Decomposition of Coordinated Acetylacetonate in Lead Zirconate Titanate (PZT) Precursor Solutions

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Introduction

Metal−organic chemical vapor deposition (MOCVD) and sol−gel processing are two increasingly important processes used in the preparation of speciality ceramics and electronically or optically active thin films. There has been a substantial effort to develop stable metal complexes which can be routinely used in these applications without recourse to special processing conditions. Acetylacetone (acacH) and a wide range of analogues have often been used as chelating ligands or modifiers to stabilize the solution against hydrolysis. For example, acac complexes of titanium and zirconium were used in recent studies[1−5] of lead titanate (PT) and lead zirconate titanate (PZT) precursor solutions. These were subjected to refluxing in a range of diols to give reproducible sols which were suitable for thin film deposition, and which exhibited long-term stability. The reactions between the diol and the metal complexes, however, are not well characterized. Part of our interest lies in the chemistry occurring prior to sol formation in this and related sol precursor systems, and in particular in determining the fate of the acac ligands. This paper describes the initial reactions occurring between some titanium or zirconium acac complexes with refluxing alcohols or diols. By following the decomposition processes by NMR and GC we have identified the reaction products and arrived at a reasonable mechanism to explain our observations. Throughout this work, we have attempted to avoid the presence of moisture, hydroxo anions, and oxo species, to simplify the reactions and rule them out as possible vectors in the reaction.

Experimental Section

All syntheses were carried out under an atmosphere of dry nitrogen. ^{1}H and ^{13}C NMR were recorded using a Bruker AC300 NMR Spectrometer. Samples were dissolved in $CDCl_3$ and $SiMe_4$ was used as an internal reference. Titanium di(isopropoxide) bis(acetylacetonate), 75% solution in 2-propanol (Aldrich) was used as supplied. Alcohols and diols were dried and distilled using standard techniques. Reactions of metal complexes with alcohols and diols employed a common methodology and representative examples are described below. Products were identified from ^{1}H and ^{13}C NMR spectra and gas chromatography data which were compared to reference samples. A Pye Unicam 4550 Gas Chromatograph was employed, equipped with a nonpolar methylsilicone (DB-1) 30 m column with 0.53 mm internal diameter, and flame intensity detector.

Reaction of $Ti(OPr^i)_2(acac)_2$ with 1,3-Propanediol (1). 1,3-Propanediol (1.52 g, 0.02 mol) was added to titanium di(isopropoxide) bis(acetylacetonate), $Ti(OPr^i)_2(acac)_2$ (9.71 g of a 75% solution, 0.02 mol), with vigorous stirring to ensure rapid mixing of the reagents. After stirring at room temperature for 16 h, a sample was taken to record ^{1}H and ^{13}C NMR spectra. The reaction was heated in a distillation apparatus for 4 h, and the solvent fraction boiling <80 °C was removed. ^{1}H and ^{13}C NMR spectra were recorded for the distillate and remaining reaction mixture. The reaction mixture appeared as a clear orange solution, which became slightly cloudy on cooling. Heating to >150 °C in vacuo failed to remove any other volatiles.

Reaction of $Ti(OPr^i)_2(acac)_2$ with 1,3-Propandiol (2). 1,3-Propanediol (10 g) was added to $Ti(OPr^i)_2(acac)_2$ (9.71 g of a 75% solution, 0.02 mol) with vigorous stirring to ensure rapid mixing of the reagents. After stirring at room temperature for 16 h, a sample was taken to record ^{1}H and ^{13}C NMR spectra. The reaction was heated in a distillation apparatus for 4 h, and the solvent fraction boiling <80 °C was removed. ^{1}H and ^{13}C NMR spectra were recorded for the distillate and remaining reaction mixture. Vacuum distillation of the higher boiling solvent was carried out to 55 °C at 0.2 mbar. ^{1}H and ^{13}C NMR spectra were recorded for the distillate. The remaining white precipitate was washed with dry ethanol and dried in vacuo. Anal. Calcd for $C_6H_{12}O_4Ti$: C, 36.8; H, 6.2. Found C, 37.0; H, 6.5.

Reaction of $Zr(acac)_4$ with *n*-Propanol. Zirconium tetrakis(acetylacetonate), $Zr(acac)_4$ (6.1 g, 12.5 mmol), was refluxed in *n*-propanol (15 mL) for 4 h. On cooling, ^{1}H and ^{13}C NMR spectra were recorded. The volatile products were distilled off, and ^{1}H and ^{13}C NMR spectra were recorded for the distillate and remaining reaction mixture. No $Zr(acac)_4$ remained in the reaction mixture.

Discussion

A PZT precursor solution was prepared according to the method of Calzada and Milne[4] such that a lead precursor prepared from lead acetate trishydrate $Pb(OAc)_2{\cdot}3H_2O$ and 1,3-propanediol was added to a solution prepared from $Ti(acac)_2(OPr^i)_2$ and $Zr(acac)_4$ in 1,3-propanediol. The volatile fraction of the solvent was distilled off as prescribed (bp <80 °C) and subjected to NMR and GC studies. Further distillates were removed under reduced pressure (bp <55 °C at 0.2 mbar) and examined similarly. It was determined that the lighter fraction contained 2-propanol, isopropyl acetate, and acetone, while the higher boiling fraction contained 1,3-propanediol, 3-hydroxypropyl acetate, and 1,3-propanediacetate. Of particular interest were the unexpected presence of acetone and the absence of significant quantities of acacH. To characterize the reactions occurring in the solution, it was decided to isolate a number of separate reactions from the system. To this end the Ti and Zr reagents were used in separate reactions, under anhydrous conditions, and in the absence of acetates and acetic acid.

On stirring the $Ti(OPr^i)_2(acac)_2$ in 2-propanol solution with a single equivalent of 1,3-propanediol at room temperature, the isopropoxide groups were completely substituted. Proton and carbon NMR spectra showed the presence of free 2-propanol, with only a trace of free 1,3-propanediol remaining. The coordinated 1,3-propanediolate showed equivalent OCH_2 signals in accordance with its bidentate nature. The cis isomers of titanium dialkoxide bis(acetylacetonate) complexes are known to be more stable in solution.[6,7] The isopropoxide complex **1** used here illustrates this nicely, with axial and equatorial termini of the acac ligands being clearly distinguished in the proton

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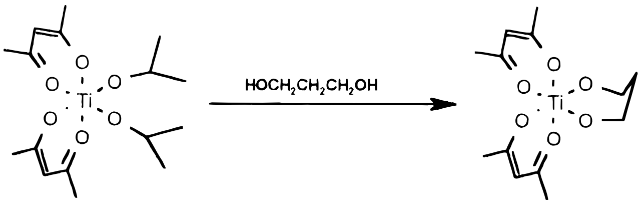
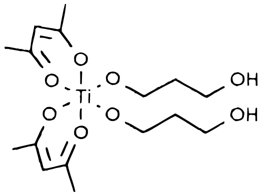
Scheme 1



1 **2**

and carbon NMR spectra. The 1,3-diolate complex, **2**, however, shows coalescence of the acac methyl signals below room temperature. This has been attributed to racemization (Scheme 1).[6]

A second experiment was carried out whereby a five-times excess of 1,3-propanediol was used. As before, the isopropoxide groups were rapidly substituted. The same chelated 1,3-diolate complex was seen as before, but an additional product was apparent in the ^{13}C NMR. This was consistent with the formation of a bis diolate complex, **3**, where 1,3-propanediol was bound as monodentate alkoxide species. The approximate ratio of mono:bis complex was 10:1.



3

Refluxing the reaction mixture resulted in further reaction of the complex with the diol. Distillation of the volatile solvents (<80 °C) was followed by continued heating to complete the reaction. The higher boiling solvent fraction was separated from a white precipitate by vacuum distillation (<55 °C at 0.2 mbar). C and H microanalysis suggested the formulation Ti(OCH$_2$CH$_2$CH$_2$O)$_2$. (Anal. Calcd for $C_6H_{12}O_4Ti$: C, 36.8; H, 6.2. Found: C, 37.0; H, 6.5.) This reaction was not characterized by a straightforward ligand exchange because NMR examination of the reaction solution and distillates failed to show the presence of the liberated acacH. The lower boiling fraction contained the 2-propanol plus some acetone and trace amounts of isopropyl acetate. The higher boiling fraction contained some remaining 1,3-propanediol plus some mono- and diacetylated 1,3-propanediol in a ratio of ca. 10:1.

A proposed mechanism for the reaction is shown in Scheme 2.

The reaction of the coordinated acac described above can be described as an alcoholysis reaction. The acac is cleaved to yield acetone and the ester of the reacting alcohol or diol. This mechanism does not require the formation of an intermediate acetate ligand.

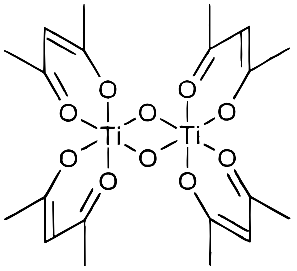
Using 1,2-ethanediol in place of the 1,3-propanediol produced a similar result, although no diacetylated ethanediol was identified in the ^{1}H and ^{13}C NMR spectra or GC traces.

Attempts to carry out this decomposition using monoalcohols in place of diol were made. The lighter alcohols were less reactive, so that refluxing the Ti(OPr^i)$_2$(acac)$_2$ complex up to 24 h in 2-propanol, *n*-propanol, or butanols resulted in only trace amounts of acetone and acetylated alcohols. Using the higher boiling alcohol, 2-ethylhexanol resulted in the complete decomposition of the acac in the same way as in the diol reactions, to yield 2-ethylhexyl acetate and acetone. The initial product of alkoxide exchange, Ti [OCH$_2$CH(C$_2$H$_5$)C$_4$H$_9$]$_2$(acac)$_2$, was observed in the NMR, prior to its conversion to tetrakis(2-ethylhexyl)titanate.

Table 1. Reactivities of acac Complexes with Alcohols and Diols

alcohol	Ti(OPr^i)$_2$(acac)$_2$	Zr(acac)$_4$
ethanol		traces of products
n-propanol	traces of products	complete reaction
isopropanol	traces of products	traces of products
n-butanol	traces of products	complete reaction
tert-butanol	no reaction	no reaction
2-ethylhexanol	complete reaction	complete reaction
1,2-ethanediol	complete reaction	complete reaction
1,3-propanediol	complete reaction	complete reaction

Alternative reaction pathways were considered for the decomposition of the acac. These included the participation of moisture, reaction of uncoordinated acacH, and the formation of intermediate acetate complexes. These possibilities were finally ruled out after conducting a number of further reactions. Addition of moisture to a solution of Ti(OPr^i)$_2$(acac)$_2$ immediately resulted in the formation of the oxo dimer **4**.[8]



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Heating this complex in 1,3-propanediol, as for previous reactions, did not noticeably impact on the acac cleavage reaction, thus ruling out moisture, hydroxyl or oxo species as participants in the reaction. The possibility that 1,3-propanediol reacted with free acacH was discounted, as a reaction involving refluxing a 50/50 mixture of acacH with 1,3-propanediol did not result in acetylated products. It is possible that intermediate acetato complexes were formed, but these were never detected during this work. If metal acetates had been formed and subsequently reacted to esterify the refluxing alcohol or diol solvent, water. However, no hydrolysis products indicative of the presence of water were apparent in the final solutions. Thus, the formation of intermediate acetato complexes was seen as an unlikely possibility.

As a comparison, samples of Zr(acac)$_4$ and Ti(OPr^i)$_2$(acac)$_2$ were refluxed in a range of alcohols for 4 h. NMR and GC studies of the resulting solutions were obtained to determine whether the alcohol had reacted with the coordinated acac. The products of all these reactions always included acetylated alcohol or diol and acetone. The results in Table 1 clearly show the increased reactivity of the Zr(acac)$_4$ complex compared to the Ti(OPr^i)$_2$(acac)$_2$ complex. Most notably Zr(acac)$_4$ decomposed readily in refluxing *n*-propanol to form *n*-propyl acetate and acetone. Within 4 h reaction time, no detectable quality of Zr(acac)$_4$ remained.

A further observation is that primary alcohols react more readily with coordinated acac in comparison with secondary or tertiary alcohols. It is likely that steric factors are the important influence here.

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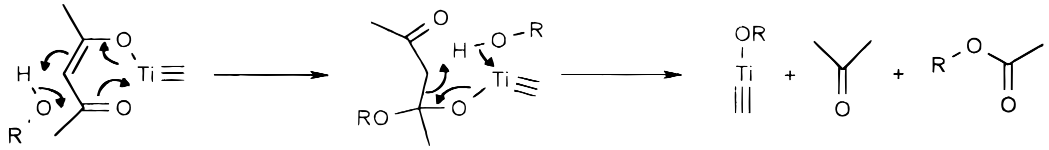
Scheme 2



The reactivity of coordinated acac described above could be important for other systems where acacH is used. Two recent reports involving lanthanide complexes[9,10] describe the room-temperature cleavage of acac, resulting in unexpected products. The first report involved the addition of excess acacH to a solution of $Y_5O(OPr^i)_{13}$ which led to the formation of acetato ligands.[9] It was described as a retro-Claisen reaction and it was postulated that the acetate derived from the acac. Further examples involved hexafluoroacetylacetonato complexes of lanthanides.[10] The origin of the unusual products was readily identified due to the fluorination present on the products and starting materials. These studies suggest that acacH should be used with caution as a modifier in metal alkoxide systems, as its reactivity could unexpectedly modify the chemistry. This is particularly important in sol−gel applications where reliable reproducibility of the sol properties is an important requirement.

The zirconium complex resulting from the reaction with 1,3-diolate was insoluble, as was the case for the titanium complex. C and H microanalyses of both Ti and Zr species were consistent with the formulation $M(OCH_2CH_2CH_2O)_2$. In the sol precursor solutions for PT and PZT,[1−5] the chemistry is complicated by the presence of water and acetate groups. Further reaction prevents the isolation of the $M(OCH_2CH_2CH_2O)_2$ species, and well controlled hydrolyses and condensations to form M−O−M and M−O−M′ linkages, result in clear sols. Related studies of PT precursor sols[11,12] have identified the types of reactions occurring.

Conclusions

Heating metal acac complexes in the presence of diols or certain alcohols results in an alcoholysis reaction, whereby the coordinated acac reacts to acetylate the alcohol or diol and release acetone. The metal alkoxide or diolate thus produced is then available for hydrolysis or reaction with acetates or other reagents. Using this route, the condensation of metal oxide species to form a sol, is a slow and controlled process.

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