

# Formation of dibutyl carbonate and butylcarbamate via CO<sub>2</sub> insertion in titanium(IV) butoxide and reaction with *n*-butylamine



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**This work is dedicated to the memory of Prof. M.D. Grillone and Prof. M. Schiavello.**

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## ABSTRACT

The species resulting from insertion of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> into titanium(IV) butoxide is for the first time fully characterized by means of infrared and nuclear magnetic resonance spectroscopy. Results show formation of Ti-monobutylcarbonate, that easily undergoes nucleophilic attack by an aliphatic amine. The hydrolysis of the resulting species produces butylcarbamate and dibutylcarbonate as the only main products. Characterization results of the carbonate-like adduct, along with its reactivity with amine molecules open the route to new ways of CO<sub>2</sub> utilization as building block for valuable organic compounds.

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## 1. Introduction

Organic carbonates, yearly produced in multiton scale, are widely used compounds e.g. as protecting groups, in polymer science, organometallic reactions, solid phase synthesis, enzymatic reactions [1,2] and as solvents in synthesis and catalysis [3,4]. Among them, dibutyl carbonate (DBC) is extensively used for the production of various organic and polymeric materials, and it is important for petrochemical industry, because of its high thermal oxidative stability and solubility [5].

The industrial routes to linear carbonates, as DBC, mainly use phosgene as the starting material [1,6]. Therefore, even if organic carbonates are considered green solvents, their actual production is surely not a "green" process [3]. Therefore, finding environmental friendly alternatives to the traditionally used reaction of phosgene with *n*-butanol represents a challenging issue [1].

Among different routes proposed [1,7,8], CO<sub>2</sub> has been selected instead of phosgene as reactant, thus avoiding the use of a toxic reagent combined to the benefits related to CO<sub>2</sub> sequestration and

use. However, the severe operative conditions to be applied for these processes make difficult their implementation [1,2]. Indeed, nowadays only few industrial processes use CO<sub>2</sub> as raw material, essentially for its thermodynamic stability and kinetic inertness. "High-energy" starting materials as hydrogen, unsaturated compounds, small-membered ring compounds and organometallics are used to react with CO<sub>2</sub>. Focusing on these last, carbon dioxide can coordinate in several modes with transition metal compounds [9]; in particular, high valent metal complexes with nucleophilic ligands as alkoxides or amides [10,11] allow formation of a carboxyl group through nucleophilic attack. In the latter case, CO<sub>2</sub> is inserted in the M—O or M—N bond to give a metal-alkylcarbonate or metal-alkylcarbamate, respectively.

In general, most metal alkoxide complexes react reversibly with carbon dioxide [12–18], presumably because the metal alkoxide and metallo-alkylcarbonate possess similar M—O bond strengths.

Insertion of CO<sub>2</sub> into the M—O bond was demonstrated for different transition metals. Zinc complexes, as Zn<sub>2</sub>Br<sub>4</sub>(μ-OCHRCH<sub>2</sub>NC<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (R = H, CH<sub>3</sub>) [19], or Cobalt complexes, as [Co(TCT)(OR)]BPh<sub>4</sub> (R = Et, Ph; TCT = *cis,cis*-1,3,5-*tris*(cinnamylideneamino) cyclohexane) [20], activate carbon dioxide via insertion, although in some case release of CO<sub>2</sub> occurred even in a stream of argon. Rhenium complexes like *fac*-(CO)<sub>3</sub>L<sub>2</sub>-ReOCH<sub>3</sub> (L = PMe<sub>3</sub>; L<sub>2</sub> = diars) showed reversible carbon dioxide insertion into the rhenium oxygen bond [21]. Also various alkyl vanadium(III) alkoxide complexes reversibly insert carbon dioxide [22].

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Molybdenum systems [23] like Mo<sub>2</sub>(OiPr)<sub>4</sub>(L)<sub>4</sub> (L = PMe<sub>3</sub>, HOiPr) react with carbon dioxide to give Mo<sub>2</sub>(O<sub>2</sub>COiPr)<sub>4</sub> and Mo<sub>2</sub>(O<sub>2</sub>-COiPr)<sub>4</sub>(PMe)<sub>4</sub>. Some copper(I) alkoxide [24] also reacts with carbon dioxide at low temperatures.

Interestingly, similar CO<sub>2</sub> insertion was demonstrated also for a zirconia catalyst [25], vanadium based heterogeneous catalysts [26] and for organotin alkoxides immobilized on mesoporous silica [27].

CO<sub>2</sub> insertion was also hypothesized to occur in CO<sub>2</sub>-starting synthesis catalyzed by tin [28], cobalt [29], nickel [30], and niobium [31,32] complexes.

The insertion of CO<sub>2</sub> in titanium alkoxide complexes has been mainly invoked in literature to explain the reactivity of these complexes for the synthesis of organic carbonates from the corresponding alcohols and CO<sub>2</sub> [33]. Notably, titanium alkoxides and polyether ligands [34] (e.g., crown ethers or polyethylene glycols) showed a relatively high activity. However, characterization studies are almost absent, probably because these complexes are easily affected by the presence of water, being destroyed by hydrolysis. Furthermore, while reactions with heterocumulenes and titanium isopropoxide are known [35], reactions of CO<sub>2</sub> are not. In fact, supercritical CO<sub>2</sub> is used as a solvent for Ti(OiPr)<sub>4</sub> [36]. There is just one brief communication by Ghosh et al. [37] describing the importance of water traces in the insertion of CO<sub>2</sub> in titanium tetraisopropoxide. Authors report the formation of an isopropyl carbonate cluster which has been crystallographically characterized.

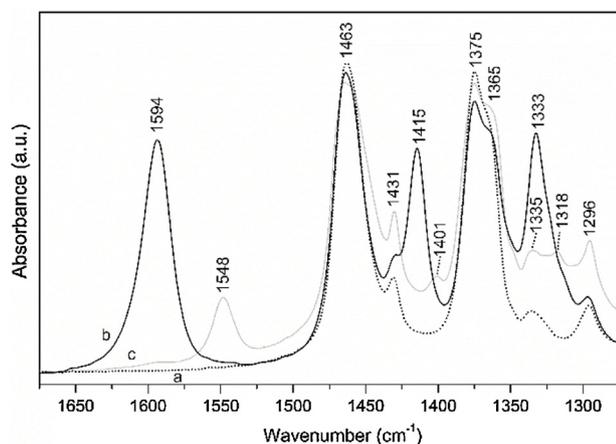
However, a deeper characterization is important to understand the intrinsic properties of the complex and to utilize the CO<sub>2</sub> sequestration capability for synthetic purposes.

In this study we report a thorough IR and NMR characterization of the complex resulting from insertion of CO<sub>2</sub> in a commercial available titanium(IV) butoxide complex.

Moreover, the reactivity of intermediate Ti-monobutylcarbonate species towards an amine was evaluated as an extension of the carbamation amines with organic carbonates. At the best of our knowledge, this reaction was studied until present only using dimethylcarbonate as alkylation agent [38,39]. Noteworthy carbamation is among the reaction producing value-added chemicals by exploiting the chemical conversion of CO<sub>2</sub> through C–N bond formation [40].

## 2. Experimental

Titanium(IV) butoxide (TTB, Sigma–Aldrich, purity 98%) and *n*-butylamine (Sigma–Aldrich, purity 99%) were used as received



**Fig. 1.** IR spectra of TTB (a), after bubbling <sup>12</sup>CO<sub>2</sub>, [TTB-<sup>12</sup>CO<sub>2</sub>] (b) and after bubbling <sup>13</sup>CO<sub>2</sub>, [TTB-<sup>13</sup>CO<sub>2</sub>] (c).

without further purification. The actual dryness was checked by IR spectroscopy (see Fig. 1 curve a, and related comment). The CO<sub>2</sub> was purchased from Airliquide with a global purity of 99.998% (N48). CO<sub>2</sub> insertion occurred at atmospheric pressure and room temperature simply by bubbling CO<sub>2</sub> for 15 min through pure TTB. <sup>13</sup>CO<sub>2</sub> was purchased by Icon Isotopes <sup>13</sup>C@99atom%. The reaction of <sup>13</sup>CO<sub>2</sub> with TTB was carried out as follow: (i) a small glass balloon (ca. 10 mL) was partially filled with ca. 5 mL of TTB in a glove-box; (ii) the above gas phase was removed by pump-freeze-thaw cycles; (iii) <sup>13</sup>CO<sub>2</sub> was admitted in the balloon; (iv) the balloon was shaken for 15 min.

A drop of the solution obtained was then placed between two KBr plates in order to obtain a thin film and analysed by means of IR spectroscopy, in a Bruker Vector 22 equipped with a DTGS detector (resolution of 4 cm<sup>-1</sup>, by accumulating 100 scans, to attain a good signal-to-noise ratio).

NMR spectra were recorded with a JEOL EX 400 spectrometer (<sup>1</sup>H operating frequency 400 MHz) at 298 K; data were treated by Jeol Delta Software. <sup>1</sup>H and <sup>13</sup>C chemical shifts are relative to TMS (δ = 0 ppm) and referenced against solvent residual peaks (CDCl<sub>3</sub> at 7.26 and 77.16 ppm for <sup>1</sup>H and <sup>13</sup>C, respectively).

*n*-Butylamine was dosed in molar ratio 4:1 in respect with Ti atoms in the TTB–CO<sub>2</sub> complex affording TTB–CO<sub>2</sub>–AM compound. Solutions resulting from TTB after interaction with CO<sub>2</sub> (TTB–CO<sub>2</sub>) and from TTB after interaction with CO<sub>2</sub> and *n*-butylamine (TTB–CO<sub>2</sub>–AM) were hydrolysed with distilled water in slight excess with respect to stoichiometric amount (mole ratio between water molecules and titanium atoms 4:1). The resulting white solid, Ti(OH)<sub>4</sub>, was separated by filtration and washed several times with toluene in order to extract the obtained organic compounds.

The toluene solution was then concentrated under vacuum at 60 °C until an oily residue was obtained, then analyzed by means of GC–MS (Thermo Finnigan Trace). A blank experiment was carried out as follows. Powdered Ti(OH)<sub>4</sub> was separately synthesized by hydrolysing pure TTB with distilled water and drying the obtained white solid. Thereafter, 1.5 g of Ti(OH)<sub>4</sub> were dispersed in 150 mL of *n*-butanol at 60 °C and CO<sub>2</sub> was bubbled through the suspension for 6 h. The suspension was then dried under vacuum at 60 °C and the obtained white solid was washed with toluene and filtered. The toluene solution was concentrated and analyzed by means of GC–MS.

## 3. Results and discussion

The IR spectrum of titanium(IV) butoxide (TTB) is reported in Fig. 1, curve a. In the 1675–1275 cm<sup>-1</sup> range, different signals are present, assigned to the vibrations of the alkyl chains [41a]. No signal due to water bending mode, expected in the 1650–1620 cm<sup>-1</sup> range, is observed. When CO<sub>2</sub> was bubbled in TTB liquid, new bands appeared located at 1594, 1415 and 1333 cm<sup>-1</sup> (Fig. 1, curve b). The newly formed compound (TTB–<sup>12</sup>CO<sub>2</sub>) was stable against subsequent bubbling with argon (see Fig. S1 in the Supplementary material, hereafter SM). The same experiment was carried out by bubbling <sup>13</sup>CO<sub>2</sub>. Also in this case three new signals appeared, but downshifted to 1548, 1401 and 1318 cm<sup>-1</sup> (Fig. 1, curve c). This proved the occurrence of the insertion of the carbon atom of CO<sub>2</sub> molecules in the newly formed species. Focussing back on the three new bands obtained for TTB–<sup>12</sup>CO<sub>2</sub> species, their positions appeared similar to what reported for the –O(CO)O– moiety of monodentate methyl carbonate on ZrO<sub>2</sub> [42], where the lower frequency with respect to molecular alkyl carbonates could be justified by the interaction with the transition metal centers.

The experimental isotopic ratios were compared with the calculated ones on the basis of a diatomic CO oscillator for the 1594/1548 cm<sup>-1</sup> pair and of a triatomic OCO oscillator for the 1415/

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