

AD-A204 790

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS DTIC FILE CODE	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report Number 6		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Microelectronics Center of North Carolina	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Defense Contract Administration Services Management Area - Atlanta	
6c. ADDRESS (City, State, and ZIP Code) 3021 Cornwallis Road, Research Triangle Park, N.C. 27709		7b. ADDRESS (City, State, and ZIP Code) 805 Walker Street, Marietta, Georgia 30060-2789	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-85-C-0871	
8c. ADDRESS (City, State, and ZIP Code) Dept. of the Navy 800 N. Quincy Street Arlington, VA 22217-5000		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) The Relative Stabilities of Tungsten Hexacarbonyl, Silver Neodecanoate, some Metal Acetyl- and Hexafluoroacetyl-acetonates and the Thermal Properties of the Palladium(II) acetonates.			
12. PERSONAL AUTHOR(S) Shelly Lucie Poston, Arnold Reisman			
13a. TYPE OF REPORT Technical Report #6	13b. TIME COVERED FROM 8/1/88 TO 1/31/89	14. DATE OF REPORT (Year, Month, Day) 1989, February, 3	15. PAGE COUNT 32
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Abstract is attached.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Pamela K. Adams		22b. TELEPHONE (Include Area Code) 919-248-1426	22c. OFFICE SYMBOL

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OFFICE OF NAVAL RESEARCH

Contract N00014-C-85-0871

Technical Report No. 6

The Relative Stabilities of Tungsten Hexacarbonyl, Silver Neodecanoate,
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of the Palladium (II) acetonates.



by

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Prepared for Publication

in the

Journal of Electronic Materials

North Carolina State University
Department of Chemistry
Department of Electrical and Computer Engineering
Raleigh, North Carolina

Accession For	
NTIS GRA&I	☒
DTIC TAB	☒
Unannounced	☐
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February 3, 1989

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Abstract

The relative stabilities of silver neodecanoate, tungsten hexacarbonyl, and a series of metal acetyl- and hexafluoroacetyl- acetonates, were determined using differential thermal analysis(DTA) and weight loss analysis. In general, the acetylacetonates decompose in the solid state at relatively low temperatures(100-200°C), with several of them exhibiting appreciable vapor pressures at temperatures below which their decomposition rate is significant. Hexafluoro derivatives of these compounds are, in general, more volatile and decompose at higher temperatures.

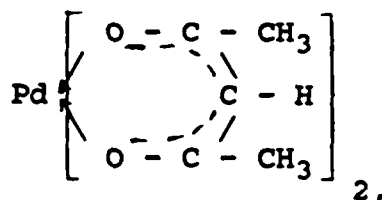
The thermal decomposition behavior of palladium(II) acetylacetonate and palladium(II) hexafluoroacetylacetonate were each investigated using DTA at atmospheric pressure and under each compound's equilibrium or decomposition product(s) vapor pressure, weight loss analysis, X-ray analysis, emission analysis, and chemical composition analysis. At the heating rates employed, $< 2^{\circ}\text{C}/\text{min}$, palladium(II) acetylacetonate tends to decompose upon heating in either an inert or oxidizing atmosphere before significant quantities volatilize. On the other hand, palladium(II) hexafluoroacetylacetonate tends to volatilize completely before any signs of decomposition are observed under the same conditions. Heating palladium(II) acetylacetonate in argon, at $\leq 2^{\circ}\text{C}/\text{min}$, shows the onset of

an endotherm at approximately 196°C , at the conclusion of which a product containing 75% palladium was found, the remainder comprised of carbon, hydrogen and oxygen. In an oxidizing atmosphere at the above mentioned heating rate, Palladium(II) acetylacetonate decomposes exothermically at 180°C yielding essentially pure palladium. Continued heating in oxygen, to 800°C results in pure PdO . At 900°C , the PdO decomposes yielding pure palladium.

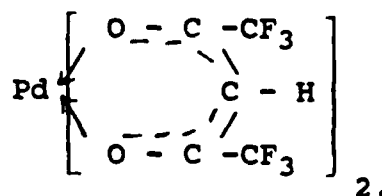
Depending upon the heating rates applied, one or two endotherms may be observed during the heating of palladium(II) hexafluoroacetylacetonate. Heating at $2^{\circ}\text{C}/\text{min}$ in either an argon or oxygen atmosphere, results in an endothermic transition due to fusion at 105°C in argon(101°C in oxygen), followed by a second endothermic transition at 231°C in argon(223°C in oxygen), due to the normal boiling point being achieved. If heating rates are slow enough, e.g. $0.1^{\circ}\text{C}/\text{min}$, complete volatilization may occur before the normal boiling point is reached.

1. INTRODUCTION

In the ongoing study of the physical, thermal and optical characterization of a series of metal-organic compounds for use as thin film preparation alternatives[1,2,3], the present report describes the relative stabilities of silver neodecanoate, tungsten hexacarbonyl some metal acetyl- and hexafluoroacetyl- acetonates and the thermal properties of their palladium analogues. The acetylacetonates(acac), and hexafluoro derivatives of these(hfa) are forms of metal-organic compounds known as β -diketonates, in which the metal is covalently coordinated to the bidentate ligand of acetylacetonate or its fluorinated derivative. Examples are, $\text{Pd}(\text{acac})_2$,



and palladium(II) hexafluoroacetylacetonate(hfa),



In order to use these compounds as alternatives to conventional thin film deposition approaches in

microelectronics, it was desirable to differentiate the metal-organic compound characteristics of the acacs and hfas according to their physical and chemical properties. Volatility and thermal decomposition behavior each represents an important form of such differentiation, since it could determine how a given metal-organic might best be used to form thin films. By heating at a slow rate, $2^{\circ}\text{C}/\text{min}$, in an attempt to approximate thermodynamic equilibrium, a differentiation was sought to establish which compounds 1) would tend to decompose upon heating before significant volatilization occurred and 2) would tend to volatilize completely upon heating before significant amounts of decomposition occurred.

Once these rough classifications had been made they could be used to optimize possible alternative approaches to current thin film formation techniques. For instance, those which possess appreciable vapor pressure could be used for both solid state or chemical vapor transport applications utilizing optical stimulation when appropriate[3]. Those which decompose significantly upon heating might be more appropriate for use in optical-thermal assisted decomposition in the solid state. Other approaches such as the use of the less stable acacs and hfas in "inks" also suggest themselves, depending upon the properties of the starting material[4].

The present paper will discuss the temperature stability of a number of acacs and hfas, as well as silver

neodecanoate and tungsten hexacarbonyl. In addition, detailed analyses of two of the more potentially important compounds in the acac and hfa series for microelectronic applications, palladium(II) acetylacetonate and palladium(II) hexafluoroacetylacetonate, will also be presented.

2. EXPERIMENTAL

A. Thermal Investigations

The thermal behavior was studied using a differential thermal analyzer(DTA) designed by one of the authors and described previously[1,5]. Samples were compared with a reference which consisted of a closed fused silica crucible containing aluminium oxide, Al_2O_3 (Fisher Sci. Co., Raleigh Branch Office, P.O. Box 40339, Raleigh, N.C. 27629). Supporting analytical techniques such as X-ray, emission analysis, etc. are described below.

B. Materials

The acetylacetonates and hexafluoroacetylacetonates were purchased from Strem Chemicals Inc.(7 Mulliken Way, Newburyport, Ma. 01950). Silver neodecanoate was purchased from Electrink, Inc.(7414 Trade St., San Diego, Ca. 92121), and tungsten hexacarbonyl from Alpha Products(152 Andover St. , Danvers, Ma. 01923). The metal-organics were stored in the containers in which they were received, in a desiccator

over a desiccant, (TM)Drierite(Fisher Sci. Co., Raleigh Branch Office, P.O. Box 40339, Raleigh, N.C. 27629).

Metal content was determined by atomic absorption and the carbon and hydrogen analysis was determined by combustion analysis in an outside laboratory. Results of the analyses on the metal-organic compounds are given in reference 2. The status of some of these compounds as hydrates is also discussed in reference 2, and these compounds were studied in that form.

C. X-rays

Debeye-Scherrer powder diffraction studies were performed on a Norelco diffractometer(type no. 12044, N. America Philllips Co.,85 McKee Dr. Mahwah, N.J. 07430) using Cu K α radiation.

3. EXPERIMENTAL RESULTS AND DISCUSSION

A. Temperature Stability

To assess the overall volatilization behavior of all the compounds studied, each compound was heated to 500°C in either an inert or an oxidizing atmosphere at 2°C/min. Weight losses were determined by weighing the sample before and after heating in the DTA. Table I lists the results obtained upon heating in these ambient atmospheres at 2°C/min. As shown in Table I, the percent weight lost(%loss) of each compound upon heating in argon(a) and oxygen(o) is compared with the theoretical percent ligand(%lig) in the

compound. For example, for palladium(II) acetylacetonate the theoretical weight percent ligand, acetylacetonate, is 65.5% (the remaining 34.5% corresponds to the percent metal, Pd). In argon, at a heating rate of 2°C/min to 500°C, a 57.0% loss is observed, while in oxygen a 59.2% loss is achieved. These data indicate that under the conditions of the experiment, the combination of decomposition and volatilization does not achieve a weight loss corresponding to the ligand content. Visual examination of the crucible after the thermal treatment indicated extensive decomposition had occurred. On the other hand, for the corresponding hexafluoro derivative of palladium, a 99.8% loss is observed in both argon and oxygen at the heating rate used. This indicates that the Pd(hfa)_2 and/or its decomposition products are volatile.

In general, from Table I we see that the acacs tend to lose less than the theoretical weight percent ligand, which indicates that the volatility of these acacs are low, and/or they decompose significantly but not completely in the solid state. Both conditions are probably true since visual examination of crucibles showed, in all cases, that decomposition was extensive. In the case of Al(acac)_3 in argon, Rh(acac)_3 in argon, silver neodecanoate in either argon or oxygen, and Pt(acac)_2 in argon and oxygen the observed weight losses corresponded to the initial theoretical percent ligand. The residues in the rhodium, aluminum, silver and platinum DTA crucibles were found to be

pure metal via X-ray diffraction. The decompositional pathway for Al(hfa)_3 appears to be different from Al(acac)_3 and is discussed at the end of the section.

For the rhodium, silver and aluminum we can assume volatility was very low and decomposition was complete by the time 500°C was achieved. With the Pt(acac)_2 it is probably the case that the volatility is also low, but not as low as for the other three since the weight loss is slightly greater than the theoretical in argon and oxygen. The platinum result appears to be in agreement with Bett[6], who studied the thermal decomposition of Pt(acac)_2 in hydrogen and air using thermogravimetric analysis(TGA) and DTA. Bett found a weight loss greater than the theoretical based on ligand loss alone. This indicates some slight volatility of the Pt(acac)_2 .

In two other cases, Cr(acac)_3 in oxygen and Cu(acac)_2 in argon, weight loss also exceeded the theoretical percent ligand, indicating some volatility had occurred. These two compounds were examined at a heating rate of 0.5°C/min to 300°C with all other parameters the same. It was found that at a heating rate of 0.5°C/min the compounds lost more weight than at a 2.0°C/min , but nothing approaching 100% weight loss. This confirms that these compounds are slightly volatile. In addition, decomposition was still apparent by visual examination of the crucibles at the conclusion of the 0.5°C/min DTA cycles.

The picture with the hfa's using DTA heating rates of $2^{\circ}\text{C}/\text{min}$ is unambiguous, except for two cases: $\text{Mg}(\text{hfa})_2$ and $\text{Zn}(\text{hfa})_2$. All other compounds showed essentially total weight loss of all material initially contained in the crucible, indicating that the compounds volatilize completely at the heating rate employed, without significant decomposition. The magnesium and zinc compounds on the other hand, appear to decompose, losing the ligand and most of the associated water of hydration.

Table II summarizes the results obtained in Table I. The first column in Table II tabulates those compounds which when heated at $2^{\circ}\text{C}/\text{min}$ tend to volatilize readily upon heating before significant decomposition has occurred. Column 2 tabulates those compounds which tend to decompose upon heating before significant volatilization has occurred. It is seen that the more volatile compounds are always hfas. This volatility has been attributed to the presence of the fluorine group on the ligand[7].

It is important to realize that this does not mean that those compounds which tend to decompose at $2^{\circ}\text{C}/\text{min}$ will not vaporize if heating rates are slower. Depending upon the vapor pressure of the compound, and the heating rates employed, various kinetic behavior is possible. For instance, the vapor pressure of the compound may be high enough so that at the heating rate employed it can be volatilized without decomposition. On the other hand, the vapor pressure may be so low that the decomposition rate

becomes appreciable prior to developing a significant vapor pressure.

Although $2^{\circ}\text{C}/\text{min}$ appears to be a low enough heating rate to maintain quasi-equilibrium or quasi-steady state conditions, it has been found that this rate may be too fast in some cases. For example, as was reported for $\text{Rh}(\text{acac})_3$ [1], the compound actually decomposed prior to melting if slow enough heating rates were employed. Heating the compound at $2^{\circ}\text{C}/\text{min}$, resulted in melting without obvious decomposition. However, at $0.1^{\circ}\text{C}/\text{min}$ decomposition occurred to completion below the melting point such that melting never occurred.

It is to be noted from the literature reviewed[8-13] on the DTA and TGA data that, in general, the heating rates employed were high($> 10^{\circ}\text{C}/\text{min}$). These rates would mitigate against achieving equilibrium. For this reason it is difficult to correlate literature data to the present results. In any event, the previous reports were not concerned with relative volatilities and/or stabilities as a function of heating rates.

As for the pathway of thermal decomposition, it is not obvious which products will result. Ideally, we would like the metal-organic compound to decompose into the metal, or perhaps a metal oxide and an organic fragment. The pathway will be influenced strongly by the conditions employed. Results by Politycki and Heiber[14] on the chemical vapor deposition(CVD) of some of the hfa compounds indicate that

the carbon content increases linearly with temperature. This work has also been confirmed in our laboratory with the chemical vapor transport of Cu(hfa)_2 [3]. Contrary to what intuition would suggest, as the temperature is raised the carbon content increases not decreases. This indicates to us that as temperature increases, both metal chelate bond breakage and chelate fragmentation start to occur simultaneously. At low temperatures, the metal-ligand bond breakage dominates while at higher temperatures both processes occur. It is probably the case that each compound has to be studied separately to determine the actual decomposition process pathway. For example, preliminary data with Al(hfa)_3 in a CVD vapor transport process at 400°C in argon indicates that bond rupture occurs at an oxygen-carbon bond site rather than a metal-oxygen site [15].

B. Thermal Properties of Pd(acac)_2 and Pd(hfa)_2

DTA was carried out in open and closed crucibles in order to observe decomposition of the compounds under atmospheric pressure, or under their own vapor pressures. The open crucible samples were heated in inert or oxidizing ambient atmospheres to observe melting and decomposition behavior isobarically.

Palladium(II) Acetylacetonate

1. Open Crucible DTA in Argon

A heating trace taken at 2°C/min of the orange palladium compound in an open crucible in an argon atmosphere exhibits one endothermic peak, as shown in Fig. 1. This peak beginning at about 196°C was found to be due to the decomposition of the compound. When the endothermic peak had almost returned to the baseline, Fig. 1, the sample was rapidly withdrawn from the DTA chamber and quenched in air. The sample consisted of a black solid product. At the heating rate of 2°C/min the sample lost 57% of its weight (the ligand accounts for 65.1%, the metal 34.9%) by the time it reached the temperature from which it was quenched. Analysis indicated a product containing 75.4% Pd, 12.3% carbon, and 0.5% H. Since oxygen could not be determined by any of the analytical techniques available to us, and it was the only element unaccounted for, its content was determined by difference and found to be 11.8%. Heating palladium(II) acetylacetonate in the DTA crucible at 2°C/min to 660°C, resulted in a 60% loss in weight and a product containing 85.4% Pd, 9.4% C, 0.1% H, and 5.2% oxygen, again by difference. Further heating to 800°C, resulted in a black/silvery product and a 61% weight loss. While this weight loss begins to approximate the theoretical percent ligand, powder diffraction studies of the sample did not indicate either a pure palladium (ASTM file #5-681) or a pure palladium oxide (ASTM #6-515, 34-1101). It appears that

ligand fragmentation accompanies the onset of decomposition of the compound such that neither a pure palladium or palladium oxide product ever results in an inert gas ambient atmosphere. Consequently, the utility of $\text{Pd}(\text{acac})_2$ for film formation purposes in an inert environment appears not to be possible.

Another question that arose was whether the decomposition occurs only during the appearance of the endotherm, or whether it is occurring below 196°C , but is masked because of the heating rate employed. In other words the question occurs, would the endotherm be observed if a slower heating rate was employed, e.g. $0.5^\circ\text{C}/\text{min}$. Heating the compound at a slower rate, $0.5^\circ\text{C}/\text{min}$, as shown in Fig. 2, still reveals an endothermic peak starting at 198°C . Continued heating to 299°C , resulted in a black product, and a 58% weight loss. Heating the compound at $0.1^\circ\text{C}/\text{min}$ to 200°C resulted in a 55.7% loss with no endotherms observed. To test for decomposition below 196°C , the sample was heated to 95°C and annealed for four hours. No weight loss was observed at this temperature. Again, heating the compound to 154°C for four hours resulted in only slight weight loss. This indicates that while decomposition probably is occurring below 196°C , the rate is extremely slow and that at 196°C the rate becomes quite high.

In 1973, Yoshida studied $\text{Pd}(\text{acac})_2$ by DTA[16]. He reported that the compound decomposed at 266°C in a nitrogen

atmosphere at a heating rate of $10^{\circ}\text{C}/\text{min}$. This is an example of how the use of high heating rates can lead to inaccurate results (266°C vs 198°C) being observed because the system is unable to achieve anything like a steady state situation.

2. Open Crucible DTA in Oxygen

The heating and decomposition of $\text{Pd}(\text{acac})_2$ in an oxygen atmosphere appears quite different, Fig. 3, from that in an inert environment, due to the oxidation of the compound. For example, if the sample is heated at $2^{\circ}\text{C}/\text{min}$, as shown in Fig. 3, one large exotherm is observed beginning at 180°C . Upon quenching the sample in air when the trace had almost returned to the baseline, a silver product was observed on the crucible walls. The sample exhibited a 64% weight loss (which is close to the ligand content of 65.1%).

Upon further heating a sample at $2^{\circ}\text{C}/\text{min}$ in oxygen up to 800°C , it was found that the compound did not lose more weight, but instead began to gain weight. For example, after heating to 530°C , the crucible which showed a 64% weight loss when heated to 250°C , showed only a 59.7% weight loss. When heated to 530°C , a black/brown product resulted. Further heating to 780°C then showed a total loss of 60.2%. This latter loss corresponds to a pure PdO product. PdO indeed, has been reported to be the most stable oxide of palladium[17]. It has also been reported that PdO is reduced to the pure metal above 800°C [7,18]. It was found in the

present case via X-ray diffraction studies, that the PdO decomposes to Pd above 800°C.

3. Closed Crucible DTA

Figure 4 shows the thermal decomposition of $\text{Pd}(\text{acac})_2$ under its own vapor pressure at a heating rate of 2°C/min. First, the onset of a small endotherm, similar to the one observed in Figure 1, is observed at 196°C. This peak is interrupted by a spontaneous exothermic decomposition of the compound at 217°C. After heating to 450°C, a black solid product was observed. The walls of the crucible were slightly discolored brown and vapors could be seen condensing inside the crucible as it cooled. Reheating of the same sample after cooling showed no thermal effects.

Palladium(II) hexafluoracetylacetonate

1. Open Crucible DTA in Argon

A heating trace of $\text{Pd}(\text{hfa})_2$ at 2°C/min in an open crucible in an argon atmosphere exhibits two endothermic peaks, as shown in Fig. 5. The first endotherm, onset at 105°C with a peak at 106°C, was found to be due to the melting of the compound. Upon completion of the peak, as determined by DTA, the sample was rapidly withdrawn from the DTA chamber. The sample was seen to be molten with an orange color. At the heating rate mentioned, the sample loses no weight. The second endotherm which begins at 194°C, and peaks at 234°C, Fig. 5, appears to represent the boiling point of the liquid

at one atmosphere external pressure. Upon quenching at the completion of the second endotherm, samples were found to have lost 99.8% of their initial starting weights (the ligand accounts for 79.6%).

The compound was quenched between the two endothermic peaks to determine if any weight loss takes place below the vaporization peak. After heating at $2^{\circ}\text{C}/\text{min}$ to 184°C and quenching the sample in air from this temperature, a 24% weight loss was measured. Reheating the same sample again at $2^{\circ}\text{C}/\text{min}$, to 194°C , which coincides with the onset of the second endotherm, resulted in a total weight loss of 89%. Heating a new sample at a slower rate, $0.5^{\circ}\text{C}/\text{min}$ in argon, Fig. 6, again shows a melting endotherm peak at 99°C , and a greatly reduced vaporization endotherm beginning at 190°C . The temperature of the onset of the evaporation endotherm must be evaluated with care since it indicates the temperature at which loss of material from the crucible becomes rapid, and not necessarily the boiling point. The boiling point is most likely represented by the region in which this evaporation peak appears isothermal, since the boiling point is a point of invariance under conditions of constant external overpressure for a quasi-unary compound. In the present case, the boiling point of $\text{Pd}(\text{hfa})_2$ appears to be at 231°C .

Thus, unlike the behavior of $\text{Pd}(\text{acac})_2$, $\text{Pd}(\text{hfa})_2$ was found to be completely volatile in an argon ambient atmosphere.

The compound melts at 96°C and reaches its boiling point at one atmosphere at 231°C .

2. Open Crucible in Oxygen

The heating and decomposition of Pd(hfa)_2 in an oxygen atmosphere at 2°C/min , Fig. 7, appears similar to the behavior in an argon atmosphere with slight decomposition occurring when the sample is heated through its boiling point at 2°C/min . The first endotherm, similar to the Pd(hfa)_2 in argon (Fig. 4) at 2°C/min , is indicative of the melting of the compound. Upon rapidly quenching the sample towards the completion of the peak, the sample was seen to be molten with an orange color. No detectable weight loss was measured. The second endotherm, onset at about 200°C , and a peak again around 230°C , represents the rapid vaporization followed by the boiling of the liquid. Upon quenching the sample at the conclusion of the peak, a 95.7% loss was observed, leaving a small amount of silvery/black material in the base of the crucible. Upon elevation to 500°C , a 99.5% weight loss was observed.

It has been suggested by Nakamura, et al[19], that the compound, Pd(hfa)_2 , sublimes between $46\text{--}55^{\circ}\text{C}$. This was not confirmed in the present study, perhaps because of differences in the exposed surface area of the samples used in the two studies. It has also been reported[20] that the compound will sublime readily at room temperature in a

vacuum (10^{-3} torr) and at 80°C at atmospheric pressure. At atmospheric pressure we could not confirm this. Although holding a sample contained in the DTA crucible at 90°C did result in a measurable weight loss after four hours, this weight loss was very small, 0.3%. A four hour anneal at 100°C resulted in a 2% weight loss. From the present studies it appears clear that a significant evaporation rate does not occur until about 190°C at which time the sample is molten. Thus, it is unlikely that a normal sublimation point was achieved, since the compound appears to exhibit a normal boiling point.

3. Closed Crucible

As shown in Fig. 8, heating of the compound under its own vapor pressure at $2^{\circ}\text{C}/\text{min}$ yields the melting endotherm as observed in Figs. 5, 6 and 7. Upon rapidly quenching the sample when it reached its peak temperature, 105°C , a molten orange liquid was observed. The melting endotherm was accompanied by a recrystallization exotherm upon cooling (not shown in Fig. 8). Continued heating of the material past its melting point fails to develop the boiling endotherm, as would be predicted from the above, but does show some irregularities in the trace starting at around 287°C and culminating in a large exotherm beginning at 310°C . A black material was found to cover the walls following this. After cooling and reheating the sample, no peaks were observed, indicating decomposition was complete.

CONCLUSIONS

In order to understand better how to use metal-organic compounds, such as the acetylacetonates and hexafluoroacetylacetonates, as alternatives to conventional thin film deposition approaches in microelectronics, it was desirable to differentiate the metal-organic compound characteristics of the acacs and hfacs according to their physical and chemical properties. Volatility and thermal decomposition behavior represent important forms of such differentiation, since they can determine how a given metal-organic might best be used to form thin films. In general, the acetylacetonates decompose in the solid state at relatively low temperatures (100-200°C), with several of them exhibiting appreciable vapor pressures at temperatures below which their decomposition rate is significant. Hexafluoro derivatives of these compounds, on the other hand are, in general, more volatile and decompose at higher temperatures.

$\text{Pd}(\text{acac})_2$ has been found by DTA to be involatile, decomposing significantly at about 200°C upon heating at 2°C/min. On the other hand, $\text{Pd}(\text{hfa})_2$ was found to be completely volatile. Thermal decomposition of $\text{Pd}(\text{acac})_2$ in an inert atmosphere produces a product that exhibits an increasing palladium composition contaminated by carbon, hydrogen, and oxygen as the temperature increases. In oxygen, the compound initially produces a compound

containing 91% metal, upon further heating in oxygen to 780°C PdO is formed. Heating above 800°C results in the dissociation of the PdO to Pd. Pd(hfa)₂ does not seem to decompose significantly until about 300°C or higher.

ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research.

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Table II. Summary of the volatility of the metal-organic compounds using DTA and heating to 550°C at 2°C/min.

<u>> 99% VOLATILE</u> (in O ₂ and Ar)	<u>DECOMPOSED</u> (in O ₂ and Ar)
Al(hfa) ₃	Al(acac) ₃
Cr(hfa) ₃	Cr(acac) ₃
Co(hfa) ₃	Co(acac) ₃
	Co(acac) ₂ xH ₂ O
Cu(hfa) ₃ H ₂ O	Cu(acac) ₂
	Mg(hfa) ₂ 2H ₂ O
	Mg(acac) ₂ 2H ₂ O
Pd(hfa) ₂	Pd(acac) ₂
Pt(hfa) ₂	Pt(acac) ₂
	Rh(acac) ₃
	Ti(hfa) ₂ (Ar only)
	Zn(acac) ₂ xH ₂ O
	Zn(hfa) ₃ 2H ₂ O
Ni(hfa) ₂ 2H ₂ O	Ni(acac) ₂ 2H ₂ O
	Silver Neodecanoate
	W(CO) ₆

Table I. Comparison of the initial percent ligand with the weight percent lost during DTA to 500°C at 2°C/min.

COMPOUND(acac)	initial weight %lig (theo)	%loss (actual)	COMPOUND(hfa)	initial weight %lig (theo)	%loss (actl)
Al(acac)3	96.7	96.8-a 96.6-o	Al(hfa)3	95.8	99.8-a 100-o
Cr(acac)3	85.1	37.1-a 89.9-o	Cr(hfa)3	92.3	100-a 99.8-o
Co(acac)2 xH ₂ O	77.1	71.8-a 68.6-o			
Co(acac)3	83.5	73.8-a 77.3-o	Co(hfa)3	91.3	99.8-a 99.8-o
Cu(acac)2	75.7	81.1-a 72.8-o	Cu(hfa)2 H ₂ O	86.7	99.4-a 99.4-o
Mg(acac)2 2H ₂ O	90.6	83.9-a 63.0-o	Mg(hfa)2 2H ₂ O	94.9	89.4-a 91.4-o
Ni(acac)2 xH ₂ O	77.2	62.0-a	Ni(hfa)2 2H ₂ O		
Pd(acac)2	65.5	57.0-a 59.2-o	Pd(hfa)2	79.6	99.8-a 99.8-o
Pt(acac)2	50.4	52.3-a 51.2-o	Pt(hfa)2	68.0	98.5-a 98.6-o
Rh(acac)3	74.3	74.1-a 77.2-o			
			Ti(hfa)2	92.8	95.4-a
Zn(acac)2	75.2	66.2-a 69.9-o	Zn(hfa)2 2H ₂ O	87.3	88.4-a 89.1-o
<u>MISCELLANEOUS</u>					
Silver Neodecanoate	61.4	61.4-a 61.4-o			
Tungsten Hexacarbonyl	47.4	98.7-a 98.4-o			

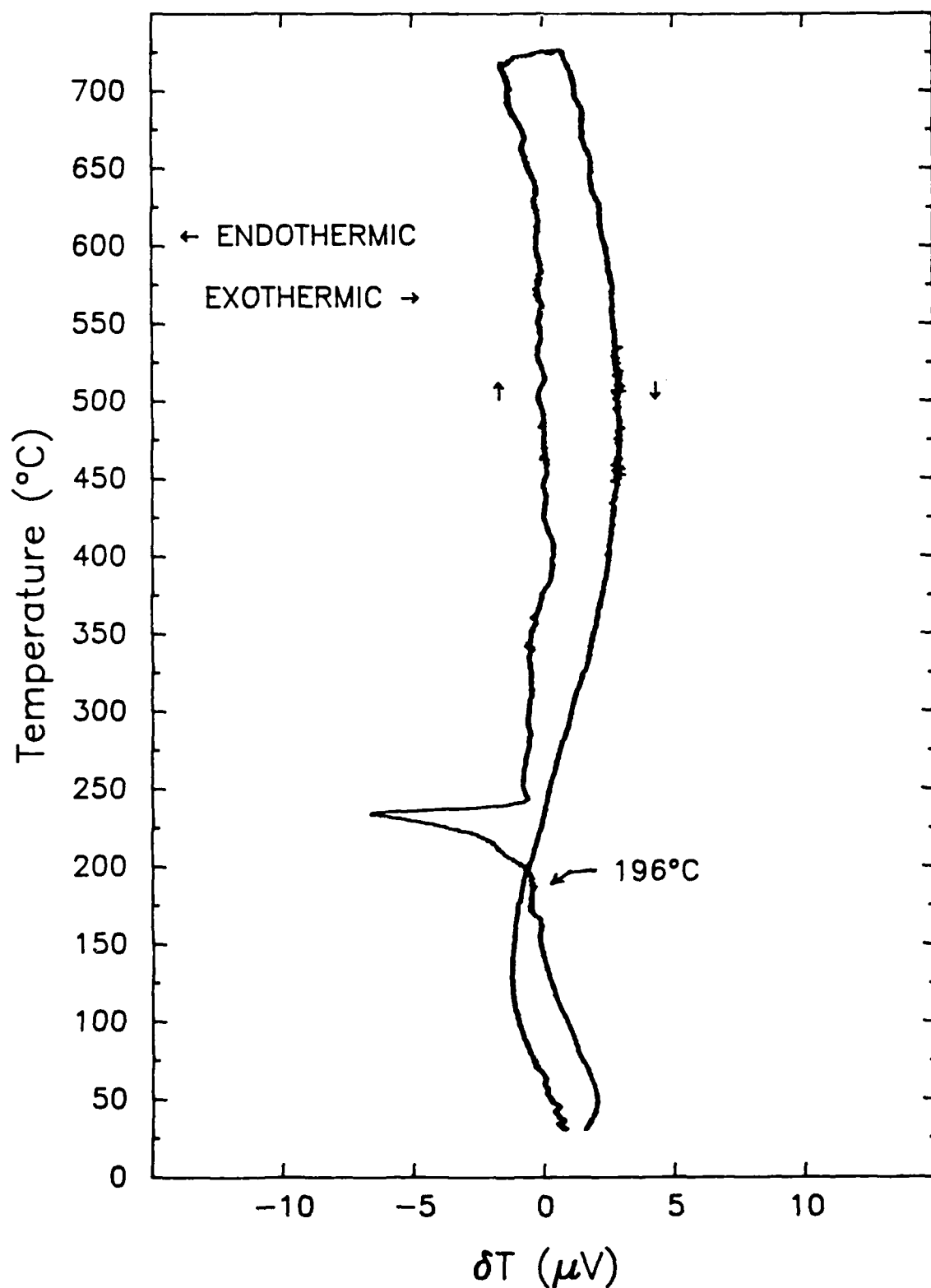


Figure 1. DTA of palladium(II) acetylacetonate at 2.0 °C/min in an argon atmosphere.

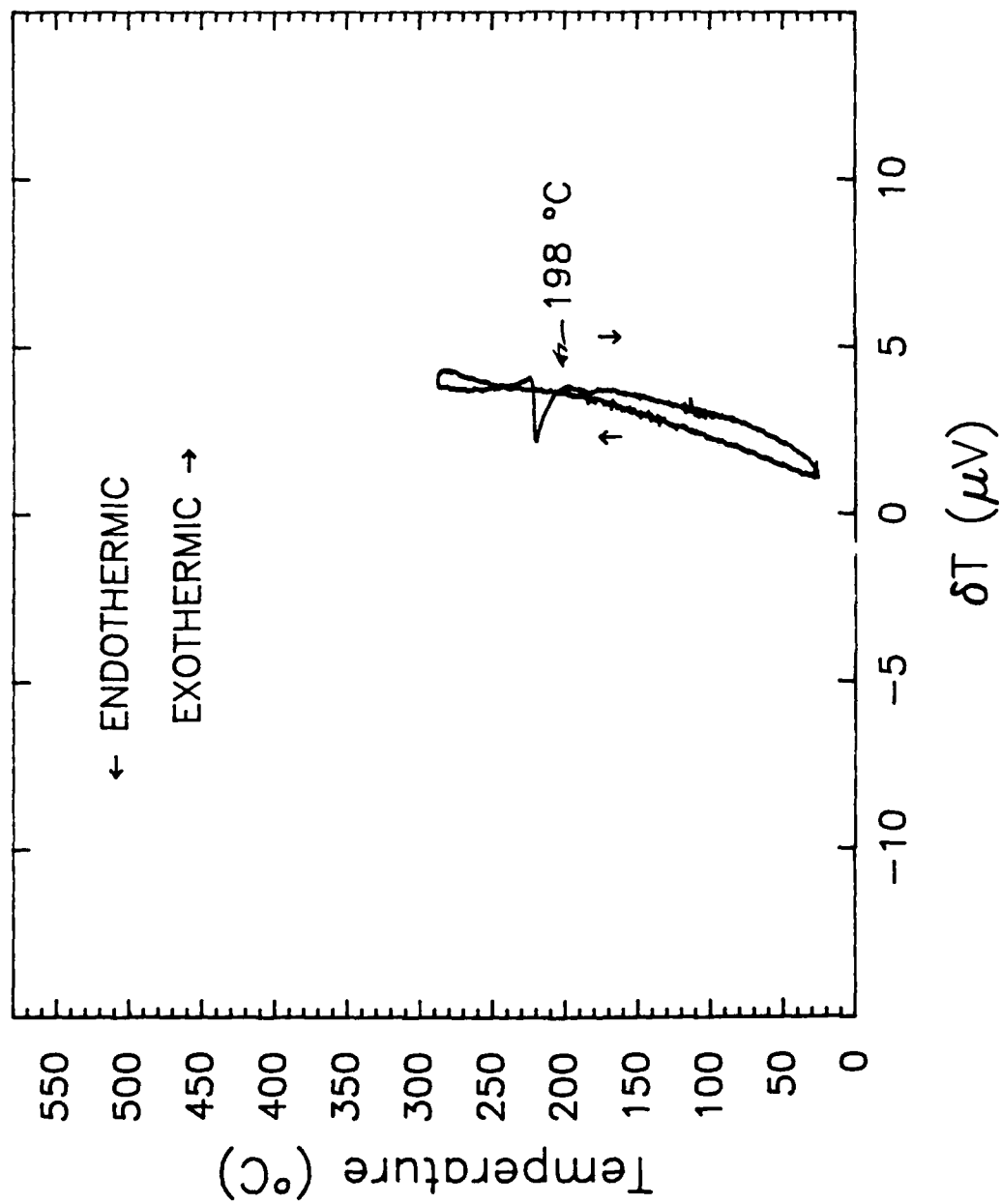


Figure 2. DTA of palladium(II) acetylacetonate at $0.5^\circ C/min$ in an argon atmosphere.

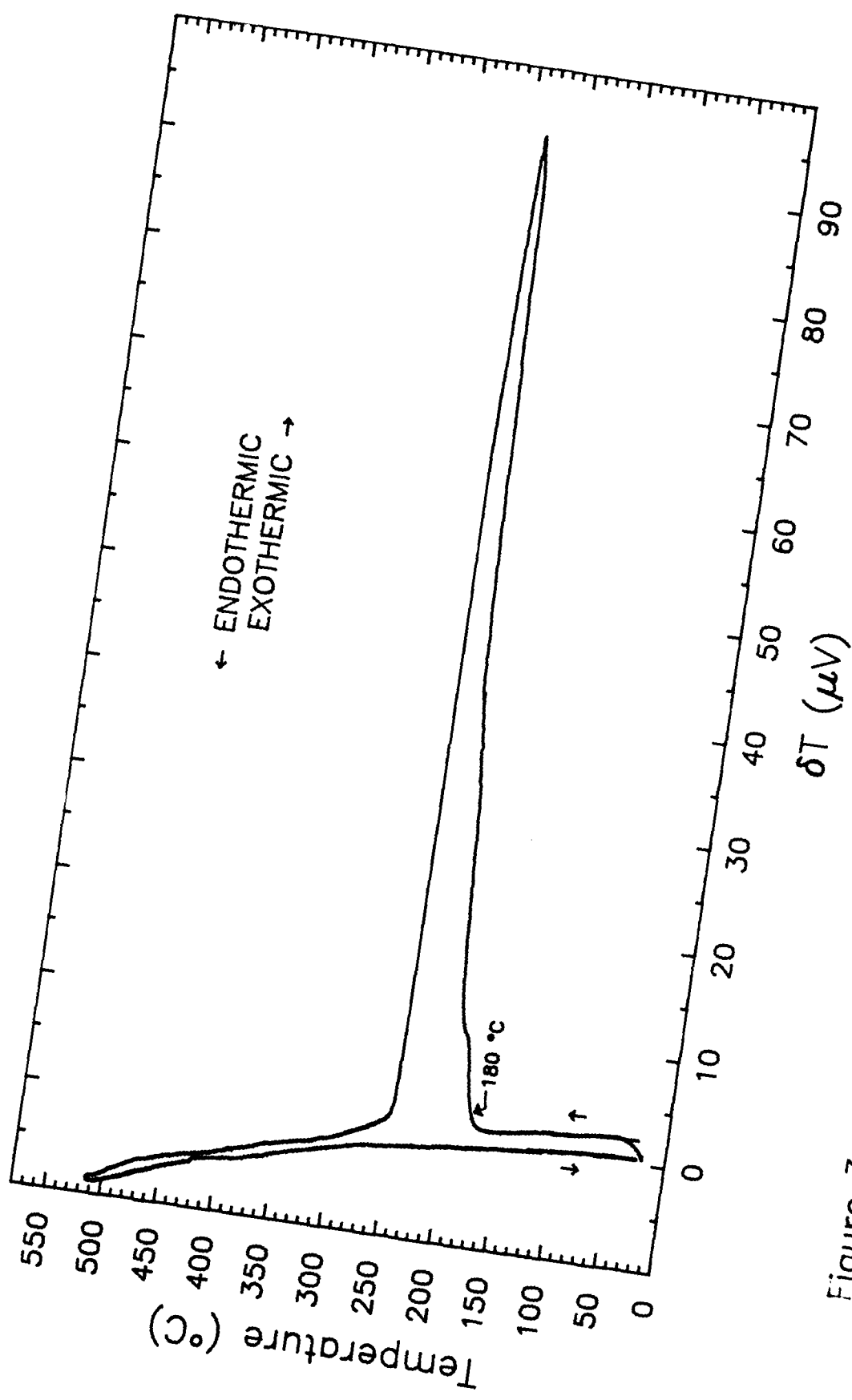


Figure 3. DTA of palladium(II) acetylacetonate at 2.0 °C/min in an oxygen atmosphere.

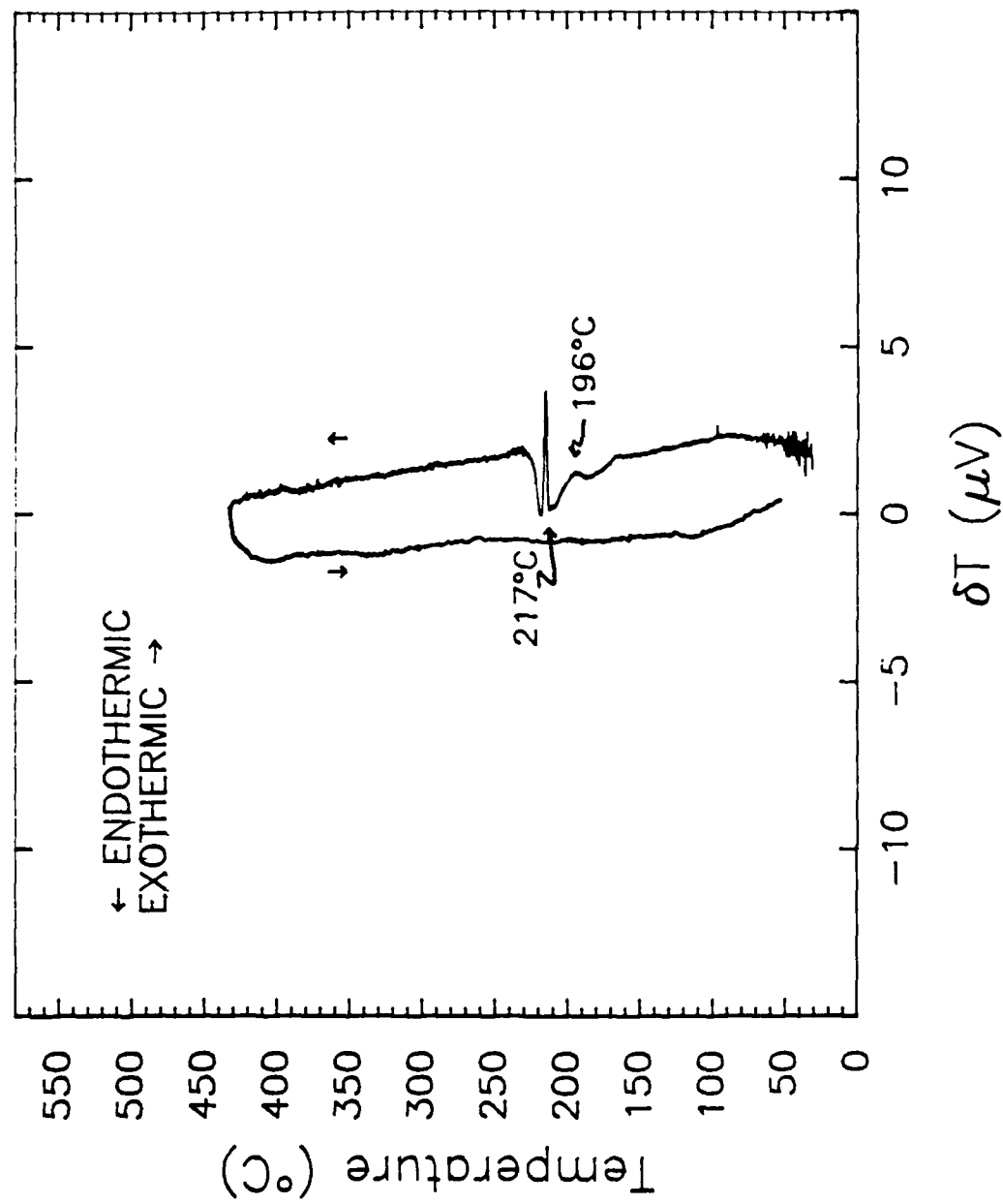


Figure 4. DTA of palladium(II) acetylacetonate at 2.0°C/min closed.

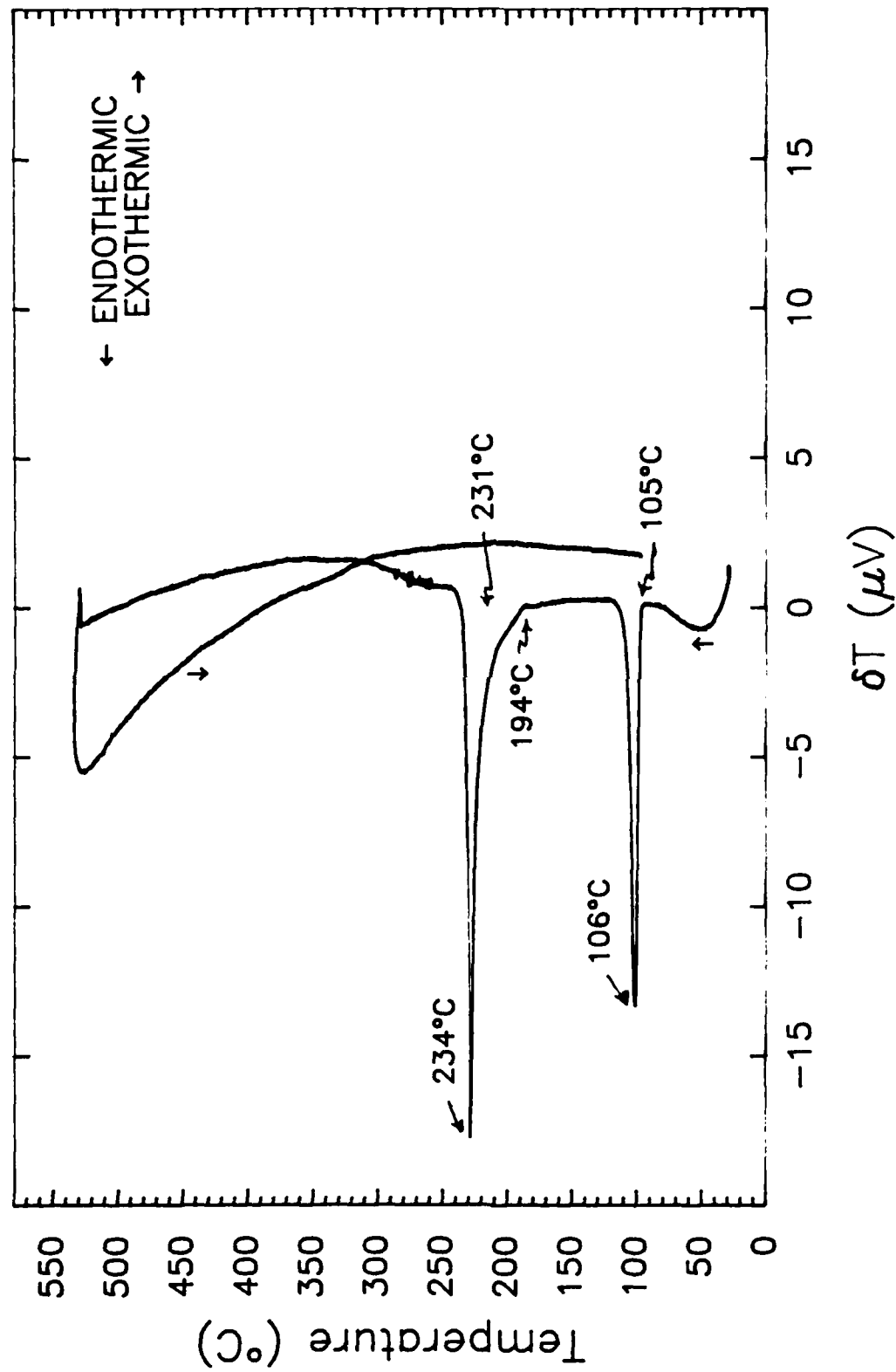


Figure 5. DTA of palladium(II)hexafluoroacetylacetonate at 2.0°C/min in argon.

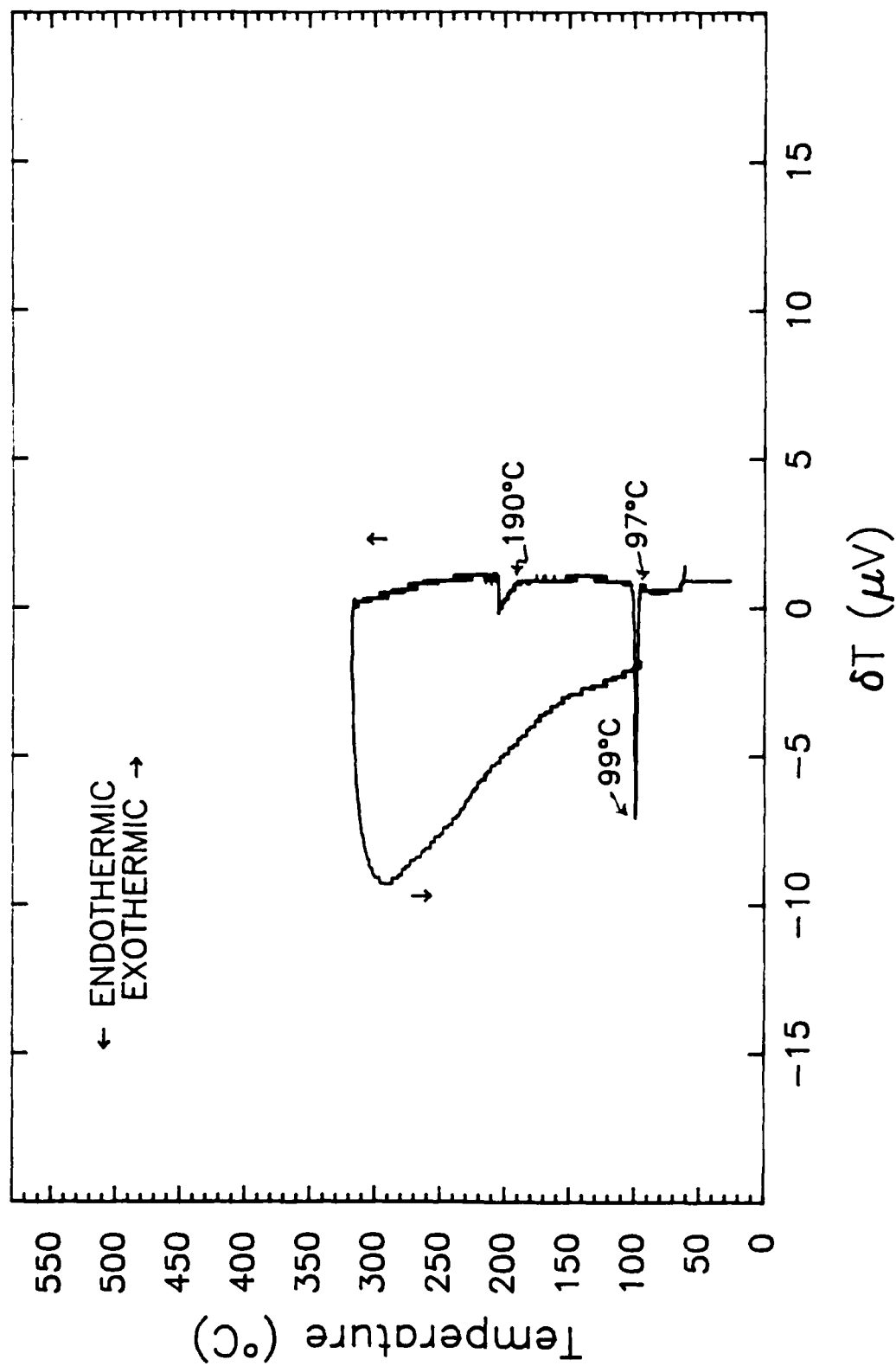


Figure 6. DTA of palladium(II)hexafluoroacetylacetonate at 0.5 °C/min in argon.

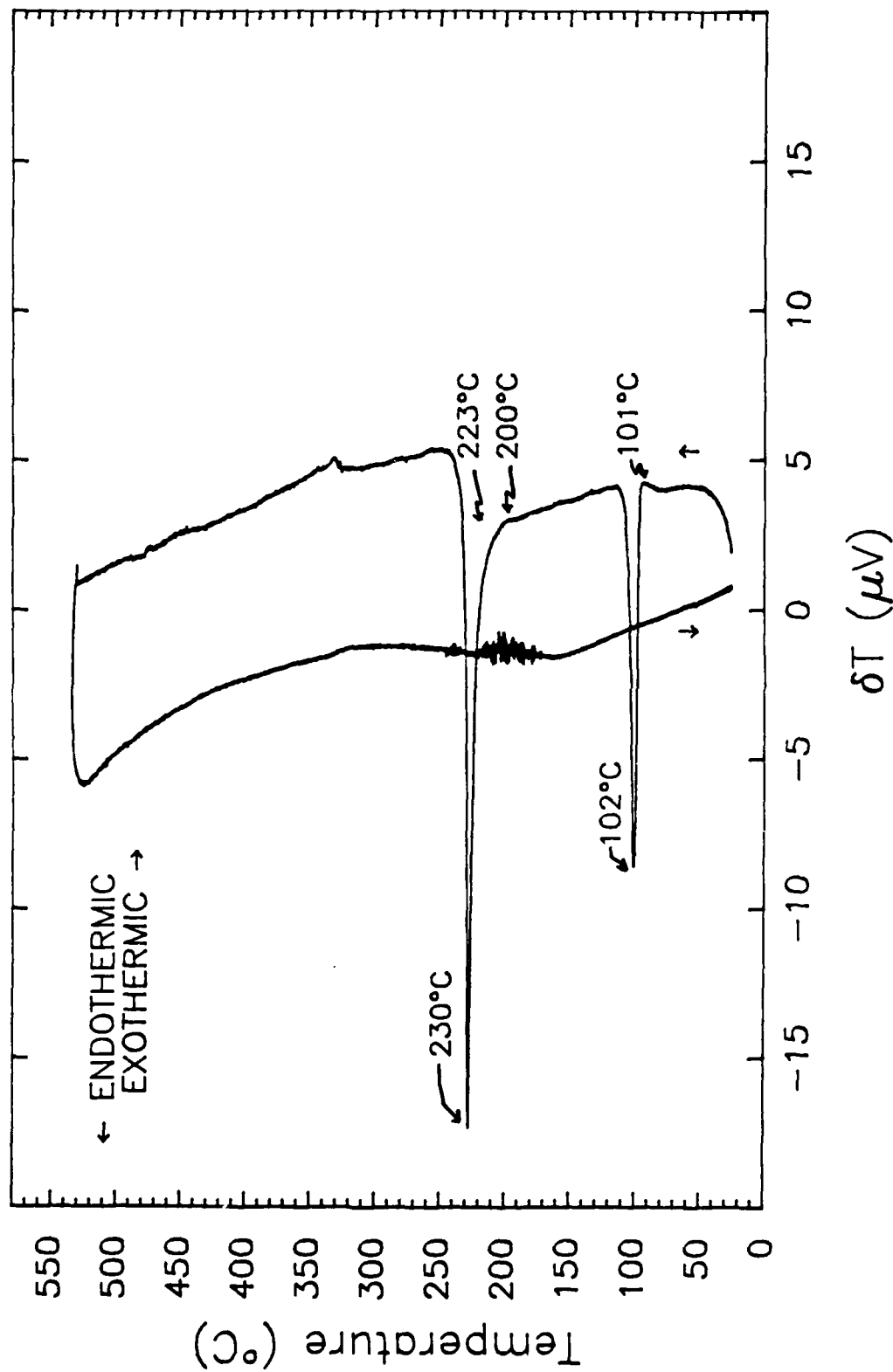


Figure 7. DTA of palladium(II) hexafluoroacetylacetonate at 2.0 °C/min in oxygen.

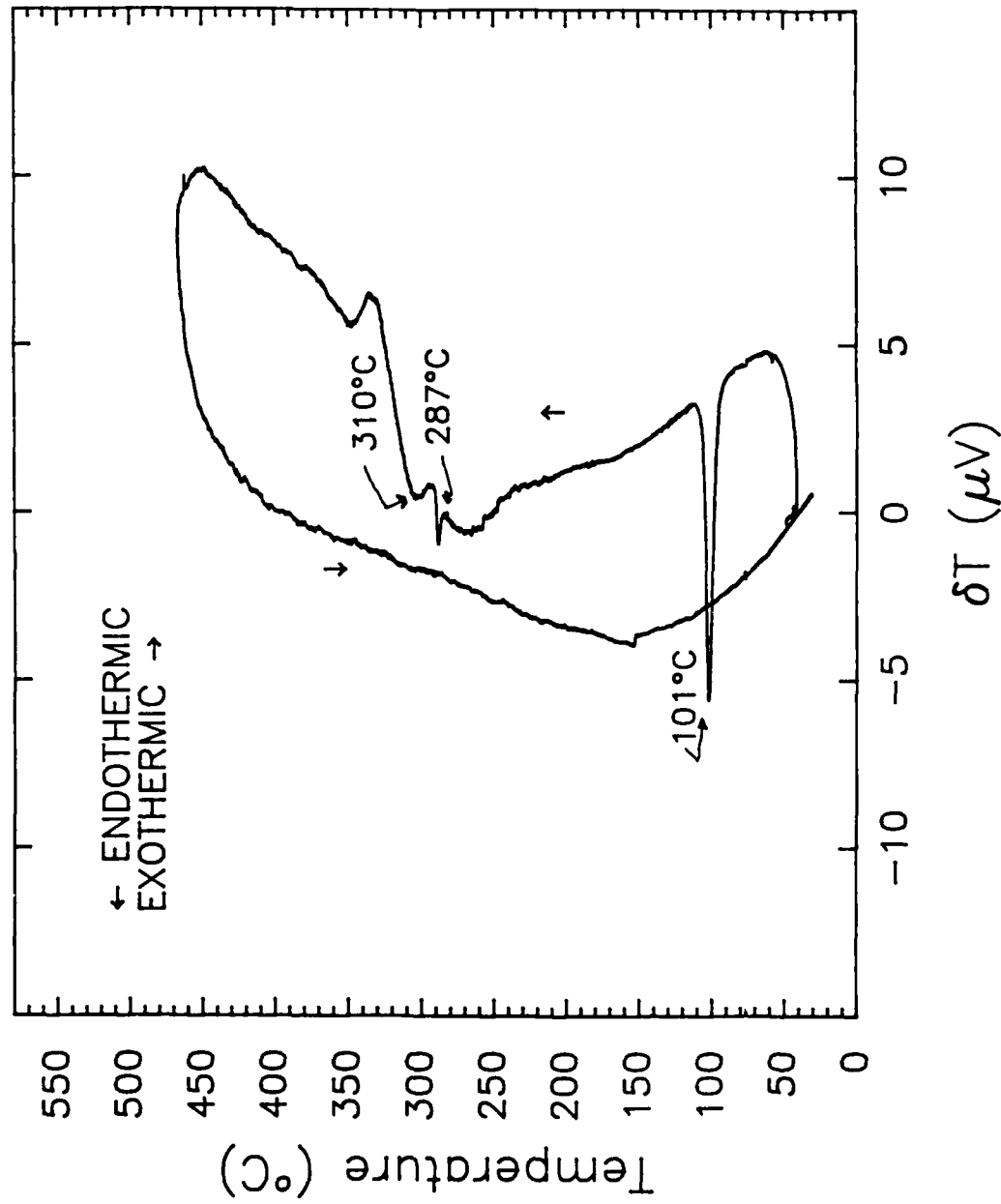


Figure 8. DTA of palladium(II) hexafluoroacetylacetonate at 2.0 °C/min closed.

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