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Thermochemistry of Gas-Phase Species Relevant to Titanium Nitride CVD

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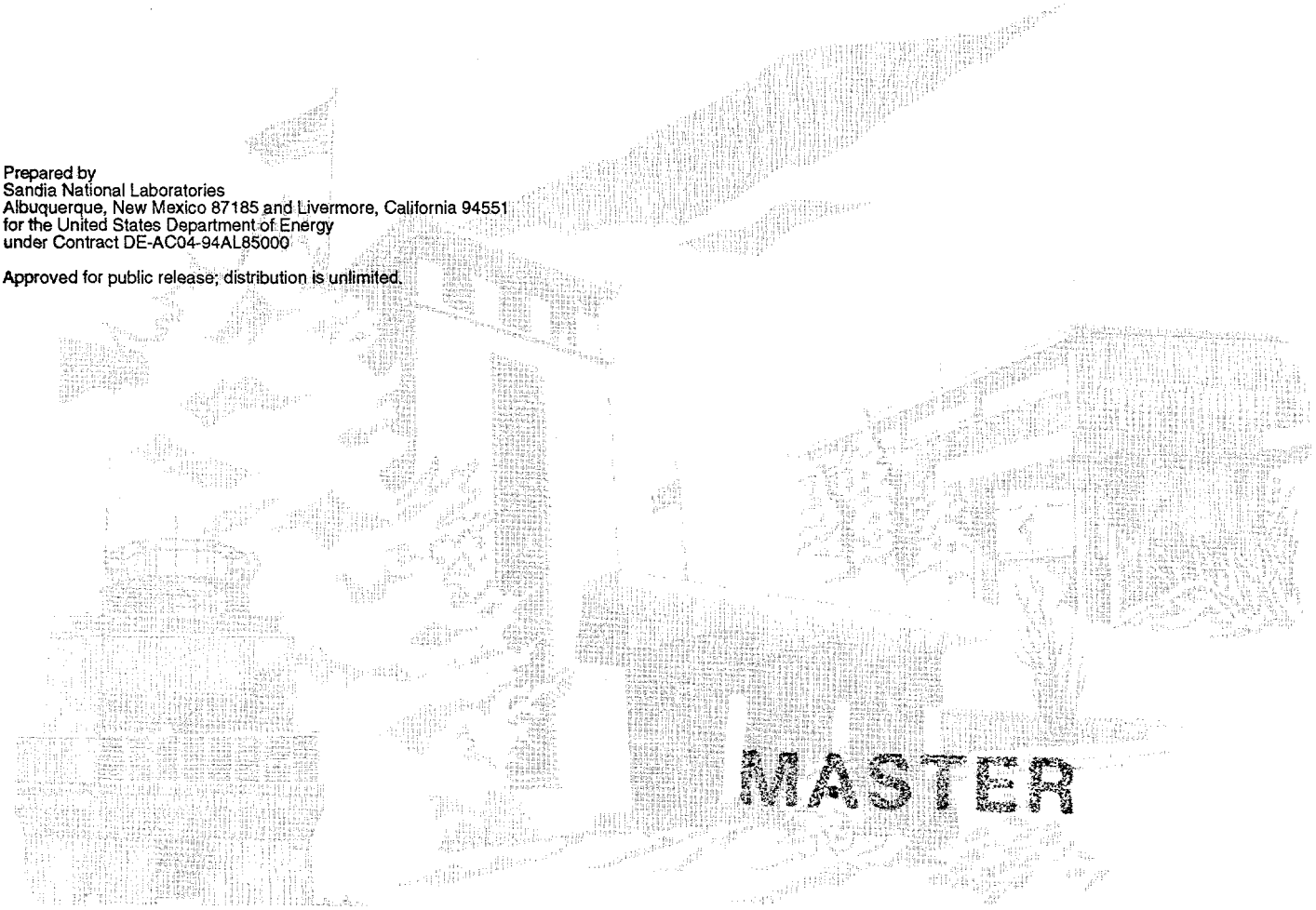

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THERMOCHEMISTRY OF GAS-PHASE SPECIES RELEVANT TO TITANIUM NITRIDE CVD*

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ABSTRACT

In this work, three different *ab initio* methods are used to predict bond dissociation enthalpies (BDE) and atomization energies for $TiCl_n$ (n = 1-4) and $Ti(NH_2)_n$ (n = 1-4) compounds, as well as for the complex $TiCl_4$:NH_3. There is considerable variation in the predicted BDEs, even for highly electron-correlated methods. However, bond-additivity corrections applied to coupled-cluster calculations at the CCSD(T) level, expected to be the most reliable of the three methods, yield Ti-Cl BDEs in good agreement with experimental results. An experimental estimate of the $TiCl_4$ BDE is also reported that is consistent with the *ab initio* results and recent experiments by others indicating that the $TiCl_3$ heat of formation reported in the JANAF Tables is too low (1). Finally, the predicted BDEs indicate that the gas-phase reaction of $TiCl_4$ and NH_3 to form the complex Cl_4Ti:NH_3 is exothermic by 17 kcal mol^{-1}. In addition, decomposition of the complex to form Cl_3TiNH_2 and HCl is endothermic by 20 kcal mol^{-1}.

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INTRODUCTION

Interest in thin films of titanium nitride (TiN) continues to increase as applications of this material to semiconductor processing expand. Originally used as a diffusion barrier, TiN is also being used to protect deposited functionalities from etching by WF_6, as an adhesion or nucleation layer between intermetal-level dielectrics and CVD tungsten, and as an antireflection layer during lithography. Currently, TiN is deposited primarily by reactive sputtering. However, as device feature sizes decrease, these techniques become less and less effective due to the poor step coverage achieved in high-aspect-ratio trenches and vias. For this reason, chemical vapor deposition (CVD) methods are becoming more attractive. One CVD method suitable for some semiconductor processing applications uses titanium tetrachloride ($TiCl_4$) and ammonia (NH_3) as precursors. Kurtz and Gordon were the first to describe an atmospheric-pressure technique (2) and since then there have been numerous reports of TiN CVD from these precursors, covering a range of temperatures (450 - 700 °C) and pressures (< 1 - 760 torr) (3-7).

Although experimental investigations by several groups suggest that gas-phase reactions may play a role in TiN CVD from $TiCl_4$ and NH_3 (2, 8, 9), little is known about this chemistry. In particular, relevant thermochemical data (heats of formation, enthalpies, and heat capacities) are unavailable for all but a few titanium compounds. The JANAF Tables (1) include data for the species in the $TiCl_x$ series (x = 0 - 4) and we are aware of recent estimates by Hildenbrand (10) of heats of formation for titanium chlorides. Since a more in-depth understanding of the $TiCl_4/NH_3$ gas-phase chemistry is necessary before accurate TiN CVD process models can be developed, a first step must be to expand the base of available thermochemical data.

The initial objective of this work is to establish theoretical methods for predicting the thermochemistry of titanium-containing compounds. In this paper, we report bond dissociation enthalpies (BDEs) and atomization energies (ΔH°_{atom}) predicted by *ab initio* electronic structure calculations for $TiCl_n$ (n = 1-4) and the complex $TiCl_4$:NH_3. Results are also reported for $Ti(NH_2)_n$ (n = 1-4) compounds, which are analogues for more complex metal organic precursors such as $Ti(N(CH_3)_2)_4$ (TDMAT). We also describe flow-reactor measurements of $TiCl_4$ decomposition rates suggesting that the Ti-Cl BDE in $TiCl_4$ is stronger than predicted from data in the JANAF Tables. Finally, we discuss the energetics of gas-phase chemical reactions that might occur when $TiCl_4$ and NH_3 are used as precursors for TiN CVD.

THEORETICAL AND EXPERIMENTAL METHODS

Electronic energies were predicted using three *ab initio* methods: Møller-Plesset (MP) perturbation theory, density functional (DFT) theory, and coupled cluster (CC) theory. Each method has been described in detail elsewhere, so we present only a short description here. In all cases, the energies reported are for 0 K and were corrected for the zero-point energy. Electronic structure calculations using MP theory (11) were performed using the Gaussian 92 quantum chemistry code (12). Equilibrium geometries and harmonic vibrational frequencies were obtained at the Hartree-Fock level of theory using the supplemented Wachters basis set of Hood et al. (13, 14) on Ti and a 6-31G* basis set on Cl, N, and H. To determine atomization enthalpies and thus

heats of formation, the effects of electron correlation were included by performing single-point calculations, using second, third, and fourth-order MP theory at the optimized geometries. MP4(SDTQ)/6-31G** calculations (fourth-order perturbation theory with single, double, triple and quadruple substitutions using the Wachters and 6-31G** basis sets) were performed to obtain the final electronic energies.

$TiCl_n$ electronic energies were also predicted from CC calculations with single and double excitations and a perturbative triples correction (CCSD(T)) (15, 16). All CC wave functions were based on RHF reference wavefunctions. Basis sets used to describe titanium were the supplemented Wachter's basis and Bauschlicher and Taylor's ANO basis set (17). Chlorine basis sets included a DZP basis set (18) with a polarization function exponent of 0.75 and the aug-cc-pVDZ basis set (19). Geometries were optimized at the CCSD level of theory using the aug-cc-pVDZ basis set on chlorine and the Wachters basis set of Hood et al. (13, 14) on Ti.

DFT is an inexpensive *ab initio* method in which the exchange and correlation energy are determined from a functional of the electron density (20). This functional may include parameters derived empirically or from accurate simulations of idealized systems such as an electron gas. The predictions of DFT are often surprisingly accurate--comparable, in some cases, to CCSD(T). However, the lack of a systematic path to improved accuracy (via successively higher levels of theory) makes DFT unattractive as a primary source of electronic energies. We applied a popular DFT exchange-correlation functional (DFT(BLYP)), which combines Becke's non-local exchange (21) with the non-local correlation functional of Lee, Yang, and Parr (22). The optimized geometries obtained from the MP calculations were used in these calculations.

Measurements of $TiCl_4$ decomposition at 40 torr were conducted in a high-temperature flow reactor (HTFR). Reactions occur within a 5.0-cm ID graphite tube enclosed within a water-cooled, insulated vacuum chamber. 50 sccm of $TiCl_4$ entered the HTFR through a water-cooled injector and mixed with 1450 sccm of preheated helium carrier gas. Under these conditions, both mixing and thermal equilibration of the injected $TiCl_4$ with the preheated carrier gas are rapid compared with the time allowed for reaction to occur. The injector is movable, allowing the $TiCl_4$ residence time to be varied with respect to a quartz probe used for sampling. Gases extracted by the probe flow past a 200-μm orifice attached to a mass spectrometer system, where a small portion is expanded into the mass spectrometer for analysis. Delivery of gases to the reactor is controlled by calibrated mass-flow controllers. $TiCl_4$ is delivered to the reactor using a temperature-controlled reservoir and mass flow controller. Reaction rates were measured by monitoring the $TiCl_4$ molecular ion signal at m/z 190 and varying the $TiCl_4$ residence time from 0 to 330 ms.

Rate coefficients for $TiCl_4$ decomposition were also calculated using RRKM theory (23). The location of the transition state was chosen by employing canonical variational transition state theory, using the modified Gorin model (23). The reaction rate at 40 torr was calculated using the biased-random-walk model for energy transfer, with an energy transfer parameter $S_{BRW} = 488.9$ cm^{-1}.

RESULTS

Ab initio predictions: Because MP successfully predicts the thermochemistry of first- and second-row compounds (24), this method was applied initially to determine electronic energies for the compounds of interest. Results of these calculations are given in Tables I and II. Five different levels of theory are shown, proceeding from the lowest to the highest: Hartree-Fock (HF), second- (MP2) and third-order (MP3) perturbation theory, and fourth-order perturbation with single, double, and quadruple excitations (MP4(SDQ)) and single, double, triple, and quadruple excitations (MP4(SDTQ)). It is evident that the HF results, which do not include the effects of electron correlation, are quite different from any of the MP predictions, demonstrating that correlation is very important in these molecules. For most of the compounds, the MP expansion converges to an approximately constant value as the level of theory increases. Exceptions to this are $TiCl_4$ and $Ti(NH_2)_4$ BDEs, neither of which converges to a constant value. Instead, the predicted BDEs oscillate from one level of theory to the next. A general convergence trend can be observed: As the number of ligands on the titanium atom increases from one to four, the magnitude of the variation in the predicted BDE increases. The variation is also larger for Cl than for NH_2. The likely cause of this behavior is mixing of excited electronic configurations with the reference wave function used for the ground state, which evidently becomes more significant as the number of ligands increases.

Better convergence behavior is expected from the CC calculations, which can more accurately predict electronic energies for compounds where multiple electronic configurations are important. Results of these calculations for $TiCl_n$ compounds are given in Table I for the highest level of theory used, CCSD(T). In contrast with MP, the CC calculations converged to a constant value with increasing level of theory for all four $TiCl_n$ compounds (results not shown), suggesting that an accurate value (within a systematic error) has been achieved. In addition, calculations using progressively larger basis sets also converged, giving confidence that the basis sets used are adequate. The resulting BDEs are substantially different from the MP4(SDTQ) predictions and ΔH°_{atom} is consistently lower, even for the cases where the MP series was well converged. Unfortunately, CCSD(T) is computationally intensive for these molecules and requires some molecular symmetry to obtain manageable computation times. Thus, it was impractical to calculate BDEs using the larger basis sets for the titanium amines, which contain minimal symmetry.

Given the large differences between the MP and CC predictions, a third method, DFT(BLYP), was applied to provide confirmation of the CCSD(T) results. As shown in Tables I and II, there is no consistent agreement between the BDEs predicted by BLYP and MP (for the $TiCl_n$ species, a complete set of BDEs could not be obtained because the calculation of the TiCl electronic energy did not converge). However, the values of ΔH°_{atom} predicted by BLYP are 24-34 kcal mol^{-1} smaller than those predicted by MP, as was the case for the CC results. Overall, therefore, these limited BLYP results are in better agreement with the CCSD(T) predictions than those of MP. It should be noted, however, that DFT exchange-correlation functionals other than BLYP can lead to widely varying results. For example, $TiCl_4$ atomization energies of 481.1, 317.2, and 393.8 kcal mol^{-1} were obtained from the local density approximation, BLYP with 50% HF exchange, and Becke exchange with Perdue's 986 correlation functional, respectively.

Table I: Predicted BDE and ΔH°_{atom} (in parenthesis) for $TiCl_n$ species, in kcal mol^{-1}.

Bond	HF	MP2	MP3	MP4 (SDQ)	MP4 (SDTQ)	CCSD(T)	DFT (BLYP)
Cl_3Ti-Cl	22.5	92.5	63.9	93.2	124.8 (476.0)	81.1 (384.1)	96.7 (416.8)
Cl_2Ti-Cl	59.5	102.5	94.5	99.7	109.0 (355.8)	96.2 (303.0)	113.3 (323.2)
ClTi-Cl	86.2	107.4	105.1	104.5	105.9 (251.3)	119.8 (206.8)	---[a] (213.5)
Ti-Cl	148.8	160.3	155.4	153.5	154.6 (154.6)	87.0 (87.0)	---[a]

[a] TiCl did not converge.

Experimental measurements of the Ti-Cl BDE and $TiCl_n$ ΔH°_{atom} are given in Table III for comparison with the *ab initio* results in Table I. Several trends are evident. First, MP4(SDTQ) consistently overpredicts ΔH°_{atom} by 25-65 kcal mol^{-1}, with no trend evident with respect to the number of Ti-Cl bonds. There is also wide disagreement with three of the four BDEs obtained from the experimental data, although the magnitude and sign of the difference varies. Second, in contrast with the MP results, the CCSD(T) predictions of both BDE and ΔH°_{atom} are consistently low with respect to both sets of experimental data. However, ΔH°_{atom} is within 28 kcal mol^{-1} of the experimental values and the amount decreases with decreasing number of Ti-Cl bonds, suggesting that a systematic error exists with respect to the Ti-Cl bond energy. Finally, the BLYP predictions of ΔH°_{atom} are within the range of values defined by the experimental eror bars for $TiCl_2$, $TiCl_3$, and $TiCl_4$. The two BDEs predicted by BLYP are within 15 kcal mol^{-1} of the experimental values. Thus, of the three methods, the limited predictions obtained from the DFT calculations are the most consistent with the available experimental data.

Table II: Predicted BDE and ΔH°_{atom} for $Ti(NH_2)_n$ species, in kcal mol^{-1}.

	HF	MP2	MP3	MP4	MP4 (SDTQ)		DFT (BLYP)	
Bond				(SDQ)	BDE	ΔH°_{atom}	BDE	ΔH°_{atom}
$(NH_2)_3Ti$-NH_2	28.5	86.2	69.1	78.3	93.5	400.6	86.1	365.4
$(NH_2)_2Ti$-NH_2	55.6	92.9	84.4	87.0	92.2	307.1	100.7	279.3
$(NH_2)Ti$-NH_2	60.5	97.7	92.3	93.4	96.3	214.9	93.7	178.5
Ti-NH_2	101.2	125.4	117.0	116.5	118.6	118.6	84.8	84.8
Cl_4Ti-NH_3	17.2	17.1	19.5	15.2	12.1		17.0	
$Cl_4TiNH_3 \rightarrow Cl_3TiNH_2$+HCl	20.1[a]	25.2[a]	21.8[a]	27.6[a]	32.6[a]		19.9[a]	

[a] Enthalpy of reaction.

Table III: Comparison of the bond-additivity-corrected CCSD(T) predictions of the Ti-Cl BDE (kcal mol^{-1}) with available experimental values.

	BAC-CCSD(T)		JANAF Tables		Other Experiments	
Bond	BDE	ΔH°_{atom}	BDE	ΔH°_{atom}	BDE	ΔH°_{atom}
Cl_3Ti-Cl	86.5-91.7	405.7-426.5	82.5±2.4	411.6±4.9	92.8[b]; ≥98[c]	411.9±4.9[b]
Cl_2Ti-Cl	101.6-106.8	319.2-334.8	101.2±4.5	329.1±5.5	100.9[b]	319.1±8.3[b]
ClTi-Cl	125.2-130.4	217.6-228.0	122.6±13.0	227.9±7.0	121.3[b]	218.2±7.5[b]
Ti-Cl	92.4-97.6	92.4-97.6	105.3±14.0	105.3±14.0	96.9[b]	96.9±6.5[b]

[a] Ref. (1). [b] Ref. (10). [c]Flow-reactor measurements; this work.

The trend in the CCSD(T) results with respect to the experimental data and the convergence trends of the CC calculations suggest that the CCSD(T) predictions represent a lower limit for the ΔH°_{atom}, with the difference between the predicted and measured values due to a systematic error caused by the finite size of the basis set used. If we assume that the magnitude of this error is proportional to the number of Ti-Cl bonds, then a bond-additivity correction (BAC) to ΔH°_{atom} can be defined by Equation [1]:

$$BAC = [\Delta H^\circ_{atom}(exp) - \Delta H^\circ_{atom}(CCSD(T))]/n \qquad [1]$$

where n is the number of Ti-Cl bonds. Performing this calculation using the experimental atomization energies in Table III and the CCSD(T) predictions in Table I for n=2-4 yields a BAC ranging from 5.4 to 10.6 kcal mol^{-1}. Applying this correction to the CCSD(T) predictions in Table I yields the BAC-CCSD(T) values shown in Table III. The corrected values compare well with both sets of experimental values. They also agree reasonably well with the DFT(BYLP) predictions in Table I.

HTFR Measurements: Recent mass-spectrometric measurements of equilibria in the Ti-Cl system by Hildenbrand (10) suggest that the heat of formation reported in the JANAF Tables for $TiCl_3$ is 10 kcal mol^{-1} too low. This discrepancy is evident in Table III, where the $TiCl_4$ BDE predicted from Hildenbrand's heats of formation is 10 kcal mol^{-1} higher than that predicted from the JANAF Tables. Both the BLYP and BAC-CCSD(T) results support Hildenbrand's revised heat of formation (note that the $TiCl_4$ heat of formation, which is based on calorimetric measurements, is considered well established (10)). To provide additional experimental evidence for this, we attempted to measure the decomposition rate of $TiCl_4$ at high temperatures to estimate the reaction enthalpy for $TiCl_4 \rightarrow TiCl_3 + Cl$.

At 40 torr in a helium bath gas, however, no decomposition of $TiCl_4$ was observed at temperatures up to 1363 K. An upper limit for the reaction rate coefficient of $k_{limit} = 0.16\ s^{-1}$ at 1363 K was determined. To estimate the BDE from k_{limit}, reaction rate coefficients were calculated using RRKM theory. The results are summarized in Table IV, which shows the calculated rate coefficients as a function of the reaction threshold (ΔH°_{rxn} at 0 K) used in the RRKM calculations. It is clear from these results that a reaction threshold based on the JANAF

thermochemistry ($\Delta H°_{rxn}$ = 82.4 kcal mol^{-1}) yields a decomposition rate that is much too large compared with the experimental observations. Better agreement is observed when $\Delta H_{rxn}°$ = 100 kcal mol^{-1}. Since RRKM theory overestimates reaction rates, possibly by as much as a factor of two (23), a reaction threshold of at least 98 kcal mol^{-1} is required to bring the RRKM prediction into agreement with the measured rate. This result suggests that the $TiCl_3$ heat of formation in the JANAF Tables is too low by at least 16 kcal mol^{-1}.

The $TiCl_4$ BDE derived from the HTFR experiments is somewhat higher than either Hildenbrand's estimate or the BLYP and BAC-CCSD(T) predictions. An overestimate of the BDE would arise if the assumption of a classical loose transition state in the RRKM calculations is incorrect. A tighter transition state, which may be caused by the apparent change in the titanium oxidation state upon loss of a chlorine atom, would lower the reaction pre-exponential factor. This in turn would result in a lower activation energy and thus, a lower BDE. To resolve this question, we are currently performing calculations at the CCSD(T) level to better define the geometry of the transition state.

Table IV. Comparison of experimental and RRKM rate coefficients at 1363 K for the reaction $TiCl_4 \rightarrow TiCl_3 + Cl$.

$\Delta H°_{rxn}$ (kcal mol^{-1})	$k_{40\ torr}$ (RRKM) (sec^{-1})	k_{exp} (sec^{-1})
82.4	26.4	< 0.16
97	0.40	
98	0.30	
99	0.23	
100	0.16	
101	0.12	

ENERGETICS OF GAS-PHASE REACTIONS

The predicted BDEs discussed above allow several qualitative observations to be made regarding the importance of gas-phase chemistry in the CVD of TiN. First, it is clear that the $TiCl_4$ BDE is too large for unimolecular decomposition ($TiCl_4 \rightarrow TiCl_3 + Cl$) to be fast at the temperatures typical of TiN CVD (450 - 700 °C for $TiCl_4$. Assuming that the reaction is in its high-pressure limits at atmospheric pressure and an Arrhenius prefactor of 10^{16} sec^{-1}, both of which are reasonable for these molecules, the reaction rate will not be faster than 1 sec^{-1} for temperatures below 980 °C. This result is supported by the flow-reactor measurements discussed above. A similar conclusion can be drawn with respect to $Ti(NH_2)_4$, with a BDE predicted by BLYP of 86 kcal mol^{-1}. If the bonding in metal-organic precursors such as TDMAT, for which deposition temperatures are typically less than 450 °C, is similar to that in $Ti(NH_2)_4$, then unimolecular decomposition in the metal organic systems should not be significant either.

A second observation to be made is that the calculations, in agreement with experiment (2), predict that $TiCl_4$ and NH_3 react at room temperature to form a stable complex:

$$TiCl_4 + NH_3 \leftrightarrow Cl_4Ti{:}NH_3 \qquad [2]$$

The strength of the Ti-N bond in this complex is predicted by BLYP to be 17 kcal mol^{-1} (Table I). This weak bond indicates that the compound will decompose into $TiCl_4$ and NH_3 at relatively low temperatures. Experiments have shown that formation of the $Cl_4Ti{:}NH_3$ precipitate is not observed at temperatures above 250 °C (2), suggesting that its decomposition to $TiCl_4$ and NH_3 is significant above this temperature.

Finally, the energetics of HCl elimination from $Cl_4Ti{:}NH_3$ (Reaction 3) predicted by BLYP (Table II) provide insight into the importance of this reaction under CVD conditions.

$$Cl_4Ti{:}NH_3 \leftrightarrow Cl_3TiNH_2 + HCl \qquad [3]$$

BLYP predicts that the reaction is endothermic by only 20.0 kcal mol^{-1}, suggesting that the rate could be significant at CVD temperatures. However, the transition state for Reaction 3 is more constrained than that of Reaction 2, leading to a much smaller (as much as two orders of magnitude) Arrhenius pre-exponential factor. Thus, Reaction 3 will be considerably slower than Reaction (-2). This analysis suggests that concentration of Cl_3TiNH_2 will be low and that $TiCl_4$ and NH_3 will be the primary species interacting with the surface. Since, however, both the forward and reverse rates of Reaction 2 will be fast relative to Reaction 3, Reaction 2 may be at equilibrium under CVD conditions. If this is so, the rate of Reaction 3, and thus, the amount of Cl_3TiNH_2 formed, will depend on the equilibrium constant for Reaction 2. We are performing additional calculations to provide a quantitative estimate of the relative amounts of Cl_3TiNH_2 and $Cl_4Ti{:}NH_3$ formed.

CONCLUSIONS

Several conclusions can be drawn from this work. First, poor convergence behavior is exhibited by titanium compounds, particularly TiX_4 species, in calculations of the electronic energy. The highest levels of theory appplied in this study, MP4(SDTQ) and CCSD(T), yield BDEs for $TiCl_n$ compounds that differ by as much as 61 kcal mol^{-1}. Somewhat surprisingly, of the three methods used, the predictions of DFT(BLYP) display the best agreement with experimental results, suggesting that this method should be explored further. However, the CCSD(T) predictions, which are expected to be the most reliable, can be brought into agreement with the available experimental data if bond-additivity corrections are applied. Second, the combined results of the *ab initio* calculations and the HTFR/RRKM calculations are consistent with the revised heat of formation for $TiCl_3$ measured by Hildenbrand. Finally, the energetics of gas-phase reactions between $TiCl_4$ and NH_3 are consistent with experimental observations concerning the formation of the $Cl_4Ti{:}NH_3$ complex. Additional calculations are required to determine the relative importance of the various titanium-containing species that can form to the deposition process. In future work, we will extend these calculations to other titanium-containing

compounds, with the objective of establishing a method for predicting accurate thermochemical data for these and other transition-metal compounds.

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