Mechanistic Studies of the Thermolysis of Tetraneopentyltitanium(IV). 2. Solid State and Ultra-High-Vacuum Studies of the Chemical Vapor Deposition of TiC Films

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Abstract: The chemical pathway responsible for the conversion of the organotitanium compound tetraneopentyltitanium to titanium carbide has been studied under chemical vapor conditions and on single crystals in ultra-high vacuum. For every equivalent of TiNp$_4$ consumed in the deposition process, 3.28 equiv of neopentane and 0.16 equiv of isobutane are produced; other organic species are also formed but in relatively small amounts. About 93% of the carbon and hydrogen originally present in the precursor can be accounted for in these products. Thermolysis of the specifically deuterated analogue Ti(CD$_2$CMe$_3$)$_4$ yields a 2.25:1 ratio of neopentane-d_3 and neopentane-d_2; this result combined with a kinetic isotope effect of 4.9 at 385 K shows unequivocally that the first step in the deposition pathway under CVD conditions is α-hydrogen abstraction. The α-hydrogen abstraction step produces 1 equiv of neopentane and a titanium alkylidene, which undergoes further α- (and eventually γ-) hydrogen activation processes to generate the second and third equivalents of neopentane. In the last stages of the thermolysis sequence, neopentyl (or neopentyl-derived) organic groups evidently fragment and generate the carbon atoms that eventually form the titanium carbide phase. Spectroscopic studies with IR and HREELS techniques have also been carried out in order to provide additional evidence about the nature of the species present when single crystal surfaces dosed with TiNp$_4$ are heated. A band at 1121 cm^{-1} is tentatively ascribed to the ν(M≡C) band of surface-bound neopentylidene groups.

Introduction

Over the past decade, metal−organic chemical vapor deposition (MOCVD) techniques have been increasingly employed for the preparation of thin film devices owing to the low deposition temperatures, high growth rates, high purities, and ease of process control characteristic of this approach.[1−11] Unfortunately, our understanding of the chemical reactions that underlie these deposition processes is often very limited. Recently, mechanistic studies of the reactions responsible for the conversion of transition metal precursors to metallic thin films (e.g., Cu, Pd, and Pt) have started to appear,[12−17] but similar studies of the growth of ceramic thin films (e.g. metal

carbides and nitrides) are scarce.[18−21] Such studies of the deposition pathways are necessary in order to develop better organometallic precursors and to improve and extend MOCVD techniques.

We have reported a metal−organic chemical vapor deposition (MOCVD) method for the deposition of amorphous thin films of titanium carbide at temperatures as low as 150 °C by using the organotitanium precursor tetraneopentyltitanium (TiNp$_4$).[22,23] Mechanistic studies of the early stages of the thermolysis of TiNp$_4$ in solution have been described in a separate paper.[24] In hydrocarbon solution, the neopentyl complex thermolyzes to

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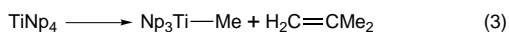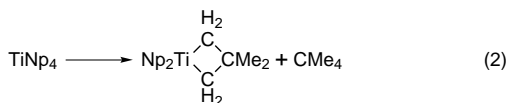
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eliminate 2.1 equiv of neopentane as the principal organic product. The initial step of the thermolysis is an α-hydrogen abstraction process which leads to the formation of a titanium alkylidene species; in reactive solvents such as hydrocarbons the alkylidene intermediate activates solvent C−H bond intermolecularly, whereas in inert solvents such as fluorocarbons it activates its own α- and γ-C−H bonds.

In order to evaluate whether the mechanism by which TiNp$_4$ thermolyzes in solution is relevant to the processes that take place during the deposition of TiC films, we have undertaken a study of the reactions of TiNp$_4$ and of the thermolytic pathways responsible for its conversion to TiC under CVD conditions and on single-crystal surfaces in ultra-high vacuum. Deuterium-labeling studies combined with temperature programmed desorption (TPD), reflection−absorption infrared (RAIR), and high-resolution electron energy loss spectroscopic (HREELS) studies have allowed us to elucidate several of the processes that take place when TiC is deposited from TiNp$_4$ under CVD conditions. These results may be of general relevance to the deposition of other metal carbide phases from MNp$_4$ (M = Zr, Hf, Cr) precursors.[25−29]

Results and Discussion

Our solution studies of the thermolysis of TiNp$_4$ have shown that the initial reaction step is α-hydrogen abstraction to give a titanium alkylidene and neopentane (eq 1).[24] Other possible first steps, such as γ-hydrogen abstraction to give a titanacyclobutane and neopentane (eq 2), β-methyl elimination to give a Ti−Me complex and isobutylene (eq 3), or homolytic cleavage of the Ti−C bond to give a Ti^{III} intermediate and a neopentyl radical (eq 4) were ruled out by measurements of deuterium kinetic isotope effects for TiNp$_4$ labeled at the α positions ($k_{\alpha(H)}/k_{\alpha(D)} = 5.2 \pm 0.4$) and by analyses of the organic byproducts generated during thermolysis.[24]

$$TiNp_4 \longrightarrow Np_2Ti{=}CHCMe_3 + CMe_4 \qquad (1)$$

$$TiNp_4 \longrightarrow Np_2Ti\begin{array}{c}H_2\\C\\\diagup\quad\diagdown\\\quad CMe_2\\\diagdown\quad\diagup\\C\\H_2\end{array} + CMe_4 \qquad (2)$$

$$TiNp_4 \longrightarrow Np_3Ti{-}Me + H_2C{=}CMe_2 \qquad (3)$$

$$TiNp_4 \longrightarrow Np_3Ti + {}^{\bullet}Np \qquad (4)$$

It is possible, however, that under actual CVD conditions (i.e. at a gas/solid interface rather than in solution) TiNp$_4$ reacts by one of the other three mechanisms.

Gaseous Byproduct Distribution Generated from TiNp$_4$ under CVD Conditions. Since different organic byproducts are predicted by the four reactions above, an analysis of the gases evolved under CVD conditions should help to discriminate among them. *In situ* quadrupole mass spectrometric studies of the gaseous products formed during the deposition of TiC under CVD conditions (250 °C, 10^{-4} Torr) show that the principal gaseous product is neopentane: peaks at $m/e = 57, 41, 39, 29,$ and 27 are seen in the correct ratios for this species, except

Table 1. GC/MS Analysis of Volatile Products from Thermolysis of TiNp$_4$ at 250 °C and 10^{-2} Torr

product	mol %	product	mol %
neopentane	90	isobutylene	<1
isobutane	6	ethylene	<1
2,2,5,5-Me$_4$-hexane	2	methane	<1
propane	2		

that the intensity of the $m/e = 41$ peak was somewhat larger than expected (see Supporting Information). The absence of significant amounts of isobutylene among the products demonstrates conclusively that the β-methyl abstraction mechanism (eq 3) is not the pathway by which TiNp$_4$ thermolyzes under CVD conditions. The other three mechanisms all predict that neopentane should be a major component of the organic byproducts, however, and cannot be distinguished on this basis.[30]

In order to establish a mass balance, TiNp$_4$ was thermolyzed in a static vacuum CVD apparatus that allowed us to collect and analyze the organic products quantitatively by NMR and GC/MS methods.[31] The NMR results show that 3.28 mol of neopentane and 0.16 mol of isobutane are formed per mole of TiNp$_4$. Traces of dineopentyl (2,2,5,5-tetramethylhexane), isobutylene, propane, ethylene, and methane were also observed (Table 1). The presence of isobutane among the reaction products explains the anomalously high intensity of the $m/e = 41$ peak in the mass spectrometric studies described above. The thin film deposited during the experiment has the composition TiC$_{1.18}$H$_{0.57}$ by elemental analysis. Together, the organic products and the TiC film account for 91% of the carbon and 93% of the hydrogen originally present in the precursor.

The static-vacuum results show that the following reaction best describes the formation of TiC from TiNp$_4$:

$$Ti(C_5H_{11})_4 \longrightarrow TiC + 3.28C_5H_{12} + 0.16C_4H_{10} + ...$$
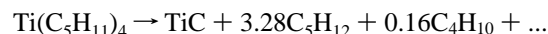
where the balance of carbon and hydrogen atoms generate a distribution of other hydrocarbons, all present in small amounts. These residual atoms are probably also responsible for the excess carbon that is present in the non-stoichiometric "TiC$_{1+x}$" deposits formed from TiNp$_4$ at lower deposition temperatures.[22,23]

Thermolysis of Deuterium-Labeled TiNp$_4$ under CVD Conditions. The α-hydrogen abstraction mechanism can be distinguished from the other mechanisms by studying the thermolysis of the deuterium-labeled molecule Ti(CD$_2$CMe$_3$)$_4$ (TiNp$_4$-d_8) at 250 °C under CVD conditions in a static vacuum. A mass spectrometric analysis of the gaseous thermolysis products shows the following distribution of neopentane isotopologs; 56% d_3, 32% d_2, 11% d_1, and 1% d_0 (see Supporting Information).[32] The large amount of neopentane-d_3 formed immediately suggests that a major decomposition pathway is α-hydrogen abstraction; in contrast, both the radical and the γ-hydrogen abstraction mechanisms predict that the predominant neopentane isotopolog should be neopentane-d_2.[30,33,34] The

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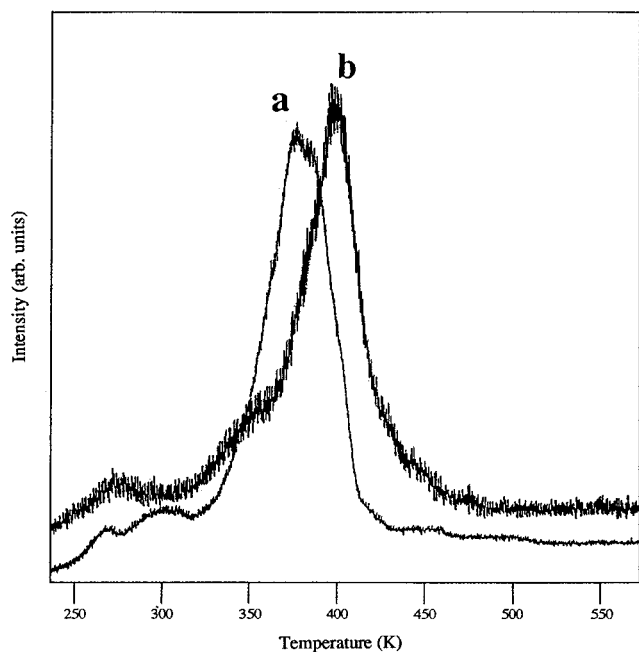
Figure 1. Temperature-programmed desorption profile of neopentane ($m/e = 57$) produced from a Cu(111) single crystal dosed at 235 K with a submonolayer coverage of (a) TiNp$_4$-d_0 and (b) TiNp$_4$-d_8, respectively.

formation of significant amounts of other neopentane isotopologs, however, shows that other processes must be occurring as well. Because approximately 3 equiv of neopentane are formed *in toto* per mole of TiNp$_4$, these other processes are likely occurring later in the thermolysis sequence.

Definitive information about the mechanism of thermolysis of TiNp$_4$ under CVD conditions has been obtained from UHV studies, to which we now turn.

Ultra-High-Vacuum Studies of TiNp$_4$ on Cu(111) Single Crystals. A Cu(111) single crystal surface in an ultra-high-vacuum (UHV) environment was dosed at 235 K with a submonolayer coverage of TiNp$_4$ and then heated. Temperature-programmed desorption (TPD) studies show that desorption of neopentane occurs between 330 and 420 K ($T_{max} = 385$ K) as followed by the $m/e = 57$ channel (Figure 1, trace a). Integrated desorption mass spectra (IDMS) show that neopentane is the predominant species desorbing from the surface in the 320–420 K temperature range (Figure 2a).[35]

In order to determine whether the α-hydrogen abstraction process is also operative under UHV conditions, we repeated the TPD experiments with the deuterium-labeled precursor TiNp$_4$-d_8. The TPD studies again show that neopentane desorbs between 340 and 430 K, but the peak maximum of 402 K is some 17 K higher than that seen for the unlabeled precursor (Figure 1, trace b). The IDMS spectrum taken in the 350–450 K temperature range showed that several neopentane isotopologs were present in the desorbing flux (Figure 2b). Analysis of the relative intensities of the mass 57 to mass 60 peaks in the IDMS spectrum indicates that the neopentane isotopolog distribution is 69% d_3, 27% d_2, 1% d_1, and 3% d_0.[32] Thus, of the 3.25 equiv of neopentane evolved in all, about 2.25 equiv is neopentane-d_3, and 1 equiv is neopentane-d_2. The implications of this result will be discussed in more detail below.

From the TPD peak maxima ($T_{max} = 385$ K for TiNp$_4$ and $T_{max} = 402$ K for TiNp$_4$-d_8), a kinetic isotope effect for the α-hydrogen abstraction step can be computed as follows. First,

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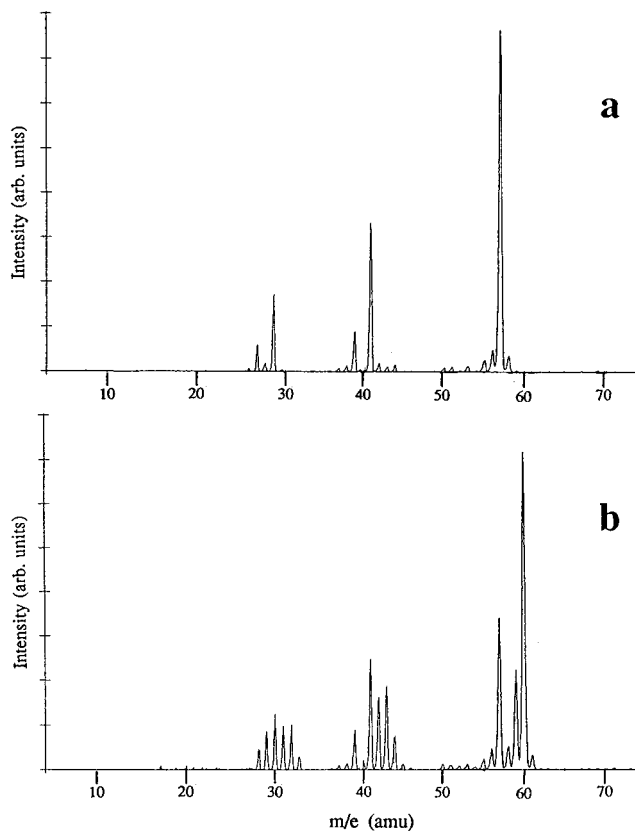(35) At higher doses, desorption of TiNp$_4$ from the multilayer occurs at ~200 K.

Figure 2. Integrated desorption mass spectra obtained (a) between 320 and 420 K from a submonolayer dose of TiNp$_4$-d_0 and (b) between 350 and 450 K from a submonolayer dose of TiNp$_4$-d_8. The Cu(111) crystal was dosed at 235 K.

the activation energies of the reactions were calculated from eq 5:

$$E_a = RT_p\left\{\ln\frac{\nu_1 T_p}{\beta} - 3.64\right\} \qquad (5)$$

where ν_1 is the pre-exponential factor, T_p is the temperature of the desorption maximum, R is the gas constant, and β is the heating rate.[36] The shapes of the TPD peaks seen for the desorption of neopentane suggest that the desorption process is unimolecular. Taking a typical pre-exponential factor for a unimolecular process of $\sim 1 \times 10^{13}$ s^{-1}, eq 5 yields activation energies of $E_a^H = 26.4$ kcal/mol and $E_a^D = 27.6$ kcal/mol for desorption of neopentane from TiNp$_4$-d_0 and TiNp$_4$-d_8, respectively. These activation energies are essentially identical with those measured for the thermolysis of TiNp$_4$-d_0 and TiNp$_4$-d_8 in solution.[24]

Second, the kinetic isotope effect was calculated from these activation energies by using the Arrhenius equation (eq 6).

$$\frac{k_{\alpha(H)}}{k_{\alpha(D)}} = e^{-(E_a^H - E_a^D)/RT} \qquad (6)$$

The kinetic isotope effect calculated from the activation energies for neopentane desorption is 4.9 at 385 K. If the kinetic isotope effect is calculated at 353 K (80 °C), a value of 5.5 is obtained. This large kinetic isotope effect indicates that an α-C−H bond is broken in the rate-determining step. This observation rules out the γ-hydrogen abstraction and radical mechanisms; overall, the TPD and IDMS results are only consistent with the α-hydrogen-abstraction mechanism as the rate-determining step

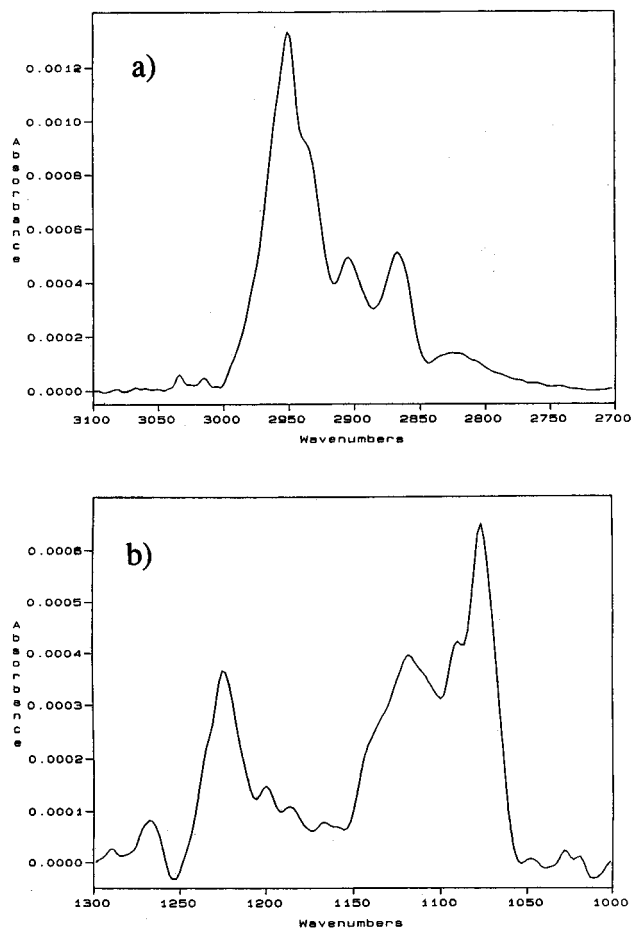<hr>

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Figure 3. The RAIR spectrum of ~1 monolayer of TiNp$_4$-d_8 dosed on Cu(111) at 235 K: (a) the 2700−3100-cm^{-1} region and (b) the 1000−1300-cm^{-1} region.

in the thermolysis pathway. The kinetic isotope effect for the thermolysis of TiNp$_4$ obtained from the UHV study agrees very well with that of 5.2 obtained at 80 °C in solution by ^{1}H NMR spectroscopy.[24]

The reactions of TiNp$_4$ on Cu(111) were also followed by Auger electron spectroscopy (AES). After the crystal was dosed with TiNp$_4$ at 235 K and heated to 330 K to remove the multilayer, AES showed that within experimental error the C:Ti ratio of the surface-bound species was near the 20:1 ratio expected for TiNp$_4$. After the surface was heated to 450 K and neopentane had been eliminated, the AES spectrum showed that a titanium carbide phase had formed: the C:Ti ratio was approximately 2:1 (although the error in this number is large) and the AES carbon signal at 272 eV, which was sharp and symmetrical, clearly indicated the presence of carbidic carbon.[37,38]

Infrared and HREELS Studies of the Thermolysis Process. In an attempt to identify the structures of the surface species present at various temperatures, we have carried out reflection−absorption infrared (RAIR) studies of the Cu(111) surfaces dosed with TiNp$_4$-d_8 (Figure 3). After the Cu(111) crystal had been dosed at 235 K, the C−H stretching modes (2951, 2904, 2868, and 2821 cm^{-1}) and bending modes (1268, 1225, 1200, 1187, 1119, 1090, and 1077 cm^{-1}) were monitored as a function of crystal temperature. As is often the case, the oscillator strengths of the α-C−D stretching modes were low and these absorptions could not be detected; these modes occur
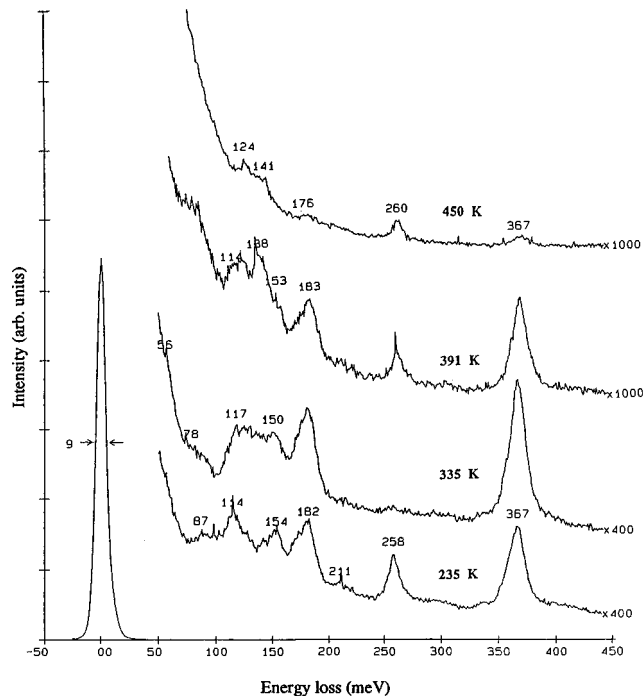
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Figure 4. Temperature dependence of the HREELS spectrum of TiNp$_4$-d_8 dosed on Cu(111) at 235 K. To convert from meV to cm^{-1}, multiply by 8.066. The peak near 260 meV is due to adventitious carbon monoxide.

in the 2000−2100-cm^{-1} region as shown by the FTIR spectrum of a bulk sample of TiNp$_4$-d_8 (see Supporting Information).

As the crystal was heated from 235 to 350 K, most of the bands became less intense. An exception was the growth of a band at 1121 cm^{-1}, which at 350 K was the most intense in the spectrum. The frequency of this band is lower than the 1270−1420-cm^{-1} frequencies reported for the ν(M≡C) stretches of metal carbynes[39] and is in the region expected for metal−carbon double bond stretches. Above 350 K, the peak intensities decreased rapidly, and only very weak C−H absorptions were observed above 500 K.

Surface vibrational spectra of TiNp$_4$-d_8 adsorbed on Cu(111) single crystals were also recorded by using high-resolution electron energy loss (HREEL) spectroscopy. The crystal was first dosed with a submonolayer coverage of TiNp$_4$-d_8 at 235 K, and then HREEL spectra were taken at 110 K after the crystal had been heated briefly to 335, 391, and 450 K. The HREEL spectrum taken after dosing at 235 K showed the presence of neopentyl groups: peaks at 2957, 1466, 1241, 918, and 701 cm^{-1} are consistent with those present at 2987, 1462, 1227, 914, and 708 cm^{-1} in the infrared spectrum of a bulk sample of the precursor. As the crystal was heated to progressively higher temperatures, changes in the low-frequency region were evident. In particular, a feature at 138 meV (1113 cm^{-1}) grew in and was the most intense low-frequency band at 391 K. The frequency of this band is similar to that of the 1121-cm^{-1} feature in the RAIR studies (see above) and is tentatively ascribed to formation of a neopentylidene group. By 450 K, the HREEL spectrum contained only very weak absorptions due to C−H vibrational modes (Figure 4). These results are entirely consistent with those of the IR study. The HREEL spectra obtained upon heating a Cu(111) surface dosed with excess TiNp$_4$ (so that a multilayer formed) were very similar to those above.

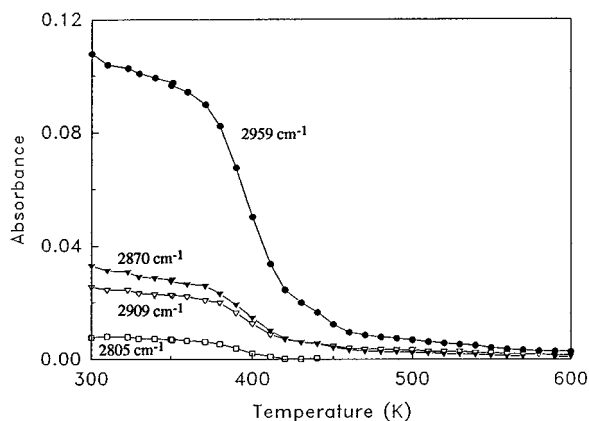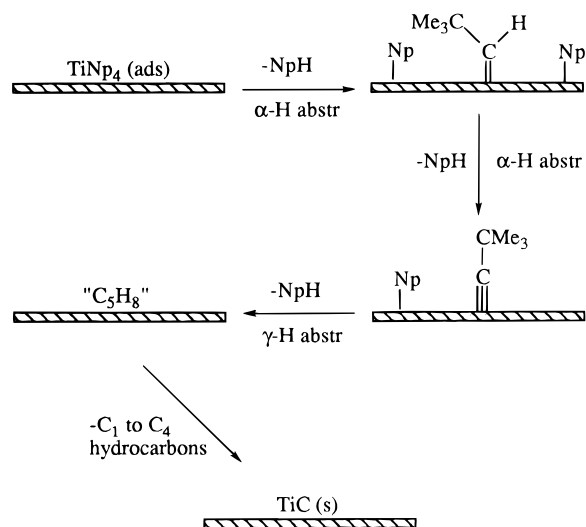(39) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988; Chapter 4.

Figure 5. Temperature dependence of the FT-IR peak intensities upon heating a monolayer of $TiNp_4$-d_0 dosed on SiO_2 at 300 K.

Scheme 1. Mechanism Proposed for the Deposition of TiC from $TiNp_4$

Transmission FT-IR studies of the thermolysis of $TiNp_4$-d_0 supported on a SiO_2-coated Ta grid were also performed. Four C−H vibrational bands (2959, 2909, 2870, and 2805 cm^{-1}) were studied as a function of temperature (Figure 5). Below 370 K, little change in the IR peak intensities is seen; above this temperature, the peak intensities decrease rapidly and are essentially zero at 450 K. Little further change in the IR spectrum is apparent from this temperature up to 600 K.

All these TPD, IR, and HREEL studies are consistent and clearly suggest that the major decomposition process of $TiNp_4$ occurs between 350 and 450 K, and that the rate-determining step is α-hydrogen abstraction with a deuterium kinetic isotope effect of 5.5 at 353 K.

Overall Mechanistic Scheme for the Thermolysis of $TiNp_4$ under CVD Conditions. From the UHV and static vacuum studies, a mechanistic scheme for the thermolysis of $TiNp_4$ precursor to TiC films can be proposed (Scheme 1).

In agreement with our previous studies of the thermolysis of $TiNp_4$ in solution, the kinetic isotope effect seen under UHV conditions clearly establishes that α-hydrogen abstraction is the first step in the thermolysis sequence; this step results in the liberation of 1 equiv of neopentane-d_3. The following steps in the sequence, which involve the fate of "$Ti(=CDCMe_3)Np_2$", are less clear,[40] but some information can be obtained from an analysis of the distribution of neopentane isotopologs evolved in these subsequent reactions. We showed above that 3.25 equiv of neopentane are evolved in all; of this amount, 2.25 equiv is neopentane-d_3 and 1 equiv is neopentane-d_2. Since 1 equiv of

neopentane-d_3 is evolved in the α-hydrogen-abstraction step, the subsequent steps must result in the evolution of nearly equal amounts of neopentane-d_2 and neopentane-d_3.

The simplest explanation of this result is that the surface alkylidenes [Ti]=CDCMe$_3$ undergo a second α-abstraction to yield the surface alkylidyne [Ti]≡CCMe$_3$; transfer of the liberated deuterium atoms to nearby [Ti]−CD$_2$CMe$_3$ groups yields 1 equiv of neopentane-d_3. At the same time, transfer of γ-hydrogen atoms from the neopentylidene or neopentylidyne groups to nearby [Ti]−CD$_2$CMe$_3$ groups yields neopentane-d_2.[41] Other mechanistic sequences are also possible, such as γ-hydrogen abstraction from surface-bound [Ti]−CD$_2$CMe$_3$ groups to yield surface-bound metallacyclobutanes, but it is unclear whether the latter should decompose under our conditions to give isobutylene as seen for discrete molecular species.[42,43] At best, only traces of isobutylene are present among the organic byproducts generated upon thermolysis of $TiNp_4$.

In the last steps of the thermolysis sequence, the remaining hydrocarbons (dehydrogenated fragments of neopentyl groups) decompose via multiple C−C and C−H bond cleavage reactions that eventually result in the formation of TiC along with isobutane and smaller amounts of other organic byproducts such as ethylene, methane, and propane (Table 1). The 0.16 equiv of isobutane formed upon thermolysis of $TiNp_4$-d_8 under CVD conditions affords some insight into the latter stages of the bond-breaking processes that take place during thermolysis. GC/MS analysis shows that the distribution of isobutane isotopologs is 33% d_0, 37% d_1, 22% d_2, and 7% d_3. The presence of significant amounts of the d_0 and d_1 isotopologs suggests that one pathway for the formation of isobutane is cleavage of the α−β carbon−carbon bond of neopentyl or neopentyl-derived groups: addition of hydrogen or deuterium to the resulting *tert*-butyl fragment would give isobutane-d_0 and -d_1. Elimination of a C$_4$ fragment from a C$_5$ species would afford surface-bound C$_1$ products that might lead directly to the formation of titanium carbide. Since only 0.16 equiv of isobutane is generated upon thermolysis of $TiNp_4$, however, this last pathway cannot be the only route to TiC.

It is of interest to compare our results with the behavior of neopentyl groups on nickel surfaces, which has recently been studied by Zaera and Tjandra.[44,45] Their studies strongly suggest that the surface-bound neopentyl groups undergo α-hydrogen elimination processes to generate neopentylidene species. The hydrogen atoms generated in this way can react with other neopentyl groups to yield neopentane. Unlike our system, however, upon further thermolysis the neopentylidene groups decompose to isobutylene via a unimolecular process. As noted above, isobutylene is not formed in significant amounts upon thermolysis of $TiNp_4$. This difference could reflect the different chemistries of neopentyl (and neopentylidene) groups attached to titanium vs nickel, or the different surface concentrations in the two experiments, which could alter the relative importance of bimolecular decomposition processes (leading to neopentane)

(40) The following discussion does not explicitly take into account the possibility that the titanium alkylidene intermediate oligomerizes on the surface. Dimerization of tantalum neopentylidenes generated by α-hydrogen abstraction has been observed: Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746−12750.

(41) Hydrogenation of surface-bound Zr-Np groups to neopentane has been observed: Quignard, F.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1991**, 1589−1590.

(42) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491−7496.

(43) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880−4890.

(44) Zaera, F.; Tjandra, S. *J. Am. Chem. Soc.* **1993**, *115*, 5851−5852.

(45) Zaera, F.; Tjandra, S. *J. Am. Chem. Soc.* **1996**, *118*, 12738−12746.

vs unimolecular decomposition processes (leading to isobutyl-ene). In any event, Zaera's results do not contradict our contention that α-hydrogen abstraction is a rate determining step that controls the early events in the chemical pathway that leads from TiNp$_4$ to TiC.

Finally, we can compare the rate of the α-elimination step with the reaction-limited rate of deposition of TiC from TiNp$_4$ under CVD conditions (∼0.3 μm h^{-1} at 175 °C).[22,23] This growth rate and the bulk density of TiC allow us to calculate that approximately 2 × 10^{14} molecules of TiNp$_4$ must thermolyze per cm^2 per second under CVD conditions. The volume of a TiNp$_4$ molecule is approximately 600 Å^3; if we make the (probably poor) assumption that TiC film growth occurs from a densely-packed monolayer (∼1 × 10^{14} molecules/cm^2), then the first-order rate constant for deposition is ∼1 s^{-1} at 175 °C. Taking the pre-exponential factor to be ∼10^{13} s^{-1}, this rate corresponds to an activation energy of ∼27 kcal/mol for the growth of TiC. This value is comparable to the activation energy for decomposition of TiNp$_4$ of about 28 kcal/mol (see above). The comparison suggests that the rate limiting step in the growth of TiC from TiNp$_4$ is α-hydrogen abstraction rather than a later step in the thermolysis pathway (such as the generation of surface-bound C$_1$ fragments or their conversion to carbide carbons). The uncertainties implicit in deriving activation energies from growth rates, however, make such a conclusion tentative.

Concluding Remarks

The mechanistic sequence responsible for the deposition of titanium carbide from the organotitanium compound tetraneopentyltitanium has been in large part elucidated. Studies of the thermolysis of TiNp$_4$ under CVD and UHV conditions show that the first step in the thermolysis pathway is the same as that previously seen in solution: α-hydrogen abstraction to form neopentane and a titanium alkylidene intermediate. This conclusion is supported by the very similar distribution of organic products obtained in both cases, by the similar activation energies seen, and by the essentially identical kinetic isotope effect observed upon deuterating the α-hydrogen positions of TiNp$_4$. The subsequent fate of the titanium alkylidene, however, is not the same as in solution: under CVD/UHV conditions it undergoes further α- (and eventually γ-) hydrogen activation processes, whereas in solution it activates solvent C−H bonds.

In the last stages of the thermolysis sequence under CVD/UHV conditions, neopentyl (or neopentyl-derived) organic groups fragment to give a variety of lower hydrocarbon products, isobutane being formed in the largest amounts. The surface-bound C$_1$−C$_4$ hydrocarbon fragments that lead to these lower hydrocarbon species also are undoubtedly the source of the carbon atoms that eventually form the titanium carbide phase; this part of the mechanistic sequence remains the least understood. At present, it is not clear whether the formation of the TiC product is simply driven thermodynamically, or whether the neopentyl (or neopentyl-derived) organic groups actually facilitate the formation of this product by providing low-energy pathways to generate C$_1$ species that transform smoothly to a carbide phase. We suspect that the thermodynamic driving force is not alone sufficient to overcome the kinetic barrier for the formation of TiC at 250 °C: instead it seems more reasonable to propose that the chemical source of the carbon atoms plays an important kinetically-controlling role at such low temperatures.

Experimental Section

General Methods. All manipulations were carried out with standard Schlenk and cannula techniques under argon or in vacuum. The

preparations of tetraneopentyltitanium, Ti(CH$_2$CMe$_3$)$_4$, and tetraneopentyltitanium-d_8, Ti(CD$_2$CMe$_3$)$_4$, are described in a separate paper.[24] The determination of the distribution of deuterated neopentane isotopologs from the mass spectrometric ion intensities was carried out by solving a set of linear equations according to a procedure described elsewhere.[24]

Elemental analyses were performed by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois. ^{1}H NMR and ^{13}C NMR spectra were recorded on a General Electric QE300 instrument at 300 and 75.44 MHz, respectively. ^{1}H and ^{13}C NMR chemical shifts are reported in δ units (positive chemical shifts to higher frequency) and are referenced with respect to SiMe$_4$. Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrometer as Nujol mulls dispersed between KBr plates. A Hewlett Packard 5890 gas chromatograph with a 5970 series mass selective detector was used to obtain the GC/MS data. The mass selective detector was calibrated by using the 31, 50, and 69 amu peaks of perfluorotributylamine. The column used was a 30-m RSL-160 capillary column (5 μm thick poly-(dimethylsiloxane) film, 0.32-mm i.d., Alltech).

Static Vacuum CVD Apparatus. In order to collect and analyze quantitatively the gaseous products generated under CVD conditions, TiNp$_4$ was thermolyzed under a static vacuum (10^{-2} Torr) at 250 °C in a closed-system CVD apparatus. This apparatus consisted of a solvent reservoir, a precursor reservoir, a deposition zone, and an NMR tube.[31] The solvent reservoir was charged with a 1:3 mixture of benzene and benzene-d_6 (0.423 g). [The concentration of protons in this solvent (3.0 mmol/mL) had been previously established by dissolving hexamethylbenzene (0.0142 g, 0.87 mmol) in the solvent mixture (0.570 g) and measuring the intensity of the C$_6$H$_6$ peak relative to the C$_6$Me$_6$ peak in a ^{1}H NMR spectrum taken with a 120-s post-acquisition delay.] After the solvent mixture had been degassed with 3 freeze−pump−thaw cycles, the solvent reservoir was isolated from the rest of the apparatus until the deposition step was complete. The precursor reservoir was charged with TiNp$_4$ (0.10 g, 0.3 mmol) and cooled to −78 °C. After the apparatus had been evacuated to 10^{-2} Torr, it was isolated from the pump and remained under a static vacuum for the thermolysis step. The NMR tube was cooled to −196 °C, and the precursor reservoir was heated at 45 °C to sublime the TiNp$_4$ through the deposition zone, which was heated externally to 250 °C. A dark film deposited on the walls of the deposition zone and the organic byproducts were collected in the NMR tube. After the precursor had sublimed and the deposition was complete, the deposition zone was cooled to room temperature. The contents of the solvent reservoir were transferred into the liquid nitrogen cooled NMR tube, which was then flame sealed. The NMR tube contents were analyzed by ^{1}H and ^{13}C NMR spectroscopy. In order to ensure accurate integrations, the post-acquisition delay times were greater than 5 times the longest T_1 and, for ^{13}C NMR spectra, NOE effects were suppressed by turning the decoupler off between acquisitions. Head-space corrections are detailed elsewhere.[24]

The ^{13}C{^{1}H} NMR spectrum of the organic products from the static vacuum CVD experiment showed the presence of neopentane and isobutane [δ 31.2 (C*Me*$_3$), 27.5 (*C*Me$_4$), 24.4 (HC*Me*$_3$), 23.2 (H*C*Me$_3$)], along with trace amounts of isobutylene. Dineopentyl, propane, ethylene, and methane, which were found in trace quantities in the GC/MS study, were not detectable in the ^{13}C{^{1}H} NMR spectrum. The relative intensity of the C*Me*$_4$ and HC*Me*$_3$ peaks in the ^{13}C NMR spectrum was 100:3.6, which corresponds to a neopentane:isobutane mole ratio of 100:4.8. This result, combined with calibrated peak integrals from the ^{1}H NMR data [δ 0.88 (s, CMe$_4$), 0.86 (d, J_{HH} = 7 Hz, HC*Me*$_3$)], showed that 3.28 mol of neopentane and 0.16 mol of isobutane had been evolved per mole of TiNp$_4$ consumed. The black deposit was analyzed and found to have a stoichiometry of TiC$_{1.18}$H$_{0.57}$. After NMR analysis of the byproducts, the sealed NMR tube was broken and the formation of neopentane and isobutane was confirmed by GC/MS methods.

The static vacuum thermolysis of TiNp$_4$-d_8 was carried out with use of the same apparatus as above, except that no NMR solvent was introduced and the captured byproducts were analyzed only by GC/MS.

The solid state thermolysis of TiNp$_4$-d_0 and -d_8 was carried out under vacuum in flame-sealed 5-mm NMR tubes at 250 °C for 30 min. After

the thermolysis was complete, the sealed tubes were broken and the volatile organic byproducts were analyzed by GC/MS (Table 1).

Ultra-High-Vacuum Studies. Experiments were performed in a diffusion and titanium-sublimation pumped ultra-high-vacuum chamber with a base pressure of ca. 1×10^{-10} Torr. The system was equipped with four-grid low-energy electron diffraction optics (Varian), a single pass cylindrical mirror analyzer (PHI) for Auger electron spectroscopy, a differentially pumped quadrupole mass spectrometer (Vacuum Generators) for temperature-programmed desorption, and a high-resolution electron energy loss spectrometer (McAllister Technical Services). For the HREELS experiments, the angle of the incident electron beam (60° to the surface normal) and its energy (4−5 eV) were held constant and electrons were collected only in the specular direction. The elastic scattering peak from an adsorbate-covered surface had an intensity of $> 10^5$ cps and a full width at half maximum of 9−11 meV (72−88 cm^{-1}). During TPD and integrated mass spectrometry (IDMS)[46] experiments, the heating rate was 1 deg K/s.

Infrared spectra were collected in either reflection or transmission mode on a Fourier transform infrared spectrometer (Mattson Instruments) and a liquid nitrogen cooled, narrow band, MCT detector. Typically, 2048 scans were averaged at 4-cm^{-1} resolution. In the variable-temperature experiments, the temperature of the crystal was raised to the indicated temperature for ∼2 s and then cooled to the dosing temperature before data collection was initiated.

(46) Dubois, L. H. *Rev. Sci. Instrum.* **1989**, *60*, 410−413.

A 1-cm-diameter Cu(111) single-crystal disk (>99.999%, Monocrystals) was oriented, cut, and polished by using standard techniques. The sample was mounted on a molybdenum button that can be heated to 1200 K by a tungsten filament or cooled to 100 K via copper braids connected to a liquid nitrogen reservoir. Chromel−alumel thermocouples were used to monitor the crystal temperature. Samples were cleaned by cycles of sputtering with Ne$^+$ ions (1 keV, 20 μA/cm^2) at both 300 and 900 K followed by annealing at 900 K. The crystals were sputtered and annealed before each experiment and their cleanliness was monitored by AES.

Dosing of the TiNp$_4$-d_0 and TiNp$_4$-d_8 precursors was carried out with an effusive molecular beam doser. The samples were held about 1 mm from the mass spectrometer skimmer during TPD and IDMS experiments.

Supporting Information Available: Figures of the mass spectrum of the products exiting the hot zone during CVD of TiC from TiNp$_4$-d_0 at 250 °C and 10^{-4} Torr, the mass spectrum of neopentane obtained from the thermolysis of TiNp$_4$-d_8 at 250 °C and 10^{-2} Torr, and the FTIR spectrum (Nujol mull) of bulk TiNp$_4$-d_8 (3 pages). See any current masthead for ordering and Internet access instructions.

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