

## Research Article

# Synthesis and Characterization of Heterometallic Ca(II)-Ti(IV)- $\mu$ -Oxomixedisopropoxide

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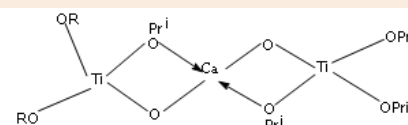
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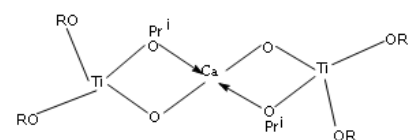
## Abstract

The cyclopentanol, cyclohexanol and cycloheptanol derivatives of heterobimetallic- $\mu$ -oxoisopropoxide  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$  have been prepared as a result of many reactions of  $\mu$ -oxoisopropoxide with cyclopentanol (HCA<sup>1</sup>), cyclohexanol (HCA<sup>2</sup>), and cycloheptanol (HCA<sup>3</sup>) in different molar ratios (1:1-1:4). The derivatives of the type  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_{6-n}(\text{CA})_n]$  (where n is 1-4 and CA = cycloalkanol anion) were obtained. The cycloalkanol derivatives have been characterized by elemental, spectral (IR, <sup>1</sup>H, <sup>13</sup>C NMR), thermal and molecular weight measurement. Hydrothermally assisted sol-gel process gives the hydrolyzed product and thermal study of these products favors the formation of multicomponent oxides. The studies reveal that derivatives are monomeric in nature and low susceptible to hydrolysis as compared to parent compound and may prove excellent precursors for the mixed metal oxides.

**Keywords:** Heterobimetallic- $\mu$ -oxoisopropoxide; Calcium; Titanium; cycloalkanol; thermoanalysis



Suggested structure of  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{RSAL})_2]$



Suggested structure of  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{CA})_4]$  (CA=OR)

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## Introduction

The control of particle size and the morphology of the oxide are of crucial importance nowadays both from the fundamental and industrial point of view [1]. The mixed metal oxides prepared from heterometallic- $\mu$ -oxoalkoxides [2-5] have been used for absorbing harmful chemicals [6] and decontaminating chemical warfare agents [7]. The investigation and the use of heterometallic alkoxides as single-source molecules precursors for synthesis of oxides have seen a rapid growth during the last more than one and half decade. The bimetallic oxo complexes, the true precursors play a significant role in the phase formation of complex oxides. The M-O-M bridges in bimetallic oxo complexes provide homogeneity of the newly formed oxide phases at the molecular level. The above-considered peculiarity in the composition, stoichiometry, solubility and reactivity of ortho- and oxoalkoxides are widely used in the sol-gel synthesis of a series of very important composites [8]. Nano-structured oxide, the new type of materials shows properties different from materials with  $\mu\text{m}$ -scale microstructures are gaining more and more interests during the past few years. A variety of chemical routes have been developed to prepare ceramic nano-structures, because the traditional solid-state method could not meet particle size requirements and versatility of synthesis process. Some chemical methods offer possibly a preparation at lower temperatures, a homogenous primary structure and limited higher order aggregation and a small distribution of particle sizes. The alkaline earth metal titanates like barium titanate, calcium titanate ( $\text{CaTiO}_3$ ), strontium titanate ( $\text{SrTiO}_3$  and  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ) due to their exceptional properties expose potential applications in multilayer ceramic capacitors, electro-optic, dielectric and piezoelectric devices [9-12]. The perovskite  $\text{CaTiO}_3$  with its unique structure, higher stability and biocompatibility, finds potential application

in the fields of communication, electronics and in biotechnology [13–15]. The ability of immobilizing the rare earths of  $\text{CaTiO}_3$  by forming solid solutions with highly radioactive wastes makes the  $\text{CaTiO}_3$  useful for disposal of highly radioactive wastes [16, 17]. Recently, calcium titanate has also been used as a competent anticorrosion pigment for paints [18]. Apart from their role as precursors for mixed metal oxides, the bimetallic- $\mu$ -oxoalkoxides of transition metals have been found to rank among the excellent catalysts for the polymerization of heterocyclic monomers like lactones, oxiranes, thiiranes and epoxides [19, 20].

In the present investigation, the derivatives of heterobimetallic  $[\text{Ca(II)-Ti(IV)}]_{\mu}\text{-oxoisopropoxide}$  are prepared from the condensation of  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$  with different Cycloalkanols in molar ratios (1:1–1:4), and the reaction proceeds with stepwise formation of Cycloalkanol derivatives of bimetallic  $[\text{Ca(II)-Ti(IV)}]_{\mu}\text{-oxoisopropoxide}$ , which are the molecular species that can be purified by distillation, allowing the isolation of pure molecular precursors.

## Experimental

### *Instrumentation, Reagents and general techniques*

All the operations were carried out in dry nitrogen atmosphere using a vacuum line. Hydrocarbon solvents and reagents used were purified and dried by standard methods. The general technique and physical measurement were carried out as described elsewhere [21–26]. Hydrated calcium acetate (Aldrich) was made anhydrous with acetic anhydride and titanium isopropoxide  $[\text{Ti}(\text{OPr}^i)_4]$  (Aldrich) used without further purification. The cyclopentanol ( $\text{HCA}^1$ ), ethyl cyclohexanol ( $\text{HCA}^2$ ), and cycloheptanol ( $\text{HCA}^3$ ) were purchased from Ranbaxy and purified before use. The isopropoxy groups in the  $\mu$ -oxoisopropoxide and liberated isopropanol formed in preparation of cycloalkanol derivatives were estimated oxidimetrically. Calcium was determined complex metrically and gravimetric estimation has been done for titanium [25]. Titanium was estimated as  $\text{TiO}_2$  via the formation of titanium-phenazone complex [25]. Perkin-Elmer 1710 FTIR spectrometer over the range  $4000\text{--}400\text{ cm}^{-1}$  used to record the Infrared spectra. The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on Bruker Avance II 400 NMR spectrometer. TG study has been made on Diamond TG/DTA PerkinElmer instrument. Elemental analyses were carried out by PerkinElmer 2400 II series CHNS/O Analyzer.

### *Synthesis of derivatives of $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$ with Cycloalkanols*

The  $[\text{Ca(II)-Ti(IV)}]_{\mu}\text{-oxoisopropoxide}$  was synthesized by reported methods on thermal condensation of  $\text{Ca}(\text{OAc})_2$  and  $\text{Ti}(\text{OPr}^i)_4$  in mixture of xylene and decalin in 1:2 molar ratio [21–24].

*Reaction of  $\mu$ -oxo compound with methyl cycloalkanol in 1:1 molar ratio:* The  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$  (0.666 g, 1.282 mmol) and cyclopentanol (0.195g, 1.282 mmol) were refluxed in benzene were refluxed in ~ 50 ml benzene in a flask connected to a short distillation column on an oil bath for about 7 h. The isopropanol liberated at  $72\text{--}78\text{ }^\circ\text{C}$  was fractionated as the binary azeotrope of isopropanol-benzene. The azeotrope was collected and checked for completion of the reaction. The excess of the solvent was then removed under reduced pressure yielding a yellowish semi-solid product. The syntheses of other cycloalkanol derivatives were carried out by similar procedure and the analytical results have been summarized in **Table 1**.

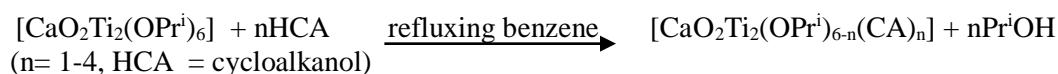
The hydrolyzed product of cycloalkanols of  $\mu$ -oxo compound obtained by hydrothermally assisted sol-gel processing. For the hydrothermally assisted sol-gel processing, cycloalkanol derivatives were diluted 20 times by weight with isopropanol, the mixture was loaded into a glass container and transferred into a 300 ml stainless steel autoclave. Dilution of cycloalkanol derivatives and their transfer into autoclave was performed in moisture-free atmosphere to prevent their hydrolysis before introducing into a hydrothermal chamber. The gap between glass container and chamber was filled with 40 ml of distilled water and then the autoclave was tightly closed. The chamber was heated  $120\text{ }^\circ\text{C}$  for five hours, the autoclave was cooled and the product was filtered off and dried overnight at  $100\text{ }^\circ\text{C}$ .

**Table 1** Analytical and physical data of studied compounds

S. No.	Compound g(mmol)	Ligand g(mmol)	Refluxing time(h)	Product (%)	Anal. Found (calcd.)					
					OPr <sup>i</sup> (g)	Ca (%)	Ti (%)	C (%)	H (%)	O (%)
1	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.717 (1.38)	HCA <sup>1</sup> 0.141 (1.63)	8	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>5</sub> (CA <sup>1</sup> ) <sub>1</sub> ] 78.6	0.03 (0.03)	7.57 (7.42)	18.84 (18.78)	42.68 (42.35)	8.58 (8.51)	17.57 (17.34)
2	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.746 (1.435)	HCA <sup>1</sup> 0.271 (2.98)	9½	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> (CA <sup>1</sup> ) <sub>2</sub> ] 79.4	0.06 (0.06)	6.87 (6.72)	17.57 (17.66)	46.44 (45.71)	8.48 (8.37)	16.81 (16.0)
3	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.688 (1.323)	HCA <sup>1</sup> 0.385 (3.97)	10	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (CA <sup>1</sup> ) <sub>3</sub> ] 81.2	0.09 (0.09)	6.69 (6.58)	16.69 (16.54)	48.67 (48.67)	8.49 (8.43)	15.87 (15.7)
4	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.608 (1.17)	HCA <sup>1</sup> 0.434 (4.68)	12	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>2</sub> (CA <sup>1</sup> ) <sub>4</sub> ] 78.6	0.11 (0.12)	6.89 (6.81)	15.32 (15.12)	50.34 (51.94)	8.52 (8.5)	15.27 (15.11)
5	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.647 (1.245)	HCA <sup>2</sup> 0.138 (1.38)	7	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>5</sub> (CA <sup>2</sup> ) <sub>1</sub> ] 78.6	0.03 (0.03)	7.08 (7.14)	16.94 (16.78)	44.51 (45.0)	8.16 (8.21)	16.97 (17.14)
6	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.611 (1.175)	HCA <sup>2</sup> 0.287 (2.87)	8½	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> (CA <sup>2</sup> ) <sub>2</sub> ] 79.4	0.06 (0.06)	6.57 (6.66)	15.67 (15.66)	48.24 (48.0)	8.31 (8.33)	16.21 (16.0)
7	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.599 (1.152)	HCA <sup>2</sup> 0.397 (3.97)	11	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (CA <sup>2</sup> ) <sub>3</sub> ] 81.2	0.09 (0.09)	6.14 (6.25)	14.65 (14.68)	50.48 (50.62)	8.38 (8.43)	14.87 (15.0)
8	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.567 (1.092)	HCA <sup>2</sup> 0.468 (4.68)	14	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>2</sub> (CA <sup>2</sup> ) <sub>4</sub> ] 78.6	0.11 (0.12)	5.77 (5.88)	13.78 (13.82)	52.69 (52.94)	8.53 (8.52)	14.07 (14.11)
9	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.647 (1.245)	HCA <sup>3</sup> 0.142 (1.245)	6	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>5</sub> (CA <sup>3</sup> ) <sub>1</sub> ] 79.3	0.03 (0.03)	6.59 (6.96)	16.35 (16.37)	45.74 (45.99)	8.14 (8.36)	16.64 (16.72)
10	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.611 (1.175)	HCA <sup>3</sup> 0.268 (2.350)	9	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> (CA <sup>3</sup> ) <sub>2</sub> ] 77.8	0.06 (0.06)	6.29 (6.36)	14.87 (14.97)	49.57 (49.68)	8.5 (8.59)	15.14 (15.28)
11	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.599 (1.152)	HCA <sup>3</sup> 0.394 (3.456)	10½	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>3</sub> (CA <sup>3</sup> ) <sub>3</sub> ] 79.7	0.09 (0.09)	4.84 (4.81)	13.84 (13.78)	52.73 (52.78)	8.76 (8.79)	13.87 (14.07)
12	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> ] 0.567 (1.092)	HCA <sup>3</sup> 0.498 (4.368)	13	[CaO <sub>2</sub> Ti <sub>2</sub> (OPr <sup>i</sup> ) <sub>4</sub> (CA <sup>3</sup> ) <sub>4</sub> ] 75.8	0.11 (0.12)	4.69 (4.54)	12.71 (12.77)	55.24 (55.43)	8.79 (8.96)	12.96 (13.04)

## Results and Discussion

A number of reactions of [Ca(II)-Ti(IV)]- $\mu$ -oxoisopropoxide were carried out with cycloalkanol (HCA) i.e. cyclopentanol (HCA<sup>1</sup>), cyclohexanol (HCA<sup>2</sup>), cycloheptanol (HCA<sup>3</sup>) in different molar ratios in refluxing benzene, yielding the products of type [CaO<sub>2</sub>Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>5</sub>(CA)], [CaO<sub>2</sub>Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>(CA)<sub>2</sub>], [CaO<sub>2</sub>Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>3</sub>(CA)<sub>3</sub>] and [CaO<sub>2</sub>Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>2</sub>(CA)<sub>4</sub>]. The preparation of the Cycloalkanol derivatives of [CaO<sub>2</sub>Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>6</sub>] follows the following reaction *scheme 1*:



### Scheme 1

The  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$  and its cycloalkanol derivatives are susceptible to hydrolysis and soluble in common organic solvents such as benzene, chloroform and carbon tetrachloride etc. The isopropanol liberated during the course of the reaction was collected azeotropically (isopropanol-benzene) and estimated oxidimetrically to check the progress of the reaction. It was observed that only four out of the six isopropoxy groups of  $[\text{Ca}(\text{II})\text{-Ti}(\text{IV})]\text{-}\mu\text{-oxoisopropoxide}$  could be replaced by cycloalkanol. Further replacement of isopropoxy groups could not be achieved even with an excess of ligand (cycloalkanol) and prolonged refluxing time (26 h). This indicates the non-replacement of bridging isopropoxy groups and that only terminal isopropoxy groups are substituted by cycloalkanol.

### Spectral Analysis of Cycloalkanol derivatives of $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$

#### IR Spectra

IR spectra of  $[\text{Ca}(\text{II})\text{-Ti}(\text{IV})]\text{-}\mu\text{-oxomixedalkoxides}$  mixed have been studied and important bands have been tentatively assigned contributing to assigning the structure of  $[\text{Ca}(\text{II})\text{-Ti}(\text{IV})]\text{-}\mu\text{-oxomixedisopropoxides}$  are discussed as follows.

The strong bands observed at  $1610\text{ cm}^{-1}$  and  $1435\text{ cm}^{-1}$  due to asym  $\text{C}=\text{O}$  and sym  $\text{C}=\text{O}$  stretch in the IR spectrum of calcium acetate are found absent in the spectrum of  $[\text{Ca}(\text{II})\text{-Ti}(\text{IV})]\text{-}\mu\text{-oxoisopropoxide}$  indicates the complete removal of acetate groups in  $\mu\text{-oxo}$  compound. The spectrum of the  $\mu\text{-oxoisopropoxide}$  shows absorption bands at  $\sim 1360\text{ cm}^{-1}$  and  $\sim 1165\text{ cm}^{-1}$  are the characteristics of *gem*-dimethyl portion and combination band  $\nu(\text{C-O+OPr}^i)$  of the terminal and bridging isopropoxy group respectively. A band appearing at approximately  $950\text{ cm}^{-1}$  is assigned to  $\nu(\text{C-O})$  stretching of bridging isopropoxy group. A number of vibrations are observed in the region  $700\text{-}400\text{ cm}^{-1}$  due to M-O stretching vibrations in  $\mu\text{-oxo}$  compound.

The IR spectra cyclic alcohol derivatives of  $[\text{Ca}(\text{II})\text{-Ti}(\text{IV})_6]$  show absorption bands in the region  $1360\text{-}1340\text{ cm}^{-1}$  which are the characteristics of *gem*-dimethyl portion of isopropoxy group. A number of bands are observed in the range of  $1165\text{-}1150\text{ cm}^{-1}$  and  $1135\text{-}1115$  due to combination bands  $\nu(\text{C-O+OPr}^i)$  of the terminal and bridging isopropoxy group respectively. No peak is observed at  $1165\text{ cm}^{-1}$  in the spectrum of 1:4 derivative of  $\mu\text{-oxo}$  compound indicates the absence of terminal isopropoxy group. A band appeared at approximately  $950\text{-}925\text{ cm}^{-1}$  is due to  $\nu(\text{C-O})$  stretching of bridging isopropoxy group. A broad band observed at  $\sim 3350\text{ cm}^{-1}$  in the spectra of cyclic alcohols due to  $\nu(\text{O-H})$  stretch is found absent in the spectra of  $\mu\text{-oxomixedalkoxides}$  indicates the deprotonation of cyclic alcohols. A number of vibrations are observed in the region  $700\text{-}400\text{ cm}^{-1}$  are due to M-O stretching in  $\mu\text{-oxo}$  compound and its cycloalcoholates [27–29].

#### NMR spectra

$^1\text{H}$  NMR spectra of all the cycloalkanol derivatives of  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$  show broad multiplet centered between  $\delta 0.7\text{-}1.3$  ppm due to the intermixing of methyl protons of isopropoxy groups. A broad multiplet centered at  $\delta 3.8\text{-}4.2$  is due to the methine proton of isopropoxy groups in the spectra of all derivatives. Very similar spectra obtained for compounds formed by reactions of 1:5 and 1:6 molar ratios of  $\mu\text{-oxo}$  compound and cycloalkanols as of 1:4 cycloalkanol derivatives of  $\mu\text{-oxoisopropoxide}$ . This confirms the non-replacement of bridging isopropoxy groups by Cycloalkanols.

The  $^1\text{H}$  NMR spectra of cycloalkanols show a broad singlet at  $\sim \delta 12.9$  ppm due to phenolic O-H proton, the absence this peak in the derivatives confirms their deprotonation. The peak at  $\sim \delta 3.9$  ppm due to methyl protons of methyl cycloalkanol and methene proton of the ethyl cycloalkanol is found to overlap with the multiplet centered at  $\delta 4.2$  ppm due to methine protons of the isopropoxy group in the derivatives of  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$ . A broad doublet centered at  $\sim \delta 1.2$  ppm is observed in mono to tri derivatives is due to the methyl protons of different types of isopropoxy groups (terminal and intramolecularly bridged). However, a fairly sharp doublet at  $\delta 1.1$  ppm is observed in methyl and phenyl cycloalkanol tetra derivatives indicate the presence of only one type of isopropoxy group/s

(probably bridging). In case of ethyl cycloalkanol derivatives the methyl protons are mixed with the methyl protons of the isopropoxy group resulting in a broad peak centered at  $\delta$  1.1 ppm.

The  $^{13}\text{C}$  NMR spectra mono derivatives of  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_6]$  shows two prominent peaks at  $\delta \sim 25.8$  and  $\delta \sim 27.7$  ppm assignable to the methyl carbon of terminal and intermolecularly bridged isopropoxy moiety and two different type of methine carbons of isopropoxy group is confirmed by the two signals observed at  $\delta \sim 62.8$  ppm and  $\delta \sim 64.1$  ppm [30]. The spectra of 1:4 cycloalkanol derivatives of  $\mu$ -oxoisopropoxide show the absence of terminal isopropoxy group. Very similar spectra obtained for compounds formed by reactions of 1:5 and 1:6 molar ratios of  $\mu$ -oxo compound and cycloalkanols as of 1:4 cycloalkanol derivatives of  $\mu$ -oxoisopropoxide. This confirms the non-replacement of bridging isopropoxy groups by Cycloalkanols.

### Thermal Studies

The thermal decomposition of cycloalkanol derivatives of  $[\text{CaO}_2\text{Ti}(\text{OPr}^i)_4]$  have been examined by thermogravimetric analysis under a flow of dry nitrogen, up to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The minor weight loss (1.84-2.12 %) starts at  $55\text{-}58^\circ\text{C}$  and completed at  $183\text{-}191^\circ\text{C}$  with a weight loss of due to presence of moisture and fraction of solvent present, if any. The second and major one starts at  $184\text{-}192^\circ\text{C}$  and is completed at  $362\text{-}365^\circ\text{C}$ , resulting in a residue amounting to 13.254-15.971% of the initial weight, probably due to the decomposition of partially hydrolyzed  $\mu$ -oxo cycloalkanol into metal/mixed metal oxides suggesting the volatile nature of compound [31].

The thermogravimetric analysis of various hydrolyzed product of different cycloalkanol derivatives have been performed up to  $800^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ . Thermograms of various hydrolysed Cycloalkanol derivatives studied as, the weight loss in stage (a) observed due to the traces of water and solvent present in hydrolyzed product of  $\mu$ -oxo compound. The major weight loss in stage (b) occurs probably due to the elimination of hydroxy groups and organic moieties present in the hydrolyzed product which is directly followed by last stage (c) ranging from  $342\text{-}360^\circ\text{C}$  to  $800^\circ\text{C}$ , leaving a residue that is less than the calculated for mixed metal oxide and metal oxides ( $\text{CaTiO}_3$  and  $\text{TiO}_2$ ). The detailed study of thermograms of hydrolyzed product of various Cycloalkanol derivatives is summarized in **Table 2**. The molecular weight measurement carried out in dry benzene using cryoscopic method suggests monomeric nature of cycloalkanol derivatives.

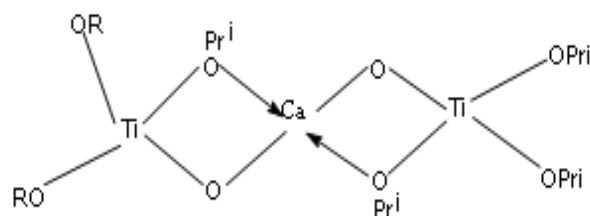
### Conclusion

The aforementioned studies reveals the suggestive structures of cycloalkanol derivatives of oxo complex of the type  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{CA})]$ ,  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{CA})_2]$ ,  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{CA})_3]$  and  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{CA})_4]$ . TGA study reveals the volatile nature of derivatives and their hydrolysed product may fabricate the mixed metal oxides. The proposed structures double and terta derivatives are given in **Figure 1** and **Figure 2** respectively.

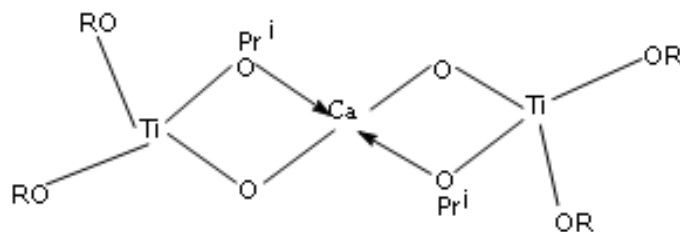
**Table 2** Study of thermograms of hydrolyzed product of various Cycloalkanol derivatives of  $[\text{CaO}_2\text{Ti}(\text{OPr}^i)_4]$

Sr. No.	Compound	Temperature range ( $^\circ\text{C}$ )	Weight loss (%)
1.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{CA}^1)]$	(a) 55-225	(a) 5
		(b) 225-355	(b) 42.41
		(c) >355	(c) No significant loss
2.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{CA}^1)_2]$	(a) 54-224	(a) 6
		(b) 224-351	(b) 53.39
		(c) >349	(c) No significant loss
3.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{CA}^2)_3]$	(a) 59-225	(a) 5
		(b) 225-356	(b) 60.89
		(c) >356	(c) No Significant loss

4.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{CA}^1)_4]$	(a) 53-222 (b) 222-357 (c) >357	(a) 5 (b) 67.52 (c) No significant loss
5.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{CA}^2)]$	(a) 57-224 (b) 224-348 (c) >348	(a) 4 (b) 43.25 (c) No significant loss
6.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{CA}^2)_2]$	(a) 54-229 (b) 229-357 (c) >357	(a) 5 (b) 53.23 (c) No significant loss
7.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{CA}^2)_3]$	(a) 55-224 (b) 224-352 (c) >352	(a) 5 (b) 63.58 (c) No significant loss
8.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{CA}^2)_4]$	(a) 57-230 (b) 230-359 (c) >359	(a) 4 (b) 70.98 (c) No significant loss
9.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_5(\text{CA}^3)]$	(a) 53-229 (b) 229-349 (c) >349	(a) 6 (b) 46.75 (c) No significant loss
10.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{CA}^3)_2]$	(a) 54-226 (b) 226-353 (c) >353	(a) 6 (b) 59.7 (c) No significant loss
11.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_3(\text{CA}^3)_3]$	(a) 57-222 (b) 222-358 (c) >358	(a) 6 (b) 67.99 (c) No Significant loss
12.	$[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{CA}^3)_2]$	(a) 55-227 (b) 227-360 (c) >360	(a) 5 (b) 71.54 (c) No significant loss



**Figure 1** Suggested structure of  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_4(\text{CA})_2]$  ( $\text{CA}=\text{OR}$ )



**Figure 2** Suggested structure of  $[\text{CaO}_2\text{Ti}_2(\text{OPr}^i)_2(\text{CA})_4]$  ( $\text{CA}=\text{OR}$ )

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