

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Formation of dibutyl carbonate and butylcarbamate via CO₂ insertion in titanium(IV) butoxide and reaction with n-butylamine This work is dedicated to the memory of Prof. M.D. Grillone and Prof. M. Schiavello

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1643315> since 2017-06-27T18:16:16Z

Published version:

DOI:10.1016/j.jcou.2015.12.002

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in JOURNAL OF CO₂ UTILIZATION, 13, 2016, 10.1016/j.jcou.2015.12.002.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), 10.1016/j.jcou.2015.12.002

The publisher's version is available at:

<http://linkinghub.elsevier.com/retrieve/pii/S221298201530024X>

When citing, please refer to the published version.

Link to this full text:

<http://hdl.handle.net/2318/1643315>

Formation of dibutyl carbonate and butylcarbamate via CO₂ insertion in titanium(IV) butoxide and reaction with *n*-butylamine

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

F. Parrino., C. Deiana. M.R., Chierotti., G. Martra., L. Palmisano.

a

Dipartimento di Energia, Ingegneria dell'Informazione e Modelli Matematici (DEIM), University of Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy

b

Department of Chemistry and Centre for “Nanostructured Interfaces and Surfaces-NIS”, University of Torino, Via P. Giuria 7, 10125 Torino, Italy

Abstract

The species resulting from insertion of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ 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_2 utilization as building block for valuable organic compounds.

Keywords

Dibutyl carbonate
CO₂ insertion
Titanium alkoxides
Carbamate

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_2 has been selected instead of phosgene as reactant, thus avoiding the use of a toxic reagent combined to the benefits related to CO_2 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_2 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_2 . 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_2 is inserted in the $\text{M}-\text{O}$ or $\text{M}-\text{N}$ 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 $\text{M}-\text{O}$ bond strengths.

Insertion of CO_2 into the $\text{M}-\text{O}$ bond was demonstrated for different transition metals. Zinc complexes, as $\text{Zn}_2\text{Br}_4(\mu\text{-OCHRCH}_2\text{NC}_5\text{H}_5)_2$ ($\text{R} = \text{H}, \text{CH}_3$) [19], or Cobalt complexes, as $[\text{Co}(\text{TCT})(\text{OR})]\text{BPh}_4$ ($\text{R} = \text{Et}, \text{Ph}$; $\text{TCT} = \text{cis,cis-1,3,5-tris(cinnamylideneamino) cyclohexane}$) [20], activate carbon dioxide via insertion, although in some case release of CO_2 occurred even in a stream of argon. Rhenium complexes like $\text{fac}(\text{CO})_3\text{L}_2\text{-ReOCH}_3$ ($\text{L} = \text{PMe}_3$; $\text{L}_2 = \text{diars}$) showed reversible carbon dioxide insertion into the rhenium oxygen bond [21]. Also various alkyl vanadium(III) alkoxide complexes reversibly insert carbon dioxide [22]. Molybdenum systems [23] like $\text{Mo}_2(\text{OiPr})_4(\text{L})_4$ ($\text{L} = \text{PMe}_3, \text{HOiPr}$) react with carbon dioxide to give

$\text{Mo}_2(\text{O}_2\text{COiPr})_4$ and $\text{Mo}_2(\text{O}_2\text{COiPr})_4(\text{PMe})_4$. Some copper(I) alkoxide [24] also reacts with carbon dioxide at low temperatures.

Interestingly, similar CO_2 insertion was demonstrated also for a zirconia catalyst [25], vanadium based heterogeneous catalysts [26] and for organotin alkoxides immobilized on mesoporous silica [27].

CO_2 insertion was also hypothesized to occur in CO_2 -starting synthesis catalyzed by tin [28], cobalt [29], nickel [30], and niobium [31,32] complexes.

The insertion of CO_2 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_2 [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_2 are not. In fact, supercritical CO_2 is used as a solvent for $\text{Ti}(\text{OiPr})_4$ [36]. There is just one brief communication by Ghosh et al. [37] describing the importance of water traces in the insertion of CO_2 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_2 sequestration capability for synthetic purposes.

In this study we report a thorough IR and NMR characterization of the complex resulting from insertion of CO_2 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_2 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 without further purification. The actual dryness was checked by IR spectroscopy (see Fig. 1 curve a, and related comment). The CO_2 was purchased from Airliquide with a global purity of 99.998% (N48). CO_2 insertion occurred at atmospheric pressure and room temperature simply by bubbling CO_2 for 15 min through pure TTB. $^{13}\text{CO}_2$ was purchased by Icon Isotopes $^{13}\text{C}@99\text{atom}\%$. The reaction of $^{13}\text{CO}_2$ 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) $^{13}\text{CO}_2$ was admitted in the balloon; (iv) the balloon was shaken for 15 min.

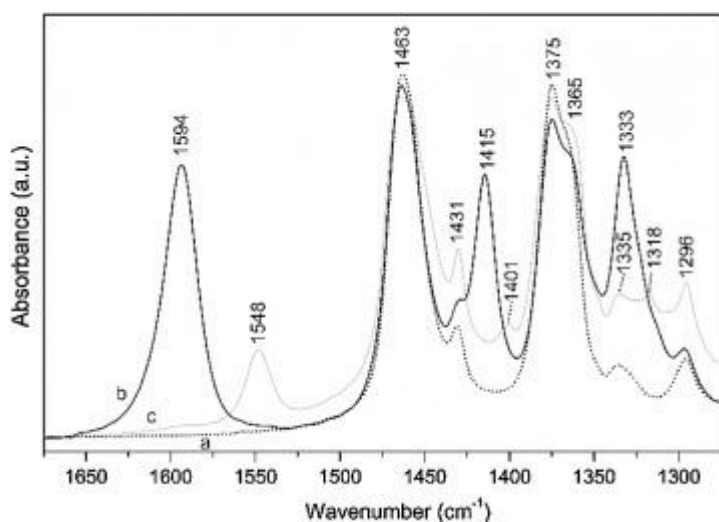


Fig. 1. IR spectra of TTB (a), after bubbling $^{12}\text{CO}_2$, [TTB- $^{12}\text{CO}_2$] (b) and after bubbling $^{13}\text{CO}_2$, [TTB- $^{13}\text{CO}_2$] (c).

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^{-1} , by accumulating 100 scans, to attain a good signal-to-noise ratio).

NMR spectra were recorded with a JEOL EX 400 spectrometer (^1H operating frequency 400 MHz) at 298 K; data were treated by Jeol Delta Software. ^1H and ^{13}C chemical shifts are relative to TMS ($\delta = 0\text{ ppm}$) and referenced against solvent residual peaks (CDCl_3 at 7.26 and 77.16 ppm for ^1H and ^{13}C , respectively).

n-Butylamine was dosed in molar ratio 4:1 in respect with Ti atoms in the TTB- CO_2 complex affording TTB- CO_2 -AM compound. Solutions resulting from TTB after interaction with CO_2 (TTB- CO_2) and from TTB after interaction with CO_2 and n-butylamine (TTB- CO_2 -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, $\text{Ti}(\text{OH})_4$, 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 $60\text{ }^\circ\text{C}$ 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 $\text{Ti}(\text{OH})_4$ was separately synthesized by hydrolysing pure TTB with distilled water and drying the obtained white solid. Thereafter, 1.5 g of $\text{Ti}(\text{OH})_4$ were dispersed in 150 mL of n-butanol at $60\text{ }^\circ\text{C}$ and CO_2 was bubbled through the suspension for 6 h. The suspension was then dried under vacuum at $60\text{ }^\circ\text{C}$ 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 $1675\text{--}1275\text{ cm}^{-1}$ range, different signals are present, assigned to the vibrations of the alkyl chains [41a]. No signal due to water bending mode, expected in the $1650\text{--}1620\text{ cm}^{-1}$ range, is observed. When CO_2 was bubbled in TTB liquid, new bands appeared located at 1594, 1415 and 1333 cm^{-1} (Fig. 1, curve b). The newly formed compound (TTB- $^{12}\text{CO}_2$) was stable against subsequent bubbling with argon (see Fig. S1 in the Supplementary material, hereafter SM). The same experiment was carried out by bubbling $^{13}\text{CO}_2$. Also in this case three new signals appeared, but downshifted to 1548, 1401 and 1318 cm^{-1} (Fig. 1, curve c). This proved the occurrence of the insertion of the carbon atom of CO_2 molecules in the newly formed species. Focussing back on the three new bands obtained for TTB- $^{12}\text{CO}_2$ species, their positions appeared similar to what reported for the $\text{—O}(\text{CO})\text{O—}$ moiety of monodentate methyl carbonate on ZrO_2 [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^{-1} pair and of a triatomic OCO oscillator for the 1415/1401 and 1333/1318 cm^{-1} pairs (see Table 1). A good agreement was found for both types of oscillators, indicating they should be only weakly coupled each other, in agreement with the supposed different bond order between the $\text{C}=\text{O}$ and $\text{O}-\text{C}-\text{O}$ moieties in the newly formed carbonate.

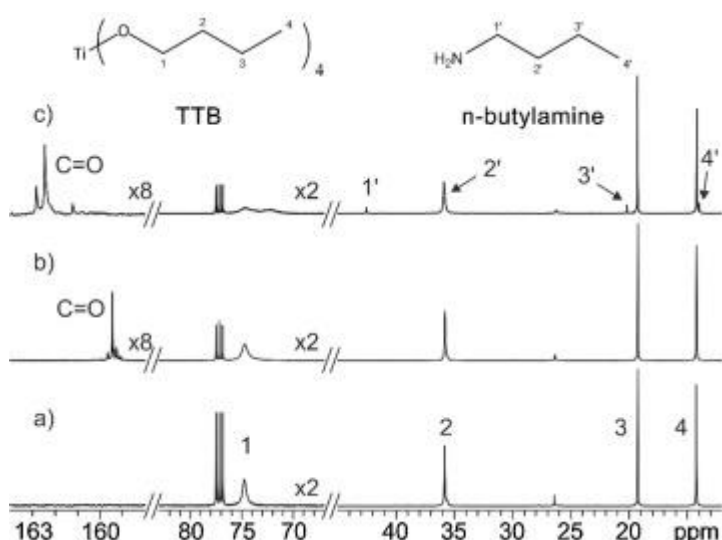
Table 1. Comparison of experimental and calculated isotopic shift.

Observed frequency ν_{CO} (cm^{-1})		Experimental isotopic ratio		Calculated isotopic ratio	
$^{12}\text{CO}_2$	$^{13}\text{CO}_2$	Formula	Value	Formula ^a	Value
1594	1548	$\nu_{^{13}\text{CO}}/\nu_{^{12}\text{CO}}$	0.9711	$\mu_{^{12}\text{CO}}/\mu_{^{13}\text{CO}}$	0.9777
1415	1401	$\nu_{\text{O}^{13}\text{CO}}/\nu_{\text{O}^{12}\text{CO}}$	0.9901	$\nu_{\text{O}^{13}\text{CO}}/\nu_{\text{O}^{12}\text{CO}}$	0.9850
1333	1318	$\nu_{\text{O}^{13}\text{CO}}/\nu_{\text{O}^{12}\text{CO}}$	0.9887	$\nu_{\text{O}^{13}\text{CO}}/\nu_{\text{O}^{12}\text{CO}}$	0.9850

a

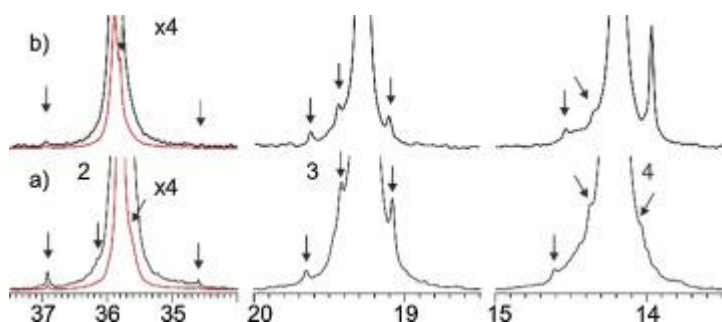
Reduced masses (μ) calculated accordingly to Ref. [41b].

In order to further elucidate the structure of the newly formed compounds, the product TTB- $^{13}\text{CO}_2$ was then analyzed by NMR spectroscopy. All ^{13}C chemical shifts and assignments are reported in Table S1 in the SM, whereas all the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra and a zoomed view of some aliphatic peaks are shown in Figs. 2 and 3, respectively. For atom numbering, we refer the reader to Scheme in Fig. 2. As expected, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of TTB does not present any signal in the carbonyl region (Fig. 2a). On the other hand, when $^{13}\text{CO}_2$ is bubbled (Fig. 2b), five new resonances appeared in the carbonyl region at 159.65, 159.44, 159.38, 159.25 and 159.07 ppm (see zoomed view in Fig. S2 in the SM). In the same time, in the aliphatic region, several small peaks/shoulders appeared close to the signals of unreacted TTB (Fig. 3a). This is in agreement with the formation of new species where the butoxide chains are still preserved although their chemical environment results slightly changed. Among the five new carbonyl species, one, characterized by the signal at 159.44 ppm, is the most abundant by far while the others are present in almost the same quantity. In agreement with IR data, the new carbonyl species arise from the CO_2 insertion between metal and butoxide ligands.



Download full-size image

Fig. 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of TTB (a), of TTB- $^{13}\text{CO}_2$ (b), of n-butylamine dosed on TTB- $^{13}\text{CO}_2$ (c). Upper part of the figure: structures with atom number for pure TTB and n-butylamine.



Download full-size image

Fig. 3. Aliphatic regions of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of TTB- $^{13}\text{CO}_2$ (a) and n-butylamine dosed on TTB- $^{13}\text{CO}_2$ (b). Arrows indicate peaks and shoulders attributed to the new achieved species.

Noteworthy, a signal at 159 ppm in ^{13}C NMR was observed by Ghosh et al. [37] for alkyl carbonates resulting from the insertion of CO_2 in titanium isopropoxide. Finally, the reaction of CO_2 on TTB is characterized by a low yield <10%; estimated from $^{13}\text{C}\{^1\text{H}\}$ no NOE (Nuclear Overhauser Effect) NMR spectra of $^{12}\text{CO}_2$ dosed on TTB (spectrum not shown). Such low value might depend in large extent on the gas-liquid regime adopted for carrying out the reaction and the limited bubbling time (15 min). Additionally, the anhydrous conditions adopted for the reaction indicate that the CO_2 insertion in TTB can occur in dry conditions, differently with what observed by Ghosh et al. in the case of Ti-isopropoxide [37]. In that case, the reactivity was ascribed to the presence of tetrameric Ti complexes, promoting the formation Ti-OC(OTi)-OR species.

At this stage monobutyl carbonate still linked to Ti atoms (see IR data and related comments) were formed. However, attempts to obtain dibutyl carbonate by further reaction with ButOH (adopting the procedure reported for the production of dimethyl carbonate [34]) were unsuccessful.

Thus, a further reaction pathway involving the C atoms from CO_2 in the TTB- CO_2 species was explored. Because of the importance of the formation of C—N bonds [40], the reactivity towards an amine, namely n-butylamine, was investigated.

Therefore, n-butylamine was added to TTB-CO₂ and the resulting IR spectrum is reported in Fig. 4, Panel A along with the one of TTB-CO₂.

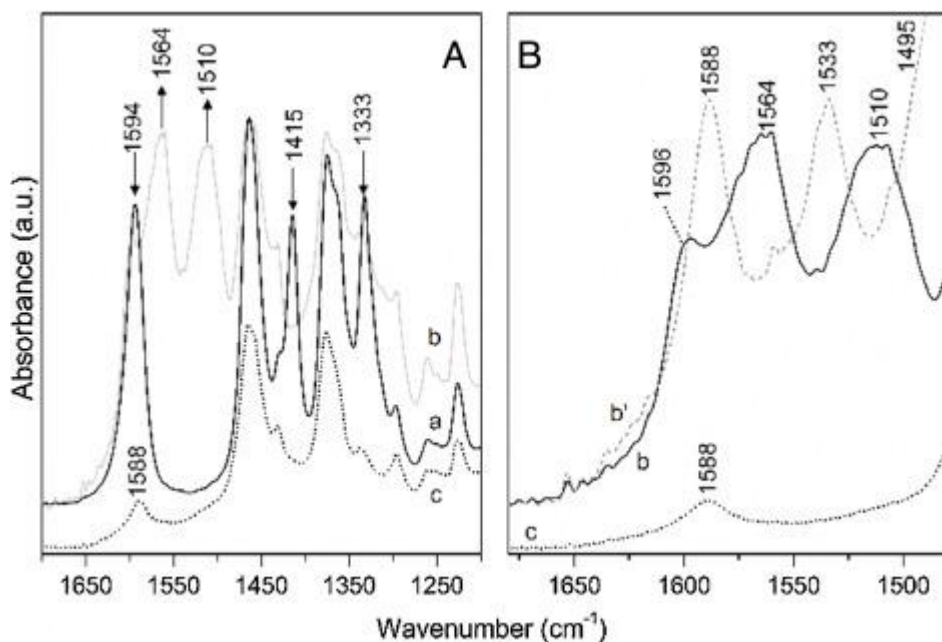


Fig. 4. Panel A: IR spectra of TTB-12CO₂ before (a) and after dosing n-butylamine [TTB-12CO₂-AM] (b). Curve (c): n-butylamine dosed on TTB [TTB-AM], for the sake of comparison. Panel B: IR spectra TTB-13CO₂-AM (b'); curves b and c the same as in Panel A.

The addition of amine molecules to TTB-12CO₂ resulted in the consumption of large part of signals at 1594, 1415, 1333 cm⁻¹ (curve a), which are converted in two new signals at 1564 and 1510 cm⁻¹ (curve b). New signals due to CH₃ and CH₂ groups appear, due to the alkyl chains of amine molecules in interaction with TTB (curve c). Moreover, the δ NH₂ band of possible unreacted amines should contribute to the high frequency shoulder of the peak at 1564 cm⁻¹. The reaction was tested also on TTB-13CO₂ and three new signals appeared at 1588, 1533 and 1495 cm⁻¹ (Panel B, curve b').

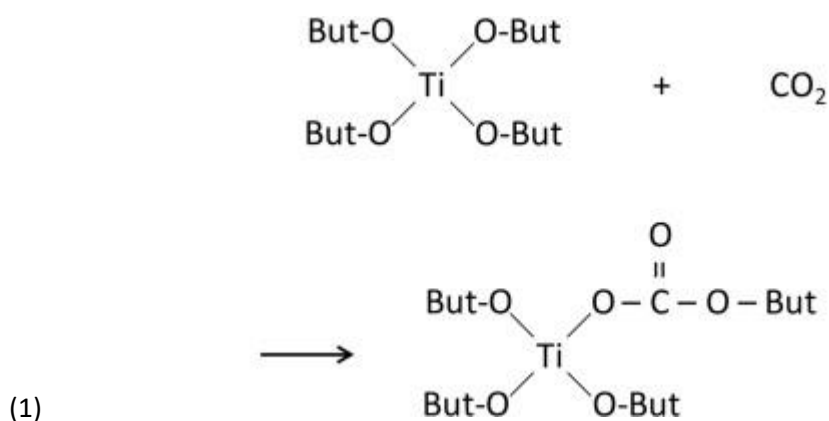
The first one corresponds to the δ NH₂ of n-butylamine in interaction with TTB (curve c), indicating the presence of unreacted amine molecules. The other two, downshifted with respect to the previous case, confirmed that some of the amine molecules reacted with ex CO₂ C atom in TTB-CO₂. In particular, these signals might be due to ν C=O (1564/1533 cm⁻¹) and ν C-N + δ CNH (1510/1495 cm⁻¹) of carbamate species. The position of the band assigned to ν C=O is rather lower than for molecular carbamates [41c], but it is proposed that this could be an effect of the coordination with Ti centres. Also in this case, the experimental isotopic ratio (0.9802 for the 1564/1533 cm⁻¹ pair) was in good agreement with the calculated one (0.9777; see Table 1), on the basis of a diatomic CO oscillator. Conversely, it was not possible to precisely identify the frequency of the shoulder located at ca. 1495 cm⁻¹, due to its overlapping with the signals of alkyl chains, thus preventing the calculation of the experimental isotopic ratio for the 1510/1495 cm⁻¹ pair.

The reaction between TTB-13CO₂ and amines was also monitored by NMR spectroscopy. By dosing n-butylamine on TTB-13CO₂, all carbonyl resonances around 159 ppm disappeared from the ¹³C{¹H} NMR spectrum (Fig. 2c). In the same time, 3 new signals appeared at 162.84, 162.48 and 161.24 ppm, with the second the most intense. The aliphatic region again is characterized by several small peaks/shoulders close to the signals of unreacted TTB (Fig. 3b) together with the signal of unreacted n-butylamine. The relevant change in the position of the carbonyl resonances are compatible with the insertion of the nitrogen atom in the TTB-CO₂ adducts to form carbamate species. Noteworthy, all carbonyl species are completely converted into new carbamate compounds with a 100% yield (likely an effect of the liquid-liquid regime).

On the other hand, blank experiments indicated that n-butylamine is not able to directly react with the unreacted TTB.

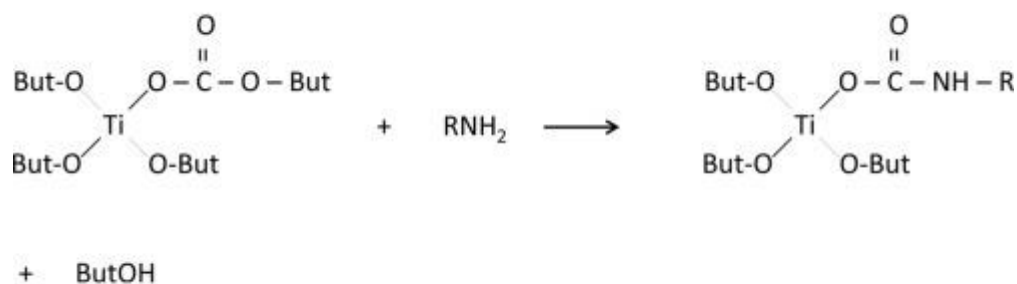
As the combined IR and NMR investigation pointed out the formation of organic carbonate- and then carbamates-like species, we then tried to extract the formed organic products (see Experimental). The separation of alkylcarbonates and carbamates is a challenging issue that requires specific efforts, as reported in a very recent paper [43]. However, the GC–MS analysis of the extracted products revealed only the presence of two peaks at m/z equal to 174 and 175 (Fig. S3 in the SM).

These mass signals may be attributed to formation of butylcarbamate and dibutylcarbonate considering the following proposed mechanism. Reaction of TTB with CO_2 produces metal organic carbonates, the most abundant of such species being schematically represented in Eq. (1).



By taking into consideration that the CO_2 insertion has an estimated yield lower than 10% and of the large excess of TTB, it is reasonable to suppose that butoxide ligands are still present in the TTB– CO_2 complex.

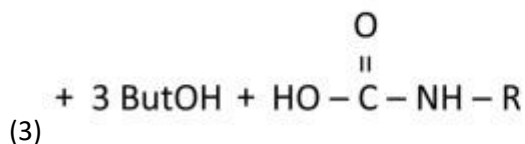
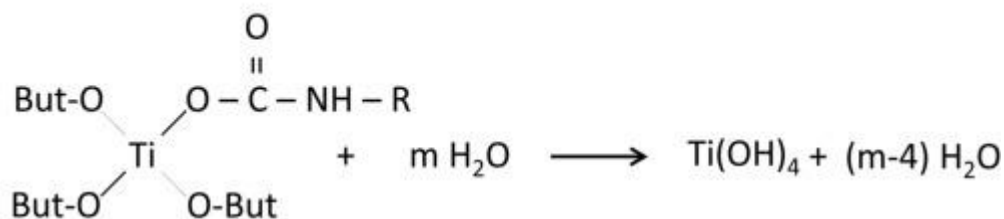
Nucleophilic attack of the amine molecule to the carbon atom deriving from CO_2 insertion gives rise to formation of a carbamate ligand as shown in Eq. (2).



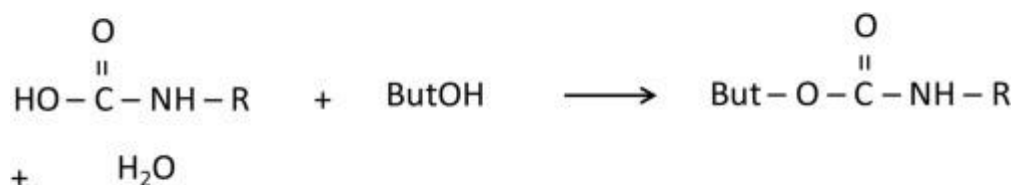
(2)

This reaction (R-NH_2 in large excess, where $\text{R} = \text{But}$) occurs with 100% yield as evidenced by NMR investigation, so that no metal organic carbonates are present in the solution.

Adding water produces hydrolysis of the complexes so that butanol and carbamic acids are produced along with titanium hydroxide, according to Eq. (3).

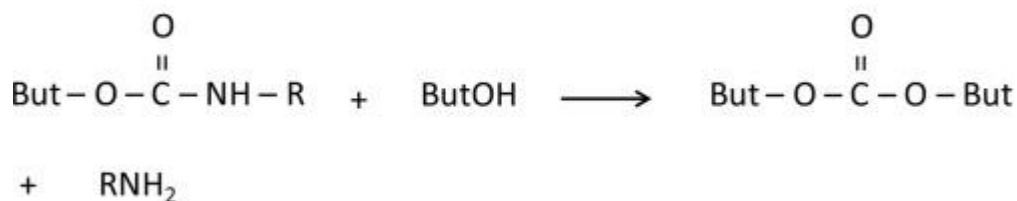


The instable carbamic acid formed easily reacts with butanol producing water and butylcarbamate (Eq. (4)) responsible for the mass signal at $m/z = 174$.



(4)

Further reaction between carbamate molecules and butanol (Eq. (5)) produces an amine molecule and dibutyl carbonate, as evidenced by the mass signal with $m/z = 175$.



(5)

A reaction similar to Eq. (5) is reported by Ball et al. [44] in the presence of catalysts possessing both weak acidic and basic Lewis properties. In this case the role of the solid Ti(OH)_4 as the catalyst for this reaction step cannot be excluded.

It is worth to note that, although the whole process is not catalytic as it implies destruction of the metal complex, the amine molecule is restored at the end of the process. The role of the amine molecule is essential in the production of DBC as it is necessary to obtain the carbamate key intermediate. Indeed, blank tests carried out in the absence of amine did not result in organic carbonate production. A direct production of DBC from CO_2 and butanol on the surface of the solid Ti(OH)_4 can be excluded as no DBC was detected by bubbling CO_2 in a butanol suspension of Ti(OH)_4 at 60°C .

4. Conclusions

The complex deriving from CO₂ insertion in titanium(IV) tetrabutoxide is for the first time thoroughly characterized by means of IR and NMR spectroscopies. Although the yield of CO₂ coordination is estimated to be quite low (ca. 10%), among the different coordination modes the carbonate-like species resulted the most abundant. Furthermore, reaction of an aliphatic amine with the coordinated CO₂ is hereby reported and the deriving C—N bond formation demonstrated. Hydrolysis of the resulting complex produced butyl carbamate and dibutyl carbonate as the only products detected by means of mass spectroscopy. A tentative mechanism for this reaction is proposed whereby the role of the amine molecule in formation of the key carbamate intermediate is highlighted. Although of difficult application, these basic results allow to shine some light on the chemistry and reactivity of carbon dioxide coordinated in metal complexes opening the route to new catalytic processes for organic carbonates production. In perspective, future developments could imply the study of the possible beneficial effect of trace amount of water in increasing the relative amount of carbonate-like species, and then, if successful, the set-up of proper separation procedures.

Acknowledgements

Dr. Roberto Buscaino and Dr. Claudio Magistris are kindly acknowledged for mass spectrometry analysis, MIUR-PRIN 2010–2011 (project no. 2010A2FSS9) and MIUR PON 01_02257 project for financial support.

References

- [1] A. Dibenedetto, A. Angelini *Adv. Inorg. Chem.*, 66 (2014), pp. 25-81
- [2] J.P. Parrish, R.N. Salvatore, K.W. Jung *Tetrahedron*, 56 (2000), pp. 8207-8237
- [3] B. Schaffner, F. Schaffner, S.P. Verevkin, A. Borner *Chem. Rev.*, 110 (2010), pp. 4554-4581
- [4] M. Bellardita, V. Loddo, A. Mele, W. Panzeri, F. Parrino, I. Pibiri, L. Palmisano *RSC Adv.*, 4 (2014), pp. 40859-40864
- [5] F. Ouyang, Z.Z. Wang, Y. Zhou, Z. Cheng, Z.H. Lu, Z. Yang, D.J. Tao *Appl. Catal. A-Gen.*, 492 (2015), pp. 177-183
- [6] K. Teranishi, T. Kayakiri, M. Mizutani, M. Hisamatsu, T. Yamada *Biosci. Biotechnol. Biochem.*, 58 (1994), pp. 1537-1539
- [7] V. Eta, P. Maki-Arvela, A.R. Leino, K. Kordas, T. Salmi, D.Y. Murzin, J.P. Mikkola *Ind. Eng. Chem. Res.*, 49 (2010), pp. 9609-9617
- [8] E. Leino, P. Maki-Arvela, V. Eta, D.Y. Murzin, T. Salmi, J.P. Mikkola *Appl. Catal. A-Gen.*, 383 (2010), pp. 1-13
- [9] M.E. Vol'pin, I.S. Kolomnikov *Pure Appl. Chem.*, 33 (1973), pp. 567-582
- [10] C.L. Boyd, E. Clot, A.E. Guiducci, P. Mountford *Organometallics*, 24 (2005), pp. 2347-2367
- [11] C.S. McCowan, T.L. Groy, M.T. Caudle *Inorg. Chem.*, 41 (2002), pp. 1120-1127
- [12] D.J. Darensbourg, K.M. Sanchez, J.H. Reibenspies, A.L. Rheingold *J. Am. Chem. Soc.*, 111 (1989), pp. 7094-7103
- [13] E.C.Y. Tam, N.C. Johnstone, L. Ferro, P.B. Hitchcock, J.R. Fulton *Inorg. Chem.*, 48 (2009), pp. 8971-8976
- [14] T. Tsuda, T. Saegusa *Inorg. Chem.*, 11 (1972), pp. 2561-2563

- [15] M.H. Chisholm, F.A. Cotton, M.W. Extine, W.W. Reichert *J. Am. Chem. Soc.*, 100 (1978), pp. 1727-1734
- [16] S.K. Mandal, D.M. Ho, M. Orchin *Organometallics*, 12 (1993), pp. 1714-1719
- [17] D.J. Darensbourg, W.Z. Lee, A.L. Phelps, E. Guidry *Organometallics*, 22 (2003), pp. 5585-5588
- [18] J.C. Choi, T. Sakakura, T. Sako *J. Am. Chem. Soc.*, 121 (1999), pp. 3793-3794
- [19] H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang *Angew. Chem. Int. Ed.*, 39 (2000), pp. 4096-4098
- [20] S.J. Archibald, S.P. Foxon, J.D. Freeman, J.E. Hobson, R.N. Perutz, P.H. Walton *J. Chem. Soc. Dalton* (2002), pp. 2797-2799
- [21] R.D. Simpson, R.G. Bergman *Organometallics*, 11 (1992), pp. 4306-4315
- [22] G.A. Razuvaev, L.I. Vyshinskaya, V.V. Drobotenko, G.Y. Mal'kova, N.N. Vyshinsky *J. Organomet. Chem.*, 239 (1982), pp. 335-343
- [23] M.H. Chisholm, K. Folting, J.C. Huffman, R.J. Tatz *J. Am. Chem. Soc.*, 106 (1984), pp. 1153-1154
- [24] T. Yamamoto, M. Kubota, A. Yamamoto *Bull. Chem. Soc. Jpn.*, 53 (1980), pp. 680-685
- [25] K. Tomishige, T. Sakaihorii, Y. Ikeda, K. Fujimoto *Catal. Lett.*, 58 (1999), pp. 225-229
- [26] X.L. Wu, M. Xiao, Y.Z. Meng, Y.X. Lu *J. Mol. Catal. A-Chem.*, 238 (2005), pp. 158-162
- [27] B.B. Fan, H.Y. Li, W.B. Fan, J.L. Zhang, R.F. Li *Appl. Catal. A-Gen.*, 372 (2010), pp. 94-102
- [28] D. Ballivet-Tkatchenko, T. Jerphagnon, R. Ligabue, L. Plasseraud, D. Poinot *Appl. Catal. A-Gen.*, 255 (2003), pp. 93-99
- [29] M. Abla, J.-C. Choi, T. Sakakura 50th Symposium on Organometallic Chemistry, Osaka, Japan (2003), p. PB233
- [30] T.S. Zhao, Y.Z. Han, Y.H. Sun *Fuel Process. Technol.*, 62 (2000), pp. 187-194
- [31] M. Aresta, A. Dibenedetto, C. Pastore *Inorg. Chem.*, 42 (2003), pp. 3256-3261
- [32] A. Dibenedetto, C. Pastore, M. Aresta *Catal. Today*, 115 (2006), pp. 88-94
- [33] J. Kizlink, I. Pastucha *Collect. Czech. Chem. C*, 60 (1995), pp. 687-692
- [34] K. Kohno, J.C. Chol, Y. Ohshima, H. Yasuda, T. Sakakura *ChemSusChem*, 1 (2008), pp. 186-188
- [35] R. Ghosh, A.G. Samuelson *Chem. Commun.* (2005), pp. 2017-2019
- [36] T. Nakanishi *Kobunshi Ronbunshu*, 58 (2001), pp. 710-713
- [37] R. Ghosh, M. Nethaji, A.G. Samuelson *Chem. Commun.* (2003), pp. 2556-2557
- [38] M. Aresta, A. Dibenedetto, E. Quaranta *Green Chem.*, 1 (1999), pp. 237-242
- [39] M. Selva, P. Tundo, A. Perosa *Tetrahedron Lett.*, 43 (2002), pp. 1217-1219
- [40] Z.Z. Yang, L.N. He, J. Gao, A.H. Liu, B. Yu *Energy Environ. Sci.*, 5 (2012), pp. 6602-6639
- [41] (a) N.B. Colthup, L.H. Daly, S.E. Wiberley *Introduction to Infrared and Raman Spectroscopy* (second edition), Academic Press, New York (1975), p. 225 (b) N.B. Colthup, L.H. Daly, S.E. Wiberley *Introduction to Infrared and Raman Spectroscopy* (second edition), Academic Press, New York (2015), p. 179 (c) N.B.

Colthup, L.H. Daly, S.E. Wiberley Introduction to Infrared and Raman Spectroscopy (second edition), Academic Press, New York (2015), p. 308

[42] K.T. Jung, A.T. Bell J. Catal., 204 (2001), pp. 339-347

[43] P.X. Wang, S.M. Liu, L.J. Lu, X.Y. Ma, Y.D. He, Y.Q. Deng Rsc. Adv., 5 (2015), pp. 62110-62115

[44] P. Ball, H. Füllmann, W. Heitz Angew. Chem. Int. Ed., 19 (1980), pp. 718-720