

Molecular orbital studies of titanium nitride chemical vapor deposition: gas phase β -elimination

Jason B. Cross, H. Bernhard Schlegel *

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

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Abstract

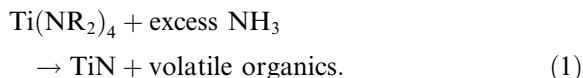
Chemical vapor deposition (CVD) of titanium nitride can be carried out using $\text{Ti}(\text{NR}_2)_4$ and NH_3 ($\text{R} = \text{Me}$ or Et). Imido compounds are thought to be key intermediates in this process. Formation of $\text{Ti}(\text{NR}_2)_2=\text{NH}$ from $\text{Ti}(\text{NR}_2)_4$ can proceed by ligand exchange with NH_3 followed by elimination of NHR_2 . When $\text{R} = \text{Et}$ there is an alternate β -elimination pathway that also leads to imido formation. At the B3LYP/6-311G(d) level of theory, this pathway has a barrier of 51.1 kcal/mol and the reaction is endothermic by 68.0 kcal/mol. By comparison, ligand exchange has a barrier of 35.5 kcal/mol, suggesting that β -elimination does not contribute significantly to $\text{Ti}(\text{NR}_2)_2=\text{NH}$ formation. © 2001 Published by Elsevier Science B.V.

1. Introduction

It is well known that titanium nitride (Ti–N) thin films have many properties that are desirable for commercial and industrial uses. These properties include extreme hardness, chemical resistivity, excellent electrical conductivity, and optical properties similar to those of gold. When combined, these characteristics make Ti–N thin films ideal for use as wear-resistant coatings for tools, barrier materials and conductive coatings for microelectronics, solar coatings for glass, and decorative coatings [1–4].

The semiconductor industry prefers the use of chemical vapor deposition (CVD) to physical deposition when preparing Ti–N thin films be-

cause CVD produces good conformal coatings that are required for submicron devices [2]. High temperature CVD processes (500–1000°C) utilize TiCl_4 as a precursor along with N_2 or NH_3 as a nitrogen source [5–7]. Semiconductor applications require low temperatures (300–400°C), and high quality films that can be prepared from Ti(IV) amido precursors with an excess of ammonia [8–10]:



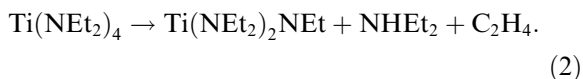
Gas phase reactions are key elements of the Ti–N CVD process at atmospheric pressure [5]. A combination of experimental and computational work is shedding some light on the details of this process. In previous work, we have computed the gas phase heats of formation of potential intermediates in the Ti–N CVD process at the G2 level of theory [11]. These results are in agreement with

* Corresponding author. Fax: +1-313-577-8822.

E-mail address: hbs@chem.wayne.edu (H.B. Schlegel).

recent experimental values for TiCl_n [12], and the theoretical bond dissociation energies should be accurate to ± 2 kcal/mol. We have subsequently calculated the reaction paths and barrier heights for complex formation, ligand exchange, and elimination reactions involving TiCl_4 and $\text{Ti}(\text{NH}_2)_4$ with NH_3 [13]. The exchange reactions are facile, and gas phase elimination of NH_3 to form $\text{Ti}(\text{NH}_2)_2\text{NH}$ is practical under CVD conditions [13]. Further elimination from $\text{Ti}(\text{NH}_2)_2\text{NH}$ is unlikely, [13] but experimental evidence suggests that imido compounds play a significant role as intermediates in Ti–N film growth [14]. Dubois has experimental evidence for the formation of oligomers from these complexes [15] and our calculations show that the formation of a dimer from $\text{Ti}(\text{NH}_2)_2\text{NH}$ is a barrierless reaction resulting in a large (99.1 kcal/mol) binding energy [16]. Subsequent elimination of hydrazine from the imido dimer complex is highly endothermic, suggesting that reduction of Ti(IV) to Ti(III) may occur on the surface rather than in the gas phase [16].

The growth of Ti–N films using $\text{Ti}(\text{NMe}_2)_4$, $\text{Ti}(\text{NMeEt})_4$ and $\text{Ti}(\text{NEt}_2)_4$, as well as a number of complexes with cyclic amido groups, as precursors have been studied experimentally [10,17,18]. Films made using $\text{Ti}(\text{NMeEt})_4$ and $\text{Ti}(\text{NEt}_2)_4$ had higher step coverage, better stability and lower resistivity [10,18]. There is a more direct reaction path available to $\text{Ti}(\text{NEt}_2)_4$, and any similar compound with hydrogens on a β -carbon, that is not accessible to other precursors:



In this Letter we explore the β -elimination pathway for formation of $\text{Ti}(\text{NH}_2)_2\text{NH}$ from $\text{Ti}(\text{NH}_2)_3\text{NHet}$ (a model for $\text{Ti}(\text{NEt}_2)_4$) and compare this pathway to those studied previously [13].

2. Method

Molecular orbital calculations were carried out using the GAUSSIAN 98 [19] series of programs. Equilibrium geometries for complexes and transition states were optimized using the B3LYP hybrid

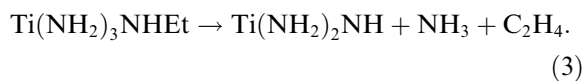
density functional method [20–22] with the 6-311G(d) basis set [23–27]. (For titanium, this corresponds to the 14s,9p,5d Wachters–Hay [25–27] basis set contracted to 9s,5p,3d and augmented with an f-type Gaussian shell with an exponent of 0.690.) Vibrational frequencies and zero-point energies were computed at this level of theory and were used without scaling since the B3LYP frequencies compare favorably with experimental values for a wide range of second and third period compounds [28]. Thermal and free energy corrections to the energies were calculated by standard statistical thermodynamic methods [29] using the unscaled B3LYP frequencies.

The B3LYP/6-311G(d) level of theory proved to be the best compromise between cost and accuracy. Most of the systems studied in this Letter involve up to 7 heavy atoms, which is too costly for high accuracy methods, such as the G2 method [30]. For a more complete discussion supporting this choice of level of theory, see the Methods section of our previous paper [13].

3. Results and discussion

Structures on the $\text{Ti}(\text{NH}_2)_3\text{NHet}$ reaction path are found in Fig. 1; relative energies are plotted in Fig. 2. Transition state structures are labeled with **TS** and complexes representing minima are labeled with **C**. Computed heats of formation, entropies, relative enthalpies, and free energies at the B3LYP/6-311G(d) level of theory are listed in Table 1.

As studied in our previous paper [13] $\text{Ti}(\text{NH}_2)_2\text{NH}$ (**C4**) can be formed by a ligand exchange reaction involving $\text{Ti}(\text{NR}_2)_4$ and NH_3 , followed by elimination of NHR_2 . This is the only obvious path available for $\text{R} = \text{H}$ and $\text{R} = \text{Me}$. For $\text{Ti}(\text{NEt}_2)_4$ and other precursors with hydrogen atoms bonded to β carbons, there is a more direct pathway that involves β -elimination with no ligand exchange. The simplest model for the $\text{Ti}(\text{NEt}_2)_4$ precursor has all but one ethyl group replaced by hydrogen. Thus, the model reaction is:



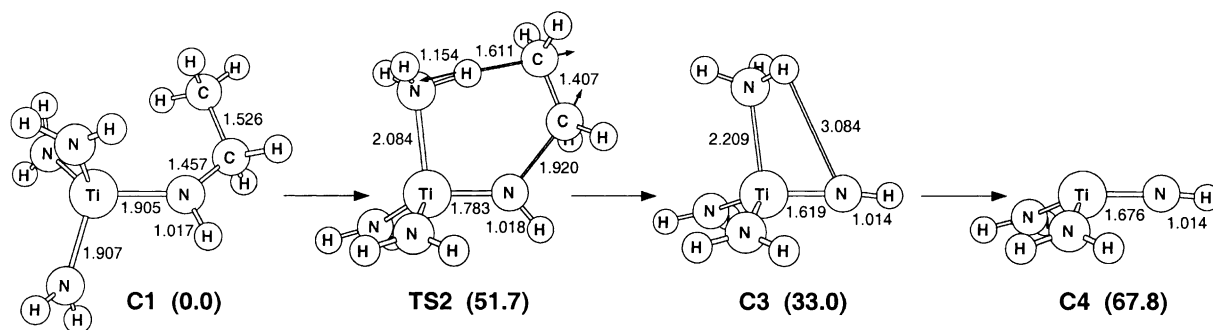


Fig. 1. Structures on the β -elimination reaction path, including molecules and complexes (denoted by C), and transition state with transition vectors (denoted by TS). Relative enthalpies at 0 K in kcal/mol are included in parentheses.

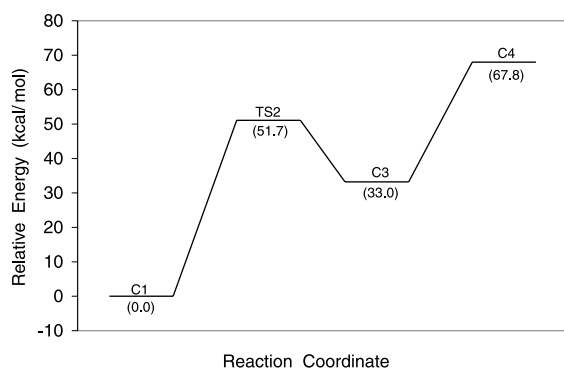


Fig. 2. Energy profile for the β -elimination reaction path. Relative enthalpies at 0 K in kcal/mol are included in parentheses.

The structures on this reaction path are in Fig. 1. The reaction is calculated to be endothermic by 67.8 kcal/mol with a transition state barrier of 51.7 kcal/mol. The transition state (**TS2**) structure can

be characterized as late, which is consistent with an endothermic reaction. The Ti–NH imido double bond formation is well underway (1.905 Å in **C1** to 1.783 Å in **TS2**, compared to 1.676 Å in **C4**) and the Ti–NH₃ bond has elongated to 2.084 Å from 1.904 Å in the reactant (**C1**). Hydrogen transfer is proceeding as well, with the TiNH₂–H bond nearly formed (1.154 Å compared to 1.015 Å in the complex (**C3**)). The product side complex (**C3**) is the same one that was obtained in our previous study, with C₂H₄ not bound to the complex and a dative Ti–NH₃ bond between Ti(NH₂)₂NH and NH₃. It lies 18.7 kcal/mol below the transition state and 34.8 kcal/mol below products. The Ti=NH double bond is fully formed in this complex (1.691 Å) and there is a strong dative bond between Ti and NH₃ (2.209 Å).

Two competing reaction pathways were studied in our previous work [13]. The first is ligand exchange followed by elimination:

Table 1
Heats of formation, absolute entropies, relative enthalpies, and relative free energies

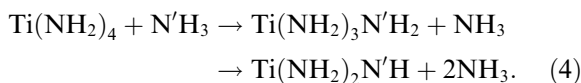
Structure	$\Delta H_{f,298}^a$ (kcal/mol)	Entropy ^b (cal/mol/K)	Rel. enthalpy ^c (kcal/mol)	Rel. free energy ^d (kcal/mol)
C1 Ti(NH ₂) ₃ NHEt	–87.4	107.8	0.0	0.0
TS2 Ti(NH ₂) ₂ NHNH ₃ Et	–36.3	102.7	51.1	53.9
C3 Ti(NH ₂) ₂ NH · NH ₃ + C ₂ H ₄	–54.3	147.5	33.2	9.3
C4 Ti(NH ₂) ₂ NH + NH ₃ + C ₂ H ₄	–19.4	180.6	68.0	23.4

^a Heats of formation at 298.15 K and 1 atm, computed using the relative enthalpies for the above compounds and Ti(NH₂)₄, the experimental $\Delta H_{f,298}$ for TiCl₄ (–182.4 kcal/mol) and NH₃ (–11.0 kcal/mol), calculated $\Delta H_{f,298}$ for HCl (–22.4 kcal/mol), and the calculated enthalpy for TiCl₄ + 4NH₃ → Ti(NH₂)₄ + 4HCl (70.4 kcal/mol).

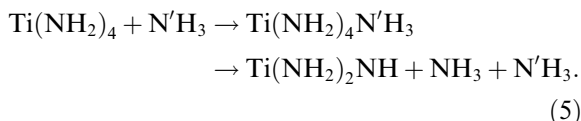
^b Absolute entropies at 298.15 K and 1 atm.

^c Enthalpies relative to **C1** at 298.15 K and 1 atm.

^d Free energies relative to **C1** at CVD conditions (523.15 K and 20 Torr).



The elimination step of this reaction is endothermic by 51.9 kcal/mol and has a barrier of 35.5 kcal/mol at the B3LYP/6-311G(d) level of theory. This compares well with our G2 values for this reaction path (46.4 and 35.5 kcal/mol for the heat of reaction and barrier height, respectively). The second reaction path studied in our previous work is an NH_3 catalyzed elimination pathway:



This pathway has a barrier of 24.0 kcal/mol at the B3LYP/6-311G(d) level of theory. This value also compares well with our previous G2 calculations for this reaction path (23.5 kcal/mol).

The ligand exchange + elimination and NH_3 catalyzed pathways described above give some indication of the accuracy of the B3LYP/6-311G(d) method used in this study compared to the G2 method used previously. The barriers for these reactions are in very good agreement, with B3LYP/6-311G(d) overestimating the barrier by a maximum of 0.5 kcal/mol relative to the G2 method. The B3LYP/6-311G(d) heat of reaction shows a larger deviation from the G2 calculations, overestimating the enthalpy by 5.5 kcal/mol. This suggests that even though the enthalpy of reaction for the β -elimination pathway may be overestimated by several kcal/mol, the barrier height is probably accurate and the β -elimination pathway is still unfavorable.

4. Conclusions

Based on gas phase relative enthalpies alone, the β -elimination pathway appears to be less favorable than the reaction path involving ligand exchange and subsequent elimination that was studied previously. The enthalpy of reaction and the barrier height for β -elimination are ca. 20 kcal/mol higher than for the ligand exchange pathway. The free energy of reaction at 250°C and 20 Torr is

lower for β -elimination (23.4 kcal/mol) than for the ligand exchange pathway (31.7 kcal/mol). However, ΔG^\ddagger for the barrier is 16.4 kcal/mol higher for the β -elimination pathway than for the ligand exchange pathway. Based on these thermodynamic considerations, it is likely that the β -elimination pathway contributes less to titanium imido formation than the ligand exchange followed by elimination.

5. Supplementary material available

Tables of total energies, Cartesian coordinates, and vibrational frequencies of the structures described in this work. This material is available free of charge via the Internet at <http://chem.wayne.edu/schlegel/>.

Acknowledgements

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