Synthesis and Characterization of (β-diketonate)Zirconium Alkoxides for Low Temperature Chemical Vapor Deposition of Lead Zirconium Titanium Thin Films

by

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Thesis submitted to the Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

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in

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APPROVED:

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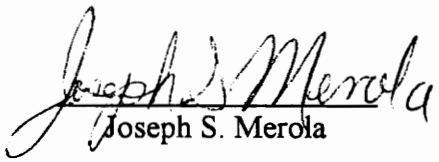

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Synthesis and Characterization of (β-diketonate)Zirconium Alkoxides for Low Temperature Chemical Vapor Deposition of Lead Zirconium Titanium Thin Films

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Department of Chemistry

(ABSTRACT)

Metal alkoxides have been known for many years. Recently, a renewed interest in these compounds has arisen as they have been found to be viable precursors for metal oxide film synthesis. Lead zirconium titanate(PZT) films have shown promise for many applications in the electronics industry. Chemical vapor deposition(CVD) of PZT thin films has been hampered by the lack of a suitable zirconium precursor for low temperature chemical vapor deposition. Currently, both zirconium alkoxides and zirconium β-diketonate complexes are employed in the CVD process of PZT films. The alkoxides, although volatile are moisture sensitive and are not easily handled under normal atmospheric conditions. Tetrakis β-diketonate complexes of zirconium are more stable than the alkoxides, but they have a deposition temperature that is too high for commercial use. A mixed (β-diketonate)zirconium alkoxide compound could provide the necessary stability while maintaining the volatility necessary for low temperature CVD.

From the above reasoning, it was decided to prepare a zirconium di-(2,2,6,6 tetramethyl-3,5 heptadione) di-*tert*-butoxide compound. The compound was

characterized and subjected to a variety of volatility studies. Thermogravimetric analysis provided evidence that the compound was volatile enough to be used in thin film synthesis. Initial attempts at film deposition, however, resulted in no film growth. Changing deposition parameters also resulted in no film growth. Visual inspection of the residue left after the deposition trials gave the first indication that the compound had undergone some change. Analysis of the material left in the reactor suggested the formation of a zirconium cluster compound. Further decomposition studies also resulted in the formation of the same zirconium cluster compound.

Attempts to make the compound more stable at deposition temperatures centered on changing the alkoxide. Tri-*tert*-butyl alcohol(tritox) was prepared, however, the synthesis of the tritox - β-diketonate zirconium complex was unsuccessful. Other changes involved using pivalic acid to replace the alkoxide. Reactions with pivalic acid and zirconium di-(2,2,6,6 tetramethyl-3,5 heptadione) di-*tert*-butoxide resulted in the decomposition of the starting material.

Other β-diketonate complexes were also investigated. Compounds synthesized from 2,4 pentadione(Acac), 1-benzoyl acetone(Bzac) and dibenzoyl methane(Dbzm) could not be purified in order to subject them to chemical vapor deposition.

A zirconium complex with two different β-diketonate ligands was also synthesized. The complex was not investigated as a precursor for chemical vapor deposition because the isomers of the complex could not be separated.

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List of Abbreviations

Acac	Acetylacetone
Bzac	Benzoylacetone
CVD	Chemical Vapor Deposition
Dbzm	Dibenzoylmethane
NMR	Nuclear Magnetic Resonance
PZT	Lead Zirconium Titanium
TGA	Thermal Gravimetric Analysis
Thd	2,2,6,6 tetramethyl-3,5 heptadione

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To My Parents

Chapter 1 Metal Alkoxides

1.1 Introduction

Metal alkoxides, of the general formula of $M^{n+}(OR)_n$, are a class of compounds in which the hydroxyl hydrogen of an alcohol is replaced by a metal. This M-O-C bond is highly polarized in part due to the electronegativity difference of the oxygen atom compared to metal. The electronegativity of the metal atom determines the properties for each alkoxide. For example, highly electronegative metals form covalent bonds with alkoxy groups and produce volatile compounds while electropositive metals form ionic solids. The nature of the alkyl group also has an effect on the properties of an alkoxide. Tertiary butoxides tend to reduce the polarization of the metal-oxygen bond and make the metal-oxygen bond more covalent. The larger alkyl groups disrupt intermolecular forces between neighboring metal and oxygen atoms which results in a more volatile compound.

1.2 Synthesis of Metal Alkoxides

1.2.1 Metals in Alcohols

The simplest method of synthesis is the direct combination of an alcohol and a metal:

$$M + xROH \rightarrow M(OR)_x + x/2\ H_2 \quad (1)$$

This method, however, is only useful in the synthesis of alkali metals alkoxides and alkoxides of other electropositive metals such as beryllium, magnesium, and aluminum.[1] The latter metals, however, need a catalyst such as iodine or mercuric chloride in order to facilitate the reaction. These are thought to remove the oxide film that makes the metal unreactive.

Lamy[2] found that thallium metal immersed in boiling ethanol is unreactive. However, when thallium metal is suspended over boiling ethanol, it is converted completely to thallium ethoxide. In this reaction it seems that oxide formation is necessary for the reaction to proceed:

$$2Tl + \tfrac{1}{2}O_2 \rightarrow Tl_2O \quad (2)$$

$$Tl_2O + EtOH \rightarrow TlOEt + TlOH \quad (3)$$

$$TlOH + EtOH \rightleftharpoons TlOEt + H_2O \quad (4)$$

Menzies[3] showed that the reaction proceeds to completion because thallium ethoxide is insoluble in ethanol and the equilibrium is forced to the right.

The nature of the alcohol employed in the alkolysis also plays a role in the reaction. Sodium, for example, reacts violently with methanol and ethanol, but the reaction is slow with isopropanol, and slower still with tertiary butanol. The variation in rates can be explained by the acidity of the alcoholic proton.

1.2.1 Reactions of Metal Hydroxides

Metal hydroxides react with alcohols to form metal alkoxides according to equation 5.

$$MOH + ROH \rightleftharpoons MOR + H_2O \quad (5)$$

The reaction can be driven to completion by removal of water. Prandtl and Hess[4] showed that hydrated vanadium pentoxide placed in boiling ethanol yields vanadium ethoxide.

1.2.2 Reactions of Metal Chlorides

The methods presented above are not satisfactory for the preparation of metal alkoxides of a metal in an oxidation state of two or greater. A simple method for the formation of these involves the alcoholysis of an anhydrous metal chloride.

$$MCl_n + n ROH \rightleftharpoons M(OR)_n + n HCl \quad (6)$$

This procedure does not necessarily remove all of the chloride from the metal, and the addition of a base, such as triethylamine, is often necessary in order to complete the reaction by removing the hydrochloric acid from the equilibrium.

Demarcay[5] attempted to make titanium tetraethoxide by the following metathesis reaction:

$$TiCl_4 + NaOEt \rightarrow Ti(OEt)_4 + 4NaCl\downarrow \quad (7)$$

The products obtained were impure due to hydrolysis of the titanium ethoxide. Bischoff and Adkins[6], however, successfully synthesized titanium ethoxide by the same method. This method cannot be applied to all metals. Zirconium tetrachloride and alcoholic sodium alkoxides do not yield zirconium alkoxides. A double alkoxide of sodium and zirconium($Na_2Zr(OR)_6$) is formed due to the fact that both zirconium tetrachloride and zirconium tetraethoxide are Lewis acids and will react with the sodium alkoxide.[7]

Nelles[8] discovered that the use of ammonia and ethanol in place of the sodium alkoxide yields pure titanium ethoxide:

$$TiCl_4 + EtOH + NH_3 \rightarrow Ti(OEt)_4 + 4\ NH_4Cl \quad (8)$$

Bradley and Wardlaw[9] used this discovery and applied it to the zirconium problem. Thus not only can zirconium alkoxides be prepared directly, but many other metal alkoxides are available by this route as well. Herman[10] streamlined the procedure with titanium by performing the reaction in the presence of an amide or nitrile. This gives a biphasic system in which the ammonium chloride dissolves in the amide or nitrile in the lower layer, while the product remains in the top layer. The need for filtration in the process was eliminated. Again this method is not general for all metals as shown by Bradley.[11]

The other major concern in this synthetic method is the effect of the alkyl group. Steric and electronic effects play a role in the reaction. Substitution by lower, straight-chained alcohols proceed smoothly, but not for highly branched alcohols. In these

reactions, it is evident that side reactions dominate. Hydrogen chloride is initially produced in the reaction between the metal chloride and the alcohol. Tertiary alcohols may then react with the hydrogen chloride to yield the alkyl chloride or an olefin (equation 11).

$$MCl_4 + ROH \rightarrow MCl_3(OR) + HCl \quad (9)$$

$$ROH + HCl \rightarrow RCl + H_2O \quad (10)$$

$$ROH + HCl \rightarrow \text{Olefin} + HCl + H_2O \quad (11)$$

It is interesting to note that water is produced in equations 10 and 11, which further reduces the yield of metal alkoxide. Steps have been taken to eliminate these side reactions. For example, Cullinane[12] was successful in the synthesis of titanium tetra-*tert*-butoxide by using pyridine to remove the hydrogen chloride generated. The use of the pyridine keeps the hydrogen chloride concentration low preventing the reactions shown in 10 and 11 from occurring.

1.2.3 Synthesis Involving Alcohol Exchange

The alcohol groups of the metal alkoxide are fairly labile and can be replaced by other alcohols. This is a pathway to the formation of new mixed alkoxide compounds. The general reaction is shown in equation 12:

$$M(OR)_4 + n\text{R'OH} \rightleftharpoons M(OR)_{4-n}(OR')_n + n\text{ROH} \quad (12)$$

This method has been employed in the synthesis of aluminum, germanium, tin(IV), zirconium, titanium, niobium, tantalum, iron(III), lanthanum, thorium, uranium and, plutonium alkoxides. The equilibrium of equation 12 can be shifted if ROH is lower boiling than R'OH. By fractional distillation, ROH can be removed and the reaction is forced to the right. Size also plays a part in this reaction. If R'OH is a large bulky alcohol, the reaction will proceed slowly and may even stop. Bradley[13] found that in an attempt to prepare zirconium tetra-*tert*-butoxide by alcohol exchange, he obtained a crystalline substance which he thought was $Zr(OMe)(O^tBu)_3$. Upon heating the compound under reduced pressure, the compound rearranged to form $Zr(O^tBu)_4$ and $Zr(OMe)_3(O^tBu)$ via equation 13:

$$3\ Zr(OMe)(O^tBu)_3 \rightarrow 2\ Zr(O^tBu)_4 + Zr(OMe)_3(O^tBu) \quad (13)$$

Zirconium tetra-*tert*-butoxide will react with one equivalent of methanol or ethanol to give the monosubstituted mixed alkoxide; the addition of two equivalents yields the disubstituted alkoxide. The replacement of a lower alcohol with a higher one may not proceed to completion; however, the reverse reaction generally goes to completion.

1.2.4 Double Alkoxides

Meerwein and Bersin[14] discovered that solutions of some metal alkoxides were acidic and could be titrated with an alkali metal alkoxide using thymolphthalein as the indicator. Later work by Bradley and Wardlaw[15] and Bartley and Wardlaw[16] found that alkali metal alkoxides react with zirconium alkoxides as shown in equation 14.

$$MOR + 2\ Zr(OR)_4 \rightarrow MZr_2(OR)_9 \quad (13)$$

The compounds generated from this reaction are volatile and were discovered to be largely covalent in nature rather than ionic salts as originally proposed.

1.3 Reactions of Metal Alkoxides

1.3.1 Reactions With Water

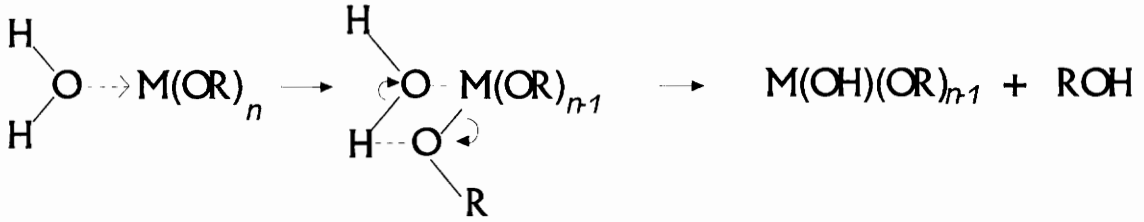
Most metal alkoxides are moisture sensitive. Reaction with an excess of water produces the corresponding metal hydroxide while in the presence of a limited amount of water the following reactions occur (equations 15-17).[17]

$$M(OR)_n + H_2O \rightarrow M(OH)(OR)_{n-1} + ROH \quad (15)$$

$$2M(OH)(OR)_{n-1} \rightarrow (OR)_{n-1}MOM(OR)_{n-1} + H_2O \quad (16)$$

$$M(OH)(OR)_{n-1} + M(OR)_n \rightarrow (OR)_{n-1}MOM(OR)_{n-1} + ROH \quad (17)$$

The reaction is thought to proceed as indicated in scheme 1.



Scheme 1
Reaction of Water With A Metal Alkoxide

1.3.2 Reactions With Halides

The reactions of metal alkoxides with halogens has been investigated by Mehrotra for a number of metals.[18] In most cases it was found that the products obtained were the same as that of the reaction of the metal halide with the alcohol. For example, Nesmeyanov[19] found that $Ti(OR)_2X_2 \cdot ROH$ is obtained from the reaction of halogens with titanium alkoxides (equation 18).

$$Ti(OR)_4 + X_2 \rightarrow Ti(OR)_2X_2 \bullet ROH \quad (18)$$

X=F, Cl, Br

1.3.3 Reactions With Carboxylic Acids

Metal alkoxides also react with compounds that contain a reactive hydroxyl group, such as carboxylic acids and the enol form of a β-diketonate. Mehrotra has shown that the reaction of metal alkoxides with carboxylic acids yields a metal-carboxylic acid compound. Reactions of aluminum alkoxides with carboxylic acids gave the tri-

substituted carboxylic acid compound.[20] However, the reaction of titanium and zirconium alkoxides with acids does not result in complete substitution even with an excess of acid. Kapor and Mehrotra,[21] obtained a zirconium oxide carboxylate($Zr_2O(O_2CR)_6$). Investigations into the mechanism showed the first three substitutions were rapid and quantitative. Isolation of the tri-substituted complex could only be performed at temperatures less than 30°C. The tri-carboxylic acid complex undergoes rearrangement by the reaction shown in 19:

$$Zr(O^iPr)(O_2CR)_3 \rightarrow ZrO(O_2CR)_2 + RCO_2{}^iPr \quad (19)$$

Since the isopropyl ester of the acid is also obtained from the reaction of the tri-substituted complex with the tetra-substituted one (equation 20), it was decided that the failure of the reaction scheme to provide the zirconium tetrakis carboxylate complex was due to equations 19 and 20 occurring during the reaction. This was further proven since the tetra-soap can be synthesized from the tetrachloride.[21]

$$Zr(O^iPr)(O_2CR)_3 + Zr(O_2CR)_4 \rightarrow Zr_2O(O_2CR)_6 + RCO_2{}^iPr \quad (20)$$

1.3.4 Reactions With β-diketonates

The enol form of a β-diketone also reacts with metal alkoxides. Titanium alkoxides have been shown to react with two equivalents of 2,4 pentanedione to yield the

di-substituted titanium complex.[22] This substitution is rapid and further substitution is slow (equation 21).

$$Ti(OR)_4 + 2\ HAcac \rightarrow Ti(OR)_2(Acac)_2 + 2\ ROH \quad (21)$$

Moving down the group to zirconium, it is found that the tetrakis acetylacetonate compound can be synthesized[22] (equation 22).

$$Zr(OR)_4 + 4\ HAcac \rightarrow Zr(Acac)_4 + 4\ ROH \quad (22)$$

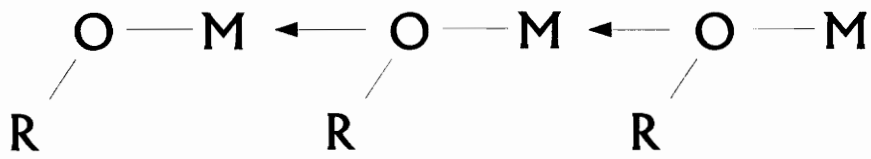
Since zirconium can exhibit a coordination number of eight, it is not unusual to see this behavior. It was also noted that the di β-diketonate titanium complex would react with higher alcohols indicating that the resistance to the third acetylacetonate substitution was due to sterics.[22]

1.4 Physical Properties

1.4.1 Volatility

Alkoxides of sodium and potassium are generally ionic in nature and therefore are not volatile, however, lithium *tert*-butoxide has been shown to have some volatility.[23] In mass spectral studies, the compound has been shown to exist as hexamers in the gas

phase.[24] Divalent metal alkoxides also tend to be non-volatile due in part to their ionic nature or their existence as large covalent molecules. Mehrotra[25] studied the volatilities of the alkoxides of groups III, IV and, V. He found that for any given metal, the volatility of the alkoxide is dependent on the alkyl chain length. The larger the chain the more volatile the alkoxide. The degree of intermolecular association is lowered with an increase in the chain length or bulk. Intermolecular association of metal alkoxides is shown in Scheme 2. The disruption of these causes a metal alkoxide to become more volatile.



Scheme 2
Molecular Interactions of Alkoxides

The steric effect of the R group will be increased if the metal atom is relatively small. Silicon n-alkoxides tend to be monomeric while zirconium alkoxides exhibit monomeric behavior beginning with *tert*-butoxides. Metals that can expand their coordination number to seven or eight also have a higher degree of polymeric behavior in their lower alkoxides.[26] Table 1 shows the boiling points of various metal alkoxides.

1.4.2 Infrared Spectroscopy

Many researchers have studied the infrared spectra of metal alkoxides. Table 2 summarizes the data for some metal alkoxides.[27] The reason for multiple bands with some of the alkoxides is due to their polymeric nature. Aluminum isopropoxide has a high degree of intermolecular attraction which gives rise to the five observed M-O stretches. Compounds with large alkoxide groups that show only one signal for the metal-oxygen stretch are monomeric in nature

1.5 Requirements of Precursor For Chemical Vapor Deposition

In order to determine the desired properties for a zirconium precursor the chemical vapor deposition process must be examined. Figure 1 shows a schematic of the chemical vapor deposition process. In the first area (I), the compound must be stable at elevated temperatures and also be volatile enough so that a large amount of the material enters the gas phase to give rapid film growth. The compound must also be thermally stable so that the vapor pressure remains constant over time. In the second area, the compound is transported to the substrate. The compound must also be stable and volatile in this region. Any decomposition or condensation in this area will result in poor film growth. The temperature of II should be the same as I or slightly higher. Too high of a temperature in II will result in thermal decomposition and unpredictable film growth.

Table 1
Volatilities of Metal Alkoxides-$M_a(OR)_n$ (°C/mm Hg)
(adapted from reference 18)

R	Metal					
	Al[30]	Fe[31]	Ti[32]	Zr[33]	Nb[34]	Ta[35]
$CH_3(CH_2)_4$	255/1.0	178/0.1	175/0.8	256/0.01	228/0.1	233/0.1
$(CH_3)_2CH(CH_2)_2$	195/0.1	decomposes	148/0.1	247/0.1	199/0.1	210/0.1
$(CH_3)(C_2H_5)CHCH_2$	200/0.6	178/0.1	154/0.5	238/0.1	183/0.1	204/0.1
$(CH_3)_3C$	180/0.8	159/0.1	105/0.05	188/0.2	126/0.1	130/.01
$(C_2H_5)_2CH$	165/1.0	163/0.1	112/0.05	178/0.05	138/0.1	153/0.1
$(CH_3)(n\text{-}C_3H_7)CH$	162/0.5	165/0.1	135/1.0	175/0.01	137/0.1	148/0.1
$(CH_3)(i\text{-}C_3H_7)CH$	162/0.6	162/0.1	131/0.5	156/0.01	139/0.1	137/0.1
$(CH_3)_2(C_2H_5)C$	-	131/0.1	98/0.1	95/0.1	-	139/0.1

Table 2
Observed IR Absorbance Frequencies for Metal Alkoxides
(adapted from reference 18)

Alkoxide	C-O(cm^{-1})	O-M(cm^{-1})
$Ti(OEt)_4$	1064,1042	625,500
$Ti(O^iPr)_4$	1005	619
$Ti(OAm)_4$	1101	615,576
$Zr(O^iPr)_4$	1101	559,548
$Zr(O^tBu)_4$	997	540
$Zr(OAm)_4$	1010	586,559,521
$Hf(O^tBu)_4$	990	567,526
$Ta(OEt)_5$	1072,1030	556
$Ta(O^iPr)_5$	1001	557,540
$Nb(OEt)_5$	1063,1029	571
$Al(O^iPr)_3$	1036	699,678,610,556,535

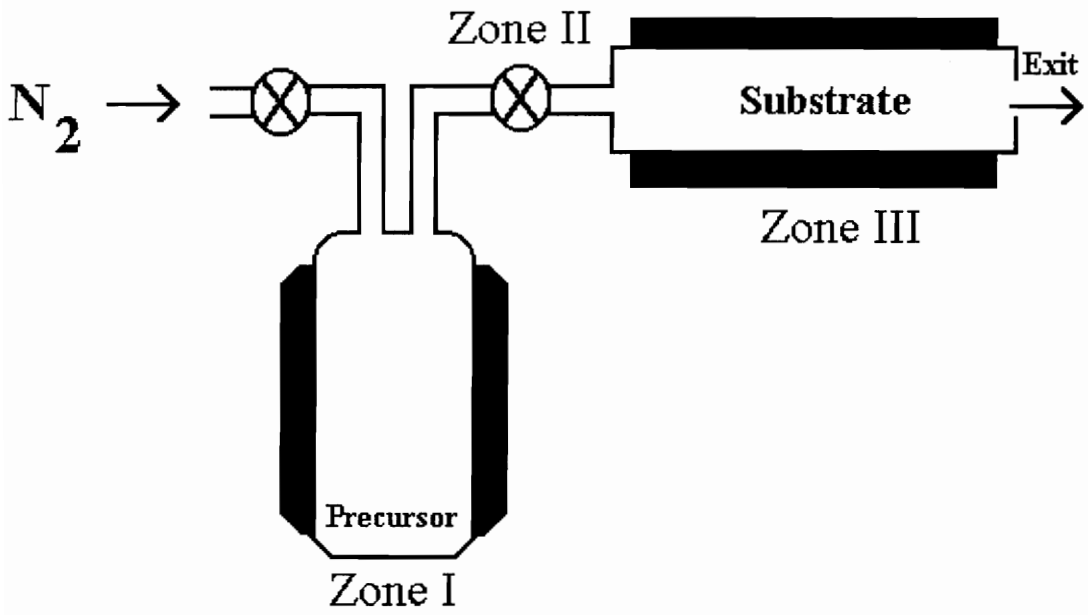


Figure 1
Chemical Vapor Deposition Apparatus

In III, the precursor must decompose rapidly with little organic contamination. A temperature in the range of 350-550°C is also necessary for efficiency of film deposition and limiting precursor reactions with the substrate.

One of the most important properties of a precursor is the ease with which it can be handled. Some of the compounds which produce good films are unstable under ambient conditions. This is especially true of the zirconium alkoxides. This instability can result in non-reproducible film growth due to compound degradation.

In summary, for a compound to be a suitable precursor it must have the following properties: [28]

1) High vapor pressure at a low temperature (10-100 millitorr at < 180°C)

2) Thermal stability at the vaporization temperature and 50°C above the vaporization temperature

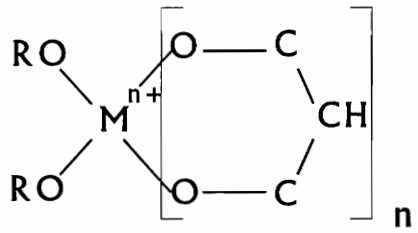
3) Rapid decomposition at a low temperature (350-550°C) with minimum organic contamination

4) Stability under ambient conditions

1.5 Precursor Design

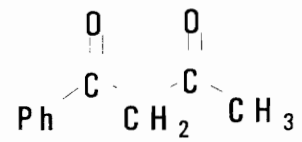
The goal of this project is the synthesis of mixed alkoxide(β-diketonate) zirconium complex. (Scheme 3) Zirconium(β-diketonate) complexes are good precursors since they are stable under ambient conditions but, they have too high of a

decomposition temperature. Zirconium alkoxides are very volatile but they are not stable under atmospheric conditions. The chelating effect of the β-diketonate should shield the zirconium center from moisture attack to provide a greater stability than the tetra-substituted alkoxide. The alkoxide portion of the complex should ensure the compound remains volatile and lowers the decomposition temperature of the compound.

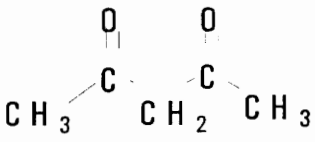


Scheme 3
Mixed Alkoxide(β-diketonate) Zirconium Complex

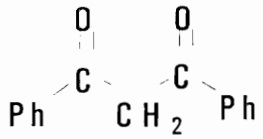
A variety of β-diketonates were selected for the syntheses of the target compounds (figure 2). The selection was based on commercial availability and steric bulk. It has been shown that the volatility of a zirconium alkoxide or β-diketonate complex is directly related to the steric bulk of the ligands coordinated to the zirconium center. After synthesis, the compounds were subjected to thermal gravimetric analysis to determine if they are volatile enough to be employed in chemical vapor deposition of films. Infrared and mass spectral analysis of decomposition products were employed in order to determine the mechanism of decomposition as well as the identity of decomposition products.



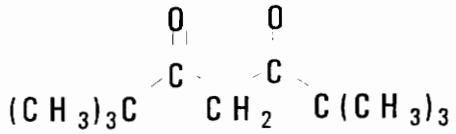
1-Benzoylacetone
(BZAC)



Acetylacetone
(ACAC)



Dibenzoylmethane
(DBZM)



2,2,6,6-Tetramethyl 3,5-heptanedione
(THD)

Figure 2
β-diketonates Used in the Synthesis of CVD Precursor

Chapter 2 Results and Discussion

2.1 Synthesis of $Zr(OR)_2(\beta\text{-diketonate})_2$

The synthesis of the zirconium precursors began by investigating the reactivity of zirconium alkoxides with an β-diketonates. The hydroxyl group present in the enol form of the β-diketonate reacts with the metal center in a fashion similar to that shown previously for the reaction of the alkoxide with water. Zirconium(IV) *tert*-butoxide was chosen as the starting material because of the compound's volatility and monomeric nature. A polymeric starting material such as $Zr(O\text{-}^{i}Pr)_4$ could form long polymers that possess a lower vapor pressure and be unsuitable for thin film synthesis using thermal decomposition. Reactions of $Zr(O\text{-}^{t}Bu)_4$ with dibenzoylmethane, acetylacetonate, and benzoylacetone all produced products that are believed to be mixtures of substitution products. Proton NMR evidence suggests the presence of the mono- di- and tri-substituted products. In all of the spectra (figures 3-5), the methyne region (5.0-7.0 ppm) shows two or more signals for the single proton in the chelate ring. The signals for the alkyl groups on the β-diketonate ligand, either methyl or phenyl also give complex patterns that indicate two or more inequivalent alkyl groups on the β-diketonate ligands. The signal for the coordinated *tert*-butoxides also indicates the presence of inequivalent *tert*-butyl groups. The lack of an alcoholic proton signal from free *t*-butanol indicates that all the *t*-butyl groups are coordinated to the zirconium center. The integration of the

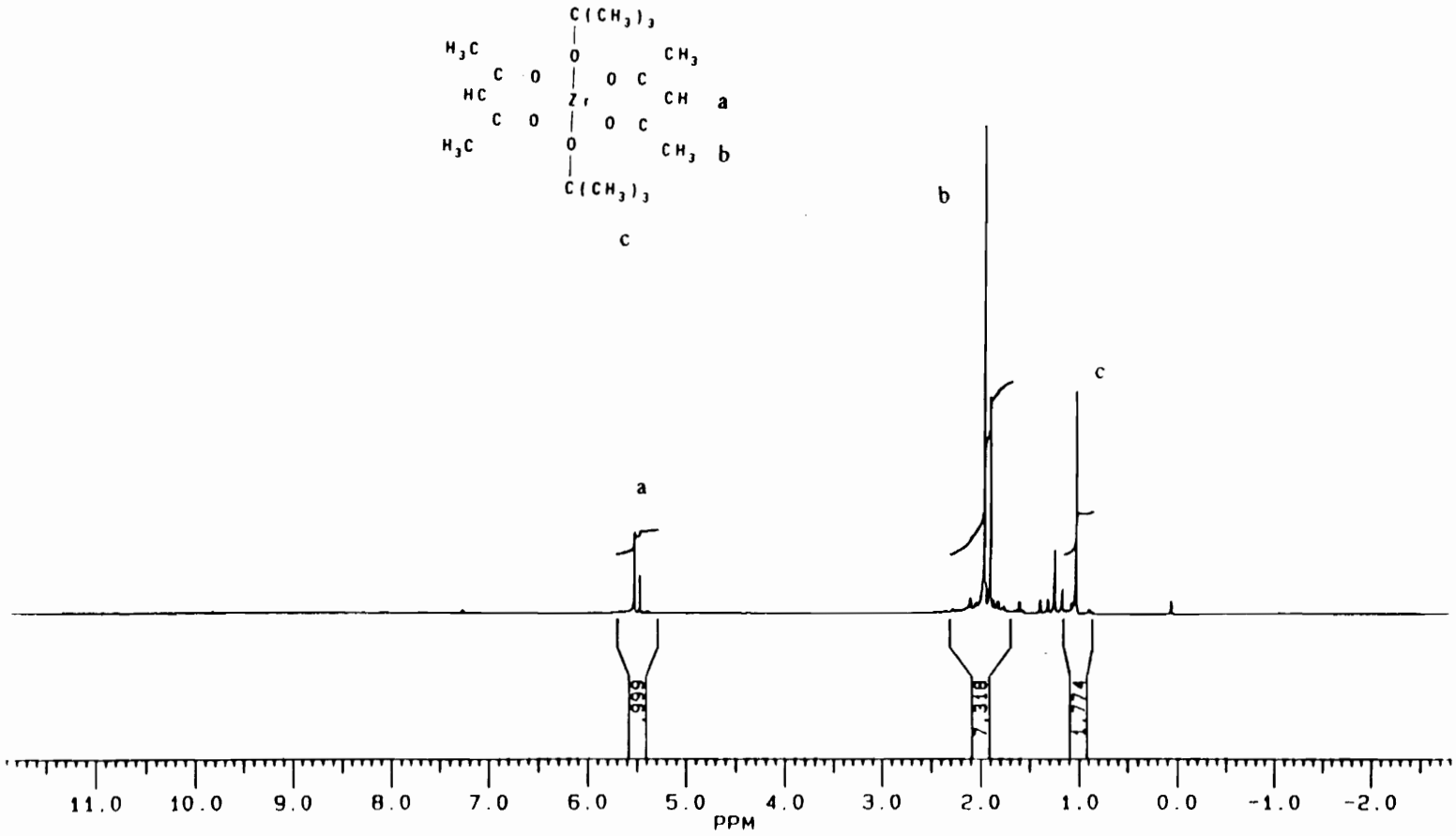


Figure 3
^{1}H NMR of Zr(O-^{t}Bu)$_2$(Acac)$_2$

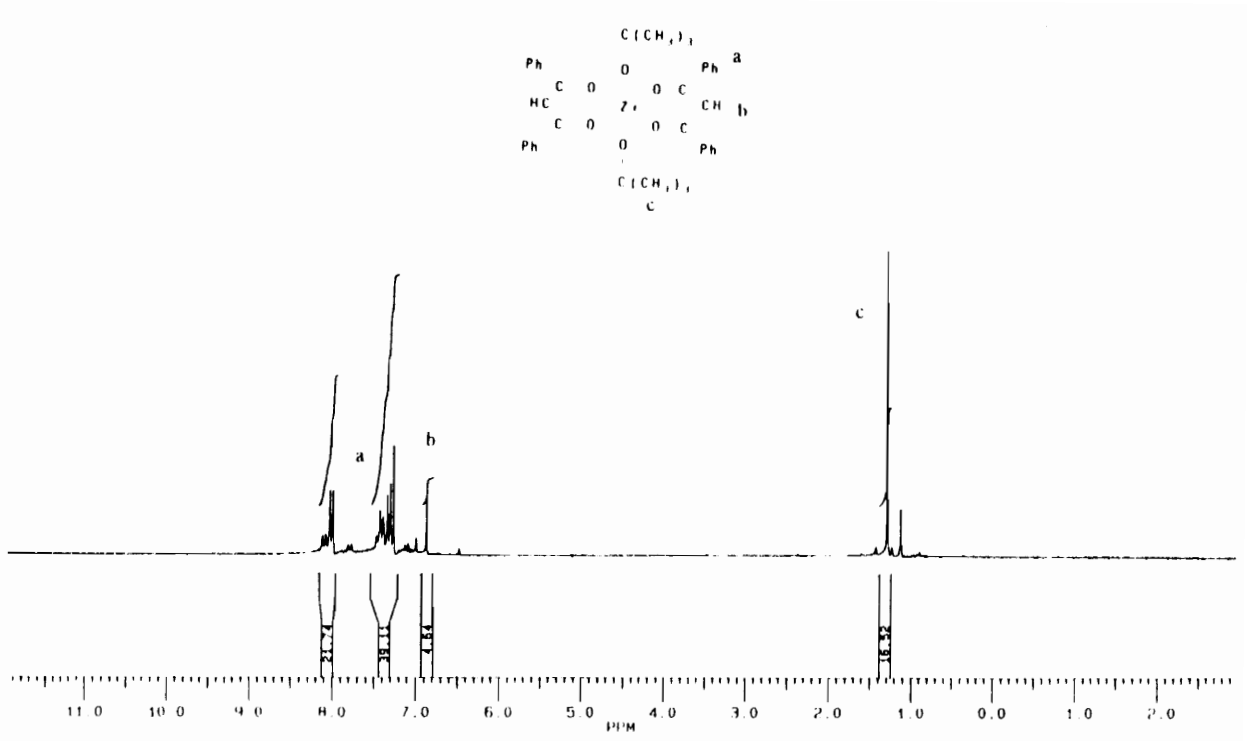


Figure 4
^{1}H NMR of $Zr(O\text{-}^tBu)_2(Dbzm)_2$

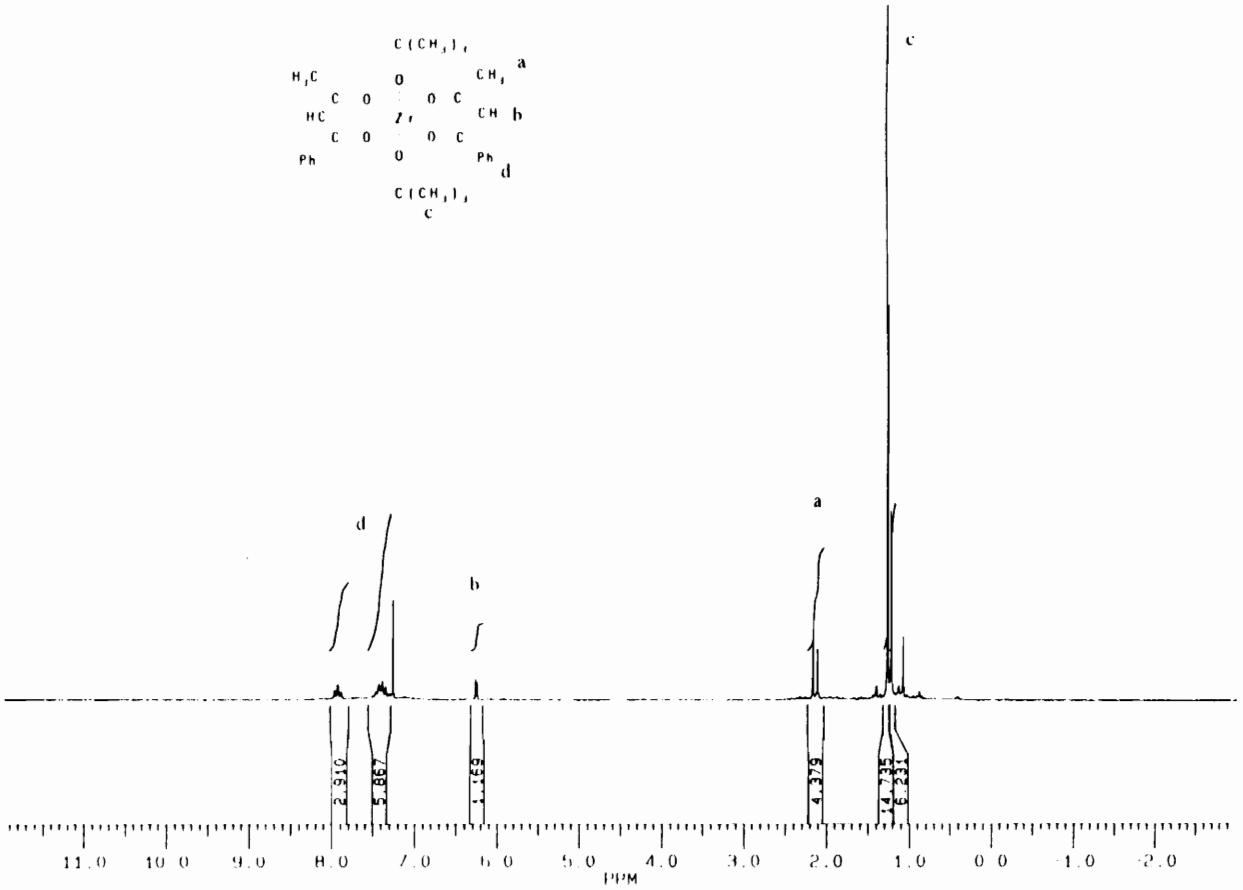


Figure 5
^{1}H NMR of Zr(O-^{t}Bu)$_2$(Bzac)$_2$

signals in the spectra, however, are inconsistent with that of a disubstituted complex. Further recrystallization of the reaction products did not afford a pure compound of any substitution pattern either mono, di, or tri. Further investigations into these reactions were not conducted due to the successful synthesis of the disubstituted 2,2,6,6 tetramethyl-3,5 heptanedione complex (see below). The successful synthesis of $Zr(O\text{-}^tBu)_2(Thd)_2$ shifted the focus of the project to the film deposition aspects.

2.1.1 Synthesis of $Zr(O\text{-}^tBu)_2(Thd)_2$

The synthesis of $Zr(O\text{-}^tBu)_2(Thd)_2$ was completed before any of the other synthetic methods. The lack of substitution products other than the di-substituted complex can be attributed to the steric bulk of Thd ligand. The first substitution is rapid, resulting in the formation of an unstable 5-coordination zirconium complex. The second substitution is also rapid and produces a stable 6-coordinate complex. The addition of a third Thd ligand does not occur most likely due to the steric congestion around the zirconium center by the two chelated Thd ligands. This shielding effect stabilizes the complex and fulfills one of desired requirements for the precursor. The crude product formed large (~10mm) clear, colorless crystals. The crystals would slowly become opaque upon prolonged exposure to air. The exposed crystals were completely soluble in pentane. If the compound began to form the hydroxide, a reduction of solubility in hydrocarbon solvents would have been noted. The exposed crystals did not undergo any

noticeable changes in the proton NMR spectrum. This evidence led to the assumption that the compound was air stable. The compound then appears to possess one of the other desirable characteristics for the precursor. The proton NMR spectrum of the complex (figure 6) consists of a single peak in the methyne region (5.6 ppm). The chelate rings in the complex are all magnetically equivalent. There is also only one peak due to the methyl groups of the *t*-butanol (1.2 ppm) ligand and a single signal from the Thd ligand's methyl protons (1.1 ppm). Although both the cis and trans isomers of the compound can be formed, the compound is probably fluctional which produces the single signal for each proton. The mass spectrum of the compound (figure 7) is also consistent with the formation of the disubstituted complex. The peak present at 529 M/Z is not the molecular ion since the molecular weight of the complex is 603. This peak is actually the weight of the complex after the loss of *t*-butoxide group. This loss proves significant in the thermogravimetric analysis of the complex. The exact conformation and structure of the compound could not be determined by x-ray crystallography. Crystals of the compound, although well-formed and large enough, did not diffract well and x-ray analysis was impossible.

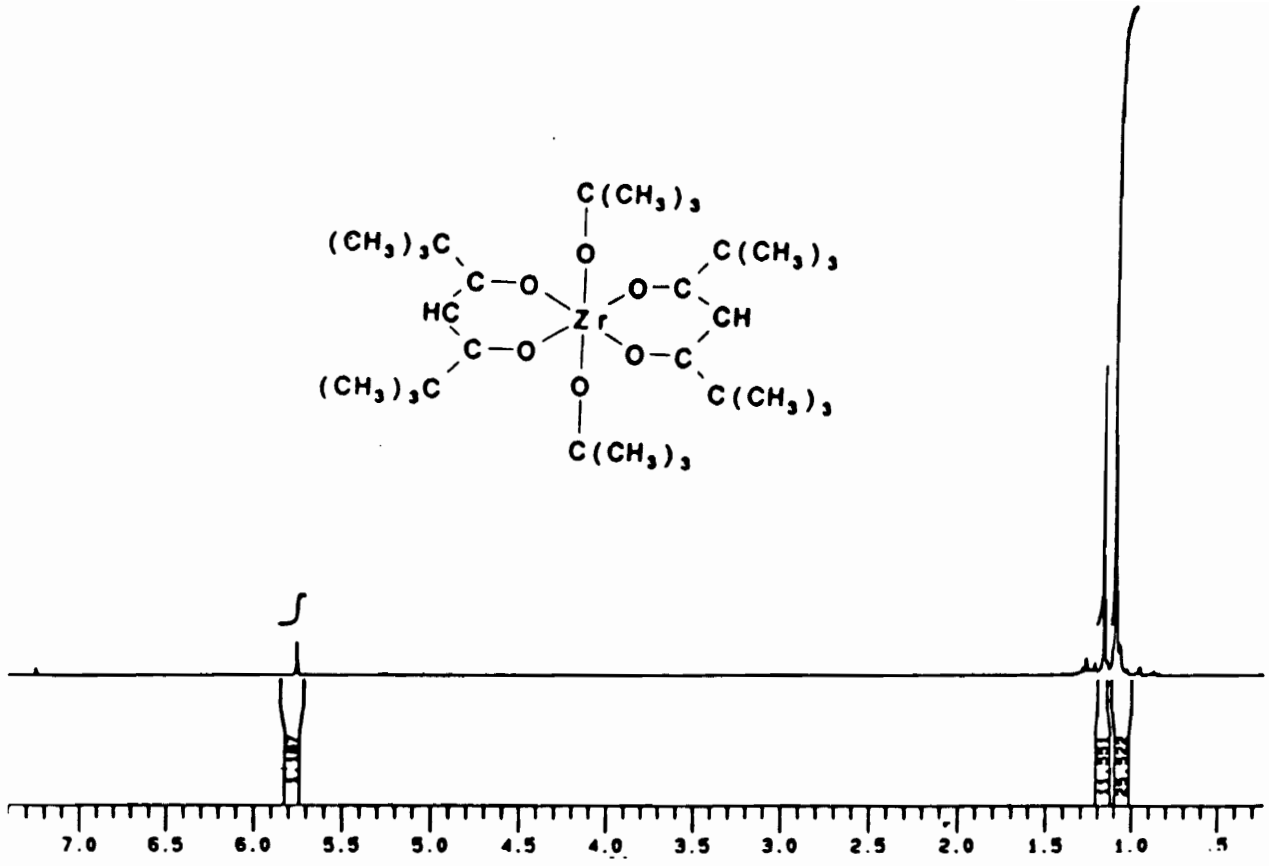


Figure 6
^{1}H NMR of Zr(O-^{t}Bu)$_2$(Thd)$_2$

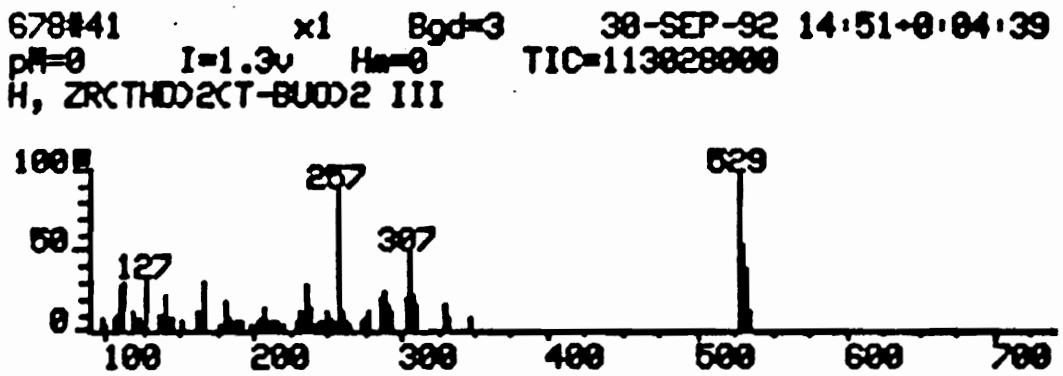


Figure 7
Mass Spectrum of $Zr(O\text{-}^tBu)_2(Thd)_2$

2.2 Film Deposition and Decomposition Studies of $Zr(O\text{-}^tBu)_2(Thd)_2$

$Zr(O\text{-}^tBu)_2(Thd)_2$ was subjected to thermal gravimetric analysis(TGA) to determine its volatility. (The TGA data is presented in appendix A). The compound was first subjected to a temperature programmed run to check if the material had enough of a vapor pressure to be used for chemical vapor deposition. In the dynamic run, the residual weight is 14.32% of the starting weight (figure 8). If the compound was not volatile and decomposed to ZrO_2 as shown in equation 23, the residual weight should have been 20.4% of the starting weight.

$$Zr(O\text{-}^tBu)_2(Thd)_2 \rightarrow ZrO_2 + \text{Volatile Organics} \quad (23)$$

Although the ideal case would have been the complete loss of material, the dynamic run indicated that the compound was volatile enough to be used in deposition trials. The compound was then subjected to a series of isothermal runs to determine what temperature film deposition should be attempted. (Appendix A) The isotherms at 100°C - 140°C show little weight loss. The isotherms between 160°C and 260°C all exhibit a gradual loss of material. Temperatures between 160°C and 180°C were chosen for the film deposition trials.

After a series of unsuccessful attempts at film deposition, the residue left in the reactor was collected and analyzed. The material was found to be soluble in pentane and mass spectral data suggests that a zirconium bi-metallic compound is formed. The pattern produced in the mass spectrum (figure 9), is indicative of a compound containing

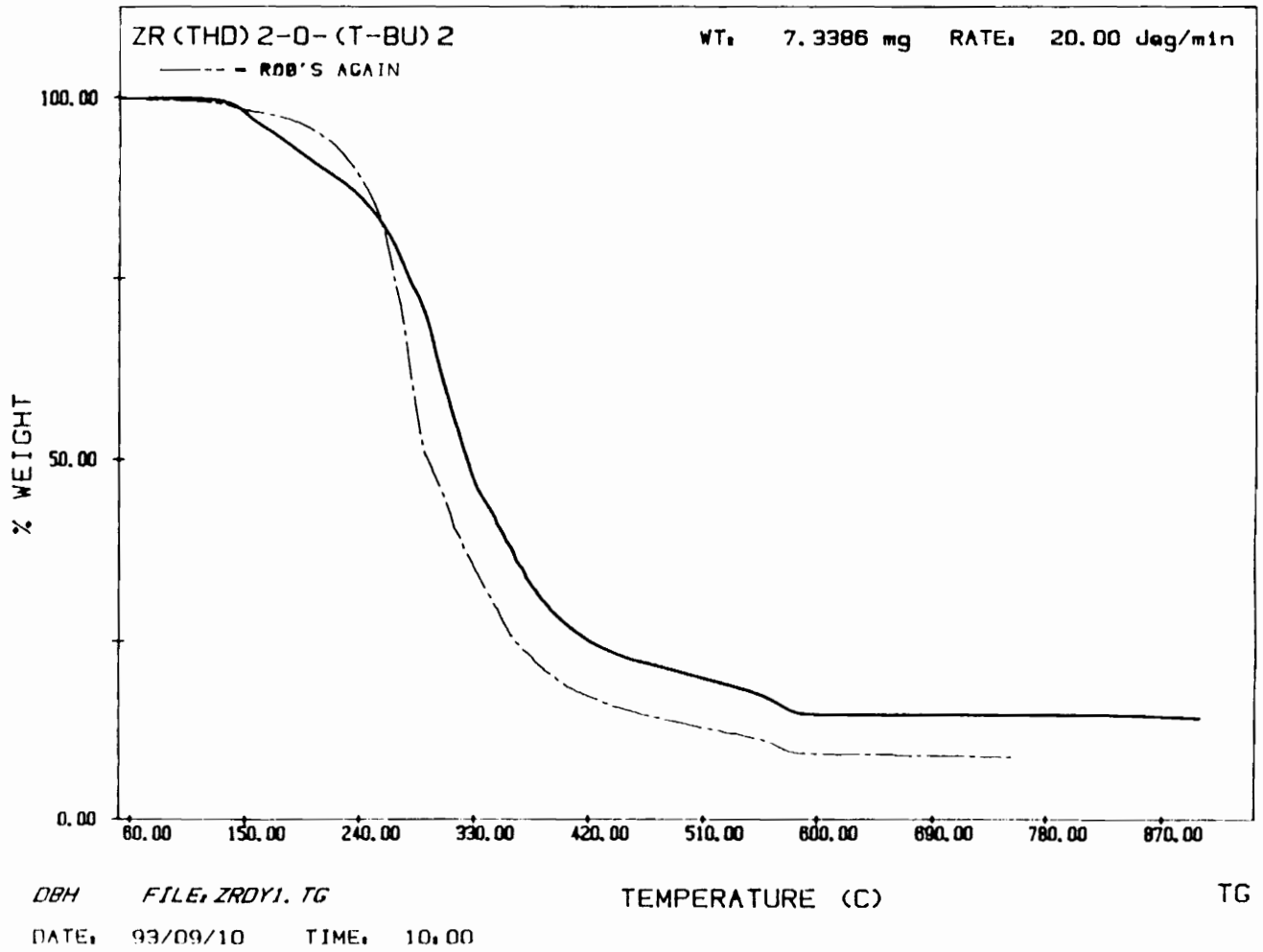


Figure8
Dynamic TGA Analysis of $Zr(O\text{-}^tBu)_2(Thd)_2$

two zirconium atoms. The ^{1}HNMR spectrum has two methyne peaks and a large group of peaks between 0.8 and 1.5 ppm (figure 10). Before further film deposition trials were undertaken, $Zr(O\text{-}^tBu)_2(Thd)_2$ was subject to a series of sealed tube decomposition studies to possibly determine what compound was being formed in the reactor and the mechanism by which it was formed. The $Zr(O\text{-}^tBu)_2(Thd)_2$ was sealed in an evacuated glass tube and then heated at 400°C for three, six and nine hours. Upon removal from the oven, the tubes were cooled and the contents analyzed. The proton NMR spectra all show the emergence of new methyne peaks as well as the t-butyl signals becoming broader. The proton NMR and mass spectrum for the material after heating at 400°C for 6 hours are shown in figures 11 and 12. The mass spectrum indicates the presence of two zirconium atoms based on the pattern found at mass 1000 M/Z.

IR analysis of the material did not provide clues to the identity of material. The presence of a peak at ~ 3000 cm-1 indicates that there is still some β-diketonate present in the material. The IR spectra did not change greatly with continued heating. IR data are presented in appendix B.

The mass spectrum of the material in the decomposition studies was the same as that obtained from the material in the reactor. The proton NMR of both compounds are also similiar. The compound formed in the sealed tube study is the same as the one formed in the reactor. Other decomposition studies to isolate compounds formed during the decomposition were unsuccessful.

Based on largely on the mass spectral evidence the following structure is proposed for the compound left in the reactor (figure 13). Two $Zr(O\text{-}^tBu)_2(Thd)_2$ combine to form the bi-metallic. During this combination, di-*t*-butyl ether is released. The molecular weight for the proposed complex is 1076. The largest signal in the mass spectrum is 1003 M/Z. This weight is the same as the bimetallic with the loss of a *t*-butoxide group. Importantly, the loss of *t*-butoxide is observed in the mass spectrum of $Zr(O\text{-}^tBu)_2(Thd)_2$.

If $Zr(O\text{-}^tBu)_2(Thd)_2$ were completely volatile the TGA data would show a weight loss of 100%. This is the ideal case for any thin film precursor. If $Zr(O\text{-}^tBu)_2(Thd)_2$ rearranges to the proposed bi-metallic, then a weight loss of 14% is expected. The isotherms produced at 160°C and 180°C (Appendix A) show a leveling off at approximately 86% of the original mass. This gives additional support to the formation of the bimetallic. If the bimetallic is volatile then the weight loss over time would again approach 100%. This case would also be ideal for chemical vapor deposition.

Since the TGA data also suggests that the material does not simply decompose to ZrO_2, a combination of vaporization and decomposition must be occurring. $Zr(O\text{-}^tBu)_2(Thd)_2$ is slightly volatile. When the compound is subjected to heat, some of the compound will enter the gaseous phase. Upon prolonged exposure to heat, the compound begins to form the proposed bi-metallic. This bi-metallic is no longer volatile and at a certain temperature begins to decompose. Using the dynamic TGA data, this temperature is about 220°C. It is at this point in the plot that the weight loss is the most rapid. Continued heating causes the compound to further decompose to zirconium oxide.

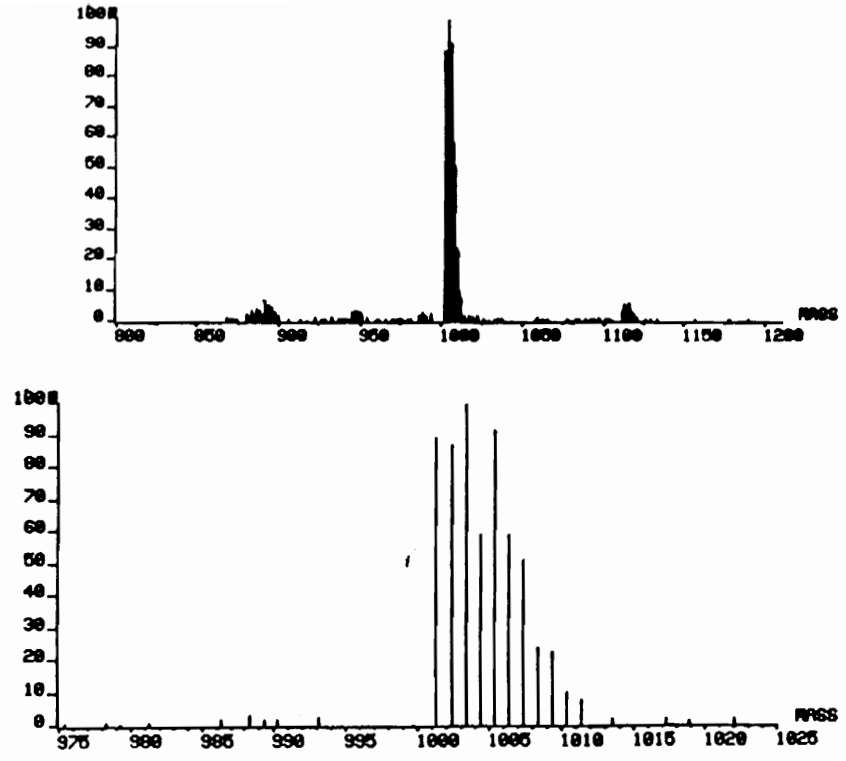


Figure 9
Mass Spectrum of the Residue Remaining in Reactor During Vapor Depostion Trials

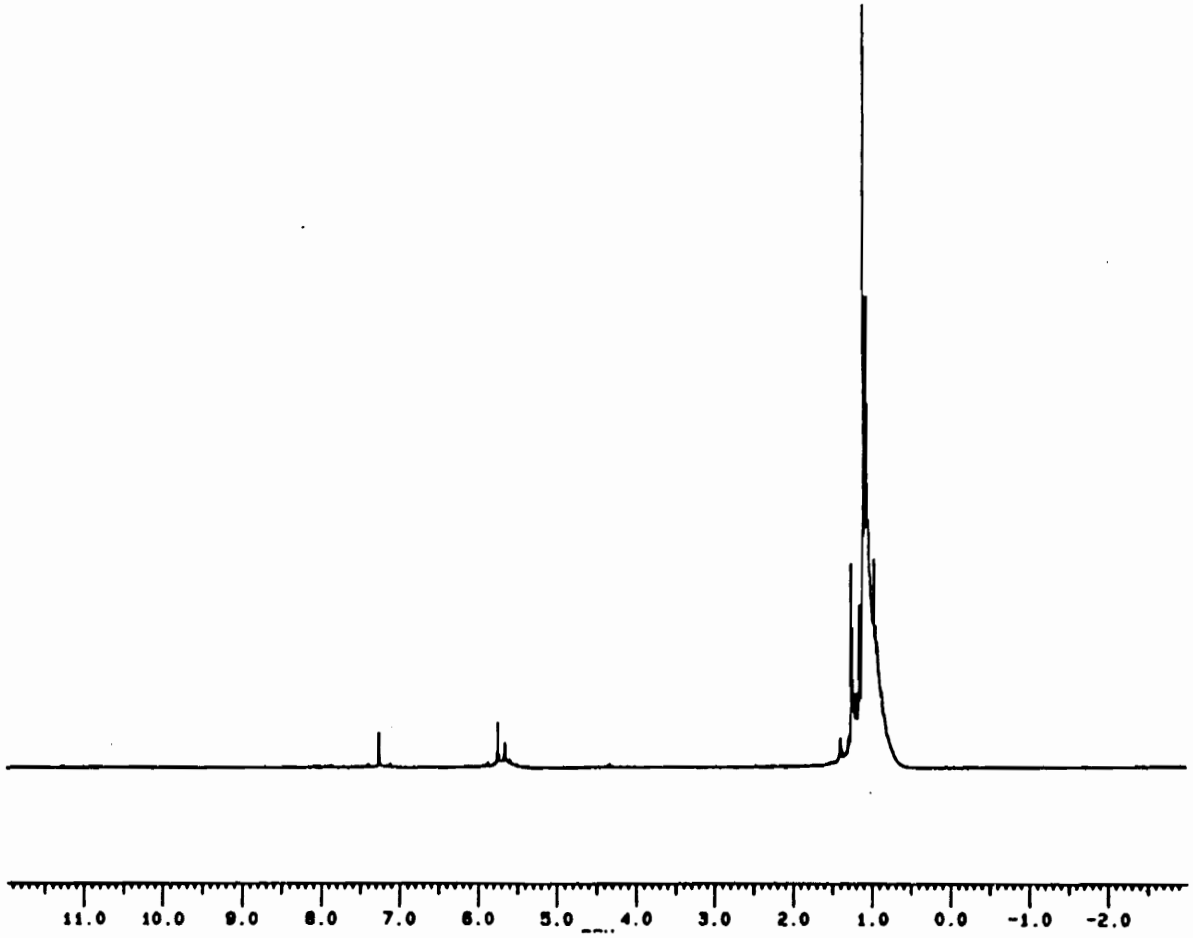


Figure 10
^{1}H NMR of the Residue Remaining in Reactor During Vapor Depostion Trials

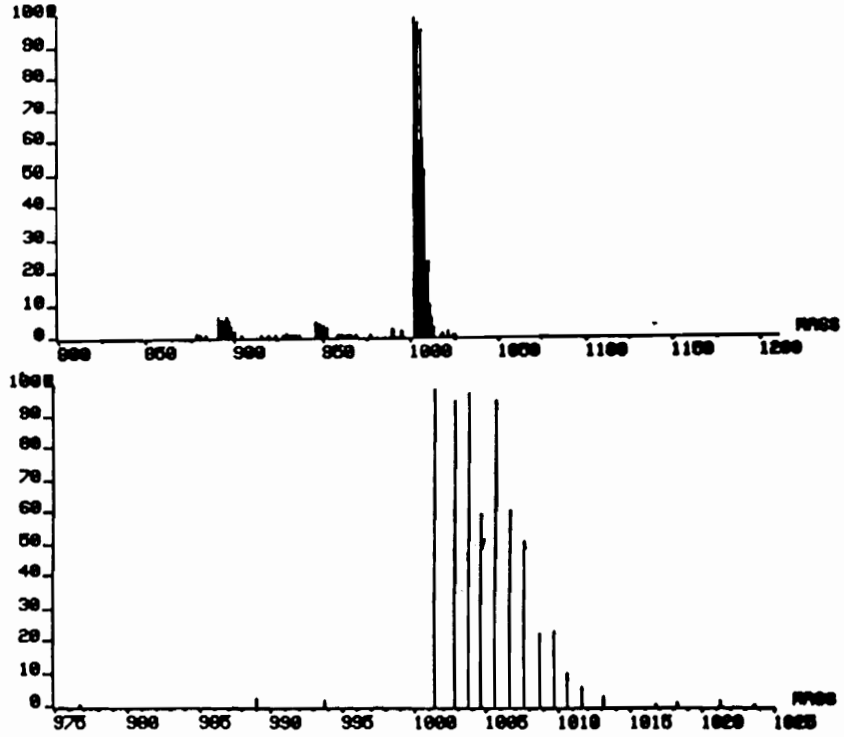


Figure11
Mass Spectrum of the Residue Remaining in Reactor During Decomposition Study

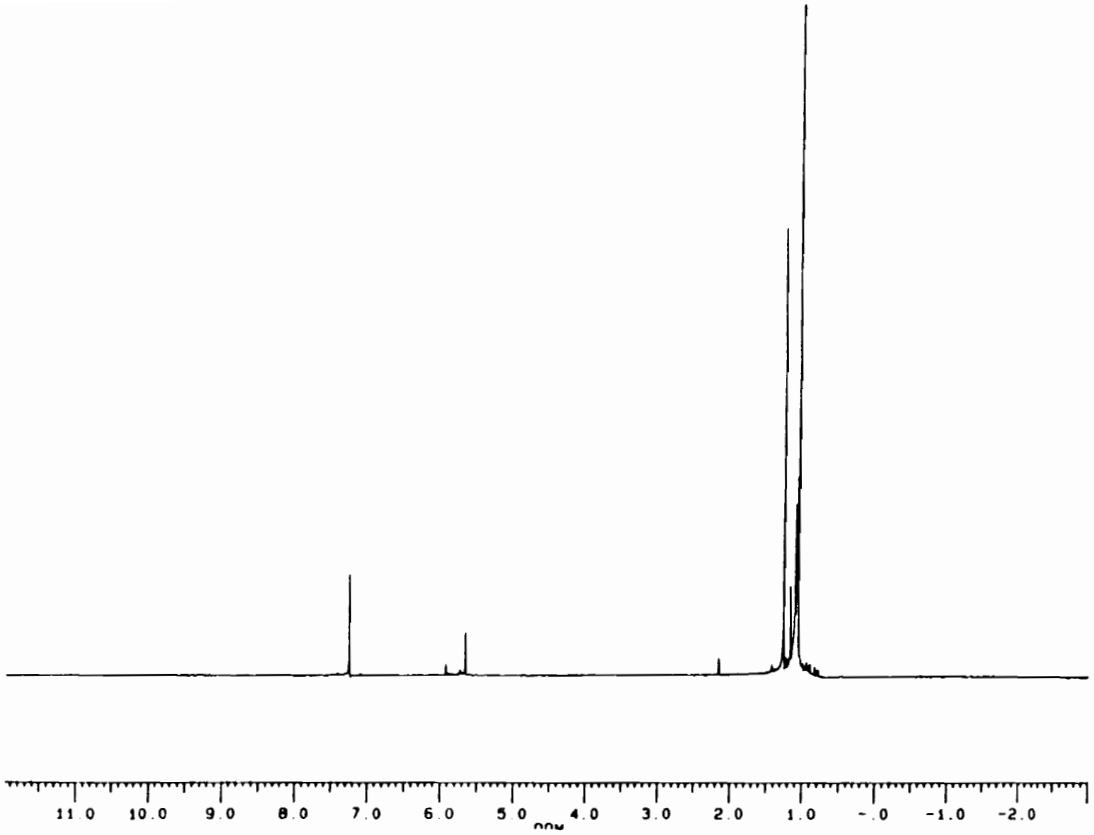


Figure 12
^{1}H NMR of the Residue Remaining in Reactor During Decomposition Study

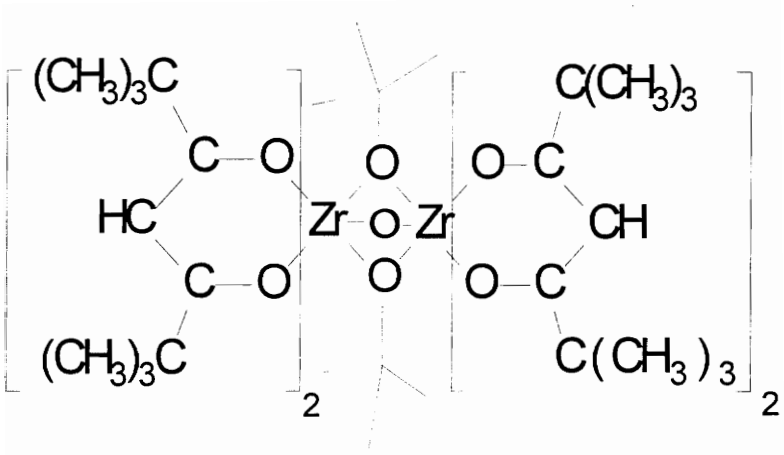


Figure 13
Proposed Structure of Decomposition Product

The weight loss levels off at 86% not the 80% expected if the compound completely decomposed to the oxide. Since the compound is initially volatile some zirconium does enter the vapor phase, this explains the 86% weight loss as not all of the compound is turned to the oxide. The amount of zirconium in the vapor phase was too low to produce detectable film growths and no deposition was noted for this compound.

2.3 Other Reactions to Improve the Precursor's Thermal Stability

The mechanism of bimetallic formation depended on the loss of a *tert*-butoxide group. If a more thermally stable substituent could be attached in place of the *tert*-butoxide group, the compound could avoid the formation of the bi-metallic and still be suitable for chemical vapor deposition applications. The reactions attempted met with little success. $Zr(O\text{-}^tBu)_2(Thd)_2$ and pivolic acid produced an insoluble white powder. The reaction generated free Thd as well as tertiary butanol. Tri *t*-butyl alcohol (tritox) was also used as to try to stabilize the complex. No reaction between the two compounds was observed most likely due to the steric effect of the two Thd molecules around the zirconium center and the size of tritox itself.

The final method was to attach another β-diketonate to $Zr(O\text{-}^tBu)_2(Thd)_2$. Acetylacetonate was added to $Zr(O\text{-}^tBu)_2(Thd)_2$. The compound generated was a white powder that was soluble in pentane. The ^{1}HNMR spectrum(figure 14) shows two signals for the Thd methine protons(5.5-5.8ppm) and three signals for the Acac methine

protons(5.2-5.5 ppm). The absence of a coordinated *tert*-butoxide signal indicates that all of the *tert*-butoxide groups have been replaced by the Acac ligand. Further purification did not produce a change in the ^{1}HNMR spectrum. Attempts to grow a crystal for x-ray diffraction did not produce crystals that were suitable for the analysis.

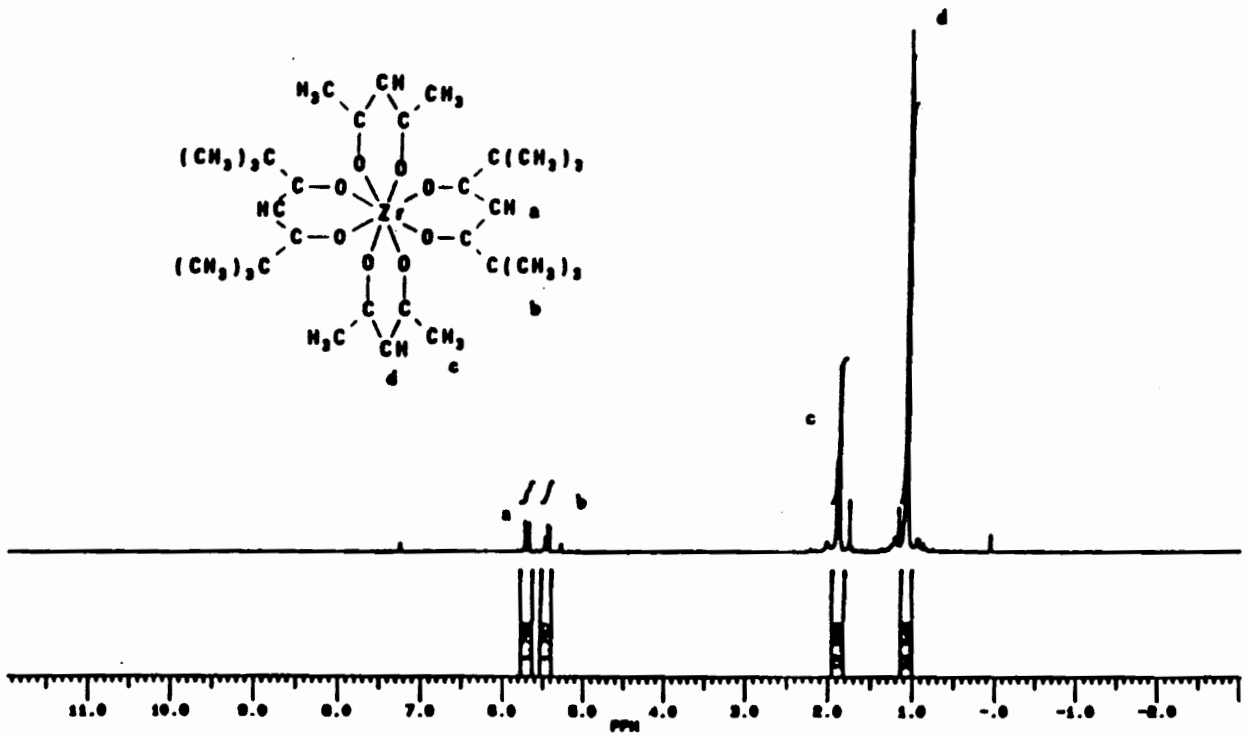


Figure 14
^{1}H NMR of Product Formed By Reaction of $Zr(O\text{-}^tBu)_2(Thd)_2$ and Acac

Chapter 3 Conclusions

$Zr(O\text{-}^tBu)_2(Thd)_2$ was not as thermally stable as was hoped. This complex, although it does not meet the desired precursor requirements, is still an interesting complex. The compound was unstable at elevated temperatures and underwent a rearrangement to form the zirconium bi-metallic which ultimately would decompose to ZrO_2. The bi-metallic it formed is another unusual compound. The thermal gravimetric data provided most of the clues as to what was occurring during the film deposition trials. The complex tends to rearrange upon prolonged heating. Characterization of the intermediates formed during heating proved to be difficult. Attempts to collect the volatile compounds that eluted from the decomposition trials were unsuccesful.

Although $Zr(O\text{-}^tBu)_2(Thd)_2$ lacks the thermal stability necessary for CVD of zirconium films, it still has other potential uses. The compound has a potential for sol-gel preparation of zirconium films. It is soluble in volatile, hydrocarbon solvents and will decompose to the oxide upon heating.

The attempts to substitute for the labile *tert*-butoxide group met with limited success. The $Zr(Acac)_2(Thd)_2$ compound has some promise as a precursor and needs to be fully characterized. This compound is a step in the right direction for producing a more thermally stable compound.

Experimental

All reactions were performed under inert atmosphere. All solvents were dried and distilled prior to use. Reagents were purchased from Aldrich Chemical Company and used without further purification. NMR data was obtained on a Bruker 200 Mhz spectrometer. IR data was collected on a PE 710 B spectrometer using a KBr pellet.

$Zr(O\text{-}^tBu)_2(Thd)_2$ To 10ml of pentane, 5 ml of $Zr(O\text{-}^tBu)_4$ (0.012 mol) was added. With constant stirring, 5.6 ml (0.024 mol) of 2,2,6,6 tetramethyl 3,5 heptadione was added dropwise. The reaction was then allowed to stir overnight. The pentane was removed slowly under a stream of nitrogen until large colorless crystals had formed. The reaction was then filtered and the crystals vacuum dried.(yield 92%). (**^{1}HNMR** δ 5.6 ppm 1H(s), 1.5 ppm 9H(s), 1.2 ppm 18H(s))

Note: The following describe procedures that did not produce the desired compounds. ^{1}H NMR data suggests that isomers exist for all of the following except tritox.

$Zr(O\text{-}^tBu)_2(Acac)_2$ Acetylacetonate was added dropwise to a solution of 1 ml(2.6mmol) of $Zr(O\text{-}t Bu)_4$ in 10ml of pentane, 0.5 ml(5.2 mmol). The reaction was allowed to stir overnight. The mixture was filtered and the white solid dried in vaccu. Repeated crystallization from pentane did not afford a pure product (**^{1}HNMR** δ 5.4 ppm 1H(d), 2.1 ppm 6H(d), 1.5-1.0 ppm 2H(m)).

$Zr(O\text{-}^tBu)_2(Dbzm)_2$ Dibenzoyl methane(1.14g(5.2mmol)) was dissolved in a minimum amount of pentane(~15ml). The solution was then slowly added to 1 ml (2.6mmol) of $Zr(O\text{-}^tBu)_4$ dissolved in 10ml of pentane. The reaction was allowed to stir overnight and then filtered and dried in vaccu The yellow solid was then recrystallized from toluene. Further recrystallization and sublimation efforts did not afford a pure compound. (**^{1}HNMR** δ 8.2-7.0 ppm 10H(m), 7.1-7.0 ppm 1H(d), 1.2-1.0ppm 4H(s))

$Zr(O\text{-}^tBu)_2(Bzac)_2$ A solution of 0.84g (5.2mmol) of 1-benzoyl acetone in 10 ml of warm pentane was added to 1 ml(2.6mmol) of $Zr(O\text{-}^tBu)_4$ dissolved in 10ml of pentane. The reaction was allowed to stir overnight then filtered. The remaining solid was dried in vaccu and recrystalized from toluene. Recrystallization and purification methods did not yield a pure product. (**^{1}HNMR** δ 8.0 - 7.2 ppm 5H(m), 2.1 ppm 3H(d), 1.2 ppm 9H(d))

Tri-*t*-Butyl Alcohol(tritox) To a 0.5M solution of *t*-Butyl Lithium in ether, 1 mol of pavolic acid in 200 ml of ether was added dropwise. The reaction was kept at -35°C during the entire addition(~40 minutes). After one hour the reaction was filtered through glass wool and poured into a flask containing approximately 500g of crushed ice. After the ice had melted, the ether layer was collected, washed with water and then dried using $MgSO_4$. The ether was removed and the residue was vacuum distilled(~15mm Hg). The product is collected a 130°C and recrystallized from methanol. (**^{1}HNMR** δ 4.0ppm 1H (s)1.2 ppm 27H(s))[29]

$Zr(tritox)_2(O\text{-}^tBu)_2$ Tritox(0.48g, 0.024 mol) in 10ml of pentane was added dropwise to 5 ml of $Zr(O\text{-}^tBu)_4$ (0.012 mol) in 10 ml of pentane. The reaction was stirred overnight and the solvent removed. The resulting solid was insoluble in all common solvents. Sublimation of the compound resulted in pure tritox and an insoluble compound left in the bottom of the sublimator. (**^{1}HNMR** δ 1.5 ppm 9H(m), 1.2 ppm 18H(m))

$Zr(Thd)_2((CH_3)_3COO)_2$ To 5g (0.008 mol)of $Zr(O\text{-}^tBu)_2(Thd)_2$ in 10ml of pentane, a solution of 1.5g (0.016 mol) in 10ml of pentane was added dropwise. The solution was stirred for 2 hours, and the pentane removed in vaccu. The white solid was recrystalized from pentane. Tertiary butanol and other unidentified products were the result.

$Zr(Acac)_2(Thd)_2$ A solution of 0.9g of Acac in 10 ml of pentane was added dropwise to 5g of $Zr(O\text{-}^tBu)_2(Thd)_2$ (0.008 mol) in 10 ml of pentane. The reaction was stirred for eight hours and then cooled with dry ice. The reaction mixture was then filtered and the mother liquor was dried in vaccu. The white solid was recrystalized from cold pentane as above. (**^{1}HNMR** δ 5.7-5.5 ppm 1H(m), 5.4-5.2 ppm 1H(m), 1.9-1.7ppm 6H(m) 1.2-1.0ppm 9H(m))

Thermal Gravimetric Analysis

Thermal Gravimetric Analysis were performed on a Perkin Elmer TGS-2/TADS Thermogravimetric Analyzer. All runs were under a nitrogen purge.

Isothermal runs from 50°C to T_f with a Δ of 40°C/min to T_f then held for the specified amount of time.

Dynamic runs were from T_i to T_f with a Δ of 20°C/min.

Decomposition Studies

$Zr(O\text{-}^tBu)_2(Thd)_2$ (~0.5g) was sealed under vacuum in 10cm glass tube (~50mm id). The tubes were placed in a muffle furnace for a specified time and temperature. The tubes were cooled and the residue was analyzed.

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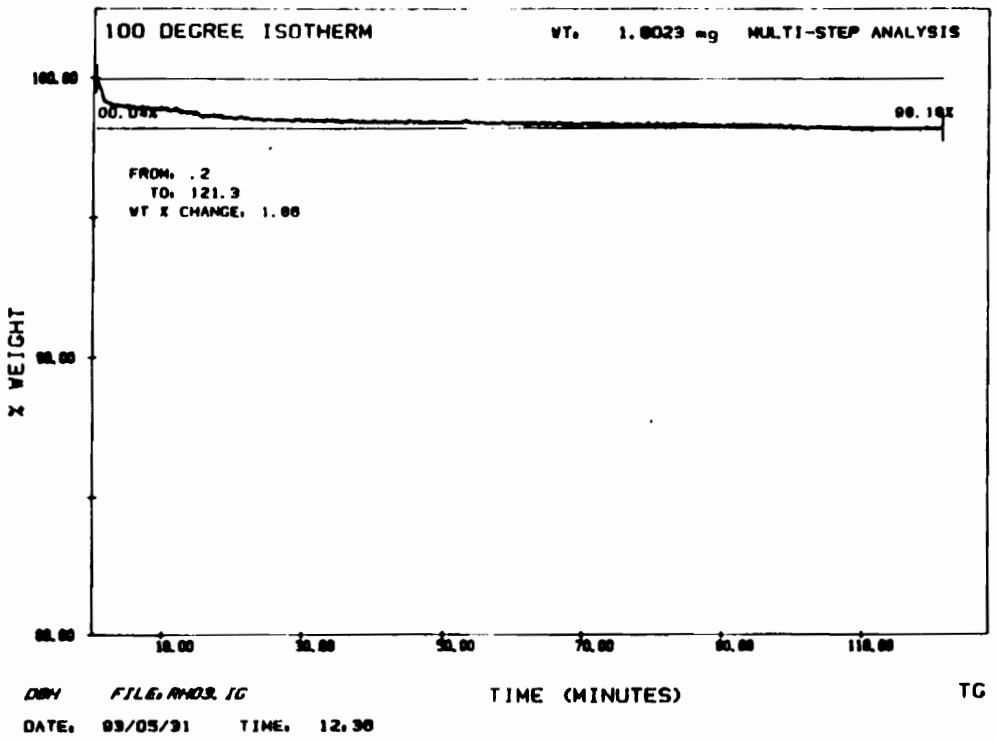
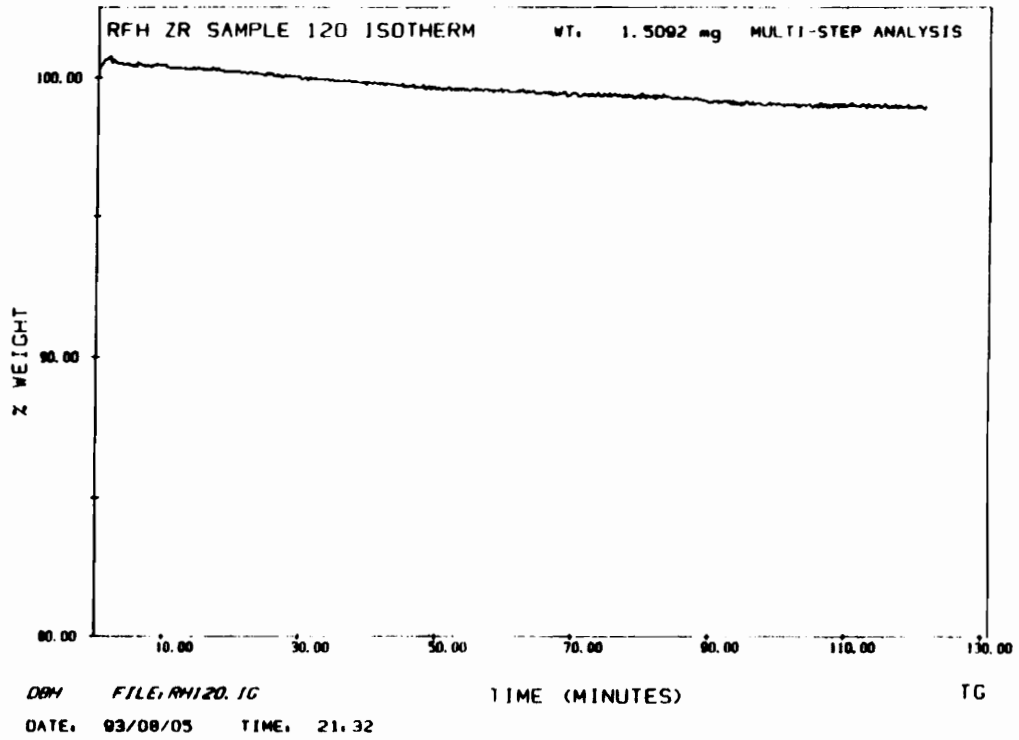
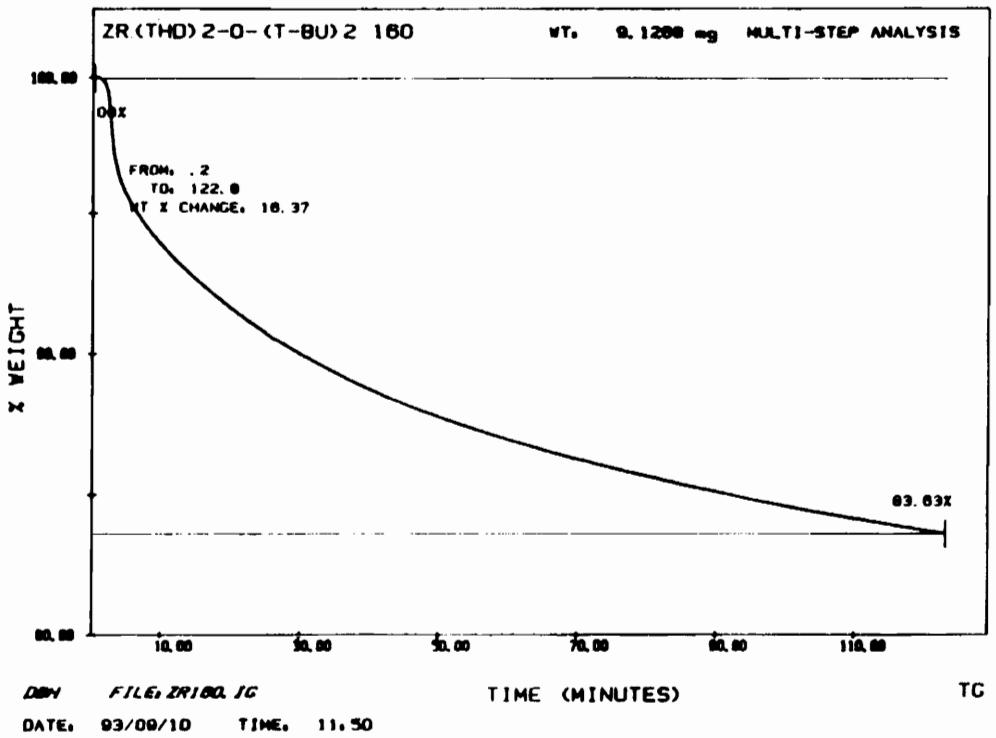


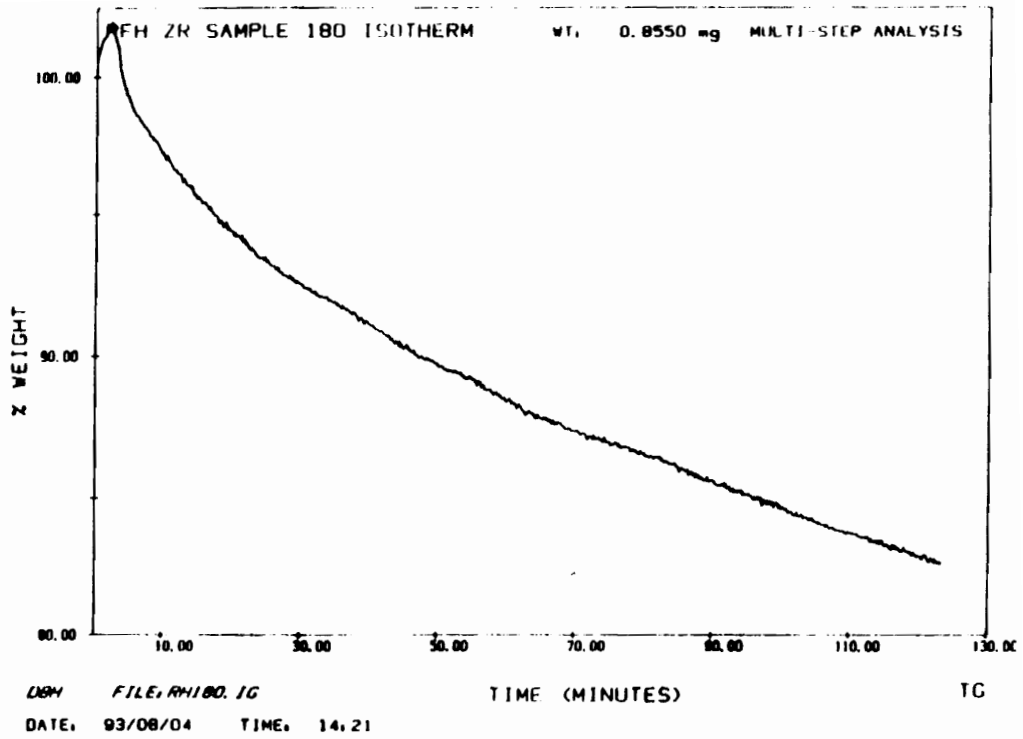
Appendix A-1
100°C Isothermal TGA of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$



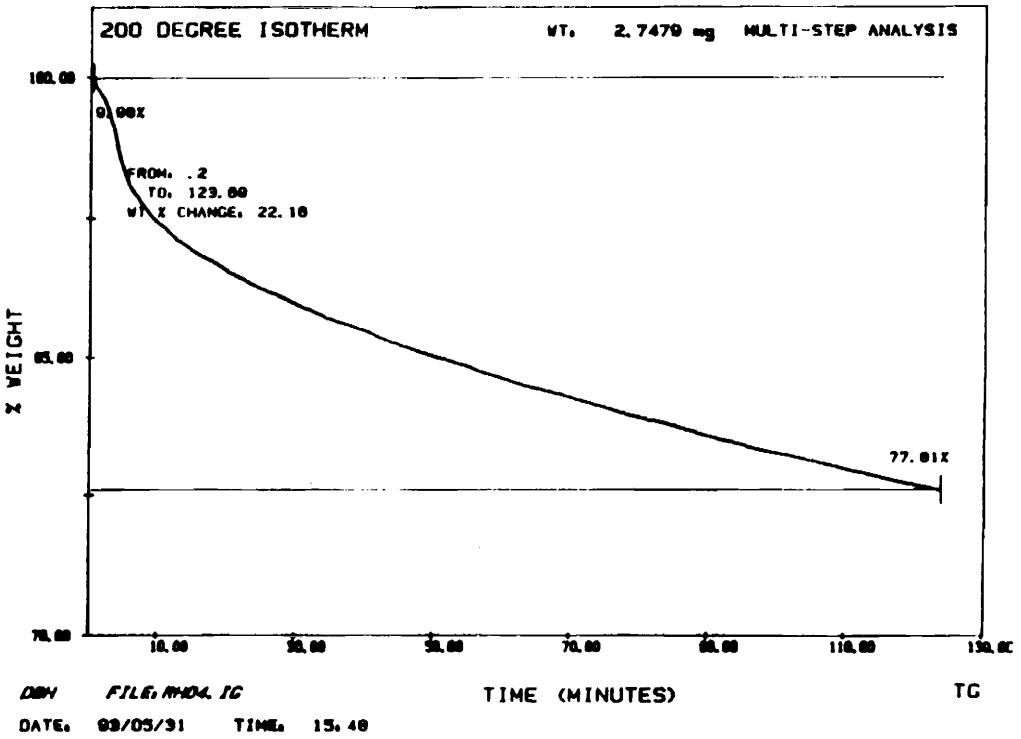
Appendix A-2
120°C Isothermal TGA of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$



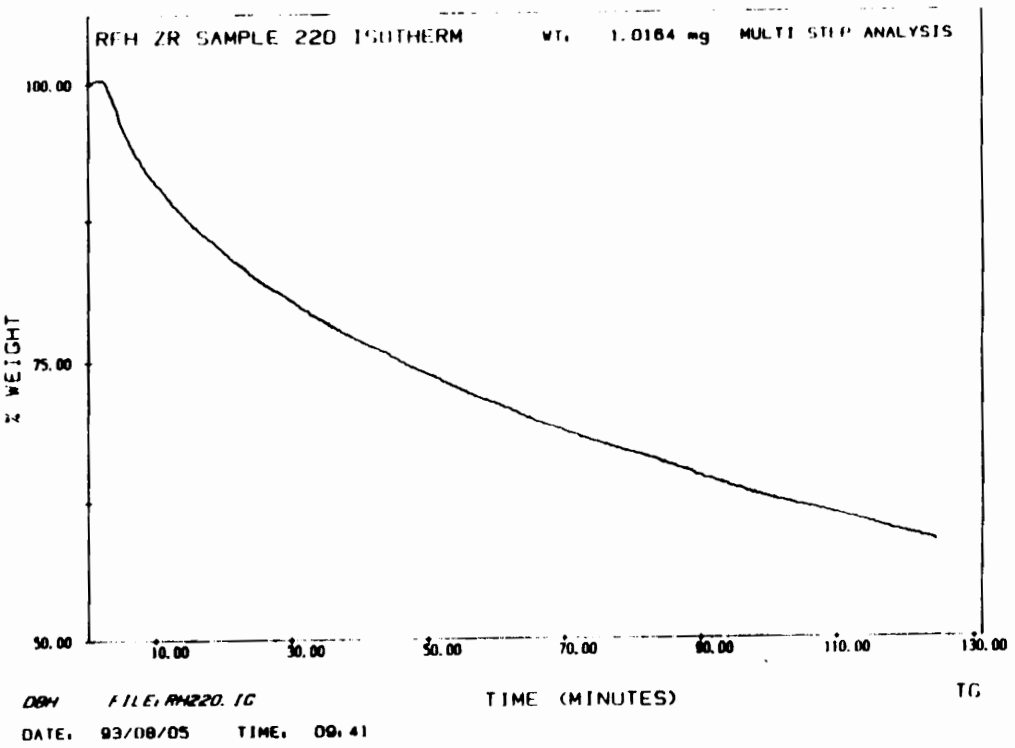
Appendix A-3
160°C Isothermal TGA of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$



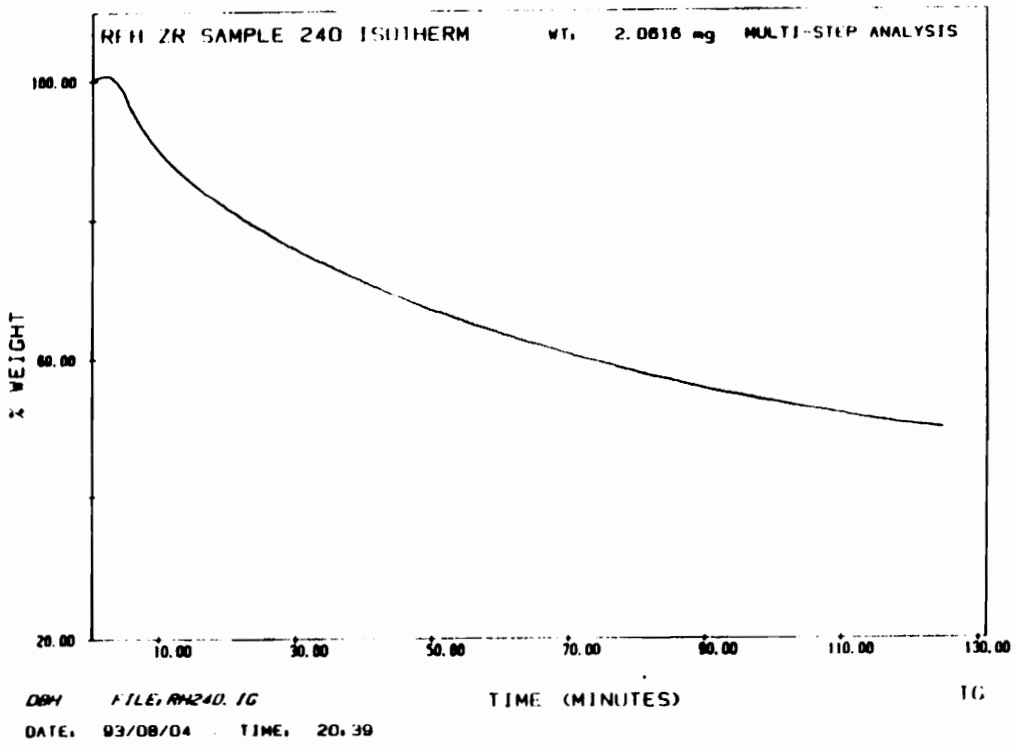
Appendix A-4
180°C Isothermal TGA of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$



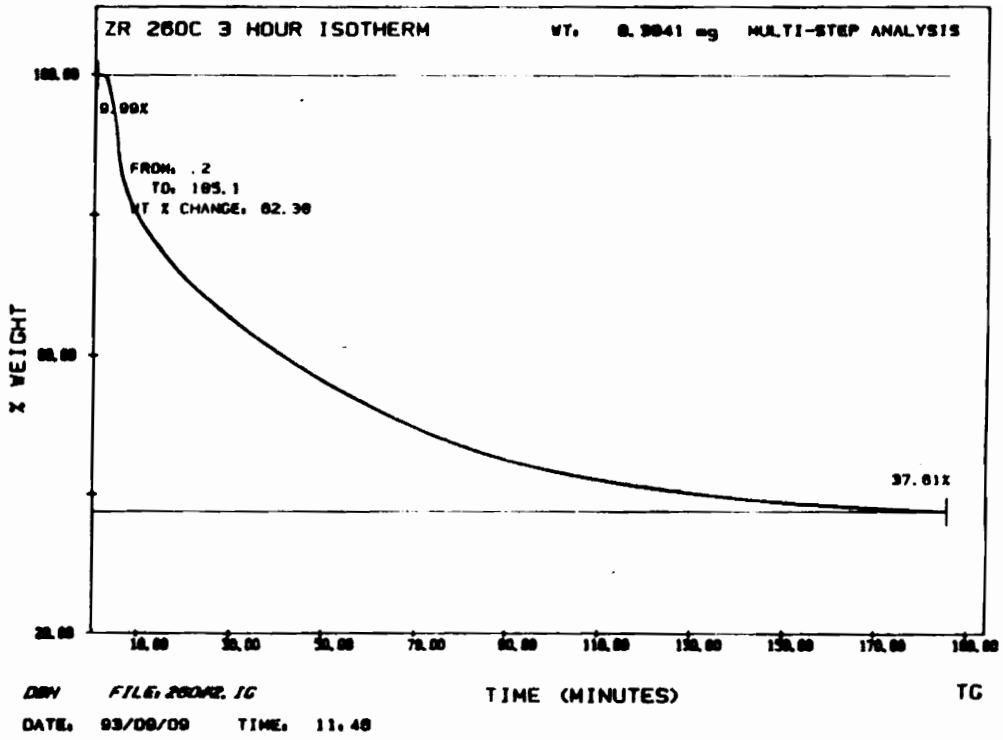
Appendix A-5
200°C Isothermal TGA of $Zr(O\text{-}tBu)_2(Thd)_2$



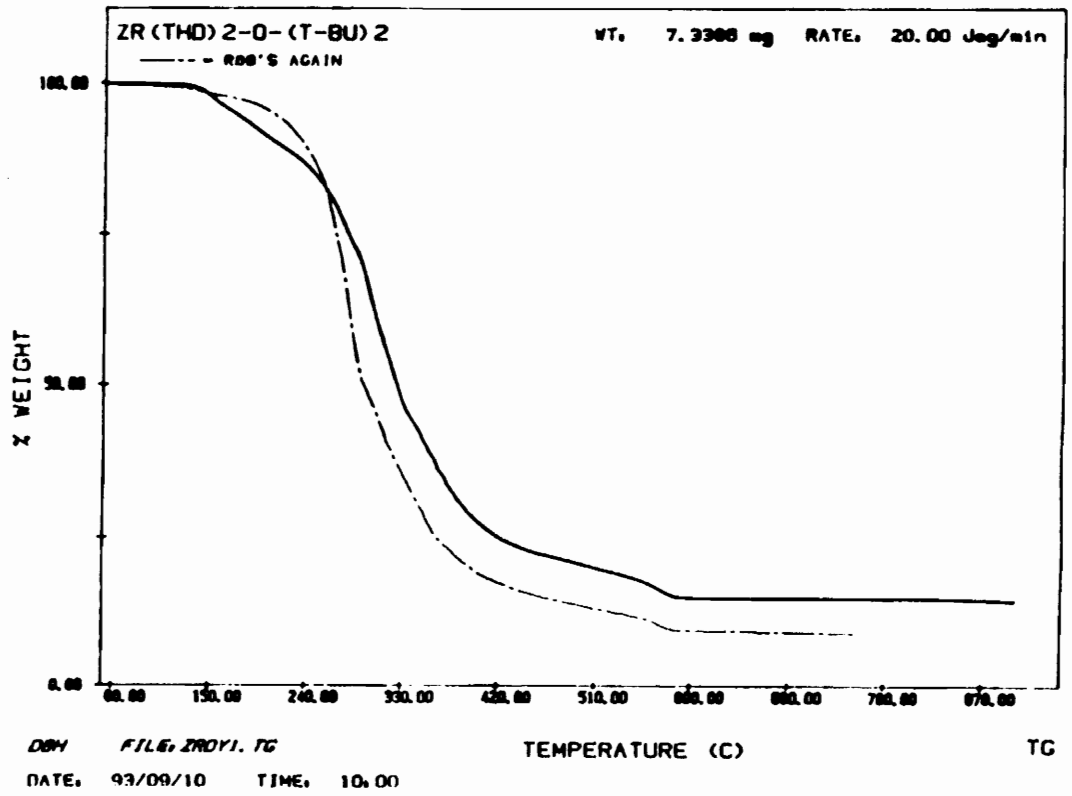
Appendix A-6
220°C Isothermal TGA of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$



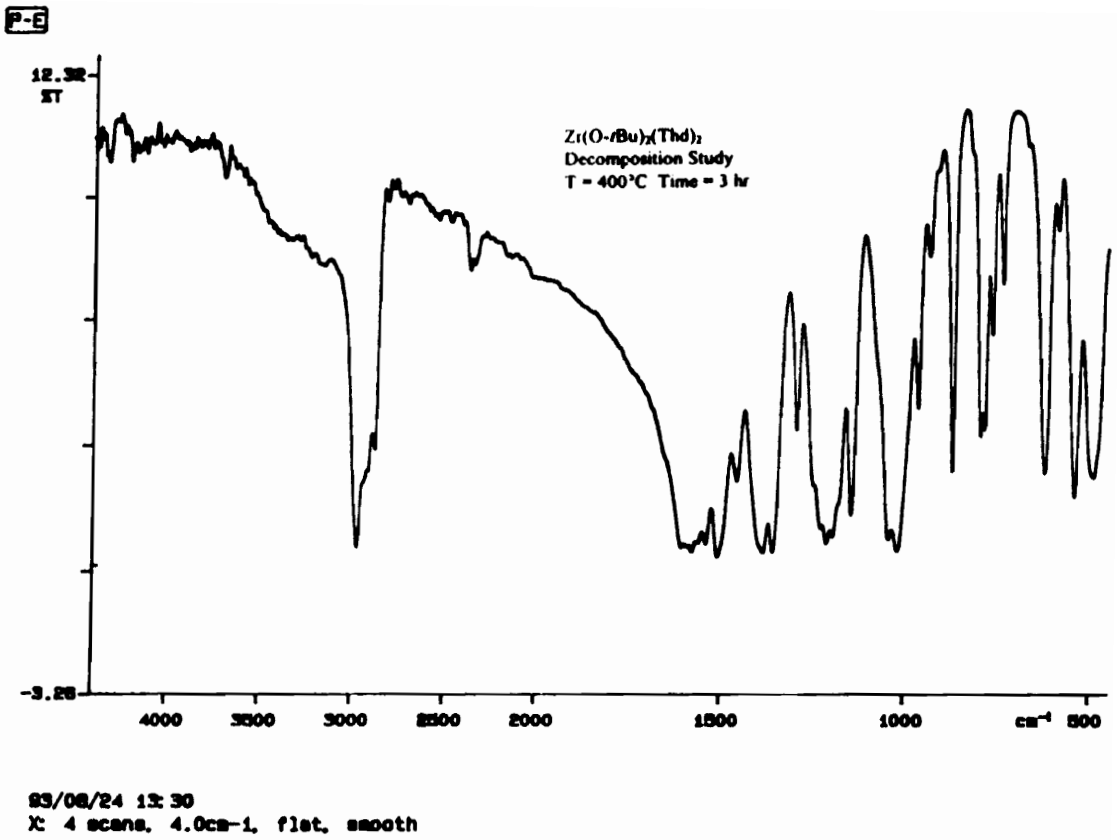
Appendix A-7
240°C Isothermal TGA of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$



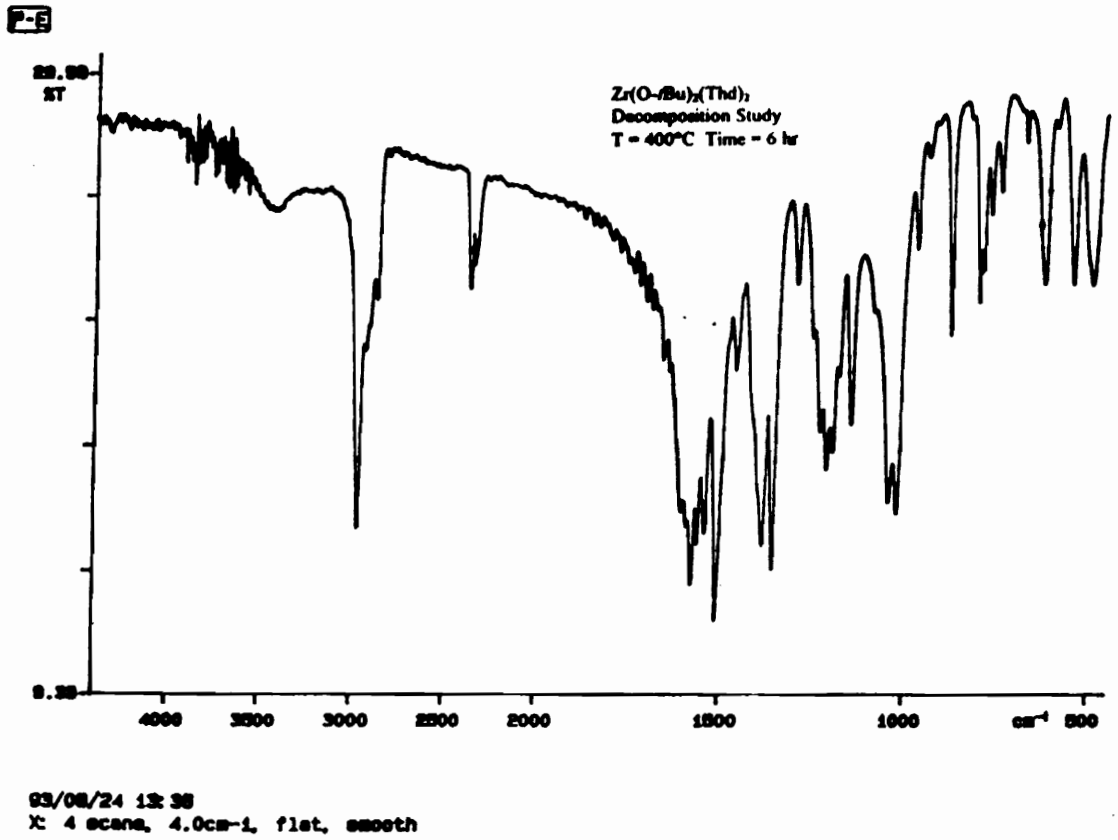
Appendix A-8
260°C Isothermal TGA of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$



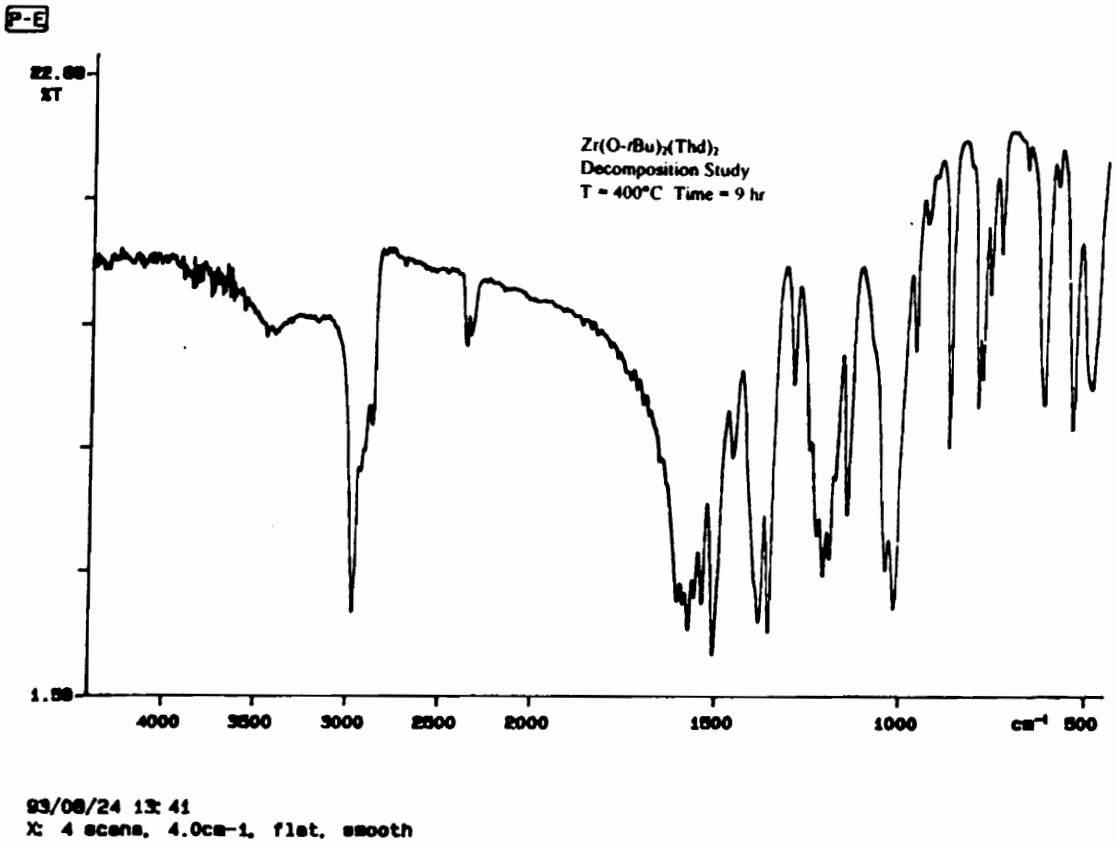
Appendix A-9
Dymanic TGA (60-900°C) of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$



Appendix B-1
IR Spectrum of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$ After 3 Hours at 400°C



Appendix B-2
IR Spectrum of $Zr(O\text{-}tBu)_2(Thd)_2$ After 6 Hours at 400°C



Appendix B-3
IR Spectrum of $Zr(O\text{-}t\text{Bu})_2(Thd)_2$ After 9 Hours at 400°C

VITA

Robert Francis Harris was born on November 7, 1968 in Augusta, Georgia. The son of a United States Army officer, he has lived in many parts of the United States as well as in the old West Germany. In May of 1986, he graduated from Stafford Senior High School in Stafford County, Virginia. In May of 1991, He received a Bachelor's of Science degree in chemistry from Virginia Polytechnic Institute and State University. Upon completion of his Bachelor's degree, he pursued a Master's of Science degree in chemistry under the guidance of Brian E. Hanson and completed his studies in April of 1994. During his studies, he received an award for distinguished teaching in undergraduate instruction for inorganic synthesis lab. He also presented this work at the 45th Southeast Regional ACS meeting in Johnson City, Tennessee. He is currently working in the labs of Dr. Kent Stewart in the Department of Biochemistry at Virginia Tech.