

# Nb(V) compounds as epoxides carboxylation catalysts: the role of the solvent

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Dedicated to Prof. Renato Ugo on the occasion of his 65th birthday

## Abstract

The synthesis of organic cyclic carbonates from epoxides and CO<sub>2</sub> is described. The role of the solvent is discussed, together with that of Nb(V) catalysts (Nb<sub>2</sub>O<sub>5</sub> and NbCl<sub>5</sub>). The reaction is very selective and affords the conversion of epoxides into the relevant carbonates in high yield.

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*Keywords:* Carbon dioxide; Catalysts; Epoxides; Organic carbonates; Solvent

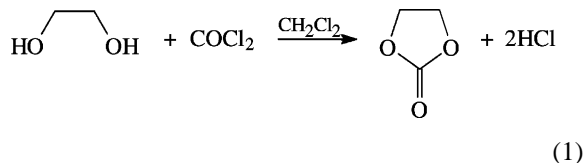
## 1. Introduction

The production of organic carbonates [1,2] either molecular (world market equal to 80 kt per year) or polymers (1.1 Mt per year), is expanding since a few decades. Organic molecular carbonates already find large use as solvents, selective reagents, fuel additives, monomers for polymers, in agricultural application as herbicides and disinfectants, in the preparation of cosmetics and personal care products. They are also used as additives for hydraulic fluids [3], and in the dyeing of textiles [2,4]. Their production will continue to grow, especially if their use as additives for fuels will expand.

This trend requires that new, environmentally friendly, synthetic methodologies are developed in order to find alternative routes to existing ones, avoid-

ing the use of toxic chemicals. Routes based on CO<sub>2</sub> respond to the raw material diversification, while implementing the atom efficiency principle with the use of clean and safe technologies [4–6].

The conventional synthesis of carbonates involves the use of phosgene, with elimination of HCl, and end production of large amounts of waste chlorinated solvents. As far as cyclic carbonates are concerned, their synthesis is reported in Eq. (1).



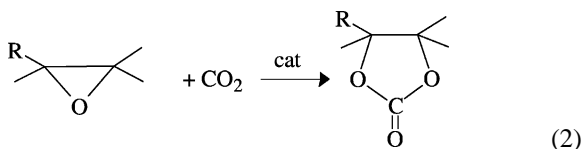
Several synthetic methodologies, alternative to the use of phosgene, have been developed, some of them are on stream [7], other require further examination for the assessment of the potential of industrial exploitation [8]. The carboxylation of epoxides (Eq. (2)) represents one of the few cases of industrial

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utilization of carbon dioxide in innovative chemical syntheses.



The reaction can be carried out using both homogeneous and heterogeneous catalysts. Several catalytic systems as alkali metal halides and phosphonium halides [9–11], organometallic complexes and organometallic halides [12], have been used as homogeneous catalysts with a major drawback due to their life. To develop new catalysts with long life-time and high selectivity is of interest for the chemical industry in order to expand the application of such methodology. Only two reports can be found in the literature on the use of metal oxides [13,14] as heterogeneous catalysts for the fixation of carbon dioxide into epoxides. We have already described the use of  $\text{Nb}_2\text{O}_5$ , that finds application in several other fields [15], as catalyst in the oxidative carboxylation of olefins [8,16].

As an extension of our work, we have studied the carboxylation of epoxides in presence of Nb species and have focused our attention on the use of Nb(IV) [17] and Nb(V) compounds with a special emphasis on  $\text{Nb}_2\text{O}_5$ , as the carboxylation of epoxides is relevant to the direct oxidative carboxylation of olefins mentioned above. In this paper we describe the results relevant to the use of  $\text{Nb}_2\text{O}_5$  and  $\text{NbCl}_5$  as catalysts, and the influence of the solvent on the carboxylation of epoxides.

## 2. Experimental

All reactions and manipulations were carried out under an inert atmosphere, by using vacuum line techniques. All solvents were dried as described in the literature [18] and stored under dinitrogen.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Varian XL-200 spectrometer. GC-MS analyses were carried out with a gas chromatograph Shimadzu 17 A (capillary column: 30 m; MDN-5S; 0.25  $\mu\text{m}$  film) detector linked to a Shimadzu GCMS-QP 5050 mass.

### 2.1. General procedure for the carboxylation of epoxides

In a typical reaction, a fixed amount of epoxide (2 ml) was dissolved in the solvent (10 ml) in a glass reactor (50 ml) which was then placed into a stainless steel autoclave (200 ml) under  $\text{CO}_2$  pressure (5 MPa). The catalyst was added as appropriate. The mixture was heated for 12 h at 408 or 423 K, as specified. After cooling to room temperature, the reaction mixture was filtered and the solvent evaporated under reduced pressure. In some cases a crystallization of the residue from THF/pentane was required to purify the product. GC analyses were carried out for evaluating the conversion yield and selectivity, while elemental analyses and NMR spectra were made to evaluate the purity of the isolated product.

### 2.2. Specific case

#### 2.2.1. Synthesis of styrene carbonate from styrene epoxide and $\text{CO}_2$ (5 MPa) in DMF

Styrene epoxide (2 ml, 17.5 mmol), dimethylformamide (DMF) (10 ml), reaction time (27 h), reaction temperature (408 K). 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*. When  $^{13}\text{C}$  was used (Entry 12, Table 2) the GC-MS gave the following peaks: 165 ( $M^+$ ), 120, 105, 91, 78, 65 *m/e*.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz, 293 K): 7.2 (m, 5H,  $\text{H}_{\text{aromatic}}$ ), 5.64 (t, 1H,  $J_{\text{H}_3-\text{H}_1} = 6.92$ ,  $J_{\text{H}_3-\text{H}_2} = 7.30$ ), 4.70 (d, 1H,  $J_{\text{H}_2-\text{H}_1} = -8.78$ ), 4.32 (t, 1H) ppm. Yield 67.7%.

The same procedure was used for all other trials and the effect of the solvent (Entries 1, 4–6, 8, 9, 15, 16, 19), of the catalyst (Entries 2, 3, 7, 10, 17, 18) and of the pressure of carbon dioxide (Entries 11–14) is reported in Table 2.

#### 2.2.2. Synthesis of propylene carbonate from propylene oxide and $\text{CO}_2$ in DMF

Propylene oxide (2 ml, 28.58 mmol), DMF (10 ml), reaction time (12 h), reaction temperature (423 K). Anal. Calcd for  $\text{C}_4\text{H}_6\text{O}_3$ : C = 47.06%; H = 5.92%. Found: C = 47.0%; H = 5.85%. GC-MS: 102 ( $M^+$ ), 87, 57, 43, 28 *m/e*.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz, 293 K): 4.78 (m, 1H), 4.48 (m, 1H), 3.95 (m, 1H), 1.41 (m, 3H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 200 MHz, 293 K):

154.979 (OC(O)O), 73.48, 70.55, 19.22 (CH<sub>3</sub>) ppm. Yield 8%.

The effect of addition of Nb<sub>2</sub>O<sub>5</sub>, CH<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, ethanol, use of dimethylacetamide (DMA) instead of DMF, use of diglyme as solvent is reported in Table 3, Entries 2–9. Reactions were carried according to the procedure reported above, and the product was characterized by the same techniques.

#### 2.2.3. Synthesis of pentene carbonate from pentene oxide in DMF

Pentene oxide (2 ml, 19.27 mmol), DMF (10 ml), reaction time (12 h), reaction temperature (423 K). Anal. Calcd for C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>: C = 55.37%; H = 7.74%. Found: C = 55.28%; H = 7.81%. GC-MS: 130 (M<sup>+</sup>), 87, 71, 57, 43, 28 m/e. Yield 20%.

The effect of addition of CH<sub>2</sub>Cl<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> is illustrated in Table 3, Entries 11–13.

#### 2.2.4. Synthesis of cyclo-pentene carbonate from cyclo-pentene oxide in DMF

Cyclo-pentene oxide (2 ml, 23.08 mmol), DMF (10 ml), reaction time (12 h), reaction temperature (423 K). Anal. Calcd for C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>: C = 56.24%; H = 6.29%. Found: C = 56.43%; H = 6.98%. GC-MS: 128 (M<sup>+</sup>), 68, 43 m/e. Yield 2%.

The effect of addition of Nb<sub>2</sub>O<sub>5</sub> and CH<sub>2</sub>Cl<sub>2</sub> is illustrated in Table 3, Entries 15–17.

#### 2.2.5. Synthesis of hexene carbonate from hexene oxide in DMF

Hexene oxide (2 ml, 16.60 mmol), DMF (10 ml), reaction time (12 h), reaction temperature (423 K). Anal. Calcd for C<sub>7</sub>H<sub>12</sub>O<sub>3</sub>: C = 58.31%; H = 8.39%. Found: C = 58.25%; H = 8.1%. GC-MS: 144 (M<sup>+</sup>), 87, 58, 43, 28 m/e. Yield 3%.

Entries 19–21 (Table 3) illustrate the effect of addition of Nb<sub>2</sub>O<sub>5</sub>, and CH<sub>2</sub>Cl<sub>2</sub>.

#### 2.2.6. Synthesis of cyclo-hexene carbonate from cyclo-hexene oxide in DMF

Cyclo-hexene (2 ml, 19.80 mmol), DMF (10 ml), reaction time (12 h), reaction temperature (423 K). Anal. Calcd for C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>: C = 59.14%; H = 7.09%. Found: C = 58.9%; H = 7.15%. GC-MS: 142 (M<sup>+</sup>), 98, 84, 70, 57, 41 m/e. Yield 1.4%.

The effect of addition of Nb<sub>2</sub>O<sub>5</sub> and CH<sub>2</sub>Cl<sub>2</sub> is reported in Table 3, Entries 23–25.

#### 2.2.7. Synthesis of octene carbonate from octene oxide in DMF

Octene oxide (2 ml, 13.10 mmol), DMF (10 ml), reaction time (12 h), reaction temperature (423 K). Anal. Calcd for C<sub>9</sub>H<sub>16</sub>O<sub>3</sub>: C = 62.76%; H = 9.36%. Found: C = 62.43%; H = 8.98%. GC-MS: 172 (M<sup>+</sup>), 87, 68, 58, 43, 28 m/e. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, 293 K): 4.64 (m, 1H), 4.45 (m, 1H), 3.98 (m, 1H), 1.71 (m, 1H, –CH<sub>2</sub>–), 1.62 (m, 1H, –CH<sub>2</sub>–), 1.38 (m, 1H, –CH<sub>2</sub>–), 1.25 (complex m, 7H, –CH<sub>2</sub>–), 0.81 (m, 3H, –CH<sub>3</sub>) ppm. Yield 10%.

The effect of addition of Nb<sub>2</sub>O<sub>5</sub> and CH<sub>2</sub>Cl<sub>2</sub> is reported in Table 3, Entries 27–29.

#### 2.2.8. Synthesis of cyclo-octene carbonate from cyclo-octene oxide in DMF

Cyclo-octene oxide (2 ml, 19.30 mmol), DMF (10 ml), reaction time (12 h), reaction temperature (423 K). Anal. Calcd for C<sub>9</sub>H<sub>14</sub>O<sub>3</sub>: C = 63.5%; H = 8.29%. Found: C = 63.89%; H = 8.5%. GC-MS: 170 (M<sup>+</sup>), 126, 112, 58 m/e. Yield 1.2%.

The effect of addition of Nb<sub>2</sub>O<sub>5</sub> and CH<sub>2</sub>Cl<sub>2</sub> is reported in Table 3, Entries 31–33.

### 3. Results and discussion

Nb<sub>2</sub>O<sub>5</sub> has revealed to be a catalyst for the fixation of carbon dioxide into several epoxides (linear and cyclic) to afford the relevant organic carbonate (Eq. (2)). Using pre-treated Nb<sub>2</sub>O<sub>5</sub> (as reported in the literature [19]) the corresponding carbonate was obtained with 100% selectivity. The yield was strongly dependent on the temperature and the solvent as specified in Tables 1 and 2, respectively, for the formation of styrene carbonate.

Table 1  
Influence of the temperature on the formation of styrene carbonate from styrene epoxide and CO<sub>2</sub> (Nb<sub>2</sub>O<sub>5</sub> as catalyst; epoxide/Nb<sub>2</sub>O<sub>5</sub> molar ratio = 50; dimethylformamide as solvent) in 12 h

Temperature	Yield (%) <sup>a</sup>
<373	0
383	11.3
393	36
408	80

<sup>a</sup> Isolated yield.

Table 2

Influence of the solvent and pressure on the yield of the carboxylation of styrene (408 K, 12 h)

Solvent (ml)	Styrene oxide (ml)	Catalyst	$P_{\text{CO}_2}$ (MPa)	Yield (%) <sup>a</sup>
(1) Xylene (10)	2	None	5	No reaction
(2) Xylene (10)	2	Nb <sub>2</sub> O <sub>5</sub> (100 mg)	5	1
(3) Xylene (10)	2	MgO (400 mg)	5	<1
(4) Xylene (5)	1	DMF (0.7 ml) <sup>b</sup>	5	No reaction
(5) Xylene (8)	0.5	DMF (3.5 ml) <sup>c</sup>	5	0.26
(6) Diglyme (10)	2	None	5	No reaction
(7) Diglyme (10)	2	Nb <sub>2</sub> O <sub>5</sub> (100 mg)	5	1
(8) Toluene (10)	2	None	5	No reaction
(9) DMSO (5)	1	None	5	(1) + side products
(10) DMSO (5)	1	Nb <sub>2</sub> O <sub>5</sub> (100 mg)	5	(5) + side products
(11) DMF (10) <sup>d</sup>	2	None	0.1	2.37
(12) DMF (10) <sup>e</sup>	2	None	0.1 <sup>13</sup> CO <sub>2</sub>	37
(13) DMF (10)	2	None	2	26
(14) DMF (10)	2	None	3	37
(15) DMF (10)	2	None	5	34.7
(16) DMF (10) <sup>f</sup>	2	None	5	67.7
(17) DMF (10)	2	Nb <sub>2</sub> O <sub>5</sub> (100 mg)	5	80
(18) DMF (10)	2	NbCl <sub>5</sub> (105 mg)	5	66.3
(19) DMA (10)	2	None	5	28

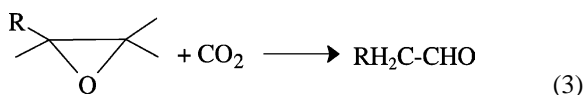
Dimethylformamide (DMF); dimethylacetamide (DMA).

<sup>a</sup> Isolated yield.<sup>b</sup> Ratio DMF:styrene oxide = 1:1.<sup>c</sup> Ratio DMF:styrene oxide = 10:1.<sup>d</sup> 6 h of reaction.<sup>e</sup> 64 h of reaction.<sup>f</sup> 27 h of reaction.

Below 373 K the conversion yield was practically zero. In *N,N*-dimethylformamide or in dimethylacetamide (DMA) at 408 K high yields were obtained (Table 2).

The insertion of CO<sub>2</sub> into a linear epoxide resulted to be in general favourite with respect to the insertion into cyclic ones (Table 3, see the relevant linear and cyclic epoxide conversion yield). The difference may be due to either steric or thermodynamic factors. The time of reaction was also important: good conversion yields were observed in general after 12 h (Entries 11 and 12, Table 2). A pressure higher than 1 MPa was necessary for a significant conversion yield (Entries 11, 13–15, Table 2). As Table 2 shows, the solvent plays a dramatic role. In solvents like xylene, diglyme, toluene a very low yield (see Table 2) was observed if not zero. In absence of solvent, the carboxylation was not observed, while the isomerisation of the epoxide to the aldehyde was the predominant process

(Eq. (3)).



### 3.1. The effect of the solvent

Table 2 shows that amides are good promoters of the carboxylation reaction, that occurs also in absence of metal systems. A similar behaviour has recently been observed for dimethylformamide in SC-CO<sub>2</sub> [20,21]. We report in this work for the first time that other amides like dimethylacetamide are also quite active promoters of the carboxylation. In both DMF and DMA the conversion of styrene oxide reached 25–30% after 12 h, and 68% after a longer reaction time (Entry 16, Table 2). The presence of a large number of molecules of the promoter per mole of styrene

Table 3  
Influence of CH<sub>2</sub>Cl<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> on the carboxylation (423 K, 12 h, 5 MPa of CO<sub>2</sub>)

Solvent (ml)	Additive	Yield (%) <sup>a</sup>
Propylene oxide (2)		
(1) DMF (10)	None	8
(2) DMF (10)	0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	30
(3) DMF (10)	0.1 ml ClCH <sub>2</sub> CH <sub>2</sub> Cl	51.5
(4) DMF (10)	100 mg Nb <sub>2</sub> O <sub>5</sub>	15.7
(5) DMF (10)	161 mg Nb <sub>2</sub> O <sub>5</sub> + 0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	88
(6) DMF (10)	0.1 ml CH <sub>3</sub> CH <sub>2</sub> OH	20
(7) DMF (10)	0.1 ml CCl <sub>4</sub>	58
(8) DMA (10)	None	8
(9) Diglyme (10)	0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	No reaction
Pentene oxide (2)		
(10) DMF (10)	None	2
(11) DMF (10)	0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	55
(12) DMF (10)	100 mg Nb <sub>2</sub> O <sub>5</sub>	9
(13) DMF (10)	89 mg Nb <sub>2</sub> O <sub>5</sub> + 0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	75
Cyclo-pentene oxide (2)		
(14) DMF (10)	None	2
(15) DMF (10)	0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	24
(16) DMF (10)	104 mg Nb <sub>2</sub> O <sub>5</sub>	8.7
(17) DMF (10)	102 mg Nb <sub>2</sub> O <sub>5</sub> + 0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	37
Hexene oxide (2)		
(18) DMF (10)	None	3
(19) DMF (10)	0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	65
(20) DMF (10)	97 mg Nb <sub>2</sub> O <sub>5</sub>	9
(21) DMF (10)	99 mg Nb <sub>2</sub> O <sub>5</sub> + 0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	75
Cyclo-hexene oxide (2)		
(22) DMF (10)	None	1.4
(23) DMF (10)	0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	4.5
(24) DMF (10)	118 mg Nb <sub>2</sub> O <sub>5</sub>	3
(25) DMF (10)	98 mg Nb <sub>2</sub> O <sub>5</sub> + 0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	10
Octene oxide (2)		
(26) DMF (10)	None	10
(27) DMF (10)	0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	80
(28) DMF (10)	114 mg Nb <sub>2</sub> O <sub>5</sub>	16
(29) DMF (10)	124 mg Nb <sub>2</sub> O <sub>5</sub> + 0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	90
Cyclo-octene oxide (2)		
(30) DMF (10)	None	1.2
(31) DMF (10)	0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	4
(32) DMF (10)	108 mg Nb <sub>2</sub> O <sub>5</sub>	2.8
(33) DMF (10)	89 mg Nb <sub>2</sub> O <sub>5</sub> + 0.1 ml CH <sub>2</sub> Cl <sub>2</sub>	10

<sup>a</sup> Isolated yield.

oxide is necessary in order to observe a positive effect. In fact, if DMF was added to a solvent like xylene, no effect was observed until the molar ratio DMF/styrene epoxide was below 10 (Entry 4, Table 2). Above such limit, the effect of DMF was observed (Entry 5, Table 2). Also DMSO promoted the carboxylation

(Entries 9–10, Table 2) but its use is prevented by the formation of several side products. The possible role of the amide is depicted in Fig. 1. It is most probably relevant to the interaction with either the epoxide or CO<sub>2</sub>, increasing the nucleophilicity of the relevant oxygen atoms.

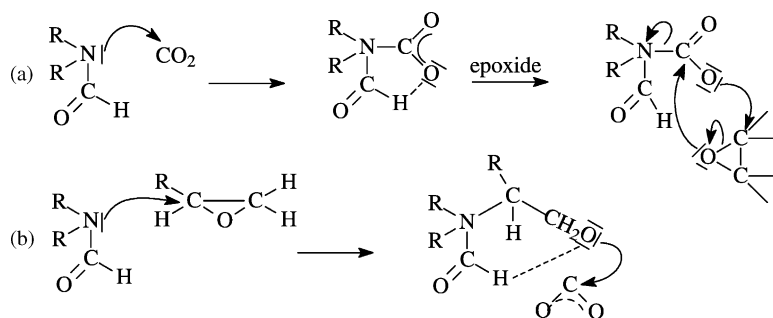


Fig. 1. Role of DMF in the carboxylation of epoxides.

An attempt to use <sup>1</sup>H and <sup>13</sup>C NMR for evidencing possible intermediates did not give any result, at least at room temperature and 0.1 MPa PCO<sub>2</sub>. As matter of fact, under such conditions, styrene epoxide and <sup>13</sup>CO<sub>2</sub> (0.1 MPa) afford the relevant labelled carbonate after a long reaction time (Entry 12, Table 2). Also at 423 K under 0.1 MPa of CO<sub>2</sub>, an adduct or intermediate could not be detected.

Very surprising, and unprecedented, is the role of methylene chloride or 1,2-dichloroethane, which affect the carboxylation yield in a very substantial mode (Table 3).

Table 3 shows that, by using DMF alone (Entry 1, Table 3) propylene carbonate was formed from propylene oxide in low yield, as confirmed also by literature data [21]. The addition of a small amount of CH<sub>2</sub>Cl<sub>2</sub> (0.1 ml) to the reactive system in either DMF alone or DMF in presence of Nb<sub>2</sub>O<sub>5</sub> considerably increases both the yield and TON (Entries 2 and 5, respectively, Table 3). The role of CH<sub>2</sub>Cl<sub>2</sub> is tentatively explained assuming that it may contribute to stabilize polar or ionic intermediates through the C<sup>δ-</sup>-H<sup>δ+</sup>, C<sup>δ+</sup>-Cl<sup>δ-</sup> dipoles. Noteworthy, if CH<sub>2</sub>Cl<sub>2</sub> was used as solvent or added to a solvent like toluene or xylene, the carboxylation of the epoxide did not take place. It seems that while CH<sub>2</sub>Cl<sub>2</sub> is a good co-promoter when added to DMF or DMA, it is not itself an effective medium for the carboxylation to occur. This can be rationalised as reported above, on the basis of the fact that DMF or DMA are bases that may interact with CO<sub>2</sub> or the epoxide and increase their reactivity by enhancing the nucleophilic character. CH<sub>2</sub>Cl<sub>2</sub> can play only the secondary, but important, role as the solvation of the intermediates. We have attempted an high temperature <sup>1</sup>H NMR in order to discover possible intermediates

that imply CH<sub>2</sub>Cl<sub>2</sub>. No evidence of such species was found. Anyway, such experiments were helpful for excluding the conversion of the organic halide, either CH<sub>2</sub>Cl<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, that was found intact at the end of the reaction, as confirmed by the position and integral of the <sup>1</sup>H signal.

### 3.2. The role of Nb<sub>2</sub>O<sub>5</sub>

The experimental results show that the addition of Nb<sub>2</sub>O<sub>5</sub> to DMF increases the conversion yield of the carboxylation reaction (compare Entries 1 and 4, 10 and 12, 14 and 16, and so on, Table 3). The metal can either promote the opening of the epoxide through co-ordination to the oxygen atom, or pre-form the carbonate moiety through the interaction of CO<sub>2</sub> with the Nb-O bonds. That the carbonate moiety is formed on Nb oxides is documented in the literature [19]. The activity of Nb<sub>2</sub>O<sub>5</sub> can be compared with that of other oxides described in the literature. Under the same reaction conditions (12 h, 408 K, DMF as solvent) the conversion yield reported for MgO [13] or Mg/Al mixed oxides [14], the only other heterogeneous catalysts described in the literature, is 60 and 90% for styrene carbonate and 41 and 88% for propene carbonate, respectively, using a molar ratio epoxide/catalyst of 0.6 (MgO) and 3.6 (Mg/Al mixed oxide) for styrene oxide and 0.4 and 3.5 for propene oxide, respectively. Such ratio is much lower than that used in this work with Nb<sub>2</sub>O<sub>5</sub>, that ranges between 50 and 1000. Consequently, the Nb catalyst, affords a much higher TON than Mg and the mixed oxide. For all such oxides, DMF is the elected solvent.

In order to verify the life-time of the catalyst, we have reloaded the epoxide several times in the



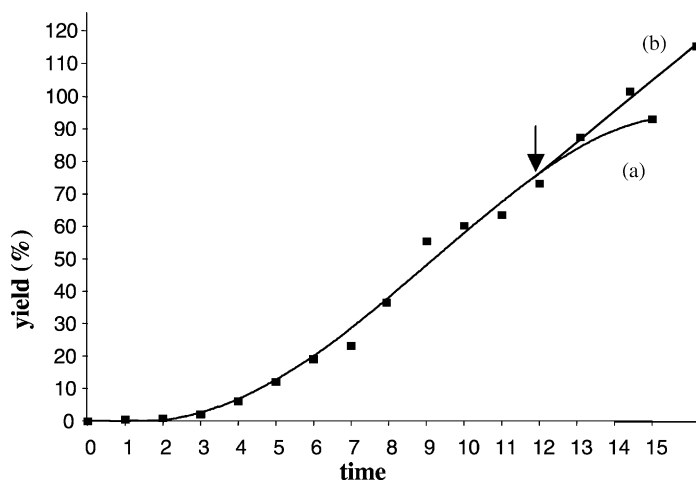


Fig. 2. Formation trend of propene carbonate at 408 K.

autoclave, and no evidence of deactivation of the catalyst was observed. Fig. 2 shows that using propylene oxide and CO<sub>2</sub> (5 MPa) at 408 K, after an induction time of ca. 2 h, 90% of the reagent was converted into carbonate in 12 h (curve (a), starting with a 47.3 molar ratio epoxide/catalyst). If the epoxide is reloaded, the catalyst is still active and the carboxylation of the epoxide continues without any induction time (see Fig. 2, curve (b)). The reloading can be repeated several times reaching a TON of several hundred moles of epoxides per mole of Nb<sub>2</sub>O<sub>5</sub> as catalyst.

Alternatively, the catalyst can be isolated and recycled several times. Studies are in progress in order to ascertain if the catalyst undergoes major structural modifications during the reaction. Using powder Nb<sub>2</sub>O<sub>5</sub> it was difficult to give an indication about the number of active centres involved into the reaction. Therefore, the TON reported above was calculated as the ratio of converted epoxide to the total number of the metal centres. In order to get information about the specific activity of Nb-centres a supported catalyst is under investigation. The formation trend of carbonate is the same for different epoxides [8], the yield of conversion depending on the molecular structure of the epoxide. After one or more runs, the reaction solution was filtered, reloaded with the epoxide and pressurized with CO<sub>2</sub>: the yield in carbonate was that typical of the run with the solvent without catalyst, showing that Nb species were not present in solution. When NbCl<sub>5</sub> was used a clear catalytic effect was

observed (Entry 18, Table 2) also if lower than with Nb<sub>2</sub>O<sub>5</sub>.

### 3.3. The effect of addition of inorganic halides to Nb<sub>2</sub>O<sub>5</sub>/DMF

As mentioned above, the addition of CH<sub>2</sub>Cl<sub>2</sub> to the Nb<sub>2</sub>O<sub>5</sub>/DMF system improves the yield, as already observed with DMF alone (Entries 4 and 5, 12 and 13, 16 and 17 and so on, Table 3). Also, the addition of an inorganic halide to Nb<sub>2</sub>O<sub>5</sub>/DMF may act as a promoter of the conversion. In fact, when 0.2 mol of KI were added per mole of Nb<sub>2</sub>O<sub>5</sub> in DMF, a 10% increase of the conversion yield of the epoxide was observed.

Such effect could be explained in two ways. It is known that halide-ions may promote the carboxylation of epoxides [12,22]. Therefore, the added halide could perform as a second catalyst operating in co-operation with the Nb oxide. Alternatively, the inorganic halide could operate as discussed above, by stabilizing some ionic [23] or polar forms, that are key intermediates in the carboxylation reaction. However, if the role of inorganic halides was easily foreseeable, the effect of adding CH<sub>2</sub>Cl<sub>2</sub> to Nb<sub>2</sub>O<sub>5</sub> and the co-operative role of DMF and an organic halide results to be very intriguing. The concerted action of DMF and CH<sub>2</sub>Cl<sub>2</sub> has a fundamental role in the activation of the hetero-cumulene and epoxide, increasing the yield of conversion and turnover number.

### 3.4. The effect of addition of alcohol or carbon tetrachloride

In order to ascertain if the C–H dipole of the organic halide or the C–Cl dipole was implied into the assistance to the reaction of carboxylation of the epoxide, we have used as additives either CCl<sub>4</sub> or ethanol. Both show a co-operative effect (Entries 6 and 7, Table 3). Such results show that solvation effects are very important in this reaction.

## 4. Conclusions

Nb<sub>2</sub>O<sub>5</sub> acts as catalyst in the carboxylation of several epoxides. Amides result to be efficient promoters of the carboxylation. The addition of an organic halide increases the conversion yield. This finding opens a new perspective for the development of efficient catalytic systems for the carboxylation of epoxides.

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