasabapathy, S.P. Gupte, R.V. Chaudhari, Ind. Eng. Chem. Res. 33 (1994) 1–6.

[13] (a) P. Giannoccaro, A. Dibenedetto, M. Gargano, E. Quaranta, M. Aresta, Organometallics 27 (2008) 967–975;
(b) B. Gabriele, G. Salerno, D. Brindisi, M. Costa, G.P. Chiusoli, Org. Lett. 2 (2000) 625–627;
(c) B. Gabriele, R. Mancuso, G. Salerno, D.M. Costa, J. Org. Chem. 68 (2003) 601–604.

[14] (a) P. Giannoccaro, C. Ferragina, M. Gargano, E. Quaranta, Appl. Catal. A: Gen. 375 (2010) 78–84;
(b) D.J. Diaz, K.G. Hylton, L. McElwee-White, J. Org. Chem. 71 (2006) 734–738.

[15] F. Qian, J.E. McCusker, Y. Zhang, A.D. Main, M. Chlebowski, M. Kokka, L. McElwee-White, J. Org. Chem. 67 (2002) 4086–4092.

[16] W. Tam, J. Org. Chem. 51 (1986) 2977–2981.

[17] D. Delledonne, F. Rivetti, U. Romano, EU, 1991, 463, 678, EniChem S.p.A.

[18] B. Gabriele, R. Mancuso, G. Salerno, G. Ruffolo, M. Costa, A. Dibenedetto, Tetrahedron Lett. 50 (2009) 7330–7332.

[19] P. Giannoccaro, C. Ferragina, M. Gargano, E. Quaranta, EuropaCat IX, Salamanca, Spain, 2009, p. 256 (abstract P2–32).

[20] J.H. Teles, N. Rieber, W. Harder, US Patent No 5,359,094 (1994).

[21] T. Mizuno, T. Nakai, M. Mihara, Heteroatom. Chem. 21 (2010) 99–102.

[22] See as an example;
(a) J. Hu, J. Li, Y. Gu, Z. Guan, W. Mo, Y. Ni, T. Li, G. Li, Appl. Catal A: General 386 (2010) 188–193;
(b) S.S.C. Chuang, Y. Chi, B. Chen, P. Toochinda, International Patent C07C26100;
(c) F. Li, C. Xia, J. Catal 227 (2004) 542–546.

[23] (a) C.M. Bartish, G.M. Drissel, Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 4, 3rd ed., Wiley-Interscience, New York, 1978, p. 772–93;
(b) M. Grayson, D. Eckroth, G.J. Bushey, L. Campbell, A. Klingsberg, L. van Nes (Eds.), Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 4, 3rd ed., WileyInterscience, New York, 1978, p. 774.

[24] D. Delledonne, F. Rivetti, U. Romano, Appl. Catal. A: Gen. 221 (2001) 241–251, and references therein. A: Gen. 386 (2010) 186-193.

[25] (a) Y.M. Shen, W.L. Duan, M. Shi, Eur. J. Org. Chem 14 (2004) 3080–3089;
(b) X.-Y. Dou, J.-Q. Wang, Y. Du, E. Wang, L.-N. He, Synlett (2007) 3058–3062.

[26] X.-B. Lu, X.-J. Feng, R. He, Appl. Catal. A: Gen. 234 (2002) 25–33.

[27] N. Cioffi, L. Torsi, I. Losito, C. Di Franco, I. De Bari, L. Chiavarone, G. Scamarcio, V. Tsakova, L. Sabbatini, P.G. Zambonin, J. Mater. Chem. 11 (2001) 1434–1440.

[28] N.S. McIntyre, S. Sunder, D.W. Shoesmith, F.W. Stanchell, J. Vac. Sci. Technol. 18 (1981) 714–721.

[29] M. Biesinger, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, Appl. Surf. Sci. 257 (2010) 887–898.

[30] R.P. Vasquez, Surf. Sci. Spectra 5 (1998) 262–266.

[31] T. Yoshida, K. Yamasaki, S. Sawada, Bull. Chem. Soc. Jpn. 52 (1979) 2908–2912.

[32] C.D. Wagner, A.V. Naumkin, A. Kraut-Vass, J.W. Allison, C.J. Powell, J.R. Rumble Jr., NIST Standard Reference Database 20, Version 3.4, 2003 (http://srdata.nist.gov/xps).

[33] C.C. Chusuei, M.A. Brookshier, D.W. Goodman, Langmuir 15 (1999) 2806–2808.

[34] G.D. Beamson, Briggs in High Resolution XPS of Organic Polymers, John Wiley and Sons Ltd, Chichester, England, 1992.

[35] M.M. Taqui Khan, S.B. Halligudi, S.H.R. Abdi, J. Mol. Catal. 48 (1988) 325–333.

[36] M.A. Pacheco, C.L. Marshall, Energy Fuels 11 (1997) 2–29.

[37] M.A. Fleet, Acta Crytallogr. Sect. B 31 (1975) 183–187.

[38] (a) J.J. Byerley, E. Peters, Can. J. Chem. 47 (1969) 313–321;
(b) J.A. Rodriguez, D.W. Goodman, Surf. Sci. Rep. 14 (1991) 1–107;
(c) M. Che, C.O. Bennet, Adv. Catal. 36 (1989) 55–172;
(d) T. Engel, G. Ertl, Adv. Catal. 28 (1979) 1–78;
(e) K.I. Choi, M.A. Vannice, J. Catal. 127 (1991) 489–511;
(f) P. Giannoccaro, A. La Ginestra, M.A. Massucci, C. Ferragina, G. Patrono, J. Mol. Catal. A: Chem. 111 (1996) 135–144;
(g) F. Rivetti, U. Romano, Chim. Ind. 62 (1980) 7–12.

[39] (a) G. Paret, G. Donati, M. Ghirardini, EP460,735 (1991), Enichem;
(b) U. Romano, R. Tesei, M.M. Mauri, P. Rebora, Ind. Eng. Chem. Prod. Res. Dev. 19 (1980) 396–403.

[40] (a) H.M. Colquhoun, D.J. Thompson, M.V. Twigg, Carbonylation: Direct Synthesis of Carbonyl Compounds, Plenum Press, New York, 1991;
(b) P. Giannoccaro, J. Organomet. Chem. 470 (1994) 249–252;
(c) P. Giannoccaro, N. Ravasio, M. Aresta, J. Organomet. Chem. 451 (1993) 243–248.

[41] For recent reviews see:
(a) N. Keller, G. Rebmann, V. Keller, J. Mol. Catal. A: Chem. 317 (2010) 1–18;
(b) Y. Sato, M. Kagotani, T. Yamamoto, Y. Souma, Appl. Catal. A: Gen. 185 (1999) 219–226;
(c) Y. Sato, M. Kagotani, Y. Souma, J. Jpn. Petrol. Inst. 43 (2000) 75–79;
(d) T. Koyama, M. Tonosaki, N. Yamada, K. Mori, EP 528,498 (1992);
(e) K. Tomishige, T. Sakaihori, S.-I. Sakai, K. Fujimoto, Appl. Catal. A: Gen. 181 (1999) 95–102;
(f) J.-C. Hu, Y. Cao, P. Yang, J.-F. Deng, K.-N. Fan, J. Mol. Cat. A: Chem. 185 (2002) 1–9.

[42] (a) H.C. Clark, K.R. Dixon, W.J. Jacobs, J. Am. Chem. Soc. 91 (1969) 1346–1350;
(b) J. Halpern, J.E. Byrd, J. Am. Chem. Soc. 93 (1971) 1634;
(c) P. Giannocaro, C.F. Nobile, Inorg. Chim. Acta 175 (1990) 133–139;
(d) J. Ruiz, M.T. Martinez, F. Florenciano, V. Rodriguez, G. López, J. Pérez, P.A. Chaloner, P.B. Hitchcock, Inorg. Chem. 42 (2003) 3650–3661;
(e) S.A. MacGregor, G.W. Neave, Organometallics 22 (2003) 4547–4556;
(f) M.A. Bennett, T.J. Yoshida, J. Am. Chem. Soc. 100 (1978) 1750–1759;
(g) R.H. Michelin, M. Napoli, R. Ros, J. Organomet. Chem. 175 (1979) 239–255;
(h) W.M. Rees, J.D. Atwood, Organometallics 4 (1985) 402–404;
(i) H.E. Bryndza, Organometallics 4 (1985) 1686.