and the theory of diffusion. For a divalent cation with a uninegatively charged ligand, the calculated K_{os} value is around 1 M^{-1}, although it depends on the estimated value of the metal to ligand distance in forming the outer-sphere complex. For uncharged ligands, values calculated with a distance of closest approach of 500 pm[11,22] are between 0.05 and 0.15 M^{-1}. For the large Cl-phen ligand, with a chlorine atom next to the binding nitrogen,[7] the distance of closest approach is probably larger. With an estimated value of a = 600 pm, the resulting K_{os} amounts to 0.02–0.07 M^{-1}. The yielded K_{os} values are in good agreement with the data derived from water-exchange and complex-formation rate constants (0.02 $M^{-1} < K_{os} < 0.14\ M^{-1}$) for Co^{2+} and Ni^{2+}. It is consistent with the starting assumption of an Eigen–Wilkins mechanism and supports the assignment of I_d for Co^{2+} and Ni^{2+}. As a parallel, we can attempt to predict or estimate k_{ex}, the water-exchange rate constants on Cu^{2+} and Zn^{2+} using eq 9: $7 \times 10^8\ s^{-1} < k_{ex} < 5 \times 10^9\ s^{-1}$ and $3 \times 10^7\ s^{-1} < k_{ex} < 6 \times 10^8\ s^{-1}$, respectively. Using incoherent quasi-electric neutron scattering, Salmon[23,24] has studied the proton-exchange rates on some aquametal ions. For these very fast exchanges on divalent cations, the proton-exchange rate can be assumed to be equal to the water-exchange rate. This method allows one to give limits for the rate of water exchange on Cu^{2+} ($k_{ex} \geq 1 \times 10^{10}\ s^{-1}$) and Zn^{2+} ($2 \times 10^8\ s^{-1} < k_{ex} < 1 \times 10^{10}\ s^{-1}$), which are close to our estimation.

In conclusion, our study together with other kinetic and neutron scattering data gives a coherent image of the substitution mechanisms on Cu^{2+} and Zn^{2+} aqua ions, both ions reacting according to a dissociative interchange, I_d, mechanism. The water-exchange rate, k_{ex}, is 1–2 orders of magnitude larger for Cu^{2+} than for Zn^{2+}.

Acknowledgment. The Swiss National Science Foundation (Grant 2.672-0.87) is greatly thanked for financial support.

Registry No. $Cu(H_2O)_6^{2+}$, 14946-74-8; $Zn(H_2O)_6^{2+}$, 15906-01-1; Cl-phen, 7089-68-1.

Supplementary Material Available: Observed pseudo-first-order rate constants, k_{obs}, as a function of temperature and pressure (Tables SI and SII) and normalized absorption spectra of Cl-phen–Cu^{2+} solutions at 298.2 K (Figure S1) (3 pages). Ordering information is given on any current masthead page.

---

(22) Burgess, J. M. A. *Metal ions in solution*; Ellis Horwood: Chichester, England, 1978; p 353.
(23) Salmon, P. S.; Howells, W. S.; Mills, R. *J. Phys. C.* **1987**, *20*, 5727.
(24) Salmon, P. S. *Physica B*, in press.
(25) McBryde, W. A. E. *A Critical Review of Equilibrium Data for Proton and Metal Complexes of 1,10-Phenanthroline, 2,2'-Bipyridyl and Related Compounds*; IUPAC Chemical Data Series No. 17; Pergamon: New York, 1978.
(26) Ducommun, Y.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1980**, *19*, 3696.
(27) Rorabacher, D. B. *Inorg. Chem.* **1966**, *5*, 1891.
(28) Diebler, H.; Rosen, Ph. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 1031.
(29) Caldin, E. F.; Grant, M. W.; Hasinoff, B. B. *J. Chem. Soc., Faraday Trans. I.* **1972**, *68*, 2247.
(30) Miceli, J. A.; Steuhr, J. E. *Inorg. Chem.* **1972**, *11*, 2763.
(31) Hague, D. N.; Martin, S. R. *J. Chem. Soc., Dalton Trans.* **1974**, 254.
(32) Holyer, R. H.; Hubbard, C. D.; Kettle, S. F. A.; Wilkins, R. G. *Inorg. Chem.* **1965**, *4*, 929.
(33) Roche, T. S.; Wilkins, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 5082.
(34) Mohr, R.; van Eldik, R. *Inorg. Chem.* **1985**, *24*, 3396.
(35) Doss, R. van Eldik, R. *Inorg. Chem.* **1982**, *11*, 4108.
(36) Ellis, P.; Hogg, R.; Wilkins, R. G. *J. Chem. Soc.* **1959**, 3308.

Contribution from the Chemistry Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Thermal Decomposition of the Halide and Pseudohalide Derivatives of Bis(cyclopentadienyl)titanium(IV)

Gilbert M. Brown

Received February 16, 1989

The thermal decomposition reactions of $Ti(Cp)_2(X)_2$, where Cp is η^5-C_5H_5 and X is Cl^-, Br^-, NCS^-, NCO^-, and N_3^-, were studied at atmospheric pressure by temperature-programmed pyrolysis with analysis of the evolved gas by mass spectroscopy. The gas evolution versus temperature profile showed that the compounds decomposed in a single, sharp, symmetrical step with the loss of cyclopentadiene observed from all compounds. The pseudohalide-containing compounds evolved products of the breakdown of this moiety simultaneously with C_5H_6. The gas evolution versus temperature profiles were used to measure ΔH^* for the decomposition of the azide and cyanate compounds. The compound $Ti(Cp)_2(N_3)_2$ was used for the chemical vapor deposition of titanium-containing films on quartz or CaF_2 substrates at 400 °C. Additional pyrolysis converts the film to an adherent, chemically resistant, refractory material. The infrared spectrum of the initial deposition product on a CaF_2 substrate was obtained. Chemical analysis and IR spectroscopy suggest the film contains a large excess of carbon over that required for stoichiometric TiC. Hydrocarbon evolution probably occurs by a hydrogen abstraction mechanism, which leads to dehydrogenation of coordinated cyclopentadienyl. This dehydrogenated ring system appears to be the source of the excess carbon in the solid film.

Introduction

The design of generalized, low-temperature synthetic routes to the carbides, nitrides, and borides of titanium is an area of active research. These materials have many desirable properties; however, the synthesis of these materials in useful forms such as fibers, whiskers, or films is a difficult task. The traditional powder metallurgical preparative methods require high temperatures and yield a product that must be further processed by grinding, sintering, and pressing.[1] Metalloorganic compounds may be attractive as precursor compounds to these refractory materials since the presence of the organic group will allow the properties of the precursor to be changed so that it can be readily processed. This strategy has been discussed within the context of polymeric precursors to ceramic materials.[2,3]

The metalloorganic chemical vapor deposition (MOCVD) technique is used in the electronics industry to prepare materials such as GaAs. It is highly desirable to find single-source precursor compounds for the chemical vapor deposition (CVD) of binary refractory materials. Girolami and co-workers[4] have demonstrated that tetraneopentyltitanium is a useful reagent for the CVD of

---

(1) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic Press: New York, 1971; pp 1–28.
(2) Laine, R. M.; Hirschon, A. S. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 373–382.
(3) Rice, R. W. *Am. Ceram. Soc. Bull.* **1983**, *62*, 889–892.
(4) Girolami, G. S.; Jensen, J. A.; Pollina, D. M.; Williams, W. S.; Kaloyeros, A. E.; Allocca, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 1579–1580.

TiC films. The conversion occurs at <200 °C. The dimethoxyethane adduct of tris(tetrahydroborate)titanium was shown to be a precursor for the CVD of TiB_2.[5] However, the pioneers in the use of organometallic compounds of Ti as precursors to TiC appear to be Norman and Whaley.[6] In two patents filed in 1959, they reported processes with compounds such as $TiCp(Cl)_3$, $TiCp(alkyl)_3$, $Ti(Cp)_2(Cl)_2$, and $Ti(Cp)_2(alkyl)_2$, where Cp is η^5-C_5H_5. The vapor of the compound is reported to react at a substrate to form a deposit. With the dichloride compound reacting at 550 °C, the deposit is reported to be Ti metal; if the deposition reaction is carried out at 700 °C, the reported product is TiC. Unfortunately, details of the analytical methods were not reported, and the deposition of titanium metal should be considered questionable. In more recent work,[7,8] complete pyrolysis of the compounds $Ti(Cp)_2(Cl)_2$ and $Ti(Cp)_2R_2$, where R is CH_3, C_6H_5, and $CH_2C_6H_5$, at 900–1000 °C led to the formation of TiC with a high content of amorphous carbon. The formation of carbon black was reduced by using a flowing stream of hydrogen at a pressure of 2–3 Torr to carry away volatile products.

Kinetics and product analysis for the thermal decomposition of $Ti(Cp)_2R_2$, where R is aryl and benzyl, have been determined.[9-11] In general the products observed in the reactions are in agreement with predictions based on the relative values of the mean bond dissociation energies of titanium–alkyl and titanium–cyclopentadienyl bonds.[12] In this paper, the thermal decomposition of the halides and pseudohalides of bis(cyclopentadienyl)titanium(IV) have been studied, both by atmospheric-pressure temperature-programmed pyrolysis and by vacuum pyrolysis. The mean bond dissociation energies of titanium–halogen bonds are greater than the mean bond dissociation energy of a titanium–cyclopentadienyl bond. Metal–pseudohalogen bond energies should be in the same range as those for metal–halogen bonds, and it was hoped that the decomposition of pseudohalides of bis(cyclopentadienyl)titanium would lead to loss of the cyclopentadiene before the pseudohalide was lost. The results will be discussed in the context of using these compounds as precursors to refractory materials.

Experimental Section

Materials, Instruments, and Chemicals. Commercially available $Ti(Cp)_2(Cl)_2$ (Alfa Inorganics) was used as received as a starting material for the synthesis of other compounds but purified by vacuum sublimation before being used for physical measurements. The compounds $Ti(Cp)_2(X)_2$, where X is NCS^- and NCO^-, were prepared by the method described by Burmeister et al.,[13] and these materials were identified by their IR and UV–vis spectra. The azide derivative was prepared by the method of Langford and Aplington[14] and purified by sublimation. The dibromo compound was prepared by refluxing $Ti(Cp)_2(Cl)_2$ with anhydrous LiBr in acetone with use of the general conditions described for the preparation of the other compounds. The identity of this material was confirmed by its UV–vis spectrum.[15] The cyanate and azide compounds appear to be sensitive to atmospheric moisture, and they were stored in an inert-atmosphere glovebox (Vacuum Atmospheres, <2 ppm water and oxygen). All other chemicals were locally available AR grade and were used without further purification. Calcium fluoride disks (1-in. diameter, 2-mm thickness) were obtained from Harshaw. Infrared spectra were run on a Digilab Model 60 FTIR spectrometer. Spectra of solids were obtained as KBr pellets in the transmission mode or by diffuse reflectance as a mixture with KBr. Gas-phase spectra were obtained in a conventional vacuum-tight gas cell with KBr windows. IR spectra of a film on a CaF_2 substrate was obtained in a vacuum-tight cell with KBr windows. The cell was loaded in an inert-atmosphere glovebox and evacuated before running the spectrum. UV–vis spectra were recorded on a Cary Model 17 spectrometer. Mass spectra were determined on a Hewlett-Packard Model 5970 mass-selective detector. A Scintag PAD V X-ray diffractometer was used for X-ray diffraction (XRD) of solid samples. Titanium was determined spectrophotometrically by dissolving the sample in hot, 50:50 HNO_3–H_2SO_4 with a few drops of HF added and then developing the color as the peroxy complex.[16]

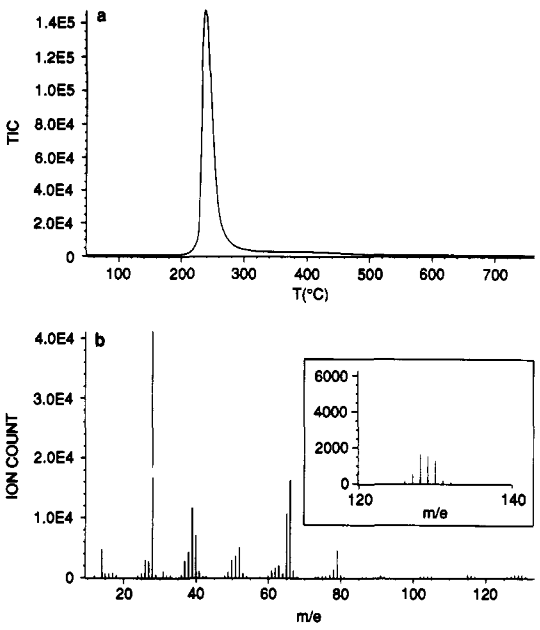

Figure 1. (a) Plot of total ion count from the mass spectrometer versus temperature for the pyrolysis of $Ti(Cp)_2(N_3)_2$. (b) Mass spectrum at the maximum of ion count versus temperature. The inset shows the region *m/e* 120–140 expanded.

Temperature-Programmed Pyrolysis. A proportional temperature controller (Barber-Coleman Model 570, chromel–alumel thermocouple) was used to ramp the temperature of the furnace at a rate of 5–20 °C/min. The sample was contained in a quartz boat within a quartz sample tube fitted with thermocouple wells. Helium or hydrogen was used as a carrier gas to sweep any volatile materials evolved from the sample via heated stainless steel lines to the mass selective detector. Correlation of temperature–time curves with the mass spectra as a function of time allowed the temperature dependence of the individual mass spectra to be constructed. The evolution of hydrogen, with helium as the carrier gas, was determined by trapping all condensable materials in a liquid-nitrogen-cooled U-trap and then passing the noncondensable gases into a Hach/Carle hydrogen-transfer system. The hydrogen gas passed through the palladium membrane, was picked up in an argon stream, and was detected on a thermal conductivity detector (Gow-Mac).

Vacuum Pyrolysis and CVD Experiments. The materials under investigation sublime under vacuum, and a special apparatus was required to carry out a vacuum pyrolysis quantitatively. A tortuous path assembly of three quartz tubes was employed; each was sealed at one end, and the tubes were nested within each other, having their openings in opposite directions. The compound was placed in the center tube, the system was pumped down, and the reaction assembly was rapidly heated under a dynamic vacuum. As the compound volatilized and was pumped out, the vapor encountered a hotter zone. By rapid heating to 400–500 °C, it was possible in some cases to react all of the compound before any vapor could leave the assembly. The reaction tube could then be heated to 800 °C to finish the reaction. CVD experiments employed a quartz tube assembly that allowed a substrate to be held in the middle of the deposition furnace. With a dynamic vacuum, the compound was heated in the vaporization zone and pumped into the deposition zone. Following the deposition reaction, the substrate could be isolated in the glovebox for spectroscopic examination or heated to higher temperatures under

---

(5) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643–1644.

(6) Norman, V.; Whaley, T. P. U.S. Patent 3061464, 1962. Norman, V.; Whaley, T. P. U.S. Patent 3061465, 1962.

(7) Vyshinskaya, L. I.; Mar'in, V. P.; Latyaeva, V. N.; Balakin, E. I.; Lebedev, A. N. *Inorg. Mater.* (*Engl. Transl.*) **1976**, *12*, 1771–1772.

(8) Latyaeva, V. N.; Vyshinskaya, L. I.; Mar'in, V. P. *Zh. Obshch. Khim.* **1976**, *46*, 627–630.

(9) Boekel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1974**, *81*, 371–377.

(10) Boekel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *102*, 161–165.

(11) Boekel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *102*, 317–320.

(12) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71–110.

(13) Burmeister, J. L.; Deardorff, E. A.; Van Dyke, C. E. *Inorg. Chem.* **1969**, *8*, 170–172.

(14) Langford, C. H.; Aplington, J. P. *J. Organomet. Chem.* **1965**, *4*, 271–277.

(15) Harrigan, R. W.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *81*, 79–85.

(16) Marczenko, Z. *Spectrophotometric Determination of Elements*; Ellis Horwood: Chichester, England, 1976; p 556.

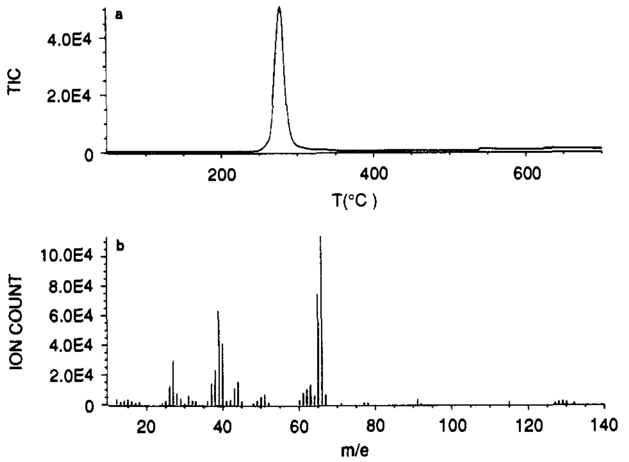

Figure 2. (a) Plot of total ion count versus temperature for the pyrolysis of $Ti(Cp)_2(NCO)_2$. (b) Mass spectrum at the maximum of ion count versus temperature.

vacuum. The mass spectroscopy system was modified to allow the volatile products to be analyzed during the deposition reaction and during the subsequent heating step.

Results

Temperature-Programmed Pyrolysis. The thermal decomposition reactions of $Ti(Cp)_2(X)_2$, where X is Cl^-, Br^-, NCS^-, NCO^-, and N_3^-, were studied by temperature-programmed pyrolysis with analysis of the evolved gas by mass spectroscopy. Figure 1 shows experimental data for the pyrolysis of bis(azido)bis(cyclopentadienyl)titanium(IV). The top portion of the figure is the total ion count from the mass spectrometer as a function of temperature. The maximum in ion count versus temperature occurs at 240 °C, and the mass spectrum of the volatile product produced at that maximum temperature is shown in the lower half of the figure. The peak at *m*/*e* 66 is due to cyclopentadiene, C_5H_6. Comparison of this spectrum with that of a known sample of cyclopentadiene shows that the signals at *m*/*e* 28 and 14 are proportionally too large, and these peaks are assigned to N_2. In addition, peaks are observed at higher mass with a parent peak at *m*/*e* 130. This region of the mass spectrum is expanded in the inset of Figure 1b. The ratio of the intensity of the peak at *m*/*e* 131 to the intensity at *m*/*e* 130 is 0.111 ± 0.003 (average of three determinations). This ratio is in excellent agreement with that calculated for the formula $C_{10}H_{10}$ as tabulated in ref 17. Therefore, this species is assigned to the dimer of the cyclopentadienyl radical, dihydrofulvalene. This dimer was previously identified in the flash vacuum pyrolysis of nickelocene.[18] The temperature maximum and the product distribution for the pyrolysis of $Ti(Cp)_2(N_3)_2$ were independent of whether hydrogen or helium was used as the carrier gas.

Figure 2 shows experimental data for the pyrolysis of bis(cyanato)bis(cyclopentadienyl)titanium(IV). The total ion count from the mass spectrometer as a function of temperature is shown in Figure 2a, and the maximum occurs at approximately 285 °C. The mass spectrum at this maximum (Figure 2b) shows the presence of $C_{10}H_{10}$ (*m*/*e* 130) and C_5H_6 (*m*/*e* 66). Comparison of this spectrum with a sample of cyclopentadiene shows that extra peaks are present at *m*/*e* 27 and 26. These are due to HCN; this assignment was confirmed by trapping a sample in liquid nitrogen and running the IR spectrum.

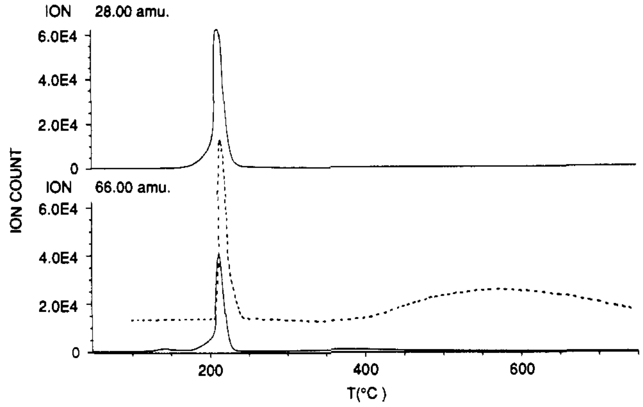

Figure 3. Plot of ion count for *m*/*e* 28 and 66 versus temperature for the pyrolysis of $Ti(Cp)_2(N_3)_2$. The dashed line is the signal from the hydrogen analyzer.

Table I. Temperature Maxima and Major Volatile Products from Temperature-Programmed Pyrolysis of Halides and Pseudohalides of Bis(cyclopentadienyl)titanium

compd	$T_{\max}$,[a] °C	major volatile products[b]
$Ti(C_5H_5)_2(Cl)_2$	310	C_5H_6, $(C_5H_5)_2$
$Ti(C_5H_5)_2(Br)_2$	320	C_5H_6, $(C_5H_5)_2$
$Ti(C_5H_5)_2(NCS)_2$	323	C_5H_6, $(C_5H_5)_2$, HCN
$Ti(C_5H_5)_2(NCO)_2$	298	C_5H_6, $(C_5H_5)_2$, HCN
$Ti(C_5H_5)_2(N_3)_2$	212	C_5H_6, $(C_5H_5)_2$, N_2

[a] Temperature program was 10 °C/min. [b] Identified by mass spectroscopy.

A plot of single ion count versus temperature for the pyrolysis of bis(azido)bis(cyclopentadienyl)titanium is shown in Figure 3. The *m*/*e* 28 signal gives the profile of N_2 evolution, and the *m*/*e* 66 signal gives the profile of cyclopentadiene evolution. In addition, the signal from the hydrogen analyzer is shown as a dashed line. All of the species shown in Figure 3 had their maxima at the same temperature. This was a characteristic feature of the reactions of the pseudohalide compounds studied in this work. The decomposition reactions occurred with the release of volatile products from pseudohalide decomposition and C_5H_6 as a single symmetrical maximum. The *m*/*e* 66 trace shows a slight rise in the base line at higher temperature. A secondary pyrolysis process seems to be occurring in which the loss of cyclopentadiene occurred from the initial pyrolysis product. Hydrogen was also given off in the secondary process, although the profile was different.

The temperature of the maximum for cyclopentadiene evolution and the major volatile products for pyrolysis of the bis(cyclopentadienyl)titanium compounds are listed in Table I. The maximum in plots of ion count from the mass spectrometer versus temperature was dependent on the temperature ramping rate. The maximum for $Ti(Cp)_2(N_3)_2$ increased from 230 °C at 10 °C/min to 240 °C at 20 °C/min. The maxima in Table I were recorded at 10 °C/min. Cyclopentadiene and the dimer of the cyclopentadienyl radical, dihydrofulvalene, were common products for all reactions studied. The halide compounds did not completely react during the pyrolysis; a significant fraction of the compound sublimed out of the furnace unreacted. There was no evidence in the mass spectra for Cl- or Br-containing products. It was assumed that the halide ions remain bound to titanium. The structures of the NCO[19] and NCS[20] compounds have been determined by X-ray crystallography, and both species have N bound to the Ti. However, a major product from the pyrolysis of these compounds was HCN. There was no evidence from the mass spectra for either S- or O-containing species. It was therefore assumed that these atoms remain bound to titanium. Thus, the decomposition reaction involved isomerization of the pseudohalide ligand. Hydrogen was observed as a product of the decomposition of the azide compound. It was not analyzed during the decomposition of the other compounds, but it was presumed to be a product of the other pyrolysis reactions.

Reaction Energetics. In an attempt to quantify the shape of the gas evolution versus temperature profiles, the temperature-programmed pyrolysis data were fitted by the method described

---

(17) Beynon, J. H.; Williams, A. E. *Mass and Abundance Tables for Use in Mass Spectrometry*; Elsevier: Amsterdam, 1963.

(18) Hedaya, E. *Acc. Chem. Res.* **1969**, *2*, 367–373.

(19) Anderson, S. J.; Brown, D. S.; Norbury, A. H. *J. Chem. Soc., Chem. Commun.* **1974**, 996–997.

(20) Villa, A. C.; Manfredotti, A. G.; Guastini, C. *Acta Crystallogr.* **1976**, *B32*, 909–914.

by Langer.[21] These profiles were sharp and symmetrical, and to a first approximation they were fitted by assuming a single rate-limiting step. The temperature of the maximum in the pyrolysis of the azide compound is 80–100 °C lower than that for the other bis(cyclopentadienyl)titanium compounds, and this appeared to be due to a lower activation energy. Langer's data treatment is similar to Redhead's method[22] used by surface chemists to account for the energetics of desorption from a surface. The reaction is assumed to be first order and to go to completion. The fraction of product formed at any temperature, α, was obtained from integrated plots of ion count versus temperature. The time derivative of α, $d\alpha/dt$, is equal to a constant (related to the surface area, etc.) multiplied by an Eyring type rate expression with an enthalpy and entropy of activation:

$$d\alpha/dt = (\mathrm{const})(k_BT/h)\exp[-\Delta H^{*}/RT]\exp[\Delta S^{*}/R] \qquad (1)$$

The heating rate, a, is constant

$$dT = a\,dt \qquad (2)$$

and after the appropriate substitutions are made, the equation can be integrated to give the approximate solution

$$\ln\,[a\alpha/T^3] = -\Delta H^{*}/RT + \ln C' \qquad (3)$$

where the term $\ln C'$ includes all of the temperature-independent terms. Thus, a plot of $\ln\,[a\alpha/T^3]$ versus $1/T$ should be linear, and ΔH^{*} can be calculated from the slope. The values were 55 kcal/mol for the azide complex and 95 kcal/mol for the cyanate compound. The plot for the thiocyanate compound was not linear; however, the instantaneous slope at values of α from 0.1 to 0.7 gave ΔH^{*} in the range 75–130 kcal/mol.

Vacuum Pyrolysis. The pyrolytic reactions of the azide and cyanate derivatives were investigated in more detail than the reactions of the other compounds. Quantitative vacuum pyrolysis of the azido derivative was accomplished for a small-scale reaction. The compound was rapidly heated to 400–500 °C and reacted before it could be volatilized out of the heated zone. The temperature of the reactor was subsequently raised to 800 °C. The residue was a dark solid, and the walls of the reaction tube assembly were coated with a shiny, dark film. Volatile products were trapped in liquid nitrogen, and IR and mass spectroscopy indicated cyclopentadiene was the only product trapped. Manometric measurements indicated approximately 1 mol of cyclopentadiene was evolved per mole of starting compound reacted. The observed weight loss during the reaction was 43%, and this loss agrees fairly well with that calculated for loss of 1 mol of cyclopentadiene, 1 mol of azide, and 2 mol of hydrogen (calculated weight loss 41.3%). However, analysis of the residue for titanium gave 27.3%, and this did not agree very well with the calculated value based on the assumption that the solid contains those elements not evolved, $\mathrm{TiC_5N_3}$ (calculated Ti 31.9%). It is apparent that the dark solid residue and the shiny metallic-looking film have a different composition, as will be noted later. Analysis of the residue by XRD indicated the material was amorphous.

Pyrolysis of the cyanate derivative could not be carried out without some of the starting material escaping unreacted. Nonetheless, this experiment also produced a shiny, metallic-looking film on the walls of the quartz apparatus. The infrared spectrum of the condensable gases given off during the reaction showed the presence of HCN, cyclopentadiene, and some unknown compound(s) with peaks at 2282 and 2258 cm^{-1}. The last two peaks are apparently due to a minor component since the mass spectra indicate only the previously identified products.

Vapor Deposition Experiments. The vacuum pyrolysis experiments indicated these compounds might be good reagents for the CVD of titanium-containing films. In fact the film produced in these experiments was adhesive and chemically inert. This film resisted hot 50:50 sulfuric acid–nitric acid and required the addition of HF for removal from the quartz. The compound $\mathrm{Ti(Cp)_2(N_3)_2}$ sublimes without decomposition at about 150 °C, and the vapor of this material was pumped into a furnace containing a quartz substrate held at 400 °C. Following the initial deposition reaction the substrate was heated under vacuum to 750–800 °C. This produced a dark, mirrorlike finish on the substrate. Unfortunately, the coating was amorphous by grazing-angle XRD. Some of the film was removed from the surface of the quartz with 5% HF, and this material also proved to be amorphous. The deposition reaction was carried out on a preweighed quartz disk, and after the reaction was complete the film was dissolved for titanium analysis. The composition of the film was 50 ± 1% titanium. With the exception of the m/e 130 species, the same products that were identified during temperature-programmed pyrolysis were observed with mass spectroscopy during the CVD experiment and the subsequent heating process. During the deposition reaction at 400 °C cyclopentadiene and $\mathrm{N_2}$ were observed. After the initial deposition reaction was over, the temperature of the deposition zone was raised to 550 °C and the ratio of nitrogen to cyclopentadiene was observed to decrease in the evolved gas. At 700 °C nitrogen in the evolved gas did not exceed background.

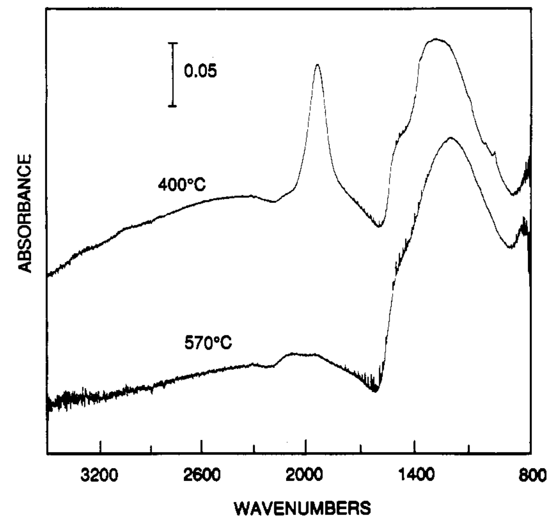

Figure 4. Infrared spectra of the product of the reaction of $\mathrm{Ti(Cp)_2(N_3)_2}$ vapor at a $\mathrm{CaF_2}$ substrate. The spectrum labeled 400 °C is that of the initial deposition product. The other spectrum is that obtained after heating under vacuum at 570 °C.

The infrared spectrum of the initial deposit was obtained with use of calcium fluoride as the substrate. $\mathrm{CaF_2}$ is transparent to infrared radiation above 900 cm^{-1}. Figure 4 shows the spectrum of the initial deposit. A prominent feature is a peak at 1995 cm^{-1}, which disappears on heating to 570 °C. This peak must be due to either a CN or NN stretching vibration. It seems improbable that azide would survive reaction at 400 °C, but it is possible that an azide decomposition product could have added to carbon. The other prominent feature of the spectrum is a peak at 1350 cm^{-1} with a shoulder at higher wavenumbers. Various carbon materials containing graphitic carbon show IR absorptions[23] at 1350 and 1590 cm^{-1}; therefore, it seems reasonable to assign this absorption to amorphous carbon.

Discussion

The similarity between $T_{\max}$ values for the halide, cyanate, and thiocyanate compounds indicates ΔH^{*} values should be approximately the same for the four compounds. The presence of the m/e 130 peak in the mass spectra indicates that cyclopentadienyl radicals were formed during the pyrolysis, although cyclopentadiene appears to be the predominant product. If Ti–Cp bond homolysis occurs during the rate-determining step, we would expect ΔH^{*} to be greater than D(M–L). The measured value for D(Ti–Cp) is 78 kcal/mol, and therefore, bond homolysis is pos-

---

(21) Langer, H. G. In *Treatise on Analytical Chemistry*, 2nd ed.; Elving, P. J., Murphy, C. B., Kolthoff, I. M., Eds.; Wiley: New York, 1983; p 229.

(22) Falconer, J. L.; Schwarz, J. A. *Catal. Rev.—Sci. Eng.* **1983**, *25*, 141–227.

(23) Friedel, R. A.; Carlson, G. L. *Fuel* **1972**, *51*, 194–198.

sible. The pseudohalide group breaks down simultaneously with C_5H_6 evolution, and other factors could be determining ΔH^*. Kinetics and product analysis have been determined for the thermal decomposition of the compounds $Ti(Cp)_2(R)_2$,[9–11] $Ti(Cp)_2(R)Cl$,[24] and $Ti(Cp)_2R$,[25] where R is aryl and benzyl. The reactions proceed by a hydrogen-abstraction mechanism, and there is little if any evidence for radical-coupling products. The products in labeling experiments show that these reactions proceed by both inter- and intramolecular pathways in which a cyclopentadienyl ring provides the hydrogen for the evolution of RH. In the work described in this paper, decomposition of the pseudohalide ligands NCO^- and NCS^- occurs simultaneously with the evolution of cyclopentadiene. Dehydrogenation of one of the cyclopentadienyl rings must be occurring to provide hydrogen for the evolution of HCN and CpH. The decomposition of the complex $Ti(Cp)_2(N_3)_2$ occurs with a lower ΔH^* value than the other reactions. The decomposition of heavy-metal azide compounds often occurs explosively since the reactions are so exothermic.[26] If breakdown of azide occurs simultaneous with or precedes the breaking of the cyclopentadienyl–titanium bond, then it is not surprising that ΔH^* is lower than the mean bond dissociation energy of the Ti–Cp bond.

The thermal decomposition of $Ti(Cp)_2(N_3)_2$ was studied in more detail than the other reactions because it appeared to be a better precursor to a refractory material. The thermal decomposition of $Ti(Cp)_2(X)_2$, where X is Cl^-, Br^-, NCO^-, and NCS^-, was studied mainly by temperature-programmed pyrolysis with analysis of the evolved gas by mass spectroscopy. The initial decomposition product retains halogen, oxygen, or sulfur. The decomposition product of $Ti(Cp)_2(Cl)_2$ was previously shown to retain most of the Cl until the temperature was over 700 °C, and then the chlorine was evolved as $Ti(Cl)_4$. Analysis of volatile products and weight-loss measurements indicate $Ti(Cp)_2(N_3)_2$ decomposes with the loss of one cyclopentadienyl group and at least one azide. The IR spectrum shows that the initial deposition product in CVD experiments retains a nitrogen-containing species (shown by the presence of a CN or NN stretching vibration). If a pathway analogous to that followed by the other bis(cyclopentadienyl)titanium compounds is followed, then the final product will contain nitrogen. Unfortunately, the product is amorphous by XRD, and thus titanium carbide cannot be distinguished from titanium nitride by this experiment.

The film resulting from CVD with bis(azido)bis(cyclopentadienyl)titanium(IV) appears to be contaminated with excess amorphous carbon. The IR spectrum of a film deposited on CaF_2 shows absorptions that can be attributed to graphitic carbon. The compounds $Ti(Cp)_2(L)_2$, where L is Cl, alkyl, and aryl, were shown to pyrolyze to TiC containing excess amorphous carbon. These bis(cyclopentadienyl)titanium compounds decompose by a pathway in which one of the rings serves as a source of hydrogen for the evolution of the other as cyclopentadiene. In addition, hydrogen is evolved from the solid. During this process σ bonds apparently form from titanium to the cyclopentadienyl ring retained by the solid, forming a polymeric material. This polymer is deficient in hydrogen and cannot eliminate the excess carbon as a hydrocarbon. A similar process occurred during the pyrolysis of carbonyl derivatives of (cyclopentadienyl)vanadium[27] to V_4C_3. Although titanium and vanadium cyclopentadienyl precursor compounds seem to retain excess carbon, several organometallic precursor compounds containing cyclopentadiene decompose without dehydrogenation of the ring. The compound $W_2(Cp)_2(CO)_4$-(DMAD), where DMAD is the dimethyl ester of acetylenedicarboxylic acid, is a precursor to W_2C,[2,28] and $(Cp)FeCo(CO)_6$ is a precursor to FeCo alloy.[29] Despite the formation of excess carbon, $Ti(Cp)_2(N_3)_2$ is a useful precursor compound for the deposition of adherent, chemically resistant titanium-containing films.

Acknowledgment. This research was sponsored by the Division of Material Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

---

(24) Waters, J. A.; Vickroy, V. V.; Mortimer, G. A. *J. Organomet. Chem.* **1971**, *33*, 41–52.

(25) Teuben, J. H. *J. Organomet. Chem.* **1974**, *69*, 241–248.

(26) Jones, K. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: London, 1973; Vol. 2, p 288.

(27) Brown, G. M.; Maya, L. *Inorg. Chem.* **1989**, *28*, 2007–2010.

(28) Laine, R. M.; Hirschon, A. S. In *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; Laine, R. M., Ed.; Martinus Nijhoff: Dordrecht, The Netherlands, 1988; pp 21–31.

(29) Czekaj, C. L.; Geoffroy, G. L. *Inorg. Chem.* **1988**, *27*, 10–13.