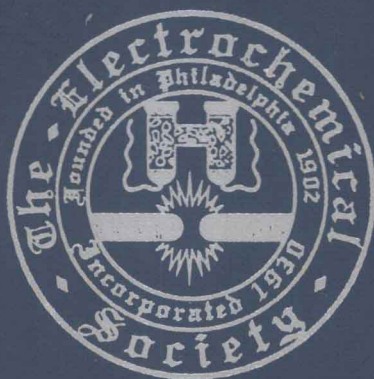


FUNDAMENTAL GAS-PHASE AND SURFACE CHEMISTRY OF VAPOR-PHASE MATERIALS SYNTHESIS



Edited by

M. D. Allendorf

M. R. Zachariah

L. Mountziaris

A. H. McDaniel

PROCEEDINGS OF THE SYMPOSIUM ON

FUNDAMENTAL GAS-PHASE AND SURFACE CHEMISTRY OF VAPOR-PHASE MATERIALS SYNTHESIS

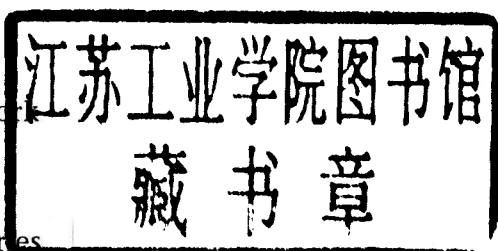
Editors

M. D. Allendorf
Sandia National Laboratories
Livermore, California

M. R. Zachariah
University of Minnesota
Minneapolis, Minnesota

L. Mountziaris
State University of New York
Buffalo, New York

A. H. McDaniel
Sandia National Laboratories
Livermore, California



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PREFACE

By definition, chemical reactions are an integral part of all processes to which the name chemical vapor deposition (CVD) is applied. Although early researchers thought that these occur only on the heated substrate, it is now clear from numerous investigations that gas-phase reactions can also play a key role. In fact, the chemistry that occurs in many CVD processes has a complexity that rivals or exceeds that of other chemical processes, such as combustion and heterogeneous catalysis. As a consequence, the development of first-principles models of CVD processes can be quite difficult. This does not minimize the need for these tools, however; increasingly stringent process requirements, particularly for CVD steps included in the manufacturing of microelectronic circuits but also for process used to make ceramic composites, optical coatings, and wear-resistant coatings, are driving expanded efforts to provide engineering tools with the ability to quantitatively predict the outcome of a CVD process.

Although there are many conferences that address the materials aspects of CVD, there have been few whose objective is to provide a forum for the latest results concerning the basic chemistry. We thus organized this conference with the hope that it would attract scientists and engineers engaged in research on topics such as gas-phase kinetics, surface science, and thermochemistry whose results are of direct importance to the understanding of CVD but who might not otherwise attend a conference dominated by the materials aspects of this complex topic. It is our intention that this symposium continue to be held in the off years from the International Conference on Chemical Vapor Deposition, so that the Electrochemical Society sponsors a major symposium on CVD technology roughly every one to one-and-a-half years. Under the current planning schedule, we expect to present this symposium next in spring 2002 in Washington, D.C.

The success of this first symposium strongly suggests that we have struck a heretofore untapped market. More than eighty papers were presented in oral and poster formats, covering a full four days and working the attendees from 8. a.m. until 6 p.m. some days. The quality of the papers, as evidenced by this book, was very high. One attendee was heard to remark that he had intended to attend some of the other symposia held at the Boston ECS meeting, but the papers presented in this symposium were so interesting he couldn't leave! Another sign of a good conference was the level of discussion following oral presentations (high) and the length of time that discussion continued after sessions concluded (long). It is thus with no small measure of pride that we present this proceedings volume, which reflects the combined efforts of a substantial cross section of the chemistry and engineering community engaged in research on this topic.

For the reader just entering the field of CVD chemistry, this preface provides a brief overview of the major topic areas addressed by the symposium with a few editorial comments concerning our perception of where the research is heading. A total of ten oral sessions were held during the four days with a general poster session one evening. The topics of the oral sessions were: applications of quantum-chemistry methods; surface

chemistry; gas-phase chemistry: kinetics and mechanisms; gas-phase chemistry: diagnostics; plasma chemistry: kinetics and modeling; aerosol processes; deposition mechanisms; reactor modeling; film properties and morphology; and novel synthetic methods.

The symposium began with a session concerning the use of quantum-chemistry methods because of the fundamental importance of molecular thermochemistry to the understanding a CVD process. With most experimental efforts to measure properties such as heats of formation largely moribund, it has fallen on the theoretical community to develop methods to predict these data. Fortunately, progress in theoretical chemistry during the last decade has been such that *ab initio* electronic-structure techniques can now predict heats of formation for many molecules to better than ± 2 kcal mol⁻¹. This achievement is exhibited by several papers in the session that discuss the application of these methods to CVD chemistries involving main-group compounds. The challenges that still lay ahead are well described by Prof. Mark Gordon's (Iowa State Univ.) invited paper, in which he discusses his group's treatment of titanium-containing species. It is apparent that quantum-chemistry methods will play an increasingly important role in the understanding of CVD chemistry and we predict that their use will become *de rigueur* within a few years.

One of the most difficult and poorly explored aspects of CVD is, ironically, surface chemistry. Although sophisticated techniques are now available for probing surface reactions, these often involve experiments in ultrahigh vacuum, which are difficult and time consuming. Furthermore, extending these results to the high-pressure realm of an actual CVD process has been problematic, to say the least. Nevertheless, new methods, such as scanning tunneling microscopy and reflectance-difference spectroscopy, are allowing surface structure and reactivity to be characterized either during or immediately after deposition. The two invited papers in this session, presented by Prof. Robert Hicks of UCLA and Dr. Randy Creighton of Sandia National Laboratories, illustrate how powerful this can be in their work on GaAs surfaces. In addition to the experimental complexities, exploration of surface chemistry is inhibited by the lack of practical theoretical techniques. However, methods such as density functional theory and molecular dynamics are showing increasing promise, as shown in a paper by Prof. Dimitrios Maroudas (U. C. Santa Barbara) presented in a later session on plasma chemistry (see below). The increasing power of computer work stations and the availability of commercial software are making such calculations accessible to a wider range of investigators. Thus, we expect theory to make a much greater impact on this complex subject in the near future.

Gas-phase chemistry is a highly developed subject, largely through efforts to understand combustion and atmospheric processes. As a result, both experimental and theoretical techniques are available and are being used to expand knowledge of gas-phase reactions relevant to CVD. The papers in this session present a particularly thorough overview of this chemistry as it pertains to silicon deposition. The invited paper by Prof. Robert Carr (U. Minnesota) provides a brief introduction to the subject of gas-phase reactions and the use of both theoretical and experimental techniques to determine rate

constants for homogeneous precursor decomposition. In addition, works by other authors in this chapter show how much progress has been made toward developing detailed elementary mechanisms for decomposition of silanes comparable to those used to model combustion processes. While most CVD chemistries are not this well understood, papers in this chapter discussing the gas-phase chemistry of GaAs, organometallic precursors, and silica formation, as well as others in a later chapter on deposition mechanisms, show that this aspect of CVD is advancing very quickly. In fact, knowledge of the gas-phase processes and species is contributing to the development of new, on-line diagnostic methods with potential for process control, as shown in the invited paper given by Prof. Michael Hitchman (U. Strathclyde).

Plasmas share many similarities with the gas-phase in terms of the experimental and theoretical methods available for exploring them. Unfortunately, like surface chemistry, they are relatively poorly characterized and are in need of systematic efforts to develop data bases of thermodynamic information and ionization cross-sections. Efforts to obtain these data experimentally are discussed by Prof. Phillip Westmoreland (U. Mass.) in his invited lecture on the application of microprobe mass spectrometry to this problem. As mentioned above, Prof. Maroudas' paper describing a combined molecular dynamics/molecular statics/Monte Carlo approach to modeling plasma-surface interactions shows the potential for theoretical methods to fill some of the many gaps in this field.

Ultimately, the point of having detailed chemical knowledge is to develop models that can be used to simulate what is occurring, allowing complex CVD processes to be optimized and scaled more quickly and efficiently. Efforts to assemble a comprehensive picture of a deposition process are described in the invited lecture given by Prof. David Cole-Hamilton (Univ. St. Andrews) in the Deposition Mechanisms chapter. He describes the use of deuterium labeling studies to identify a convincing mechanism for the MOVPE of selenium for II-VI compounds. An alternative approach is to design a precursor whose decomposition chemistry is known. This is illustrated by Prof. Roy Gordon (Harvard Univ.) in his discussion of the synthesis and reactivity characterization of novel precursors for the CVD of barium. It is encouraging that both of these papers concern CVD chemistries that are not associated with a large body of preexisting elementary reaction data, as is the case with silicon and diamond, demonstrating that the boundaries of understanding are beginning to extend beyond this traditional and relatively well-understood materials.

Understanding how to connect knowledge of the deposition chemistry with the fluid dynamics and heat transfer is no less essential than any of the other aspects discussed so far. The level of sophistication reached by these field is well displayed in the paper by Prof. Robert Kee (Colorado School of Mines) and his colleagues, where he describes a method for determining operating conditions for a CVD process in which reactor parameters vary in time. Again, the power and speed of computers is making its mark; Kee's paper shows that, given an accurate deposition mechanism, reactor models can be used to develop and "train" algorithms capable of full process control.

If there is any area of CVD chemistry less well understood than the surface reactions, it is the way in which chemistry influences the properties and morphology of the deposit. The two invited lectures in this session by Prof. Paul Sides at Carnegie Mellon Univ. and Jeffrey Roberts and colleagues at Univ. Minn. demonstrate that the two are indeed linked. Roberts et al. show that the microstructure of titanium dioxide films is independent of the precursor in a flux-limited growth regime, while in a reaction-limited regime, it is strongly dependent on the nature of the precursor. Sides et al. describe the critical role that surface energy barriers can play in determining morphology in their studies of the effects of substrate misorientation on CdTe growth.

The final chapters of this volume concern progress made toward development of new CVD methods. Among the most novel are those that use aerosol processes to generate deposition precursors. Homogeneous nucleation of particles is not always deliberate and must be controlled in cases where fine particulates can lead to the formation of defects. The invited paper by Prof. Steven Girshick (U. Minn.) describes how a combination of theoretical methods (used to generate thermochemical data for silicon clusters) and numerical modeling can be used to predict the nucleation process.

In closing, we would like to thank a number of persons whose efforts contributed to the success of this symposium. First, the members of the organizing committee must be thanked: Prof. Claude Bernard, Prof. Klaus Jensen, Dr. Meyya Meyyappan (NASA/Ames), Dr. Richard Ulrich, and Prof. Michael Zachariah (U. Minn.). We also acknowledge and thank the coeditors of this book, Dr. Anthony McDaniel (Sandia) and Prof. Michael Zachariah, both of whom invested substantial amounts of time to ensure that it was published in a timely fashion. Our colleagues who volunteered (or whose arms were twisted!) to chair sessions, thereby ensuring the smooth flow of information to the audience, must also receive our gratitude: Dr. Francis Teyssandier (CNRS/Perpignan, FR), Prof. Michael Hitchman (U. Strathclyde), Prof. Colin Wolden (Colo. School of Mines), and Prof. Karl Spear (Penn. State U.). Finally, we wish to thank the secretarial staff: Ms. Bertha Lewis (MDA), Ms. Irene Brubaker, Ms. Angela Ethridge, Ms. Darlene Innes and Ms. Susan Schebell (LM), and Kim Thompson (MRZ) who performed many unsung but critical tasks, often under deadline!

Mark D. Allendorf
Sandia National Laboratories
Livermore, California

Lakis Mountziaris
Dept. of Chemical Engineering
State University of New York at Buffalo

FACTS ABOUT THE ELECTROCHEMICAL SOCIETY, INC.

The Electrochemical Society, Inc., is an international, nonprofit, scientific, educational organization founded for the advancement of the theory and practice of electrochemistry, electrothermics, electronics, and allied subjects. The Society was founded in Philadelphia in 1902 and incorporated in 1930. There are currently over 7,000 scientists and engineers from more than 70 countries who hold individual membership; the Society is also supported by more than 100 corporations through Contributing Memberships.

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TITANIUM-MAIN GROUP CHEMISTRY

Mark S. Gordon and Brett M. Bode
Department of Chemistry
Iowa State University
Ames, IA 50011

Takako Kudo
Department of Chemistry, Faculty of General Studies
Gunma University
Tenjin-cho, 1-5-1, Kiryu-shi, Gunma-ken, 376, Japan

Gyusung Chung
Department of Chemistry
Konyang University
San-30, Naedong
Nonsan, Chungnam, 320-711
Korea

ABSTRACT

Several levels of *ab initio* electronic structure theory are used to study potential energy surfaces for several processes that involve titanium-main group interactions. The reactions discussed are: the competing unimolecular decomposition pathways for TiH_3OH and the related $\text{H}_2\text{TiO} \rightarrow \text{HTiOH}$ isomerization; a comparative study of $\text{Ti}=\text{C}$ vs. $\text{Ti}=\text{Si}$ p bond strengths; and the role of divalent Ti in the hydrosilation reaction.

I. INTRODUCTION

Recent advances in theoretical chemistry, computational methodology and computer hardware have combined to advance the reliability of quantum chemistry treatments of complex molecules and the energetics of their chemical reactions. Of particular interest to us in recent years has been the chemistry of titanium. In this paper, we summarize three reaction networks that involve interactions between titanium and main group elements. Following a presentation of the computational methods in Section II, the decomposition mechanisms of TiH_3OH are discussed in Section III. In Section IV, we consider the $\text{Ti}=\text{C}$ and $\text{Ti}=\text{Si}$ p bond energies, and in Section V the role of divalent Ti as a catalyst in the hydrosilation reaction.

II. COMPUTATIONAL METHODS

Because our primary interest is in the study of potential energy surfaces and accurate energetics for chemical reactions, the level of theory used must go beyond the Hartree-Fock (HF) approximation. If there is reasonable certainty that all of the relevant structures (usually, this means stationary points) for a particular problem can be well represented by a single electronic configuration (one Lewis structure), one can use open or closed-shell Hartree-Fock wavefunctions as a starting point to provide a "reference" wavefunction. One can then add electron correlation for improved accuracy in the prediction of energetics. The most common choices for adding electron correlation are second order perturbation theory (MP2^1) or coupled cluster theory (CCSD(T)^2). When dealing with transition metals, it is frequently difficult to describe the system of interest with a single electronic configuration, because transition metals often have multiple low-

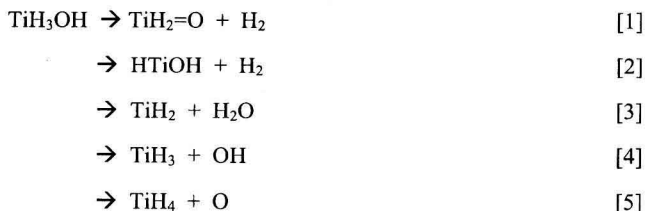
lying electronic states with varying occupations of their valence d orbitals. In such cases, Hartree-Fock is not a good reference wavefunction. Instead, one must start with a multi-configuration (MC) wavefunction, usually MCSCF. One should view an MCSCF wavefunction as the qualitatively correct starting point when Hartree-Fock is not appropriate. This means that the prediction of accurate energetics requires the addition of electron correlation corrections to the MCSCF starting point as well⁵. This is usually accomplished by the use of multi-reference perturbation theory methods, such as CASPT2⁴ or MC-QDPT2⁵ or multi-reference configuration interaction (MRCI).

It is not uncommon to perform geometry searches at the HF or MCSCF level of theory, and then to add correlation corrections for accurate energetics at the HF or MCSCF geometries. For small molecules, it is quite possible to include correlation in the geometry optimization step, and it is frequently necessary to do so. Determination of stationary points on a potential energy surface must be followed by assessment of whether these points are minima, transition states or higher order saddle points. This is accomplished by calculating and diagonalizing the matrix of energy second derivatives (hessian). A hessian with 0, 1, 2,... negative eigenvalues (force constants) indicates a minimum, transition state (first order saddle point), second order saddle point, etc. Especially for complex molecular systems, it is not necessarily clear which minima are connected by a particular transition state. Therefore, we nearly always follow the identification of a transition state by following the minimum energy path (MEP) from the transition state to the connecting reactants and products, typically using the second order method developed by Gonzalez and Schlegel⁶. This can be done for any level of theory for which energy gradients are available. In addition to its use as a revealing diagnostic, the MEP is also an important first step in the study of the reaction dynamics.

The remaining key ingredient in an *ab initio* electronic structure calculation is the atomic basis set. Since the three applications to be discussed below all use different basis sets, these will be summarized in the appropriate sections.

III. TiH₃OH DECOMPOSITION

Titanol can dissociate by the following unimolecular routes⁷:



In addition, one can have isomerization between the first two products. All geometries for this reaction were determined using MCSCF wavefunctions with a triple zeta + polarization (TZVP) basis set. Final energies were obtained using the CASPT2 method with the same basis set. The structure of the parent molecule is found to be C_{3v}, with a linear Ti-O-H angle. Reactions [4] and [5] are predicted to proceed monotonically uphill, with no intervening barrier. At the MCSCF level of theory, the endothermicities for these reactions are 114.3 and 203.2 kcal/mol, respectively. Since these are very high energy processes, they were not pursued further.

Reaction [2] is also predicted to occur without barrier. The CASPT2 endothermicity, including zero point vibrational corrections, is 30.9 kcal/mol. The endothermicity for the production of titanone, $\text{H}_2\text{Ti}=\text{O}$, is only 2.5 kcal/mol at the same level of theory, so this isomer is much lower in energy than HTiOH . However, there is an intervening barrier of 18.6 kcal/mol between TiH_3OH and $\text{H}_2\text{Ti}=\text{O}$. For the remaining reaction [3], the production of water and TiH_2 , there is an intermediate complex in which the two products are weakly bound at about 55 kcal/mol above the reactant. The products are an additional 12.5 kcal/mol higher in energy. So, the lowest energy decomposition path is clearly the one that leads to $\text{H}_2\text{Ti}=\text{O}$. Note also that the isomerization barrier from $\text{H}_2\text{Ti}=\text{O}$ to HTiOH is 48 kcal/mol, so the lowest energy route to the higher energy isomer is directly from TiH_3OH .

It is interesting to compare the electronic structure of $\text{H}_2\text{Ti}=\text{O}$ with its main group analogs $\text{H}_2\text{C}=\text{O}$ and $\text{H}_2\text{Si}=\text{O}$. The percent decrease in bond length on going from the singly bound to the doubly bound species is about 7.5% for both the Ti and Si compound. In contrast, the percent decrease for C is 14.6%, nearly twice as large. This reflects the much greater propensity for C to form double bonds. The $\text{Ti}=\text{O}$ and $\text{Si}=\text{O}$ bonds are also much more polar than $\text{C}=\text{O}$: the Mulliken charges on the metal are 0.102 (C), 0.825 (Si), 0.713 (Ti).

IV. GROUP IVA – GROUP IVB BONDING

To assess the $\text{Ti}=\text{C}$ vs. $\text{Ti}=\text{Si}$ p bonding, the internal rotation process was studied for the molecules $\text{H}_2\text{Ti}=\text{CH}_2$ and $\text{H}_2\text{Ti}=\text{SiH}_2$. Geometries were determined using MCSCF wavefunctions, optimizing the geometry of both the lowest singlet and lowest triplet states as a function of the angle between the TiH_2 and EH_2 ($\text{E} = \text{C}, \text{Si}$) planes. Both effective core potentials and the TZVP basis set were used. Final energetics were determined with the MC-QDPT2 method and the TZVP basis set. The energetics are summarized in Table 1. At the best level of theory, MC-QDPT2 with the TZVP basis set, the rotation barrier on the singlet surface is 15.8 kcal/mol for the carbon compound and 8.6 kcal/mol for the silicon species. To some degree this reflects the greater ability of Si than C to form p bonds, but note that due to the participation of the Ti d orbitals, there is significant p bonding at all rotation angles. Note also that the triplets for both species are minima at the twisted structure. Unlike the singlet states, the energy decrease for the triplets are very similar for C and Si.

The MCSCF potential energy curves are shown in Figures 1 and 2 for C and Si, respectively. Whereas the singlet remains below the triplet at all rotation angles for the carbon compound, the two curves cross in the silicon species, so that the triplet is the ground state at the twisted structure. It is also interesting that the singlet TiC distance actually *decreases* upon rotation (Figure 3) whereas the TiSi distance increases as expected (Figure 4). The origin of this behavior may be seen in Figures 5 and 6, where the natural orbital occupation numbers for the p bonding orbitals are plotted. Normally, one expects this NOON to decrease from roughly 2.0 to roughly 1.0 as the p bond is broken. This behavior is just what is found for Si (Figure 6). In contrast (Figure 5), the NOON actually increases in the carbon case. This very likely reflects the greater ability of carbon to interact with the empty Ti d orbitals as the rotation occurs. So, while the rotation barrier cannot be equated with a p bond energy, the relative rotation barriers for C vs. Si do reflect the stronger p bonds formed by C. The determination of the total $\text{Ti}=\text{Si}$ and $\text{Ti}=\text{C}$ bond energies is in progress.

V. HYDROSILATION REACTION

The hydrosilation reaction is the addition of a silane, R_3Si-H to a $C=C$ double bond, to form new carbon-silicon bonds. In the absence of a catalyst, this reaction occurs only with a very large (50-60 kcal/mol) barrier⁸. Several catalysts have been used for this reaction. The simplest is divalent titanium.

In order to assess several levels of theory, the first study was performed on the prototypical system $SiH_4 + C_2H_4$, using TiH_2 as catalyst. These calculations were performed using the TZVP basis set, at the Hartree-Fock, MP2 and CCSD(T) levels of theory⁹. It is very clear from a detailed analysis of the reaction path that correlation corrections are essential to obtain a reliable prediction of the energetics for this reaction. On the other hand, MP2 parallels the CCSD(T) calculations very well. This is an important result, since the MP2 calculations are affordable for larger species, while CCSD(T) would be out of the question. The key bottom line for this reaction is that the initial steps in the reaction, the formation of complexes between the catalyst and the two substrates is so exothermic, nearly 70 kcal/mol at the highest level of theory, that all subsequent steps have barrier heights that are more than 30 kcal/mol below the starting reactants. The overall exothermicity for this reaction is predicted to be 28 kcal/mol.

With the foregoing results in hand, several additional reactions were considered with increasingly complex reactants and catalyst. The three reactions studied were



where Cp is cyclopentadienyl. The calculations on these reactions¹⁰ were made possible by two recent advances in theory and code development: the development of very effective parallel computer codes for MP2 gradients¹¹ and the development of much more efficient gradient and Hessians for effective core potentials¹². Effective core potentials are a very effective means for studying heavier elements, since they replace inner shells with more easily evaluated one-electron potentials.

The results for reactions [6]-[8] differ in detail, but not in substance, from those for the parent reaction discussed above. Initial formation of complexes formed between the catalyst and the substrates are consistently very exothermic, so that all subsequent barriers are well below the starting reactants in energy. So, there are no net barriers for any of these reactions. The overall exothermicities for these three reactions are 37.2 kcal/mol.

VI. SUMMARY

Accurate predictions of structures and reaction energetics for compounds that contain transition metal-main group bonds is quite feasible if one uses appropriate levels of theory. Frequently, this requires the use of multi-reference wavefunctions, especially if one is dealing with unsaturated species. In the present work, we have summarized a detailed analysis of the unimolecular decomposition mechanisms for TiH_3OH , illustrating that the preferred product should be $H_2Ti=O$, an analog of formaldehyde. We have also illustrated the differences in the p bond energies for $Ti=C$ vs. $Ti=Si$ bonds. Finally, an extensive study of the hydrosilation reaction illustrates that divalent titanium compounds

are very effective catalysts for this process because they are able to form very stable intermediates. The formation of these intermediates is so exothermic that the barriers for all subsequent rearrangements lie well below the energies of the reactants.

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