

Carbon dioxide as building block for the synthesis of organic carbonates

Behavior of homogeneous and heterogeneous catalysts in the oxidative carboxylation of olefins

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Abstract

The increasing world market of organic carbonates demands for the development of new synthetic methodologies, alternative to phosgene which represents the starting material for their conventional synthesis. Innovative technologies based on CO₂ are attracting much attention as they are environmentally acceptable and may respond to the atom-economy principle.

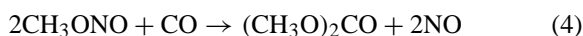
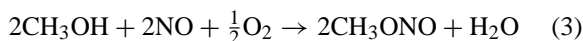
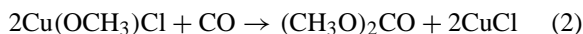
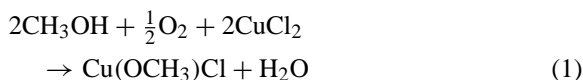
The oxidative carboxylation of olefins catalyzed by homogeneous or heterogeneous catalysts has a good potential as it uses simple starting materials to produce valuable chemicals. In this paper the conversion of styrene into styrene carbonate is discussed with emphasis on the reaction mechanism and product distribution considering either homogeneous or heterogeneous catalysts. © 2002 Published by Elsevier Science B.V.

Keywords: Carbon dioxide; Catalysts; Olefins; Organic carbonates; Oxidative carboxylation

1. Introduction

Organic carbonates have a large market (ca. 1.8 Mt/year), as they can be used as solvents, selective reagents, intermediates (for the synthesis of pharmaceuticals and agrochemicals), fuel additives, and monomers for polymers [1]. Existing technologies for the synthesis of organic carbonates are based on the use of phosgene, a toxic species which generates a large environmental impact because of the high energy demand for the synthesis of chlorine and the disposal of large amount of chlorinated solvents and inorganic chloride at the end [2].

New alternative methodologies have been developed. As examples we can consider the ENIChem [3] (Eqs. (1), (2)) and Ube [4] (Eqs. (3), (4)) processes, for the production of DMC from methanol. As catalysts CuCl, and PdCl₂/NO are used, respectively.



If we consider the two processes from the environmental point of view, the ENIChem process appears to be more acceptable. The Ube process has,

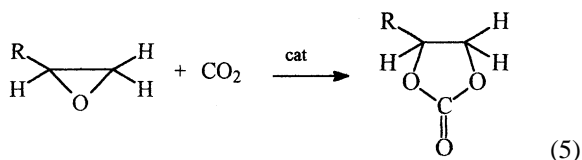
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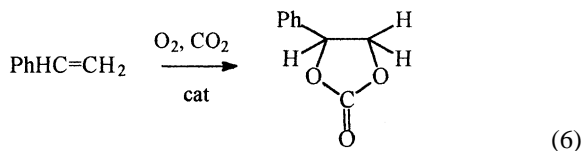
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in fact, some weaknesses: the use of nitric oxide which is toxic, the use of the mixture $\text{CH}_3\text{OH}/\text{NO}/\text{O}_2$ which is potentially explosive, and the formation of CH_3ONO .

The utilization of carbon dioxide as building block for the synthesis of chemicals is the objective of several international research programs [5]. This approach can contribute to the development of new clean synthetic methodologies, avoiding both the use of toxic substances [6,7] and the production of waste and implementing the principle of atom-economy and energy saving. In fact, an emerging methodology is the synthesis of carbonates through the fixation of carbon dioxide into epoxides. Organometallic species and metal complexes [8], classical Lewis acids [9] and metal phthalocyanines [10] are used as catalysts. Metal oxides have been seldom used as catalysts [11]. The carboxylation of epoxides is known since time (IG Farben, 1943) [12] and is now on stream in several plants (Eq. (5))



The direct oxidative carboxylation of olefins (Eq. (6)) seems to be a very interesting methodology for the synthesis of carbonates. In fact, it combines both the epoxidation and the carbonation processes, so it could be useful for industry.



2. Experimental

2.1. Materials

All solvents were dried as described in literature [13a] and stored under nitrogen. All reactions and manipulations were carried under dinitrogen atmosphere. A stainless-steel autoclave (150 ml) equipped with a withdrawal device was used.

GC analyses were carried out with a Hewlett Packard HP 6850 (capillary column: 30 m, MDN-5S, 0.25 μm film) and GC-MS analyses with a Shimadzu GCMS-QP5050 (capillary column: 60 m, MDN-5S, 0.25 μm film). ^1H NMR spectra were recorded with a Varian XL 200 or a Bruker AM 500. Standard products were synthesized as described below or purchased as commercial products. Nb_2O_5 was pre-treated at 670 K as reported in the literature [13b].

2.2. Synthesis of styrene carbonate

0.274 g (1.81 mmol) of ZnCl_2 and 0.751 mg (2.03 mmol) of TBAI (tetra-butyl-ammonium iodide) were added to 30 ml (0.262 mol) of styrene oxide in a glass reactor, that was closed into a stainless-steel autoclave and 5 atm of CO_2 were charged. The system was stirred for 96 h at room temperature, then the carbonate was isolated as pure product. Yield = 43.4%. Anal. Calcd. for $\text{C}_9\text{H}_8\text{O}_3$: C = 65.8%, H = 4.93%. Found: C = 66.3%, H = 5.12%. GC-MS: 164 (M+), 120, 105, 91, 78, 65 m/e. ^1H NMR (CDCl_3 , 200 MHz, 293 K): 7.2 ppm (m, 5H, $\text{H}_{\text{aromatic}}$), 5.64 (t, 1H), 4.70 (d, 1H), 4.32 (t, 1H).

0.18895 g (7.13×10^{-4} mol) of Nb_2O_5 were added to a solution of styrene oxide (2 ml, 1.75×10^{-2} mol) in DMF (10 ml) in a glass reactor that was placed into the autoclave and 50 atm of carbon dioxide were charged. After 12 h at 408 K, the system was cooled. The reaction solution filtered to separate the catalyst. Then the solution reaction was dried under vacuum. The yellow residue analyzes for pure carbonate with yield of 80%. Anal. Calcd. for $\text{C}_9\text{H}_8\text{O}_3$: C = 65.8%, H = 4.93%. Found: C = 65.63%, H = 5.02%. GC-MS: 164 (M+), 120, 105, 91, 78, 65 m/e. ^1H NMR (CDCl_3 , 200 MHz, 293 K): 7.2 ppm (m, 5H, $\text{H}_{\text{aromatic}}$), 5.64 (t, 1H), 4.7 (d, 1H), 4.31 (t, 1H).

2.3. Synthesis of 1-phenyl-1,2-ethane diol

0.5 g of styrene carbonate were dispersed in 5 ml of NaOH 0.1 N in water. The dispersion was stirred at room temperature for 2 h till the complete conversion of carbonate into diol, that is soluble in the reaction medium. The diol was extracted with diethyl ether, dried under vacuum and its GC-MS compared with that of an authentic sample. GC-MS: 138 (M+), 120, 107, 91, 79, 65 m/e.

2.4. Synthesis of hydroxo-esters from benzoic acid and epoxide

To a solution of benzoic acid (0.454 g, 3.7×10^{-3} mol) in DMF (10 ml) under nitrogen, 0.227 g (8.56×10^{-4} mol) di Nb₂O₅ and 1 ml (8.75×10^{-3} mol) of styrene oxide were added. The reaction mixture was heated at 393 K with stirring until the conversion of benzoic acid into esters was complete (ca. 5 h) as monitored by GC-MS. The reaction solution was cooled to room temperature, filtered to separate the catalyst, then dried under vacuum. The residue was collected and fractionated on a silica gel column (1.5 cm \times 120 cm) using as eluent diethyl ether/hexane (1:1 v/v). The fractions were analyzed by GC-MS and those containing a single product collected. Two compounds were isolated: the first was identified as 1-phenyl-2-hydroxyethyl benzoic ester (**X**), the second as 2-phenyl-2-hydroxyethyl benzoic ester (**IX**). IR (Nujol, KBr disks, cm⁻¹): 3250 (ms), 1720 (ms), 1600 (vs), 1270 (vs), 1120 (vs), 1090 (vs). GC-MS of **IX**: 242 (M+), 225, 148, 135, 121, 105, 77 m/e. GC-MS of **X**: 242 (M+), 225, 211, 165, 134, 121, 105, 77 m/e.

2.5. Synthesis of styrene carbonate from styrene, O₂ and CO₂

0.109 g (4.11×10^{-4} mol) of Nb₂O₅ were added to a solution of styrene (2 ml, 1.75×10^{-2} mol) in DMF (10 ml) under nitrogen in a glass tube. The tube was placed in the autoclave and O₂ (5 atm) and CO₂

(45 atm) charged. The autoclave was stirred for 12 h at 408 K. After cooling, the autoclave was discharged, the gas phase was condensed in a solvent at low temperature and analyzed. The residual reaction solution was analyzed by GC-MS. Yield: styrene carbonate 1.9%, benzaldehyde 7.52%, phenylacetaldehyde 0.6%, styrene oxide 0.47%, benzoic acid 6.08%, esters 5.62%, 1-phenyl-1,2-ethane diol 3.21%.

0.119 g (4.5×10^{-4} mol) of Nb₂O₅ and 0.057 g (2.1×10^{-4} mol) of NbCl₅ were added to a solution of styrene (2 ml, 0.0175 mol) in DMF (10 ml) under nitrogen. The glass tube containing the mixture was closed in the autoclave and O₂ (1 atm) and CO₂ (49 atm) charged. The autoclave was stirred for 12 h at 408 K. After cooling of the system, the autoclave was discharged, the gas phase was condensed in a solvent at low temperature and analyzed. The reaction solution was analyzed by GC-MS. Yield: styrene carbonate 11%, benzaldehyde 6.7%, phenylacetaldehyde 0.8%, styrene oxide 0.6%, benzoic acid 2.3%, esters 0.5%, 1-phenyl-1,2-ethane diol 1.56%.

2.6. Kinetic measurements

In a typical experiment, 0.21840 g of Nb₂O₅ (8.22×10^{-4} mol) were added to a solution of styrene (5 ml, 4.35×10^{-2} mol) in DMF (20 ml) under nitrogen. The glass reactor was closed into the autoclave and the gases (5 atm of O₂ and 45 atm of CO₂) or (1 atm of O₂ and 49 atm of CO₂) were charged at 298 K. The reaction system was heated for 3 h at 393 K or at 408 K

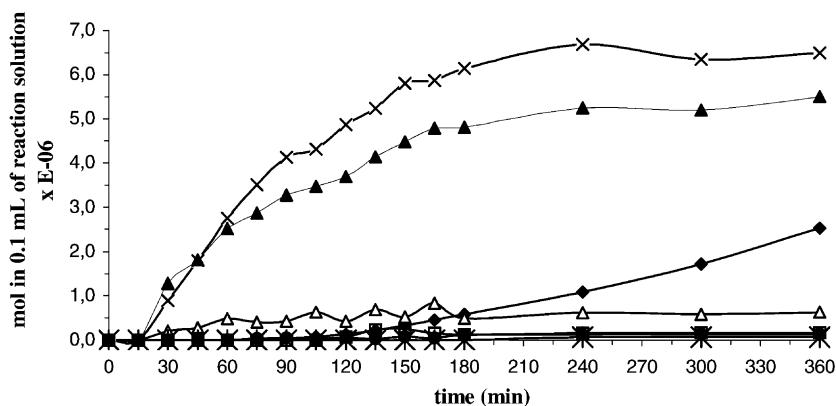


Fig. 1. Kinetics of the conversion of styrene with CO₂/O₂ catalyzed by Nb₂O₅: (—◆—) styrene carbonate; (—△—) phenylacetaldehyde; (—●—) 1-phenyl-1,2-ethane diol; (—×—) styrene oxide; (—✱—) benzoic acid; (—▲—) benzaldehyde; (—◻—) hydroxo-ester.

with stirring. At fixed times (every 15 min) a sample of the reaction solution (0.1 ml) was withdrawn and analyzed by GC. The formation trend of the all major components was monitored (see as example Fig. 1).

3. Results and discussion

Only few reports [14,15] are in the literature on the direct synthesis of carbonates from olefins, dioxygen and carbon dioxide, despite the usefulness of this reaction, that avoids the preliminary synthesis of epoxides.

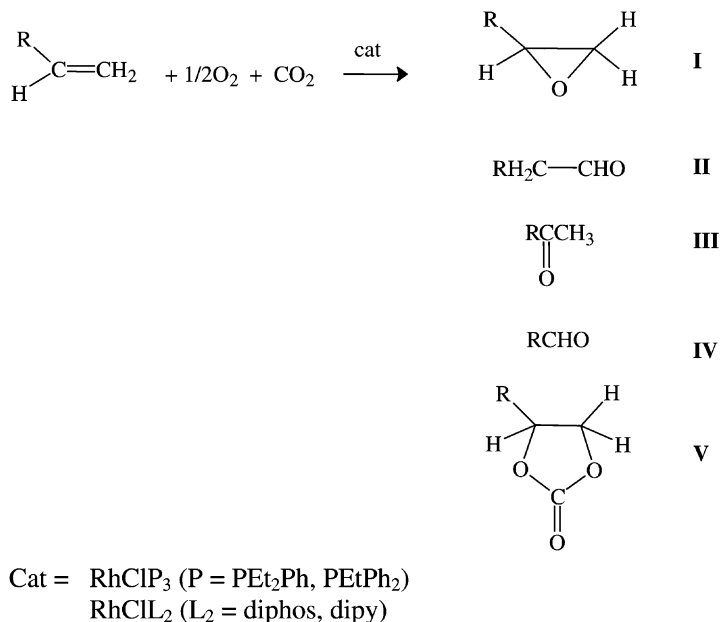
3.1. Use of homogeneous catalysts

We have been investigating the conversion of olefins into carbonates by direct oxidative carboxylation using Rh-catalysts under homogeneous condition [14]. The limitation to the implementation of the Rh-catalyzed synthetic methodology lies in the low turnover number (max TON = 3) due to the short lifetime of the catalyst under homogeneous conditions. In fact, when RhClP_3 ($\text{P} = \text{PEt}_2\text{Ph}$, PEtPh_2) or RhClL_2 ($\text{L}_2 = \text{diphos}$, dipy) is used as catalyst for the oxidative carboxylation of

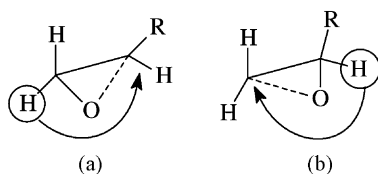
olefins, the formation of a mixture of styrene oxide (**I**), phenylacetaldehyde (**II**), acetophenone (**III**), benzaldehyde (**IV**) and styrene carbonate (**V**) is observed (Scheme 1).

The product distribution is strongly dependent on the solvent used [16], the temperature and the ligand coordinated to Rh. It also depends on the oxygen and carbon dioxide pressure. We have demonstrated that if the catalyst is a Rh-complex stabilized by monodentate phosphane, increasing P_{O_2} , it can be destroyed because of the possible oxidation of the ligand to phosphine oxide. Conversely, if the catalyst is stabilized by a bidentate phosphane or dipyriddy, during the reaction time, the active species “ $\text{Rh}(\text{L}-\text{L})\text{Cl}$ ”, formally $14e^-$, can be converted into the $18e^-$ $\text{Rh}(\text{L}-\text{L})_2\text{Cl}$ [17] that is not a catalytic species. Because of this fact, the lifetime of the catalyst is very short with a serious limitation to the potential application in synthetic chemistry.

The results obtained using Rh-catalysts have clearly shown that under the reaction conditions two processes operate (Scheme 1): “one-oxygen transfer” to the olefin which generates **I**, **II**, **III**; “two-oxygen transfer” which affords **IV**, its conversion products,

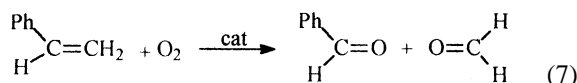


Scheme 1. Distribution of products under homogeneous conditions.



Scheme 2. Intermolecular hydrogen shift for the conversion of the epoxide into the terminal aldehyde (a) or the ketone (b).

and formaldehyde **VI** (Eq. (7)).



I can be the precursor of **II**, **III**, **V**. The formation of **II** and **III** from **I** requires an intra-molecular hydrogen shift (Scheme 2).

Such isomerization has been demonstrated to occur when **I** is heated in the presence of the Rh-complexes used as catalyst [14] for the oxidative carboxylation. **V** is the product of insertion of CO_2 into **I**. Clearly, the two-oxygen transfer uses the olefin in a pathway alternative to that affording epoxide and carbonate. In order to limit the oxidation of the olefin via the two-oxygen transfer that cleaves the double bond with formation of benzaldehyde, reaction conditions (low temperature, low oxygen pressure) must be used that favors the oxidation via one-oxygen transfer with formation, as main product, of epoxide.

Homogeneous catalysts act through the formation of peroxocarbonates (Scheme 3), that are the

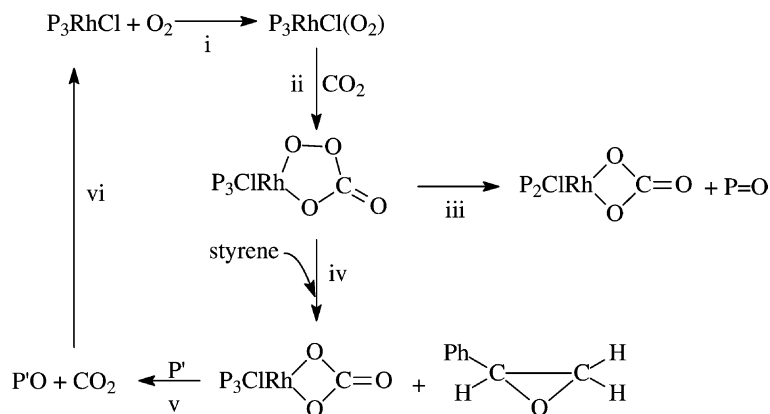
one-oxygen transfer agents. As we have shown [17], the Rh-catalysts are destroyed because the phosphane is released and acts as a one-oxygen acceptor (Scheme 3, iii) from the peroxocarbonate to afford phosphine oxide (free or coordinated) and the Rh-carbonate, an inactive form of the metal. We have also demonstrated how the catalyst is regenerated [17] (Scheme 3, v).

Increasing PCO_2 favors the one-oxygen transfer, reducing the double bond cleavage. This is due to the reduced attack by O_2 on the olefinic double bond, as it is more involved in the peroxocarbonate formation.

3.2. Use of heterogeneous catalysts

In order to have a catalytic system with a longer life, we have investigated the oxidative carboxylation of olefins using heterogeneous catalysts. We have tested several metal oxides (group 1 and 2 elements or transition metals), either as a fine powder [18] or supported on pumice [19].

The screening phase has shown that Nb_2O_5 is able to afford carbonate with a quite high TON and the catalyst can be reused for several cycles. Therefore, we have investigated in detail the oxidative carboxylation of styrene using Nb_2O_5 . The reactions were carried out using a thermostated stainless-steel autoclave equipped with a withdrawal device. Using this system it is possible to take samples of the reaction mixture and to follow the reaction pathways during the time. The reaction mixture was analyzed for all



Scheme 3.

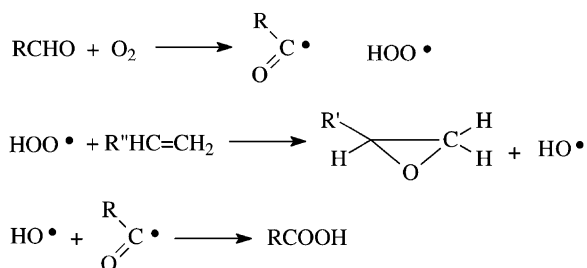
major components, namely those which represent at least 1% of the starting olefin. The total analyzed and characterized fraction represents more than 90% of the reacted styrene.

As shown in Fig. 1, benzaldehyde is formed during the first 30 min in higher amount with respect to the epoxide, which becomes the predominant product after 1 h. Besides epoxide (**I**) and benzaldehyde (**IV**), the formation of carbonate (**V**), benzoic acid (**VII**), acetophenone (**III**), phenylacetaldehyde (**II**), 1-phenyl-1,2-ethane diol (**VIII**) and benzoic acid esters (**IX**, **X**) was monitored. Products **I–V** are common to the homogeneous catalysis.

The first attempts gave a yield of carbonate of 1–2%. We have, thus, investigated in depth the reaction pathway in order to shed light on the influence of the reaction conditions on yield and selectivity.

3.2.1. Study on the distribution of the products and their role in the reaction pathway

The formation of benzaldehyde which occurs through a two-oxygen transfer to the olefin (Eq. (7)) plays two roles. If from one hand it reduces the yield of formation of carbonate because reduces the amount of olefin available for epoxidation, on the other hand can be beneficial because it can cooperate to the formation of the epoxide. It has been shown that in the



Scheme 4. Role of an aldehyde in the olefin epoxidation.

epoxidation of an olefin with O_2 , the addition of an external aldehyde can favor the one-oxygen transfer to the olefin [20]. A possible reaction mechanism is reported in Scheme 4.

We have, thus, used isobutylaldehyde as an external aldehyde in the oxidative carboxylation of styrene. The yield and selectivity towards the carbonate formation were negatively (–50%) affected (Fig. 2), while the amount of benzaldehyde was reduced by only 30% and styrene oxide was increased. All together, the addition of an external aldehyde made more complex the separation procedure, while giving quite small benefits.

However, in our system, benzaldehyde itself can operate as one-oxygen transfer promoter to styrene according to Scheme 4 ($\text{R} = \text{Ph}$), and the mechanism

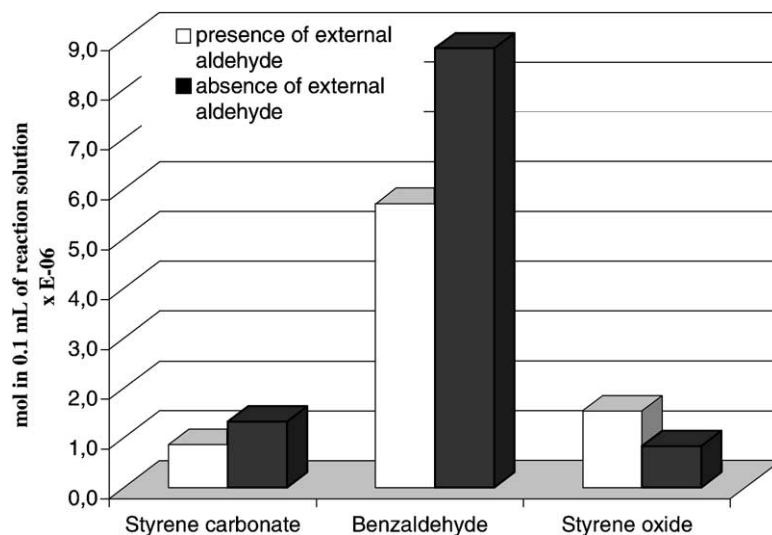
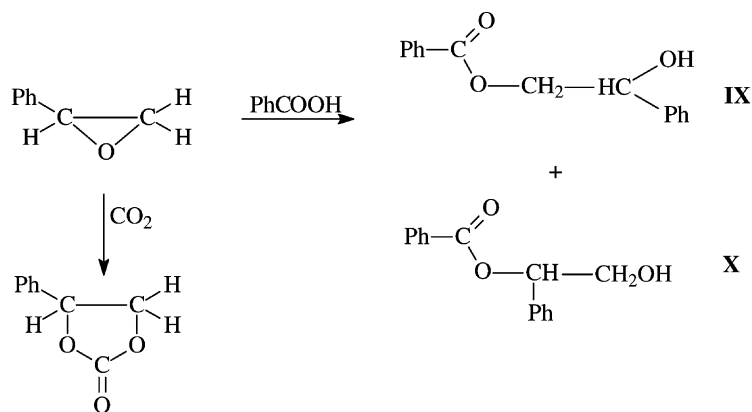


Fig. 2. Influence of an external aldehyde on the synthesis of styrene carbonate, benzaldehyde and styrene oxide via oxidative carboxylation of styrene.



Scheme 5. Formation of hydroxo-esters from epoxide and benzoic acid.

reported therein explains the formation of benzoic acid which is formed in the reaction mixture. Noteworthy, benzoic acid competes with carbon dioxide towards epoxide as it affords the hydroxo-ester (**IX** or **X**) shown in Scheme 5, which have been isolated and characterized.

Therefore, the two-oxygen transfer to styrene, reduces the amount of styrene that can be transformed into epoxide, produces benzoic acid, generated from benzaldehyde, which subtracts the epoxide to the carbonation reaction, converting it into esters. These features emphasize how important is the control of the oxidation of the olefin and confirms that the oxidative carboxylation requires strictly controlled operative conditions.

An interesting point to consider is whether or not the carbonate formation requires the preliminary formation of epoxide. In principle, the intermediate **XI** depicted in Fig. 3 may be formed during the oxidation of the olefin. **XI** can either release the organic fragment and generate the epoxide or interact with CO_2 and afford the carbonate (Scheme 6).

We have studied the carbonate formation starting either from olefin and CO_2/O_2 or from epoxide and

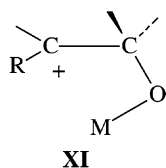
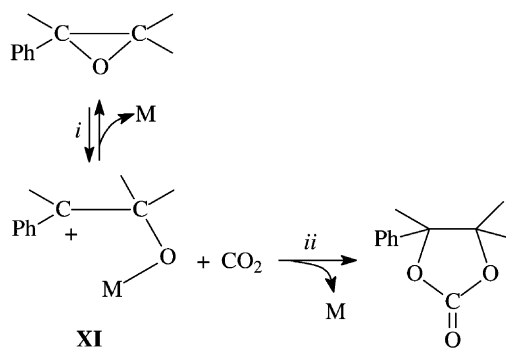


Fig. 3. Possible precursor of the epoxide.



Scheme 6. Formation of carbonate and epoxide.

CO_2 and found that the initial carbonate formation rate is higher starting from the olefin, as shown in Fig. 4.

This means that at least at the beginning of the reaction, route ii in Scheme 6 is prevalent for the

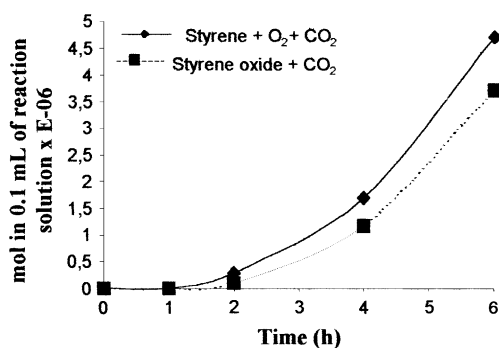


Fig. 4. Carbonate formation starting from olefin or from epoxide.

Table 1
Influence of the temperature in the carbonation of epoxide using Nb₂O₅

Temperature (K)	Yield (%) of carbonate
383	11.3
393	36
408	>80

formation of carbonate. The epoxide is concurrently formed (route i in Scheme 6) and accumulates in the reaction medium. It can become the source of carbonate through an oxidative addition to the catalyst and subsequent CO₂ insertion. In fact, at longer reaction times the yield of carbonate is higher from the epoxide and CO₂, than from olefin and O₂/CO₂ (Tables 1 and 2). In order to be able to address the reaction towards high yield of carbonate, we have investigated the role of the parameters like temperature, pressure of oxygen, solvent and addition of co-catalysts.

3.3. Effects of the reaction conditions: temperature, pressure, solvent and co-catalyst

The temperature plays a very important role in the carbonation of the epoxide. In fact, at temperature below 373 K the carbonate yield is close to zero as demonstrated by the study of insertion of carbon dioxide into epoxide [11c] using the same catalyst as in the oxidative carboxylation (Table 1).

Therefore, lowering the temperature reduces the conversion of the epoxide into carbonate. At temperature <370 K the only route to produce the carbonate is route ii in Scheme 6, the carboxylation of the epoxide is blocked and the latter accumulates. The epoxide formation per se is not sensitive to the temperature change (Fig. 5a) in the range 393–408 K, while the benzaldehyde formation (Fig. 5b) is strongly influenced.

So the temperature has a double opposite effect: an increase of temperature favors from one hand the for-

mation of carbonate from epoxide, and from the other the cleavage of the double bond of the styrene with production of benzaldehyde. The latter, as we have described above, is converted into benzoic acid that reacts with the epoxide subtracting it to the carboxylation reaction. As a matter of fact, at temperature below 370 K the formation of carbonate is very low, while epoxide is converted into the esters according to the reaction shown in Scheme 5. Therefore, the temperature requires a careful control.

The pressure of oxygen deeply influences the formation trend of the reaction products. In fact using a high pressure of oxygen, the ratio between epoxide and benzaldehyde formation decreases with time (Fig. 6a), while at lower pressure this ratio is constant with time (Fig. 6b). This means that the epoxide formation is favored by a low pressure of oxygen with respect to the formation of benzaldehyde and this influences also the formation of carbonate.

The best solvent among those used (DMF, diglyme, THF, toluene, xylene) revealed to be DMF. THF is not very effective for its low boiling point that does not allow to work in the best temperature conditions. Xylene and toluene are not very effective most probably because of their low polarity. In fact, the yield of the oxidative carboxylation is close to zero. A polar solvent is, thus, required for the carboxylation to occur, and the temperature must be higher than 373 K. This finding may help to explain why in SC-CO₂, which is not a polar medium, the formation of carbonate has not been observed [21] during the epoxidation of olefins.

An aspect which is very intriguing is the role played by chloride ions in the reaction. We have observed that, if chloride is present in the reaction medium, the yield of carbonate increases [11c]. This is not an unexpected result. In fact, halides are known to catalyze the carbonation of epoxides [8,22]. Halide ions can indeed stabilize carbocation XI [23] (Scheme 7).

The stabilization of the carbocation could favor the reaction with CO₂ (Scheme 6, route ii) reducing, thus,

Table 2
Carbonate yield in presence or in absence of a co-catalyst

	Catalyst			
	Nb ₂ O ₅	Nb ₂ O ₅ /NbCl ₅	Nb ₂ O ₅ /CH ₂ Cl ₂	NbCl ₅ /wet air
Carbonate yield (%)	0.64	11	1.9	3.92

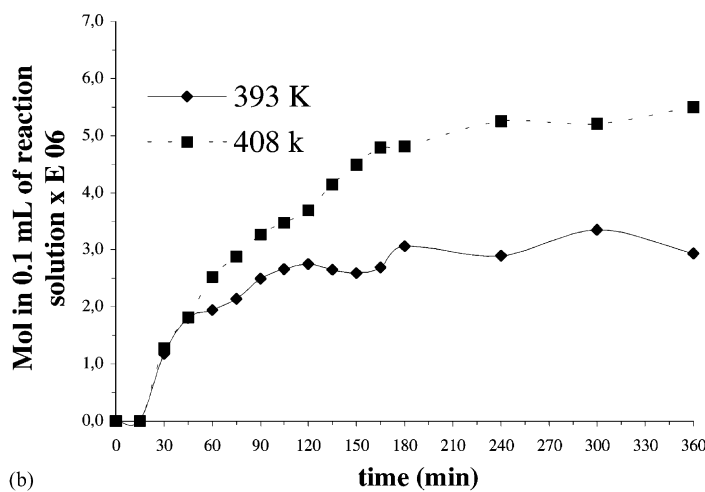
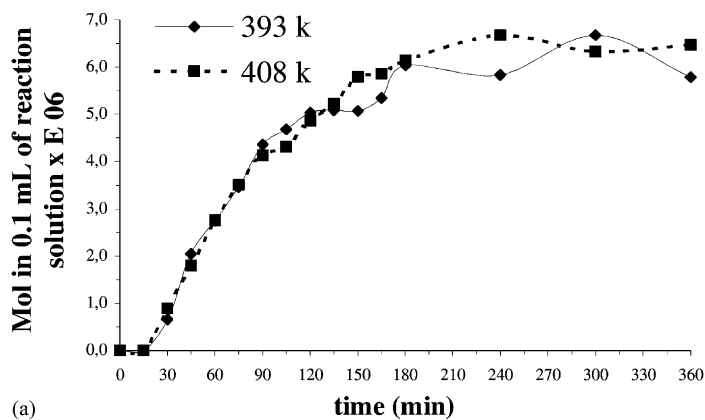


Fig. 5. Influence of the temperature on the formation of epoxide (a) and benzaldehyde (b).

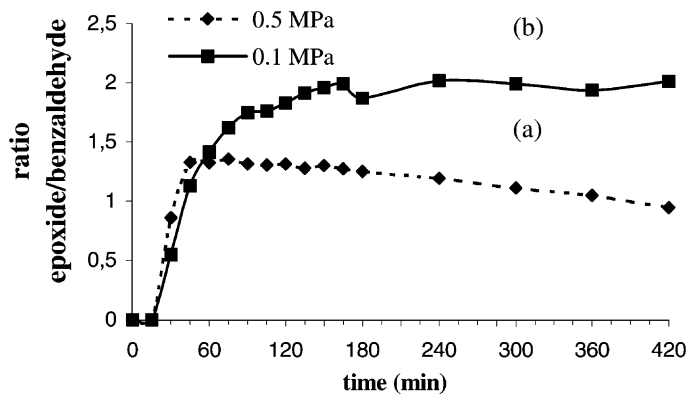
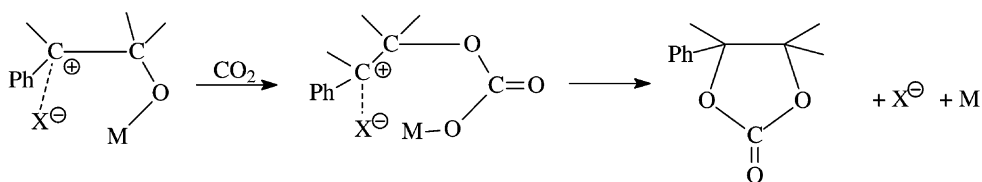


Fig. 6. Influence of the pressure of oxygen on the formation of epoxide and benzaldehyde working at the same temperature (408 K).



Scheme 7. Acid–base catalysis in the formation of carbonate.

the epoxide elimination by ring closure (Scheme 6, route i). Therefore, we have investigated the effect of addition of small amounts of a Nb-halides (NbCl_5) to Nb_2O_5 . We have also considered the addition of small amounts of CH_2Cl_2 (100 μl) to the reaction mixture. Interestingly, the yield in carbonate is increased in both cases (Table 2).

Noteworthy, if NbCl_5 is moistened in the air to afford products of formula close to NbOCl_3 , and then used as catalyst, it gives the best yield in carbonate. These findings suggest that an acid–base catalysis can operate in the synthesis of carbonate according to Scheme 7. By using NbOCl_3 as catalyst, T : 408 K with pressure of oxygen around 1 atm and pressure of CO_2 of 49 atm, in DMF, the yield of carbonate was as high as ca. 4% with respect to ca. 1–2% of the starting experiments, while the mixture $\text{Nb}_2\text{O}_5/\text{NbCl}_5$ gives a yield of 11% in carbonate.

The control of the reaction conditions has allowed, thus, to improve the carbonate yield by more than one order of magnitude. The knowledge of the reactive system and the developed skill in its control opens a new perspective to the oxidative carboxylation of olefins.

Acknowledgements

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