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Direct carboxylation of alcohols to organic carbonates: Comparison of the Group 5 element alkoxides catalytic activity
An insight into the reaction mechanism and its key steps

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Abstract

The reaction of carboxylation of alcohols is a sustainable technology for the synthesis of dialkylcarbonates that avoids the use of phosgene. In this paper we describe the behaviour of metal alkoxides of Group 5 elements as homogeneous catalysts in the above reaction, and the isolation and characterization of the active species, i.e. the hemicarbonates formed upon insertion of carbon dioxide into the M–OR bond. Ta and V alkoxo complexes are comparatively discussed with respect to the Nb-analogues, whose synthesis and catalytic properties have been published [M. Aresta, A. Dibenedetto, C. Pastore, Inorg. Chem. 42 (10) (2003) 3256, and references therein].

In this paper, we report for the first time the evidence of insertion of carbon dioxide in tantalum alkoxides $[Ta(OR)_5]_2$ [R = methyl (Me), ethyl (Et)]. The relevant hemicarbonates $Ta(OR)_4[OC(O)OR]$ have been characterized using spectroscopic techniques (IR and NMR). Tantalum alkoxides and the vanadium compound $VO(OR)_3$ are shown to be able to catalyze the carboxylation of alcohols at 413 K and 5.5 MPa of CO_2.

The trend of reactivity for the Group 5 alkoxides as catalysts for the carboxylation of alcohols is $Nb \gg Ta > V$.

Keywords: Alkoxo complexes; Carboxylation of alcohols; Group 5 elements; Hemicarbonates; Homogeneous catalysis

1. Introduction

The direct carboxylation of alcohols with CO_2 (1) has a great potential as a sustainable route to

$$2ROH + CO_2 \rightleftarrows (RO)_2CO + H_2O \quad R = Me, Et, Allyl \tag{1}$$

organic linear carbonates. The thermodynamics says that if R is an alkyl group [1] the reaction is exothermic or nearly thermally neutral, while with aromatic substituents the equilibrium is substantially displaced to the left, making the methodology not useful for practical application. Accordingly, a few homogeneous (Nb [1], Sn [2]) and heterogeneous (Ti [3], Zr [4]) catalysts are described in the literature that promote the conversion of aliphatic alcohols into the relevant carbonates, while the synthesis of diphenylcarbonate (R = Ph) is not documented at all to occur according to Eq. (1).

Some of the studies performed so far confirm that the reaction is an equilibrium and the aliphatic carbonate equilibrium concentration lies between 1 and 2% [1–4] that is in agreement with the thermodynamic data. The reaction pathway has been highlighted for Nb [1] and Sn [2], while a complete reaction pathway, including transition state (TS) energies, has been reported for the carboxylation of aliphatic alcohols (MeOH, EtOH, AllylOH) promoted by dicyclohexylcarbodiimides (DCC) [5].

The existing information is still too limited: a deeper insight into the catalyst behaviour is necessary for a better understanding of the connection of the metal properties to the reaction mechanism in order to be able to design a catalytic system that may foster the reaction kinetics to a practical application. To this end, we have investigated the chemistry of several element alkoxides towards CO_2 and gained worthwhile information that correlates the metal properties to the catalyst efficiency and reaction kinetics. In this paper we discuss in detail the reaction of $[Nb(OEt)_5]_2$ and $[Ta(OEt)_5]_2$ with CO_2 and compare the catalytic efficiency of $VO(OR)_3$, $[Nb(OR)_5]_2$ and $[Ta(OR)_5]_2$ (R = Me, Et) in the carboxylation of alcohols. We also correlate such reactivity

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to some key steps of the carboxylation process with an insight into the reaction mechanism.

2. Experimental

2.1. General

All solvents and starting reagents were RP Aldrich products. Alcohols and solvents were dried, distilled [8] and stored under dinitrogen. Carbon dioxide was from Rivoira IP (99.999% purity).

Elemental analyses were made with an analyzer EuroLab EA3000. Nuclear magnetic resonance experiments were carried out with a 400 MHz Varian INOVA apparatus using deuterated Cambrige Isotope Laboratory (CIL) solvents. FTIR spectra were recorded with a Shimadzu Prestige 21 instrument.

GC–MS analyses were carried out with a gas chromatograph Shimadzu 17 A (capillary column: 30 m; MDN-5S; Ø 0.25 mm, 0.25 μm film) coupled to a Shimadzu QP5050 A mass spectrometer. Quantitative determinations on the reaction solutions were recorded using a Hewlett-Packard 6850 GC-FID (capillary column: 30 m; MDN-5S; Ø 0.25 mm, 0.25 μm film).

$[Nb(OR)_5]_2$ [1], $[Ta(OR)_5]_2$, $VO(OiPr)_3$ [9] and $NbO(OEt)_3$ [10] were prepared as reported in the literature. High pressure reactions were carried out in a 100 mL autoclave thermostated with an electric heating jacket equipped with an inner glass reactor for avoiding metal contamination of the reagents and with a valve for continuous withdrawing of liquid samples.

The synthesis and characterization of $Nb(OC(O)OR)(OR)_4$ (R = Me, Et, Allyl) has been already published [1].

2.2. Synthesis and characterization of $Ta(OMe)_4[OC(O)OMe]$ and $Ta(OEt)_4[OC(O)OEt]$

(a) 1.35 g of $[Ta(OMe)_5]_2$ (3.93 mmol) was dissolved in methanol (5 mL) under carbon dioxide (0.1 MPa) and the solution stirred for 2 weeks. Samples were withdrawn each day and analyzed by NMR. After the third day the signals of the hemicarbonate started to become evident. When the conversion was complete, the solvent was evaporated at 290 K by bubbling carbon dioxide into the solution. An amorphous white solid remained that was characterized as the hemicarbonate.

Anal. calcd. for $C_6H_{15}O_7Ta$: C 18.96, H 3.98, Ta 47.60%; found C 19.0, H 4.1, Ta 47.8%.

IR (KBr disks, Nujol): the most important bands are at 1608 ($\nu_{as\ C=O}$), 1472, 1362 ($\nu_{sym\ C=O}$), 1164 (ν_{C-O}), 1108 cm^{-1} (ν_{C-O}).

^1H NMR (toluene-d_8, 298 K): 3.99 ppm [singlet, $-OC(O)OCH_3$], 4.20 ppm (broad singlet, OCH_3 axial and equatorial).

^{13}C NMR (toluene-d_8, 298 K): 161.5 ppm ($-OC(O)O-$), 54.3 ppm ($-OC(O)O-CH_3$) and 59.4 ppm (terminal methoxide groups).

(b) The ethyl analogue was prepared in a similar way and characterized using the same techniques.

Anal. calcd. for $C_{11}H_{25}O_7Ta$: C 29.34, H 5.59, Ta 40.20%; found C 29.0, H 5.3, Ta 40.8%.

IR (KBr disks, neat compound): the most important bands are at 1604 ($\nu_{as\ C=O}$), 1470, 1361 ($\nu_{sym\ C=O}$), 1163 (ν_{C-O}), 1108 cm^{-1} (ν_{C-O}).

The NMR spectrum is shown and discussed in Section 3.

2.3. NMR experiments

Two hundred and thirty milligrams in the case of $[Nb(OEt)_5]_2$ or 293.6 mg for $[Ta(OEt)_5]_2$ (0.72 mmol) was dissolved in 1 mL of toluene-d_8 under dinitrogen atmosphere directly in a NMR tube and the proton spectrum was recorded immediately. A sub-stoichiometric quantity of ethanol (4.5 μL, 0.078 mmol) was added to such solutions under controlled conditions and the proton and carbon spectra were again recorded. The dinitrogen atmosphere was replaced with carbon dioxide and the spectra registered again.

The same series of spectra were recorded when the Nb or Ta ethoxides were dissolved in anhydrous acetone-d_6. The spectra are shown in Section 3.

In the case of tantalum, a sample was prepared using the same quantity of $[Ta(OEt)_5]_2$ in toluene-d_8 in presence of a quasi-stoichiometric amount of ethanol (80%). The ^1H and ^{13}C NMR spectra were registered immediately. The remaining solution was stirred under a carbon dioxide atmosphere for 3 days. After this time, the sample was transferred to a NMR tube and the ^1H and ^{13}C spectra were recorded.

2.4. Carboxylation of ethanol under pressure using various Group 5 element catalysts

(a) 4.42 g of $[Nb(OEt)_5]_2$, or 3.39 g of $VO(OiPr)_3$, or 5.65 g of $[Ta(OEt)_5]_2$ (13.9 mmol in each case) dissolved in 20 mL of ethanol (347.8 mmol) was heated at 410 K under 5.5 MPa of CO_2 in the stainless steel autoclave described above. The solution was continuously monitored by GC–MS and GC-FID.

The alcohol conversion observed in the three cases is plotted in Fig. 7.

(b) 3.41 g (14.00 mmol) of $NbO(OEt)_3$ was placed in the reaction vessel into the autoclave and the same procedure as above was followed. The GC analysis on the final mixture revealed only traces of carbonate.

3. Results and discussion

We have already shown [1] that $[Nb(OR)_5]_2$ (R = Me, Et, Allyl) is able to catalyze the direct carboxylation of alcohols under mild conditions. The reaction mechanism proposed infers the dissociation of the dimer to a monomer that is carboxylated to afford a hemicarbonate $[(RO)_4Nb[OC(O)OR]]$, isolated and characterized as a monomer bearing a chelating hemicarbonate moiety. The latter interacts with alcohols to afford the carbonate. We have now carried out a more detailed ^1H and ^{13}C NMR study on the Nb-species in order to gain

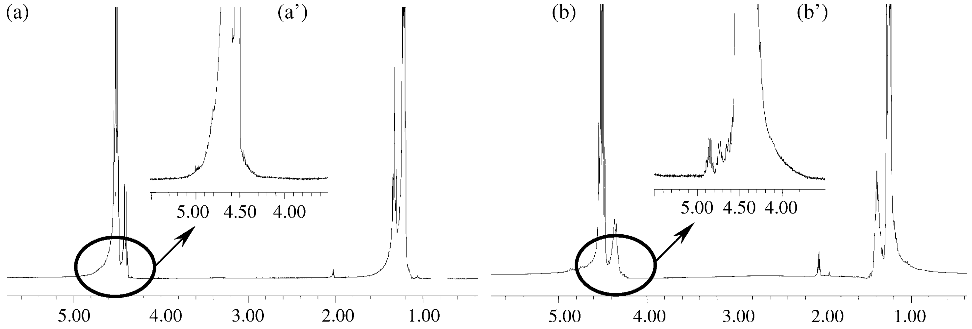
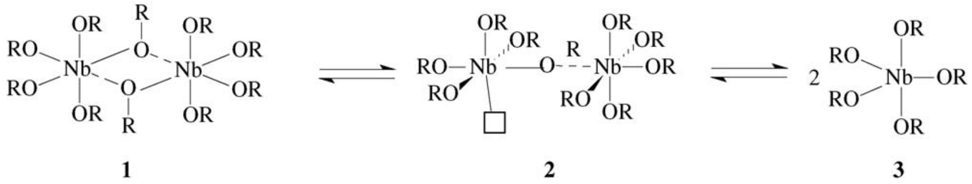


Fig. 1. (a) ^{1}H NMR of $[Nb(OEt)_5]_2$ shortly after dissolution in toluene-d_8 and (b) ^{1}H NMR of $[Nb(OEt)_5]_2$ in toluene-d_8 after 2 h.



Scheme 1. Reaction path from the dimer to the active monomeric species.

further evidence about the proposed mechanism and to better demonstrate its validity. We have also extended such studies to the Ta-analogues in order to obtain information about the relative efficiency of Nb and Ta element catalysts. Also, V(V) oxo-alkoxides have been studied under catalytic conditions and the efficiency of the three Group 5 element catalysts fully compared.

3.1. $[Nb(OEt)_5]_2$ behaviour in solution: NMR study in presence of co-ordinating molecules (or solvent)

When $[Nb(OEt)_5]_2$ **1**, is dissolved in toluene-d_8, the ^{1}H NMR spectrum shows, after 2 h besides the signals of the bridging and terminal OEt groups (Fig. 1a), new signals attributed to the product of (semi-) dissociation of **1** (Fig. 1b). Fig. 1a shows the aliphatic portion of the ^{1}H NMR spectrum of **1** (a) taken at time zero (soon after the dissolution in toluene-d_8) with a zoom (a′) on the methylenic-region. Only the signals of the dimer are evident, with the group of signals due to the terminal (more intense) and bridging ethoxo-groups.

Fig. 1b represents the spectrum of the solution at equilibrium. For sake of simplicity we limit the analysis to the methylenic portion of the spectrum that is the most informative (b′). Besides the partially overlapping quadruplets due to the CH_2 of bridging (4.35 ppm, $J_{H–H} = 7.0$ Hz) and terminal (4.51 ppm, $J_{H–H} = 7.1$ Hz) OCH_2CH_3 moieties, weak signals at 4.90 and 4.60 ppm clearly indicate the presence of a different species, i.e. the product of dissociation of the dimer. The structure of the signal is not simple and they cannot unequivocally be attributed to a single species. The multiplicity of signals suggests that the dissociation may proceed step by step, as indicated in Scheme 1 until the formation of the monomer is reached.

As we have already reported [1], the overall dissociation process is slow (k_{dis} is 0.97×10^{-5} in benzene and $1.15 \times 10^{-5}\ s^{-1}$ in ethanol) and the equilibrium is by far displaced to the left ($K_{eq} = 2.07 \times 10^{-4}$ mol L^{-1}). This agrees with the ratio of the integrals of the signals of the dimer and the dissociation product(s). Moreover, as demonstrated by the kinetic constants, the dissociation is influenced by the solvent

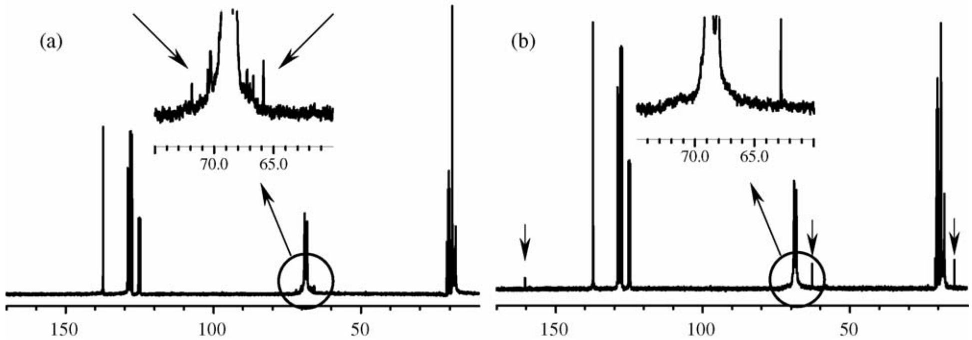


Fig. 2. (a) ^{13}C NMR of $[Nb(OEt)_5]_2$ in toluene-d_8 and ethanol and (b) ^{13}C NMR of $[Nb(OEt)_5]_2$ in toluene-d_8 and ethanol after exposure to carbon dioxide atmosphere.

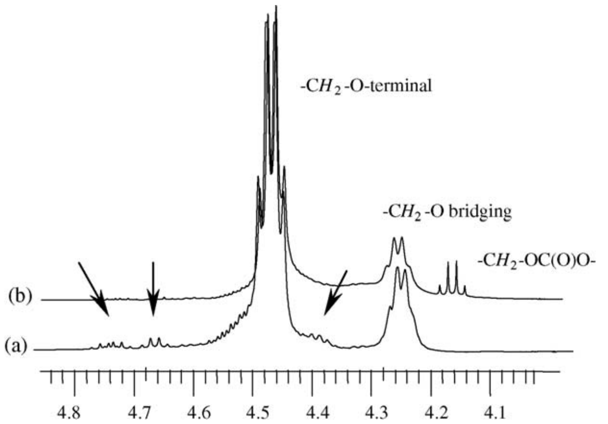


Fig. 3. ^{1}H NMR spectra for the $-CH_2-$ region for $[Nb(OEt)_5]_2$ in acetone-d_6 before (a), and after exposure to carbon dioxide (b).

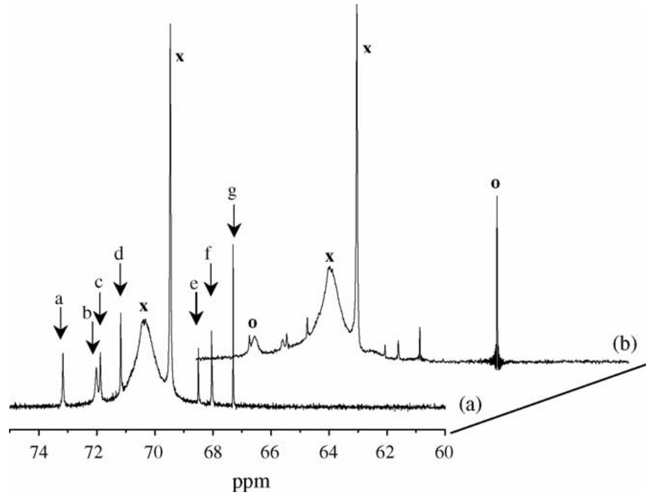


Fig. 4. ^{13}C NMR of the methylene-region for $[Nb(OEt)_5]_2$ in acetone-d_6: (a) before and (b) after exposure to carbon dioxide at 273 K. [x] are the signals of the starting species; [o] are the signals of the carboxylated species. Arrows indicate the signals attributed to the dissociated species.

and it is faster and more displaced to the right in a co-ordinating solvent. The solvent influence is demonstrated by the fact that the addition of sub-stoichiometric amounts of ethanol to a solution of **1** in toluene-d_8 increases the intensity of the signals due to the dissociated form of **1** and broadens both the dissociated and dimer signals due to an exchange of free ethanol with co-ordinated OEt moieties. Such exchange most probably proceeds through a preliminary co-ordination of ethanol to the vacant position (□) of the partially dissociated dimer **2** (see Scheme 1). The ^{13}C NMR spectrum is more informative (Fig. 2) than the ^{1}H.

In fact, upon dissolution of **1** in toluene-d_8, seven signals appear in the methylene region (Fig. 2a) in addition to the signals of the terminal and bridging CH_2 groups. Very interestingly, the addition of CO_2 to such solution causes the fast disappearance of the seven signals attributed to the dissociated form of **1**, while the signals of hemicarbonate **4** ($Nb(OEt)_4[OC(O)OEt]$) appear at 160.2, due to $-OC(O)O-$, 62.7, due to CH_2 and 14.5 ppm, due to the CH_3 of the $-OC(O)OEt$ group. The carboxylation of the monomer is quite fast (10^4 times faster) as compared to the dissociation [1], and this is in agreement with the immediate disappearance of the signals of the dissociated form of **1**. The dissociation of the dimer is assisted by any other co-ordinating solvent.

Fig. 3 shows the ^{1}H NMR spectrum of **1** in acetone-d_6 and the effect of the addition of CO_2. Again, the signals of the dissociated form disappear upon addition of CO_2. The ^{13}C NMR spectrum of **1** in acetone-d_6 confirms that this solvent is able to foster the dissociation of **1**.

In fact, as Fig. 4 shows, upon dissolution of **1** in acetone-d_6, seven signals appear, due to **2** (a–f) and **3** (g), that disappear upon exposure of the solution to CO_2. Fig. 4b clearly shows the decrease of the signals of the dissociated forms under controlled temperature conditions (273 K): at room temperature the signals' disappearance is too fast for the NMR time scale and one would observe only the signals of the carboxylated form (o) (Scheme 2).

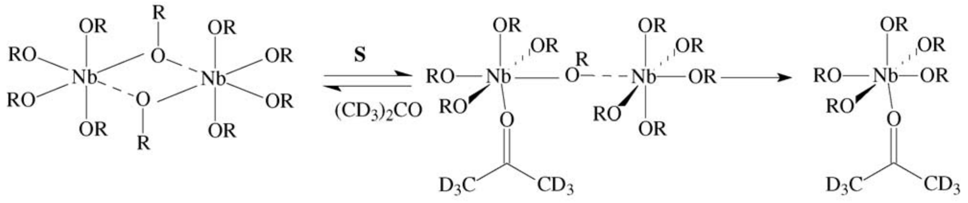
The ensemble of the above data confirms that the production of the hemicarbonate is a two-step process:

(i) dissociation of the dimer (slow);
(ii) carboxylation of the monomer (fast).

As the dissociation is assisted by polar solvents, one may expect that the formation of the hemicarbonate is faster in co-ordinating than in non-co-ordinating solvents. Alcohol can, thus, be advantageously used as solvent and reagent in such reactions.

3.2. $[Ta(OEt)_5]_2$ behaviour: NMR study

With such information in our hands, we have investigated the behaviour of $[Ta(OEt)_5]_2$, **5** towards CO_2 under the same reaction conditions used for the analogous Nb-complex. Interestingly, the Ta alkoxide is much less reactive than the Nb-analogue. In fact, when $[Ta(OEt)_5]_2$ is dissolved in toluene-d_8, only the signals of the bridging and terminal OEt methylene



1 **2** **3**

Scheme 2. Dissociation mechanism of the dimeric species of $[Nb(OR)_5]_2$ in acetone-d_6.

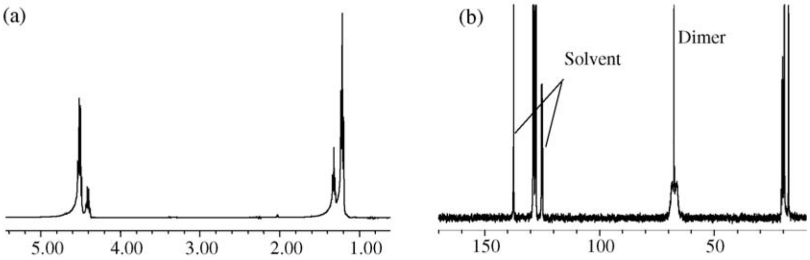


Fig. 5. (a) ^{1}H NMR spectrum of $[Ta(OEt)_5]_2$ in toluene-d_8 after 3 h and (b) ^{13}C NMR spectrum of the solution after addition of CO_2: no signals due to the hemicarbonate are evident.

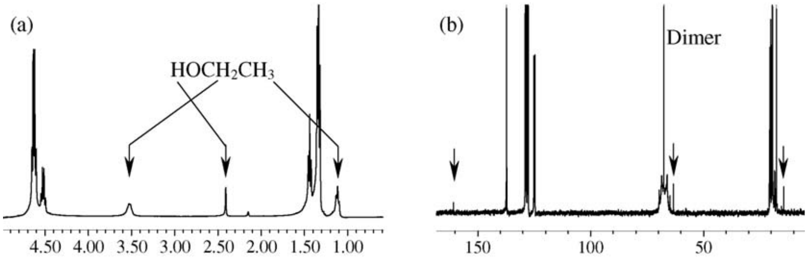


Fig. 6. (a) ^{1}H NMR of **5** in toluene-d_8 added with stoichiometric amount of ethanol after 3 h and (b) ^{13}C NMR spectrum of a solution of **5** in toluene-d_8 plus ethanol after 3 days of exposure to CO_2: the signal of the hemicarbonate starts to emerge.

groups of the dimer are observed in the ^{1}H NMR spectrum, also after some hours (Fig. 5a). Obviously, in accordance with what we have reported above, the addition of CO_2 does not cause any immediate formation of the hemicarbonate (Fig. 5b), confirming that the insertion of CO_2 occurs in the monomer and not in the dimer. As opposed to what we have described for the Nb-alkoxide, when ethanol is added to a solution of **5** in toluene-d_8, no interaction of ethanol with the Ta-alkoxide is observed after 3 h. In fact, the ^{1}H NMR spectrum of **5** + ethanol shows the separate signals of **5** and ethanol (Fig. 6a).

Only after 3 days of exposure to CO_2 (Fig. 6b) the signals of the hemicarbonate are observed. These features can be interpreted in terms of the different M–OR energy. It is well known that the Ta dimers are more stable than the Nb-analogues: in fact, it has been determined that the ΔH of dissociation for $[Ta(OiPr)_5]_2$ is greater than that for the niobium analogue [6]. We have found that by increasing the temperature from 298 to 373 K, the reaction of **5** with CO_2 can be observed, but at very low extent (the isolation of the pure carboxylated form of **5** is not easy as it is formed only in small amounts also after 48 h).

3.3. $VO(OEt)_3$ behaviour

Vanadium penta-alkoxides are not isolable, so that we have used $VO(OEt)_3$, **6** instead. This form of V^{5+} does not allow the isolation of the hemicarbonate: in this aspect **6** is similar to $NbO(OEt)_3$ [10] which does not allow the isolation of the hemicarbonate at room temperature. Moreover, differently from Nb(V) and Ta(V), V(V) undergoes a reduction to lower oxidation states (IV, III) with formation of the relevant aldehydes upon alcohol oxidation.

3.4. Comparison of the reactivity of the Group 5 metal alkoxides in the reaction of carboxylation of alcohol to afford dialkylcarbonates

These data allow us to predict that Nb must be a better catalyst than Ta and V in the carboxylation of alcohols with CO_2. As a matter of fact, when aliphatic alcohols (MeOH, EtOH, AllylOH) are reacted with CO_2 (5.5 MPa) in presence of one of the Group 5 element alkoxides, the relevant carbonate is formed, but at totally different rates, depending on the catalyst used. This is shown in Fig. 7, where the formation yield of

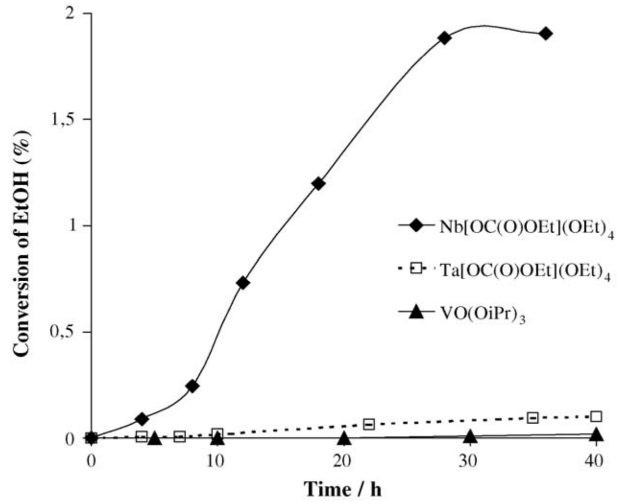
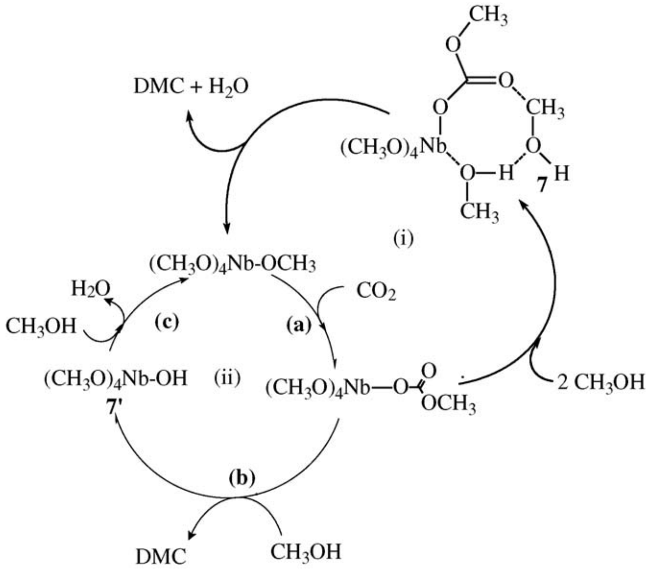


Fig. 7. Formation of diethylcarbonate, DEC (expressed as alcohol conversion) via carboxylation of ethanol with Group 5 element alkoxides as catalysts. 13.9 mmol of metal complex ($[Nb(OEt)_5]_2$ or $VO(OiPr)_3$ or $[Ta(OEt)_5]_2$) was dissolved in 20 mL of ethanol (347.8 mmol) and heated at 410 K under 5.5 MPa of CO_2 in the stainless steel autoclave described in Section 2.



Scheme 3. Proposed pathway for the Nb-promoted carboxylation of alcohols. The formation of dimethylcarbonate is shown as an example.

diethylcarbonate (DEC) is plotted versus time for the three Group 5 elements.

Clearly, Nb is the most effective catalyst. The total TON may reach values higher than 2 if the catalyst is recovered when the equilibrium is reached and reused in fresh alcohol. It is also well evident from the DEC formation curve with Nb-catalysts that there is an induction time (during which the active catalytic species is formed, i.e. the hemicarbonate), followed by a phase of growth of the concentration of DEC until the equilibrium is reached. The same trend is observed with MeOH.

As we have already demonstrated, heating the Nb-hemicarbonate in a solvent different from alcohol causes the loss of CO_2, while in alcohol the dialkylcarbonate is formed [1]. This behaviour is different from that of $Bu_2Sn(OMe)[O\text{-}C(O)OMe]$ that affords DMC and Bu_2SnO when heated in toluene under CO_2 [2].

Consequently, we propose that the formation of the dialkylcarbonates takes place in a different way in the two cases. In the case of the Sn-complex, an intramolecular alkyl-cation migration takes place from the Sn–OR group to the hemicarbonate moiety, OC(O)OR linked to Sn. In the case of Nb, the alkyl group is furnished by an external alcohol, following a more complex path that most probably may involve two alcohol molecules and **4** (see Scheme 3i).

$$CH_3OH + A \longrightarrow CH_3^+ + AOH^- \text{ (or } CH_3OHA^+) \qquad \text{(i)}$$

$$CH_3OH + B \longrightarrow CH_3O^- + BH^+ \qquad \text{(ii)}$$

$$CH_3O^- + CO_2 \longrightarrow ROC(O)O^- \qquad \text{(iii)}$$

$$CH_3OC(O)O^- + CH_3^+ \text{ (or } CH_3OHA^+) \longrightarrow CH_3OC(O)OCH_3 \text{ (+ A)} \qquad \text{(iv)}$$

Scheme 4. Dimethylcarbonate formation from methanol.

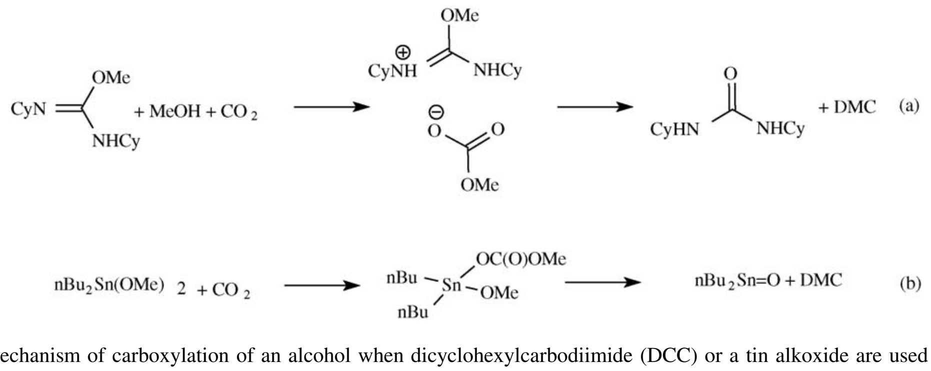
The alternative route 3ii is also possible.

Routes 3i and 3ii should have different TS energy [11], as shown by DFT calculations.

The alcohol carboxylation requires an acid 4i and a basic activation of the alcohol 4ii (Scheme 4).

In our opinion, the rate determining step in the whole process must be the alkyl group formation and migration to the hemicarbonate that must be ready to be alkylated (Scheme 4). Therefore, the acid activation of alcohol is the key determining step of the process. This hypothesis is supported by the fact that when good alkyl-releasing reagents are used (CH_3I coupled with K_2CO_3 [7], or the isourea form derived from carbodiimides [5]) the formation of the carbonate takes place under mild conditions. Conversely, when the formation of the alkyl-moiety requires harsh conditions (alcohol activation by a metal system), the carboxylation of the alcohol takes place with a low yield due to a low reaction rate. As the acid activation of the alcohol is a process that requires higher energy than the base activation, the reaction may follow an initial double basic activation of the alcohol with production of two OR moieties, one of which then must behave as an alkyl transfer agent with final formation of a E=O double bond (where E is a metal or C). This is observed in both the DCC (Scheme 5a) and Sn (Scheme 5b) cases.

Nb seems to follow an alternative reaction path (Scheme 3). In fact, the IR spectroscopy does not reveal any Nb=O bond in the catalyst recovered from the reaction solution until the catalyst ceases its activity. One can envisage that the eight-membered species **7** (involving two methanol units) may play a key role in the catalytic cycle. As preliminary DFT calculation have shown **7′** is more than 20 kcal/mol higher in energy than **7**. **7′** would most probably be related to the deactivation of the catalyst. The possible routes of formation of DMC using Nb-alkoxides have been modelled using the DFT method and the results will be available in a forthcoming publication [11].



Scheme 5. Mechanism of carboxylation of an alcohol when dicyclohexylcarbodiimide (DCC) or a tin alkoxide are used as promoters.

4. Conclusions

The investigation of the behaviour of Group 5 element alkoxides towards CO_2 has clearly shown that there is a correlation between the energy of the metal–oxygen bond and the reactivity of metal alkoxides that is relevant to the catalytic activity of the metal systems. Such information has allowed us to identify the key steps of the entire process of conversion of alcohols into the relevant carbonates. Such knowledge, combined with that relevant to the dicyclohexylcarbodiimide–alcohol–CO_2 system, is very useful for designing an effective alcohol carboxylation catalyst that we have now under study.

Acknowledgements

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