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Assembling gas-phase reaction mechanisms for high temperature inorganic systems based on quantum chemistry calculations and reaction rate theories

Mark T. Swihart*

Department of Chemical Engineering, University at Buffalo (SUNY), Buffalo, NY 14260-4200, USA

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Abstract

Detailed chemical kinetic modeling based on computational quantum chemistry has been quite successful in making quantitative predictions about some systems, particularly the combustion of small hydrocarbons and certain areas of atmospheric chemistry. The gas phase chemistry of many processes in high-temperature inorganic systems, from materials synthesis to propulsion to waste incineration, could in principle be modeled with equal or greater success using detailed chemical kinetic modeling. This contribution provides examples from our own work of how computational quantum chemistry can be used in developing gas phase reaction mechanisms for modeling of high temperature materials processing. In the context of CVD of silicon from dichlorosilane, CVD of alumina from $AlCl_3/H_2/CO_2$ mixtures, and particle nucleation from silane, this detailed chemical kinetic modeling has given us insight into gas phase reaction pathways that we would not likely have gained by other means.
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keywords: Chemical kinetics; Quantum chemistry; Reaction mechanism; Silicon; Aluminum; ab initio

1. Introduction

Detailed chemical kinetic modeling has been quite successful in making quantitative predictions about some systems, particularly the combustion of small hydrocarbons and certain areas of atmospheric chemistry. Both of these successes involve reactions of small molecules made up of light elements that are amenable to treatment by computational quantum chemistry and reaction rate theories. In addition, for both of these cases there is a database of experimentally measured elementary rate parameters that can be used in constructing detailed reaction mechanisms [1–6]. The gas phase chemistry of many processes in high-temperature inorganic systems, from materials synthesis to propulsion to waste incineration, could in principle be modeled with equal or greater success using detailed chemical kinetic modeling. However, in these cases we generally have very few experimentally measured rate parameters and may not even have experimentally measured thermochemical properties (enthalpy of formation, etc.) for many of the important chemical species. While experiments are still the most reliable source for most of this needed data, they are also in many cases prohibitively expensive and time-consuming. Therefore, we turn to computational quantum chemistry to attempt to build useful detailed chemical kinetic models of these gas-phase processes.

In this general approach, we first compute thermochemical properties of potentially important chemical species, using ab initio or density functional theory methods, and benchmark these calculations against whatever experimental results are available. We then use these same methods to characterize transition states for reactions among these species, or to identify reaction paths that have no energetic barrier. For reactions with energetic barriers, we can apply conventional transition state theory to estimate rate parameters. For barrierless reactions, we can either make empirical estimates or apply variational transition state theory. For unimolecular reactions and

* Tel.: +1 716 645 2911x2205; fax: +1 716 645 3822.
E-mail address: swihart@eng.buffalo.edu

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many chemically activated reactions, we can treat the pressure dependence of the reaction rate by using RRKM theory for the microcanonical rate constants and solving the master equation. If the reaction mechanism is too large to allow every reaction to be considered individually, as is the case in chemical nucleation of nanoparticles, we can generalize the results by fitting the thermochemical properties to a group additivity scheme, proposing reactivity rules for estimating rate parameters, and applying automated reaction mechanism generation methods that have been developed for hydrocarbon pyrolysis and combustion. Most of the above can be done using commercially or publicly available software, though some of this software requires significant expertise to produce meaningful results.

This contribution describes some of our experiences in applying these methods to problems including silicon epitaxy from chlorosilanes [7–9], nanoparticle nucleation during thermal and plasma decomposition of silane [10–15], reaction of aluminum atoms with HCl [16–18], and chemical vapor deposition of alumina [19]. We are one of many groups applying this approach to the construction of gas phase reaction mechanisms related to high-temperature materials chemistry. We do not attempt to review here the large body of work in this field, but focus on our own work because it is the most convenient source of examples. Of particular note is the large body of work of Allendorf, Melius, and co-workers, from which a few representative publications are [20–24]. Many results of their groups' work are currently available online at http://www.ca.sandia.gov/HiTempThermo/.

2. Computational methods and tools

There are a variety of commercial computational chemistry packages that can be used to carry out the ab initio and density functional theory quantum chemistry calculations that form the basis for the work described here. For the majority of our work, we have used the GAUSSIAN94 and GAUSSIAN98 packages [25,26]. Details of the methods used in each case can be found in the original publications. In order to estimate reaction rate parameters, one must not only compute the structure and energy of molecules, but also of transition states on reaction paths connecting different possible sets of reactants and products. Stable molecules are local minima in energy with respect to the positions of the atoms, while transition states are saddle points on the potential energy surface. If there is an energetic barrier to reaction, then the minimum energy path from reactants to products on the potential surface will have a maximum. This is the saddle point that we identify as the conventional transition state structure. The Gaussian programs have fairly sophisticated transition-state locating algorithms that usually allow these saddle points to be located, at least for small molecules. In many cases, one is not able to guess in advance whether a given reaction will have an energetic barrier, or whether the energy along the path from reactants to products changes monatonically. If there is no energetic barrier, then there is no saddle point, which means that one often spends substantial time searching for a saddle point that does not exist. In order to demonstrate that there is no saddle point, one must identify some path from reactants to products, along which there is no maximum in energy. This can be done using partial optimizations of the molecular geometry in which one or two bond lengths or angles are fixed at a series of values and for each of these values the other bond lengths and angles are varied to minimize the energy of the structure.

Once one has the properties (electronic energy, molecular geometry, and harmonic vibrational frequencies) of the molecules and transition states that may be important in a given reaction mechanism, the next step is to estimate reaction rate parameters. Conventional transition state theory calculations are carried out using spreadsheets or simple computer programs of our own. For unimolecular reactions and chemically activated reactions, we use RRKM theory and master equation calculations to compute the pressure and temperature dependent rate constants. For different reactions, this has been implemented using the UNIMOL program [27], the ChemRate program [28], or the Variflex program [29]. These three codes are all available from their respective authors. UNIMOL was available long before the other two, and was hence used in much of our earlier work. ChemRate has a user-friendly graphical interface and strong capabilities for treating chemically activated reactions. Variflex has the most sophisticated and realistic treatment of 'loose' transition states, for reactions with no energetic barrier to reaction.

After calculating all of the thermochemical properties of potentially important chemical species and estimating rate parameters for the reactions among them one can assemble these into a reaction mechanism. This mechanism will usually contain many reactions and some chemical species that are not actually important in the chemical processes of interest. However, it is usually difficult or impossible to guess in advance which reactions will be important. To do so, one must incorporate the reaction mechanism and rate expressions into a simple reactor model, such as a batch reactor, plug flow reactor, or perfectly mixed continuous stirred tank reactor and then solve these equations and examine the results. We usually do this either with our own simple programs in Fortran or Matlab or with the CHEMKIN suite of programs [30–34], or with some combination of the two. A more recent suite of applications and tools with many of the same capabilities as the CHEMKIN suite of programs, as well as some advantages relative to it, is the CANTERA package created by David Goodwin. This package is available from the author, via download from http://www.cantera.org. Both the CHEMKIN and Cantera codes allow one to conduct sensitivity analyses to determine the sensitivity of each species

concentration to each rate parameter, as well as to analyze species concentrations and reaction rates. By examining the reaction rates, species concentrations, and sensitivity coefficients for the time-scales and concentration ranges of interest, one can identify the most important reactions and chemical species and develop a simplified reaction mechanism that may provide insight into the most important chemical processes occurring in the system.

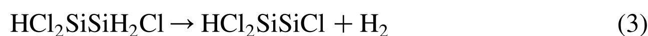
3. Examples

3.1. Gas-phase chemistry during CVD of silicon from dichlorosilane

We constructed a reaction mechanism for homogeneous decomposition of the chlorinated silanes [9] (S_3Cl, SiH_2Cl_2, and $SiHCl_3$) with rate parameters based self-consistently on ab initio molecular orbital calculations [7,8]. This mechanism predicted that thermal decomposition of dichlorosilane is accelerated by chain reactions propagated by SiH_2, SiHCl, and $SiCl_2$, and that secondary reactions convert SiHCl produced by unimolecular decomposition of dichlorosilane to $SiCl_2$. These results are consistent with experimental observations of dichlorosilane decomposition and reconcile them with predictions of ab initio calculations for the unimolecular decomposition of dichlorosilane that seemed to be in conflict with the experimental evidence. An example of a chain reaction mechanism for dichlorosilane decomposition is:

Initiation : $SiH_2Cl_2 \rightarrow SiHCl + HCl$ (1)

Propagation : $SiHCl + SiH_2Cl_2 \rightarrow HCl_2SiSiH_2Cl$ (2)


$HCl_2SiSiH_2Cl \rightarrow HCl_2SiSiCl + H_2$ (3)

$HCl_2SiSiCl \rightarrow Cl_2SiSiHCl$ (4)

$Cl_2SiSiHCl \rightarrow SiCl_2 + SiHCl$ (5)

The apparent overall reaction resulting from the above sequence of reactions is SiH_2Cl_2 decomposition to give $SiCl_2$-plus H_2. Similar chain reactions in which SiH_2 and $SiCl_2$ were the chain carriers were also found to be important. Sensitivity analysis allowed identification of the steps in these chain reaction mechanisms that had the greatest effect on the overall reaction rate and also allowed construction of a reduced reaction mechanism containing just 19 of the 39 reactions in the 'full' reaction mechanism developed based on the ab initio calculations. Fig. 1 shows schematically the reaction paths that were found to be most important in this system, with thicker arrows denoting paths with greater reaction rates.

Steps (2) and (3), shown above, could also occur as a single chemically activated reaction:

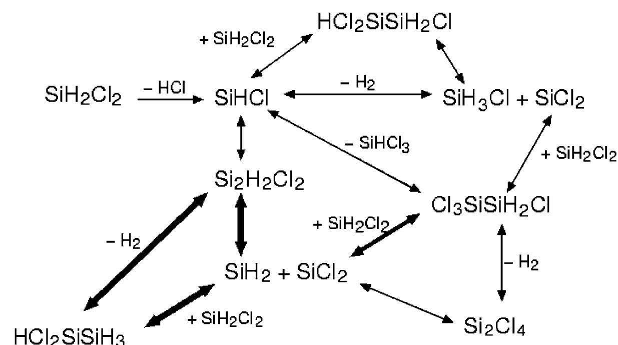


Fig. 1. Schematic representation of the overall reaction mechanism for thermal decomposition of dichlorosilane. Heavier arrows indicate greater reaction rates.

$SiHCl+SiH_2Cl_2 \rightarrow HCl_2SiSiH_2Cl^* \rightarrow HCl_2SiSiCl + H_2$ (6)

There are also several other possible sets of products that can be produced by decomposition of the activated HCl_2-$SiSiH_2Cl$* shown in reaction (6). However, it was shown in this study that the results of simply using the high-pressure limiting rate parameters for (2) and (3) provided a good approximation to the results of more rigorous and much more time consuming detailed analysis of the possible multi-channel chemically activated reactions, which was carried out for one set of reactions. This was another important lesson learned from this study. Finally, this reaction mechanism was incorporated into coupled reaction and transport models for silicon epitaxy from dichlorosilane. The conclusion drawn from these models was that under conditions commonly used for silicon epitaxy from dichlorosilane, gas phase reactions have little effect on the deposition rate.

3.2. Reactions in the Al–H–Cl system for modeling propulsion and CVD of alumina

The gas-phase chemistry of the Al–H–Cl system is of interest in at least two contexts: (1) $AlCl_3$ can be used as a precursor for deposition of aluminum-containing materials by CVD processes, often in the presence of H_2; and (2) aluminum is added to solid rocket propellant where it can react exothermically with the products of combustion of other fuels, including HCl, H_2O, CO, and CO_2. In order to construct reaction mechanisms for this system relevant to both propulsion and CVD applications, we first carried out a series of high-level ab initio calculations to determine the thermochemical properties of likely molecules in this system, many of which were previously unknown or at least uncertain [18]. This included many oxygen-containing species as well as Al–H–Cl compounds. We then identified transition states or barrierless reaction paths for the subset of this system consisting only of molecules of stoichiometry AlH_nCl_m [17]. Even for these quite small, simple molecules,

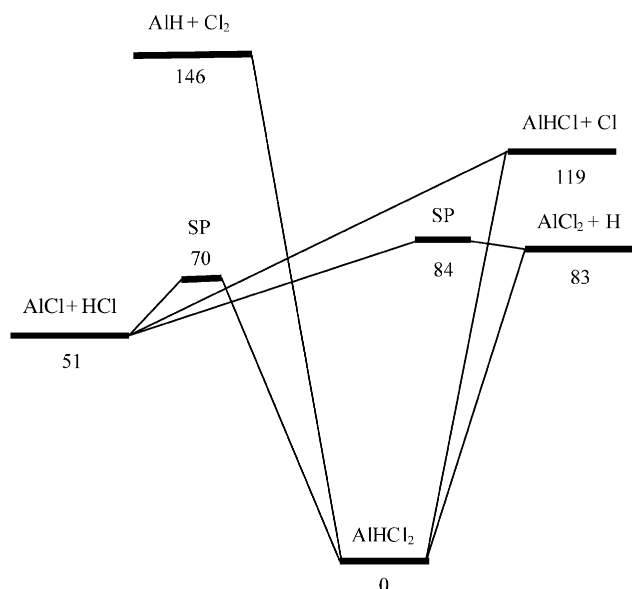


Fig. 2. Schematic energy diagram for $AlHCl_2$. Energies are in kcal/mol at 0 K, and are based on calculations using the CBS-RAD method as described in [Swihart, 2001 #1307]. SP indicates a first-order saddle point on the potential surface.

the potential energy surface turned out to be rather complex. An example is shown in Fig. 2.

On this potential surface, and on the similar surfaces for other molecules in this system, we found that there were many reactions that could occur either via a direct path, or via a chemically-activated path through a stable intermediate. For example, the reaction

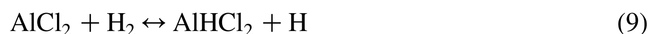
$$AlCl + HCl \leftrightarrow AlCl_2 + H \quad (7)$$

can either occur directly or through formation and decomposition of $AlHCl_2$. At sufficiently low pressures, the formation and decomposition of $AlHCl_2$ will occur as a chemically activated reaction, meaning that the $AlHCl_2$ formed from $AlCl_2+H$ does not have time to equilibrate to the temperature of the system before decomposing to $AlCl+HCl$. It was found that the vast majority of reactions in this system occurred via either barrierless direct reaction paths or via chemically activated reaction paths, and therefore we could not compute rate parameters for them using conventional transition state theory.

We used ChemRate [28] to simulate the chemically activated reaction $AlCl+HCl \rightarrow$ products. These RRKM/master equation calculations showed that in the temperature range from 500 to 4000 K and at pressures from 1 to 50 atm, stabilization of $AlHCl_2$ is negligible. That is, all of the chemically activated $AlHCl_2$ formed from $AlCl+HCl$ either decomposes to $AlCl_2+H$ or decomposes back to the reactants. In this range of conditions, the branching ratio for formation of $AlCl_2+H$ from the chemically activated $AlHCl_2$ was typically in the range of 1–10% (0.01–0.1), increasing with temperature. The apparent rate constant for the $AlCl+HCl \rightarrow AlCl_2+H$ reaction is the product of this branching ratio with the rate constant for $AlCl+HCl \rightarrow AlHCl_2^*$ (the rate constant for formation of chemically activated $AlHCl_2$). Since the branching ratio increases with temperature, the apparent activation energy for the overall $AlCl+HCl \rightarrow AlCl_2+H$ reaction is higher than the barrier for $AlCl+HCl \rightarrow AlHCl_2^*$. However, it is still significantly lower than the endothermicity of the overall reaction (as observed experimentally by Slavejkov and Fontijn [35]). For many other reactions in this system, such detailed application of reaction rate theories was not possible. For a large number of barrierless abstraction reactions in this system, we estimated rate constants by analogy with similar reactions [16].

We then constructed a reaction mechanism, based on the calculations described above, to model the gas phase chemistry during CVD of alumina from mixtures of $AlCl_3$, H_2, and CO_2 [19]. This model was able to explain several trends observed experimentally, including the promoting effect of H_2, the inhibiting effect of HCl, and the effect of temperature not directly on the alumina deposition kinetics, but indirectly on the aluminum precursor decomposition. The gas phase decomposition of $AlCl_3$ was predicted to occur primarily through the free radical chain reaction sequence

$$AlCl_3 + H \leftrightarrow AlCl_2 + HCl \quad (8)$$



$$AlCl_2 + H_2 \leftrightarrow AlHCl_2 + H \quad (9)$$

When H_2 is present, this reaction sequence is initiated by the pressure-dependent formation of H atoms from

$$H_2 + M \leftrightarrow H + H + M \quad (10)$$

Additional free radical chain carriers are produced by the chain branching reaction

$$AlHCl_2 \leftrightarrow AlCl_2 + H \quad (11)$$

Somewhat surprisingly, this model predicted that formation of water during $AlCl_3$ decomposition via the the reaction sequence

$$CO_2 + H \leftrightarrow CO + OH \text{ followed by} \quad (12)$$

$$H_2 + OH \leftrightarrow H_2O + H \quad (13)$$

(globally the water shift reaction) is unimportant. Its removal from the kinetic model did not appreciably change the computed water concentration profiles. Instead, most water was predicted to be formed by the reaction

$$AlO + H_2 \leftrightarrow Al + H_2O \quad (14)$$

This is potentially an important insight, because water is believed to play an important role in the surface reactions that lead to alumina formation. Once again, we believe that detailed chemical kinetic modeling based on quantum chemistry calculations has been able to provide new insights into the gas phase chemistry of this process.

3.3. Chemical nucleation of silicon nanoparticles during silane decomposition

Particulate contamination is a leading source of yield loss during semiconductor processing, and particles formed by homogeneous clustering reactions within process equipment are an important and growing source of this contamination. Chemical vapor deposition (CVD) processes using silane (SiH_4) are common, and particle nucleation in these processes can limit film growth rates and reactor productivity. On the other hand, intentional synthesis of silicon nanoparticles with controlled size and morphology may be of great interest due to the unique optical and electronic properties of nanostructured silicon. We have been working to develop detailed chemical kinetic models for the nucleation of these silicon nanoparticles [11–15,36–38]. This particle nucleation occurs via a sequence of reversible chemical reactions among silicon–hydrogen clusters. Once a cluster of some (unknown) critical size is formed, the cluster will continue to grow, irreversibly, into a particle. In this case, there are far more possible clusters and reactions than can be explicitly treated by quantum chemical methods. In fact, there are more possible clusters and reactions than can be practically written by hand. Therefore, one must either simplify the reaction mechanism (lumping together many similar species and reactions) or pursue computer-automated methods of generating reactions and species. We have used both of these approaches.

The starting point for this modeling was the large set of ab initio quantum chemical calculations presented by Katzer et al. [39]. In order to be able to determine the thermochemical properties (enthalpy, entropy, and heat capacity) of an arbitrary Si_nH_{2m} molecule, we fit a group additivity scheme to the properties predicted by Katzer et al. Such a scheme approximates a property (enthalpy, entropy or heat capacity) as the sum of contributions from the 'groups' from which the molecule is made up [40]. Each group consists of a non-hydrogen atom and is defined based on the bonds it makes to its nearest neighbors. Additional corrections are made for the presence of rings of varying sizes.

Given the entropy and enthalpy values from the group additivity scheme, we proposed reactivity rules to estimate rate parameters for the classes of reactions expected to occur, based on the known reactivity of small silicon–hydrogen compounds [11]. This allowed us to construct, semi-manually, a reaction mechanism including silicon–hydrogen molecules containing up to 20 silicon atoms. Reactions among those containing 10 or fewer silicon atoms were taken to be reversible, while reactions leading to the formation of molecules containing 11 or more silicon atoms were taken to be irreversible. This led to a reaction mechanism consisting of 2614 reactions among 221 species [11]. A major simplification in this description of the chemistry is the inclusion of just one isomer of each type (silane, silylene, silene) for each stoichiometry. This is equivalent to the assumption that rearrangements to form the most stable isomer are infinitely fast. In some cases, this is clearly an imperfect assumption. Thus, this mechanism, which is about as large as can practically be assembled by hand, still contains substantial 'lumping-together' of reaction steps and species.

The mechanism described above has been incorporated into several simple reactor models [11,14,38,41]. Reaction rate and sensitivity analysis allowed identification of the most important reaction paths leading to formation of clusters containing 11 or more silicon atoms. The rate of formation of these clusters was taken to be the rate of particle nucleation in an aerosol dynamics model that was fully coupled to the equations for the chemical species concentrations. This allowed prediction of particle concentration and size distribution for these different reactor configurations. Comparisons with experimental data on particle formation during low-pressure CVD of silicon from silane [38] showed good agreement for the pressure and temperature at which particle formation begins, particle sizes and growth rates, and relative particle concentrations at various process conditions. However, it overpredicted the absolute rate of particle nucleation by roughly four orders of magnitude. This strongly suggests that, for the conditions considered in that work, there are kinetic bottlenecks on the path to particle nucleation at cluster sizes larger than 10 silicon atoms. Since we arbitrarily terminated the reversible portion of the reaction mechanism at clusters containing 10 silicon atoms, this model cannot find rate-limiting reactions among larger clusters.

We are presently pursuing two approaches to simulate the nucleation of silicon particles from silane that may allow us to include both a greater level of detail (avoiding the need to arbitrarily lump together reactions or species) and larger silicon–hydrogen clusters (avoiding the need to arbitrarily terminate the reaction mechanism at a fixed size). The first of these approaches is automated reaction mechanism generation, as described and implemented by Broadbelt and co-workers [42–45]. In this approach, the computer automatically enumerates all possible reactions among the current list of chemical species and estimates the thermochemical properties of species and the rate parameters for reactions using the same group additivity scheme and reactivity rules as in the manually generated mechanism described above. New chemical species generated by the reactions are added, and the process is repeated. However, this is not as simple as it first sounds. The exponential growth in the number of possible isomers with increasing cluster size means that, if all isomers and reactions are included, the mechanism quickly becomes too large to solve in any reactor model or even to store in computer memory. Thus, strategies must be incorporated to automatically include only the most important chemical species and isomers, as well as criteria for terminating the mechanism generation process. There are existing strategies for doing this [45–47], and these are being adapted and improved to

meet the unique challenges encountered in the silicon–hydrogen system [48].

The second approach that we are using is kinetic Monte Carlo simulation of the particle nucleation process [36,37]. In this method, rather than assembling a reaction mechanism, we follow the evolution of a single cluster. For a given cluster structure, the group additivity scheme and reactivity rules are applied to generate all possible reactions that the cluster can undergo and to estimate the rate of each reaction. A reaction event is then selected at random, with the selection probability for each event proportional to the rate for that event. The cluster structure is then modified to reflect the occurrence of the selected reaction, and the elapsed time is incremented. This process is repeated until some specified time is reached, or until the cluster grown to some maximum number of silicon atoms that we consider. Finally, the whole clustering simulation is repeated many times. From these simulations, we can predict the probability of a cluster of a given size growing to a larger size or shrinking to a smaller size, at given reaction conditions. For sizes larger than the critical nucleus size, growth should be more probable than shrinkage. Conversely, for particles smaller than the critical cluster size, shrinkage should be more probable than growth. The rate at which particles grow past the critical cluster size approximately gives the particle nucleation rate. Fig. 3 shows how, for a particular set of conditions, the probability of cluster growth or shrinkage changes with cluster size. For a cluster containing seven silicon atoms, the probability of shrinkage is much greater than the probability of growth. For nine silicon atoms, the probabilities are about equal, with growth slightly more probable. Starting from 11 or 13 atom clusters, growth is much more probable than shrinkage. Thus, for these particular conditions, which strongly favor particle nucleation, the critical cluster size appears to be around eight or nine silicon atoms. When the temperature is decreased from 1200 to 1150 K, the critical cluster size appears to stay near nine silicon atoms, but when the temperature is further decreased to 1100 K, it jumps to 13 silicon atoms, and at 1050 K it is larger yet. These kinetic Monte Carlo simulations appear to provide a promising, if somewhat tedious, means of identifying the critical cluster size for this kind of chemical nucleation process.

In developing and applying the automated reaction mechanism generation and kinetic Monte Carlo schemes described above, we encountered many cluster structures for which the group additivity scheme did not perform as well as it had for the smaller set of manually generated clusters. This has inspired us to develop an improved group additivity scheme. To this end, we have recently completed high-level ab initio calculations on a set of 135 molecules containing up to seven silicon atoms and fit new group additivity parameters to it [49]. We have also extended the group additivity scheme to silyl radical species and used

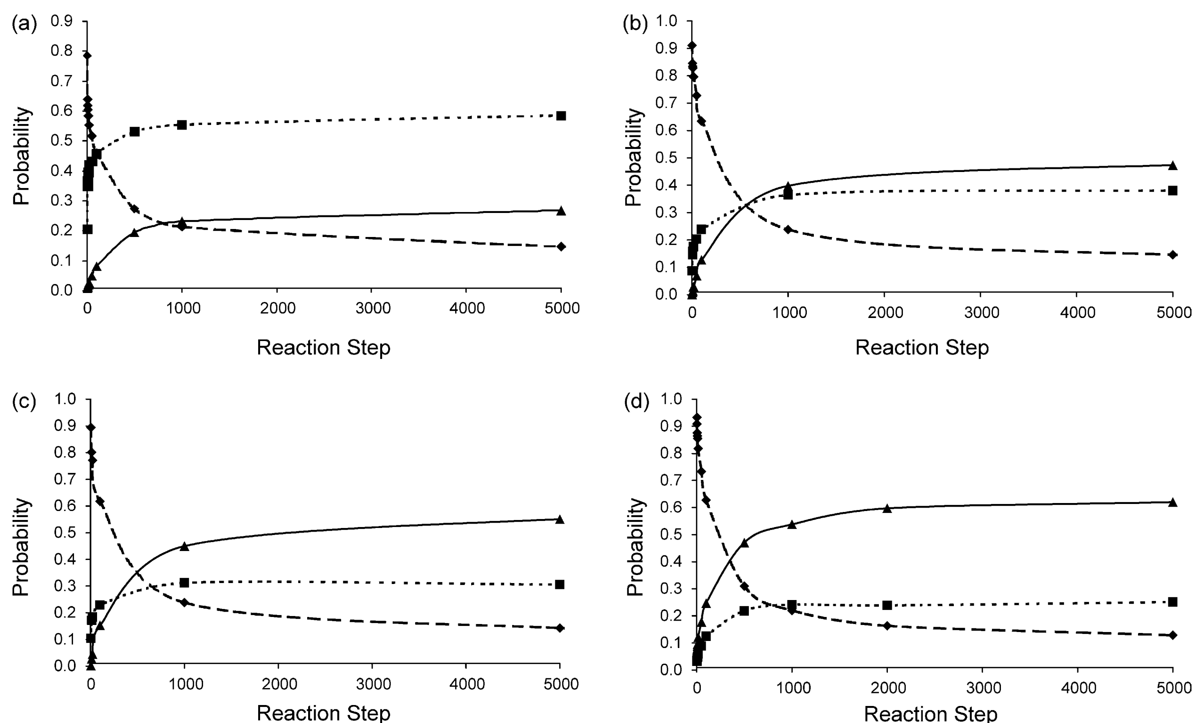


Fig. 3. Probabilities of cluster growth or shrinkage vs. number of reaction steps in the kinetic Monte Carlo simulation starting from a cluster containing (a) 7, (b) 9, (c) 11, or (d) 13 silicon atoms. In each case the solid line and triangles give the probability that the cluster has grown, the squares and dotted line give the probability that it has shrunk, and the diamonds and dashed line give the probability that its number of silicon atoms is unchanged. The number of reaction steps is related to, but not directly proportional to, time. These results are for simulations at 1200 K and 1 atm starting from 90% H_2 and 10% SiH_4.

density functional theory calculations to compute electron affinities of silicon–hydrogen molecules [13,15]. This allows the nucleation mechanism to be applied to plasma processes as well as thermal decomposition of silane. Thus, we continue to use computational quantum chemistry to refine, extend, and improve these models, even though we do not directly use it to compute species properties or reaction rates in these huge reaction mechanisms.

4. Summary

We have provided examples from our own work of how computational quantum chemistry can be used in developing gas phase reaction mechanisms for modeling of high temperature materials processing. In the context of CVD of silicon from dichlorosilane, CVD of alumina from $AlCl_3$/H_2/CO_2 mixtures, and particle nucleation from silane, this detailed chemical kinetic modeling has given us insight into gas phase reaction pathways that we would not likely have gained by other means.

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