Addition Reactions Between Silicon Centered Radicals and Olefins: An Assessment of Theoretical Procedures

by

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A thesis submitted to

the Faculty of Graduate Studies and Research

in partial fulfillment of

the requirements for the degree of

Masters Thesis

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July 21, 2004

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Acknowledgements:

I would like to acknowledge the guidance of my supervisors, Dr. Gino A. DiLabio and Dr. Keith U. Ingold.

Without their time and patience this work would have not been possible. I am very fortunate that my supervisors treated me incredibly well not only in the lab but away from the laboratory setting as well. For example, Gino was kind enough to bring me across Canada in fall 2003 for his move to Edmonton and I have nothing but great memories of our road trip. Keith has taken me waterskiing innumerable times on the Rideau River for the last four summers (!) and I am very fortunate to have been given the opportunity to talk about science in the great outdoors almost as often as in the laboratory.

I also must thank Dr. Sean Barry for his gracious hospitality in providing me with office space at Carleton University ever since Gino left for Edmonton. Sean and his students Chris Rowley, Amanda Kenney, Zhaohui Wang and Graydon Snider deserve credit for putting up with me for the last eight months; it has been great to be a "visiting" M.Sc. student in your group.

Zhengfang Lu of NRC is thanked for maintaining the laser apparatus in operation for my LFP experiments.

Erin Johnson kindly provided me with a place to stay in Edmonton for three weeks in early May 2004. I also have appreciated our stimulating theory discussions ever since my undergraduate degree.

I thank my family as well for supporting me this far in the pursuit of science and my friend Vince for all of our chess games which provided a nice break from scientific research.

Finally, I thank Nicole Halley for her unwavering support for the last four years and for making my life much more interesting than it was before.

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+ olefin reactions as a function of olefin chain length

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+ olefin reactions as a function of olefin chain length

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Abstract:

Theoretical approaches are used to determine the minimum energy reaction pathway energies for the reactions of SiH_3 , CH_3 , SiMe_3 , CMe_3 , radicals adding to ethene. The density functional theory method BHandHLYP/6-31G(d) is found to offer the best compromise of accuracy and efficiency in comparison to high-level theory and experimental results for these systems. Conventional transition state theory is compared to the generally more accurate and demanding canonical variational transition state theory and is found to give results of similar quality. Partition functions of hindered internal rotations are analysed with several correction schemes and it is found that the default method of treating internal rotations as vibrations in the harmonic oscillator framework is adequate for temperature = 298.15 K. Theoretical rate constants are determined for larger silicon centered radicals adding to larger olefins (such as $\text{Si}(\text{SiMe}_3)_3$ radical adding to 1-pentadecene) and it is found that the A-factors of these reactions (and consequently the rate constants) decrease with increasing system size. Liquid phase experiments on the same chemical systems shows no such trend; in fact, the rates of reactions increase slightly with increasing molecular size. Rationalization of these opposing trends are offered through analysis of how molecular partition functions differ in the gas and liquid phases.

Introduction:

Transition state theory (TST) (Eyring³⁵) has been successfully applied to the study of chemical reaction rates for decades (Truhlar⁹⁶, Laidler⁸⁷, Laidler⁸³, Truhlar⁸³, Pechukas⁸¹). Much of its success and extensive use can be attributed to its simplicity; to calculate a transition state theory rate constant for a bimolecular reaction one needs to calculate the properties (energies and molecular partition functions) of only three systems: the two reactants and the transition state complex. No dynamics information is required. Most applications of transition state theory have been on fairly small molecular systems (< 20 atoms or so) because these systems have the advantages of being small enough to study with accurate quantum chemistry methods and the results of these studies can often be assessed in comparison to experimental gas phase kinetic studies. Computational cost increases greatly as molecular sizes (and number of electrons) increase and this is a major limitation of the application of quantum chemistry methods to the study of chemical reactions. One must use a method that is sufficiently inexpensive and accurate to make a theoretical study worthwhile. It becomes very difficult to perform experimental gas phase kinetics studies on larger systems as well because molecular volatility quickly decreases with increasing molecular mass.

Computer power and computational methods have improved dramatically in recent years, however, and it is now becoming feasible to apply accurate quantum chemistry methods to much larger systems with many more than 20 or so atoms. Therefore, much larger molecular systems can now be studied and it is becoming possible to theoretically model difficult problems such as reactions between large molecules with quantum chemistry. However, despite modern capabilities, there has been very little work in applying transition state theory to the study of kinetics of large systems with quantum mechanical

methods. Therefore, there are currently unresolved questions concerning how one should go about studying the kinetics of large molecular systems. For example, are reactions between larger molecules in non-polar solution modelled appropriately with theoretical gas phase methods? Solvent effects are computationally expensive to include in calculations and are usually ignored for simplicity where solute-solvent interactions are expected to be weak (**Cramer99**). It is therefore of importance to test whether gas phase transition state theory can be applied to larger scale molecular reactions because it is the simplest framework to obtain theoretical kinetics.

Our group is interested in addition reactions of silicon radicals with carbon-carbon double bonded systems (olefins) (**Tong04**) and are we would like to expand the knowledge for this family of reactions.

In the literature there is very little information concerning these reactions in the gas phase. At present there is only one theoretical paper (**Bottoni97**) and one experimental paper (**Loh90**) that cover the prototypical system SiH_3 radical + *ethene*. The theoretical paper only considers the reaction barrier height and the experimental paper only yields the gas-phase rate constant of reaction. There is one new paper (**Arthur02**) that covers the kinetics and activation energy of the gas-phase reaction of $SiMe_3$ + *ethene*. There are a few older papers (**Choo74**, **Ballestri91**, **Chatgililoglu83**, **Chatgililoglu95**) that consider liquid-phase kinetics of larger silyl radicals ($SiMe_3$ radical, $SiEt_3$ radical, $Si(SiMe_3)_3$ radical) reacting with some olefins. Apart from these works and some references therein, there is no other data available. The authors of the newer paper covering the $SiMe_3$ + *ethene* system (**Arthur02**) lament the current lack of literature data on silicon centered radicals reacting with olefins.

In this work, modern electronic structure theory methods are evaluated for performance in determining the kinetics and minimum energy pathways for the family of reactions of silicon radicals adding to olefins. The similar family of reactions between carbon-centered radicals and olefins are also investigated because there is more literature data available for these systems. For small reacting systems (e.g. SiH_3 or CH_3 radicals adding to ethene) it is possible to assess computationally efficient electronic structure methods with experimental data and also with high-level correlated *ab initio* theoretical methods. For larger systems (e.g. $\text{Si}(\text{SiMe}_3)_3$ radical adding to 1-pentadecene) it is impossible to compare our efficient electronic structure methods with high-level correlated *ab initio* theory and there are also no experimental data due to the effective impossibility of studying the reactions in the gas phase. It is possible, however, to compare the theoretical gas phase kinetics data with experimental liquid phase kinetics data. Such a comparison is indirect due to the dramatically different reaction environments.

The general aspects of this project are summarized as follows. Firstly, the kinetics and minimum energy reaction pathway of the SiH_3 radical + ethene reacting system are studied from the perspective of transition state theory. From a detailed analysis of this reacting system and of the closely related CH_3 radical + ethene reacting system, a density functional theory (DFT) -based approach is chosen as optimal. The method is selected for efficiency and performance in comparison to the minimum energy pathway and kinetics of both high-level correlated *ab initio* theory and literature experimental data. The slightly larger systems of SiMe_3 and CMe_3 radicals adding to ethene are then studied for both minimum energy pathway and kinetics with the chosen DFT method and compared to literature experimental gas phase data.

Secondly, the DFT approach chosen as best for the small model systems is then applied to larger reacting systems with silicon radicals adding to olefins. These "larger" systems include all permutations of SiH₃, SiMe₃, and Si(SiMe₃)₃ radicals adding to the olefins ethene, 1-hexene, 1-decene, 1-pentadecene, styrene, and 1,1-diphenylethylene. The study of larger systems helps test the statistical thermodynamics framework of TST since there is scant literature data available for reaction kinetics of larger molecules.

Thirdly, liquid phase kinetics experiments are performed using the laser flash photolysis (LFP) method (Hadel89) on the reactions of SiEt₃ and Si(SiMe₃)₃ radicals adding to 1-hexene, 1-decene, 1-pentadecene, styrene, and 1,1-diphenylethylene (DPE) to help provide a basis for comparison the theoretical gas phase kinetics results.

Finally, the performance of gas phase transition state theory is assessed in comparison to the liquid phase kinetics of the larger reacting systems. Systematic differences between the results are considered from the perspective of how gas and liquid phase environments fundamentally differ and affect the statistical mechanics of reaction kinetics.

Theoretical Approaches:

(i) The Theoretical Problem:

We wish to solve the *Schroedinger Equation*:

$$\hat{H}\Psi = E\Psi \quad (1)$$

This is an *eigenvalue* equation, where $\hat{H}$ is the *Hamiltonian* operator, E is the *energy eigenvalue*, and Ψ is the *wavefunction* of the system under study (e.g. an atom or molecule). Since the Hamiltonian operator is known precisely, equation (1) is solved if one can obtain the appropriate wavefunction. Determining the wavefunction of a system is critically important since it allows one to obtain all possible information about that system directly through various eigenvalue equations such as equation (1) and indirectly through the methods of statistical mechanics.

Unfortunately, it is impossible to solve equation (1) exactly for any but the simplest of systems; specifically, only *hydrogen-like* systems and other two-body problems can be solved exactly. Beyond such simple systems, one must resort to approximate methods.

(ii) Hartree-Fock Theory:

The Hartree-Fock (HF) approximation is central to theoretical chemistry and is the cornerstone of *ab initio molecular orbital* (MO) theory.

The Hartree-Fock method breaks down the wavefunction, Ψ , of equation (1) into the following single determinant approximation for an N electron system:

$$|\Psi_0\rangle = |\psi_1 \psi_2 \dots \psi_{N/2}\rangle \quad (2)$$

where Ψ_0 is the HF molecular wavefunction and ψ_x is the *molecular orbital* for orbital x .

The matrix determinant in equation (2) is called a *Slater determinant*. We are now solving a modified version of equation (1):

$$\hat{H} |\Psi_0\rangle = E_0 |\Psi_0\rangle \quad (3)$$

One hopes to obtain the "best" Ψ_0 , which is the best approximation to Ψ of equation (1), by systematically varying it (Szabo96) until the Hartree-Fock energy, E_0 , is a minimum.

There is a closely related operator, denoted as $\hat{H}_0$, for which the eigenvalue equation (3) is solved exactly. This operator is defined as follows:

$$\hat{H}_0 = \sum_{i=1}^N f(i) \quad (4)$$

where $f(i)$ is the *Fock* operator of the i -th electron. Therefore we can write the new exact equation:

$$\hat{H}_0 |\Psi_0\rangle \equiv E_0 |\Psi_0\rangle \quad (5)$$

and now to solve equation (5) and obtain the Hartree-Fock approximate wavefunction for our system we need to solve each of the $N/2$ spatial integro-differential *Fock equations*:

$$\hat{f} \psi_i = \varepsilon_i \psi_i \quad (6)$$

where ε_i is the energy eigenvalue of the i -th molecular orbital.

Computationally, the task of solving the Fock equations with numerical methods is quite difficult if they are in the form of equation (6). However, Roothaan showed in 1951

(Roothaan51) that it is possible to expand each of the molecular orbitals in equation (6)

as a linear combination of a set of K known *basis functions* as shown below:

$$\psi_i = \sum_{\mu=1}^K C_{\mu,i} \phi_{\mu} \quad i = 1, 2, \dots, K \quad (7)$$

where $C_{\mu,i}$ is a weighting coefficient and ϕ_{μ} is a basis function. If the set $\{\phi_{\mu}\}$ was complete, the linear expansion would be exact. However, one is always limited to finite sets and so there is always a degree of incompleteness in the expansion of (7). Therefore the choice of the K basis functions should be made carefully to maximize the potential for describing the desired wavefunction Ψ_0 .

From (7), the problem of calculating the HF molecular orbitals reduces to the problem of calculating the set of expansion coefficients, $C_{\mu,i}$. This is done with the *Roothaan matrix equations*, which may be written as follows:

$$\mathbf{FC} = \mathbf{SC} \varepsilon \quad (8)$$

where $\mathbf{F}$ is the Fock matrix, $\mathbf{S}$ is the orbital overlap matrix, $\mathbf{C}$ is the orbital coefficient matrix, and ε is the diagonal orbital energy matrix. Using standard numerical techniques to solve matrix equations, the HF wavefunction may be practically determined from equation (8). For a particular molecular geometry, the iterative self-consistent field (SCF) procedure (Szabo96) is used to optimize the elements of the coefficient matrix $\mathbf{C}$.

The Hartree-Fock method is variational, meaning that the molecular energy obtained by calculation is by necessity an upper bound of the true molecular energy and it is also size consistent. If a method is size consistent it means that calculations of relative molecular energies (and errors of such molecular energies) are consistent with changing molecular size. Such a method can be used to calculate relative energies for the study of chemical reactions.

(iii) Basis Sets:

One must choose the form and number of basis functions to make up the set of functions used to determine the HF wavefunction Ψ_0 . It is obvious from the variational principle that including more basis functions in the set tends to make Ψ_0 better but the problem is that calculations become longer the more basis functions that are used in the calculation. One would like to obtain the best wavefunction with the least possible computational effort.

In modern calculations, gaussian type functions (GTFs) are almost exclusively used in basis sets as their form is conducive to solving the integrals required in the Roothaan equations. The form of a generic primitive gaussian-type function, G , is the following:

$$G = N_g x^i y^j z^k e^{-\alpha r^2} \quad (9)$$

with N_g a normalization constant, α is the positive orbital exponent coefficient and x, y , and z are the coordinates of 3-D space. If $i + j + k = 0$, G is of the s -orbital type; if $i + j + k = 1$, G is of the p -orbital type, etc.

GTF-derived basis functions are composed of linear combinations of primitive gaussian-type functions called contracted gaussian-type functions (CGTFs).

Thus, equation (7) may be rewritten more specifically as the following:

$$\psi_i = \sum_{\mu=1}^K C_{\mu,i} \phi_{\mu,CGTF} \quad i = 1, 2, \dots, K \quad (10)$$

with $\phi_{\mu,CGTF}$ our CGTF-based set of basis functions that can be represented as the following:

$$\phi_{\mu,CGTF} = \sum_{\tau=1}^L G_{\tau} \quad (11)$$

with L the number of primitive gaussians used in $\phi_{\mu,CGTF}$.

There are many common standard basis sets available that have primitive gaussian functions energy optimized for performance versus cost. These basis sets are seen repeatedly in the literature. For example, the STO-3G basis set is one of the most

computationally inexpensive basis sets available. The name of the basis set means that each atomic orbital is represented by a set of three CGTFs with coefficients optimized to mimic Slater-type orbitals (STOs). Slater-type functions are of the form $\exp(-\alpha r)$ and are better representatives of atomic orbitals than gaussian-type functions but are less practical numerically.

The 3-21G basis set is of the Pople-style (**Hehre86**) and uses the Pople nomenclature.

Thus, 3-21G means that each core atomic orbital (AO) is represented by a CGTF with 3 primitive gaussian functions and each valence AO is represented by one CGTF with two primitive gaussians and another with one primitive gaussian. The very common basis set 6-31G has six primitive gaussian functions in one CGTF and there are two CGTFs for the valence atomic orbitals with three and one primitive gaussian each. The basis set 6-31G(d) includes d-type polarization functions on non-hydrogen atoms and the 6-31G(d,p) further adds p-type polarization functions on hydrogen atoms; sometimes a "*" will be used in the place of a "d" or a "p" and so 6-31G(d) is equivalent to 6-31G* and 6-31G(d,p) is equivalent to 6-31G**. A "+" denotes that diffuse functions are present in the basis set; these are functions that are spatially diffuse.

There are also in common use Dunning-style basis sets for which the nomenclature is somewhat different. For example, the Dunning basis set "aug-cc-pVDZ" means that it is made of CGTFs that are augmented (includes diffuse functions), it is correlation consistent (well-suited for calculation methods that include electronic correlation) and valence orbitals are "double zeta".

(iv) Post-Hartree-Fock *ab initio* Methods:

It was stated in part (ii) of the theory section that the best possible Hartree-Fock wavefunction of a molecular system, Ψ_0 , is not the true wavefunction of Nature.

Fortunately, HF theory suffers from only one shortcoming, and there are systematic methods for improving on the HF method.

In the complete basis set limit, the Hartree-Fock energy of a molecule is always greater than the true energy. This is because HF theory does not consider electronic correlation. Specifically, what this means is that in the molecular orbital/HF approximation, electrons only interact in an "average" way; there is no explicit consideration of electron-electron interaction and hence no electronic correlation. We define this missing correlation energy as follows:

$$E_{corr} = \Xi_0 - E_0 \quad (12)$$

where Ξ_0 is the true nonrelativistic electronic energy of the system and E_0 is the HF limit energy.

This missing correlation energy is important for relative energies between reacting molecules and for determining properties of molecules such as geometries and vibrational energies.

To correct for the missing correlation energy, one may implement a *post-HF correlation method* which is a HF-based method that incorporates the effects of electron correlation. In principle such methods can give *exact nonrelativistic results*. The problem is that the

computational effort required for these approaches is prohibitive for all but the smallest of systems.

Common post-HF correlation methods are *configuration interaction* (CI), *quadratic configuration interaction* (QCI), the *coupled-cluster approximation* (CCA), and *Moller-Plesset perturbation theory* (MPPT). A brief description of each follows.

(iv, a) Configuration Interaction:

By solving the Roothaan matrix equations (equation (8)) for a system with N electrons and K basis functions, we obtain a set of 2K one-electron spin orbitals for which N are occupied. In HF theory, only the occupied MOs are explicitly considered in the Slater determinant approximation of the wavefunction (as in equation (2)); only one electronic configuration contributes to the resulting wavefunction. The configuration interaction post-HF correlation method includes more than just the ground state electronic configuration as in HF theory but also considers configurations where Slater determinants of excited configurations are included. Such determinants may be singly excited (one occupied orbital is left out of the determinant and is replaced by one virtual or empty orbital), doubly excited, triply excited, and so on. This is represented as the following equation:

$$|\Psi\rangle = c_0 |\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots \quad (13)$$

where c is the coefficient of each determinant with $a, b, \dots$ representing orbitals from which electrons are excited and $r, s, \dots$ representing orbitals to which electrons are excited.

If all possible excitations are included in equation (13), then we have what is called the full CI wavefunction. In the infinite basis set limit, this wavefunction is the exact nonrelativistic wavefunction of the system and for this reason CI is considered one of the fundamental *ab initio* post-HF methods; it can potentially give the exact molecular wavefunction and has no adjustable parameters.

Full CI is both variational and size consistent. Truncated (excluding some of the excitations in equation 13) CI is variational but unfortunately not size consistent.

(iv, b) Coupled Cluster Methods and Quadratic Configuration Interaction:

These methods are useful approximations of CI theory. Coupled cluster (CC) methods use the independent electron pair approximation (IEPA) to incorporate correlation coupling between different pairs of electrons (Szabo96). The fundamental equation of CC theory is the following:

$$\Psi = e^{\hat{T}} \Psi_0 \quad (14)$$

Where $e^{\hat{T}}$ is defined by its Taylor-series expansion:

$$\hat{e}^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \dots \quad (15)$$

and the cluster operator $\hat{T}$ is defined as:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots \quad (16)$$

where $\hat{T}_n$ is the n-electron excitation operator; so the CC method is similar to the CI method.

Terms in the CI formalism (equation 13) with pairs are simplified as below for a quadratic excited term:

$$c_{abcd}^{rstu} \cong c_{ab}^{rs} c_{cd}^{tu} \quad (17)$$

Our wavefunction therefore gets modified somewhat from equation 13 to the following:

$$|\Psi_{CC}\rangle = |\Psi_0\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a < b < c < d \\ r < s < t < u}} c_{ab}^{rs} c_{cd}^{tu} |\Psi_{abcd}^{rstu}\rangle + \dots \quad (18)$$

where we have shown only even-number excited terms for simplicity.

The most common CC method is CCSD, where the excitation operator is truncated after the second term. Including triples with CC methods is often found to be necessary and

sufficient for proper description of electron correlation. Because including triples can be prohibitively expensive, approximate methods for their inclusion have been developed.

One of the most common of these methods is denoted CCSD(T).

CC methods have a huge advantage over truncated CI methods because they are size consistent. They are not, however, variational.

Quadratic configuration interaction (QCI) (**Pople87**) methods are very similar and yield results virtually identical to CC methods but at a somewhat lower computational cost. If one includes only single and double excitations the method is called QCISD and if contributions from triples are included the method is called QCISD(T). Like CC methods, QCI methods are also size consistent but not variational.

The CC and QCI methods are practical for only very small systems (less than 5-10 non-hydrogen atoms). The methods CCSD(T) and QCISD(T), when used with large basis sets, may be thought of as computational “gold standards” (**Levine00**) which are often accurate for thermochemistry to within 1 kcal/mol.

(iv, c) Moller Plesset Perturbation Theory (MPPT):

MPPT considers the missing correlation of a HF calculation to be a slight perturbation on the HF energy (**Szabo96**). These methods are inexpensive compared to the CI, CC, and QCI post-HF method but are also often significantly inaccurate for thermochemistry.

Perturbative corrections of any order may be included in the corrections to the HF wavefunction, but the procedure becomes prohibitive quickly and so one usually stops at the second order correction; this results in the method known as MP2.

Before the advent of density functional theory, MP2 was the most common method for including correlation on fairly large systems. However, MP2 is still computationally expensive considering the quality of its results. It has therefore been largely replaced by the more efficient and often more accurate methods of density functional theory.

(v) Density Functional Theory:

Density functional theory (DFT) approaches the problem of computational chemistry from a different perspective than the HF and post-HF methods. With DFT, the goal is to determine the ground state electronic density, ρ , of a system, from which all molecular properties may be uniquely determined (**Hohenberg64, Kohn96, Cramer02**).

Use of DFT methods in quantum chemistry has been increasing dramatically since the early 1990s. The usefulness of the DFT approach is that it is in principle an exact theory, like full CI. Unlike full CI, DFT scales much more reasonably with increasing system size; the scaling is comparable to that of the much less quantitative HF theory. All DFT methods are size consistent but not generally variational.

It is not completely straightforward to determine the functional for obtaining the exact energy from the electronic density, ρ , however. The framework used is shown below (**Cramer02**):

$$E[\rho] = T_{ni}[\rho] + V_{ne}[\rho] + V_{ee}[\rho] + \Delta T[\rho] + \Delta V_{ee}[\rho] \quad (19)$$

where E is the energy, T_{ni} is the kinetic energy of non-interacting electrons, V_{ne} is the potential of nuclear-electron interaction, V_{ee} is the potential of electron-electron interaction, ΔT is the dynamic correlation term, and ΔV_{ee} is a non-classical correction to the electron-electron term (exchange correlation). In practice, the solution of the DFT problem is very similar to the HF method. The density is represented by a series of orbitals that are composed of basis functions and one solves (in analogous fashion to the Fock operator) the Kohn-Sham eigenvalue equations (**Cramer02**):

$$\hat{h}_{KS} \psi_i = \epsilon_i \psi_i \quad (20)$$

The major limitation of modern DFT methods is correctly treating the two correlation correction terms of equation 19. Unfortunately, there is no systematic way of improving the terms. So, a major focus of modern research in DFT is to improve the correlation terms such that functionals yield good agreement with high-level post-HF calculations on small systems or with experiments. This empirical procedure of obtaining the correlation functionals also explains the vast array of DFT methods currently available.

Typical DFT method nomenclature is such that the DFT approach is named as (*exchange correlation functional*)-(*dynamical correlation functional*) where the functionals are acronyms that honour their creators. Therefore, the common B3-LYP functional uses *Becke's three parameter* (**Becke93**) exchange functional and the *Lee-Yang-Parr* (**Lee88**) correlation functional. Since HF theory is in principle exact for exchange, many DFT methods incorporate a fraction of HF exchange in for the exchange term; these DFT

methods are called hybrid DFT methods. DFTs without any HF exchange contribution are called pure DFTs.

(vi) Geometry Optimization:

All the electronic structure theory methods considered above generate a molecular wavefunction based on three-dimensional geometry coordinates of nuclei. One of course not only desires to know the wavefunction and properties of a molecule for some arbitrary geometry; one would like to know the properties of the system at the correct geometry.

Therefore, one always optimizes the geometry of the molecule of interest.

Geometry optimization methods function by finding points along the molecule's *potential energy surface* (**Quapp84**) (PES) where the derivatives with respect to nuclear coordinates are zero. We see below an example of a typical two-dimensional potential energy surface and various attributes along it:

Figure 1: A schematic two-dimensional PES:

The dimensionality of a non-linear molecule's PES is $3N-6$, where N is the number of nuclei present. Therefore, it may quickly become difficult to visualize the PES of a large molecule.

If one is, as is usual, searching for energy minima along the molecular PES, the energy gradient of each of the $3N-6$ internal coordinates is calculated on the initial guess at the geometry. Based on the energy gradient, the molecular geometry will shift such that a lower energy configuration of atoms is achieved. Then gradients are calculated for this new geometry and so on until eventually, the gradient approaches zero and the molecule has become "geometry minimized" into what is the equilibrium geometry for the molecule for electronic structure theory method that was used (Levine00).

If a molecule has more than one possible geometry minima (conformation), the geometry will likely become minimized into the PES well towards which the first gradient was directed. It is therefore important to ensure that the correct conformation of the molecule is optimized if there are several possibilities.

Because the optimization procedure is usually stopped when the PES is sufficiently flat in a region, one may occasionally get a non-geometry minimized molecule if the initial geometry guess is close to a maximum in one or more of the internal coordinates.

Molecular vibrational analysis shows whether a geometry has been optimized to an energy minima.

(vii) Molecular Vibrations:

With geometry-optimized molecular coordinates it is possible to obtain the frequencies of molecular vibrations in a straightforward way (**Wilson80, Levine00**). Firstly, the 3N-6 internal coordinates are chosen so as to be orthogonal (normal, or non-coupling) to each other. Each of these independent modes of motion is then assumed to be at its energy minima. The second approximation that is used is to assume that the restoring force of any displacement along one of the internal normal coordinate modes is proportional to the distance from the equilibrium position. So, the force equation is represented as follows:

$$F = kx \quad (21)$$

where F is force, k is the force constant, and x is the distance displaced. The equation for this system is known as Hooke's Law. A corollary of this law is that the PES along the normal coordinate is a parabola. This assumption is valid for small displacements and therefore for small amplitude vibrations at temperatures ~ 300 K since the parabolic approximation of the PES is valid.

Molecular vibrations that are described in terms of Hooke's Law are said to be *harmonic*.

The energy levels of a harmonic oscillator are well known from elementary quantum mechanics and are:

$$E_{HO} = (n + \frac{1}{2})h\nu \quad n = 0, 1, 2, \dots \quad (22)$$

where n is the quantum number, h is Planck's constant, and ν is the vibrational frequency. Thus, the infinite number of quantum energy levels of the PES of a harmonic oscillator are separated by the constant amount $h\nu$.

Practically, one obtains molecular frequencies by computing mass-weighted force constant (Hessian) matrix elements, F_{ij} , for a geometry that is energy minimized:

$$F_{ij} = \frac{1}{(m_i m_j)^{1/2}} \frac{\partial^2 U}{\partial X_i \partial X_j} \quad (23)$$

where i and j range from 1 to $3N$ ($N = \#$ of atoms) and m_i is the mass of the atom corresponding to internal coordinate X_i . Then, the following set of $3N$ equations may be solved:

$$\sum_{j=1}^{3N} (F_{ij} - \delta_{ij} \lambda_k) l_{jk} = 0 \quad i = 1, 2, \dots, 3N \quad (24)$$

where δ is the Kronecker delta function, λ indicates the stiffness of the vibrational mode, and l may be used to determine the vibrational amplitude and k runs over the $3N - 6$ vibrational modes.

For a non-trivial solution to the set of equations, the following must be true:

$$\det(F_{ij} - \delta_{ij} \lambda_k) = 0 \quad (25)$$

After solving this determinant equation, we now can obtain our harmonic frequencies:

$$\nu_k = \frac{\sqrt{\lambda_k}}{2\pi} \quad (26)$$

From these molecular frequencies, ν_k , the important zero-point vibrational energy (ZPE) of the molecule may be obtained; it is a quantum correction to the “classical” energy (electronic potential energy) at the minima of the PES and is defined as follows for a harmonic potential:

$$E_{ZPE} = \sum_{k=1}^{3N-6} \frac{h\nu_k}{2} \quad (27)$$

If a molecule is not at a PES minimum but instead has one or more of its internal coordinates resting at energy maxima or saddle points, the energy gradient along such internal coordinates will be negative instead of positive. The molecular frequencies derived from the negative force constants of such modes are consequently imaginary numbers. Obtaining imaginary frequencies (which are usually denoted in software packages with a negative sign) is thus proof that the geometry is not fully energy minimized and is useful for characterizing transition states.

(viii) Molecular Partition Functions:

Up to this point, all theory has pertained only to the quantum mechanical treatment of energies, frequencies, etc. of molecules. However, quantum mechanical results are not usually directly useful for predicting how bulk quantities of molecules will behave.

However, using the partition function from the discipline of statistical mechanics, we can use the results of quantum calculations on molecules to quantitatively predict behaviour of molar quantities of such molecules.

(a) Definition:

The *molecular partition function* (or “system” partition function) Q is defined as the following:

$$Q = \sum_j e^{\frac{-\epsilon_j}{k_B T}} \quad (28)$$

where $-\epsilon_j$ is the energy of the j -th quantum state, k_B is Boltzmann's constant, and T is temperature. The molecular partition function is therefore defined as the sum over the Boltzmann factors of each quantum state of a molecule. Physically, the Boltzmann factor is a measure of how thermally accessible a quantum state is at a particular temperature. Standard physical chemistry textbooks (**Atkins98**, **Hill86**, **McQuarrie00**) show how common thermodynamic quantities such as energy, entropy, free energy, and heat capacity are uniquely defined by Q .

(b) Separation of Contributing Factors:

If one were able to easily determine all of the quantum states of a system, computation of the molecular partition function would then be possible. This task is greatly simplified if the molecular partition function is approximated as being equal to the partition functions of each contributing type of quantum state as below:

$$Q = q_{trans} q_{elec} q_{rot} q_{vib} \quad (29)$$

where q_{trans} is the translational partition function, q_{elec} is the electronic state partition function, q_{rot} is the rotational partition function, and q_{vib} is the vibrational partition function.

This approximation is valid so long as contributions to Q from molecular translation, rotation, and vibration are independent. The problem of determining Q is now feasible since there are straightforward methods for determining the partition functions from each of the contributions in equation 29. Standard equations for each of the components are well known (Atkins98, Hill86, McQuarrie00); these are the equations used in virtually all computational chemistry software packages (e.g. Gaussian).

(c) Translation:

The translational component of the molecular partition function is the following for an ideal gas:

$$q_{trans} = \left[\frac{2\pi(\sum_i m_i)k_B T}{h^2} \right]^{3/2} V \quad (30)$$

with the sum over all of the atoms in the molecule. Thus, the translational partition function is dependant only on the mass of the molecule, m , the temperature, and on the volume, V , of its container. The translational partition function is usually large and this

reflects the large number of translational states available for gaseous molecules in volumes of any substantial size.

(d) Electronic:

Due to the large gaps between energy levels of most molecules, one is usually concerned only with the ground electronic state at temperatures ~ 300 K. So, the electronic partition function is then equal to the degeneracy of the ground state; for singlets it is 1, for doublets it is 2, etc.

(e) Rotation:

For non-linear molecules, there are three rotational degrees of freedom. If the system in question is not a small hydrogen-containing molecule at low temperature (e.g. CH_4 at < 100 K) then classical treatment of rotational energy levels is justified (Hill86). We then obtain the following equation for q_{rot} :

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 I_A k_B T}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_B k_B T}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_C k_B T}{h^2} \right)^{1/2} \quad (31)$$

where I_A , I_B , I_C are the principal moments of inertia for each molecular axis and σ is the rotational symmetry factor. Due to the close spacing of rotational energy levels the

rotational partition function is often quite large but not generally as large as the translational partition function.

(f) Vibration:

The vibrational partition function is easy to calculate if one uses the harmonic oscillator treatment to describe molecular vibrations. This is because the energy level spacing for a harmonic oscillator is constant for all of the infinite number of energy levels. So, if we begin with the general definition of a partition function for a system with an infinite number of levels:

$$q = \sum_{j=1}^{\infty} e^{\frac{-\epsilon_j}{k_B T}} \quad (28a)$$

and then make the spacing of the levels to be constant; we obtain the well known geometric series result that our infinite sum can be represented as the following single term:

$$q = \frac{1}{1 - e^{\frac{-\epsilon_j}{k_B T}}} \quad (32)$$

This is the vibrational partition function for a single vibrational mode in the harmonic oscillator approximation if we set $\varepsilon_j = h\nu_j$. Because a non-linear molecule has $3N-6$ vibrations, the vibrational partition function for the whole molecule is:

$$q_{vib} = \prod_{i=1}^{3N-6} \frac{1}{1 - e^{\frac{-h\nu_i}{k_B T}}} \quad (33)$$

So, by using the harmonic oscillator model for molecular vibrations the complicated $3N-6$ dimensional problem of treating the molecular vibrational partition function has been enormously simplified as the product of the partition functions of each vibrational mode, each of which is a single term.

(g) Validity of Conventional Treatment for Partition Functions:

The above approximations used for molecular partition functions have reached the status of textbook standards because of their success in determining accurate partition functions of small molecules. This of course does not mean that these methods are not known to suffer from drawbacks and one must take care in their use and should be fully aware of the approximations used in deriving them. For example, all the derivations used assume that the system is in the (ideal) gas phase and that all contributions to Q are independent and separable into contributions from translation, rotation, vibration, and electronic states.

(i) q_{trans} :

The derivation for the translational partition function is generally valid so long as the thermal quantum wavelength of the molecule is small compared to the dimensions of the molar volume. This condition is almost always satisfied and is only a problem for light molecules such as H_2 in small containers. The derivation does not take into account solvation effects and usually uses the ideal gas law, $V = nRT/p$, for determining the molar volume.

(ii) q_{elec} :

So long as there are no low-lying thermally accessible excited electronic states, the assumption that the electronic partition function is equal to the ground state degeneracy is valid.

(iii) q_{rot} :

The rotational partition function derived in equation 31 is valid so long as the molecule is reasonably rigid and the mass and temperature are high enough that the classical treatment for rotation is valid.

(iv) q_{vib} :

The vibrational partition function is the component of equation 29 that is most likely to suffer from problems with its assumptions. In the first place, the number of degrees of freedom for q_{vib} becomes very large (scales as $3N-6$) the greater the number of atoms in the molecule. Therefore, since the molecular vibrational partition function is a product of the vibrational partition function of each vibrational mode, one can imagine that errors in treatment of q_{vib} can become larger, the more modes a molecule has.

(a) Anharmonicities:

If the electronic potential along a normal mode of vibration deviates from being parabolic, then the harmonic approximation is not completely valid and the vibrational mode is said to be *anharmonic*. For any real system the harmonic oscillator is not perfect and so all vibrations are to some extent anharmonic. The reason why the harmonic oscillator treatment is used so widely is because its partition function has a simple analytic solution and because most vibrations are indeed approximately harmonic at temperatures ~ 300 K.

It is well known (Ayala98), however, that the partition function from the harmonic oscillator model is often somewhat smaller than that of a real vibration because the potential of a parabola is too steep and all of its energy levels are evenly spaced.

Figure 2: The energy level spacing decreases with increasing energy for any curve less steep than a parabola:

The “cosine” potential energy example of figure 2 is very pertinent as it models the best known type of vibration anharmonicity; the internal rotation.

(b) Internal Rotation

Molecular vibration modes naturally fall into the categories of (i) stretches, (ii) bends, (iii) torsions, or (iv) some combination of the previous three. Stretching and bending modes are generally well treated by the harmonic oscillator approximation but torsional modes sometimes are not, especially if the barrier to internal rotation is small. If the rotational barrier is fairly small (smaller than RT or about 0.5 kcal/mol), a parabola does not well approximate the potential for $T = 300$ K. In such cases, one often uses a cosine potential to model the potential accurately; for example, a cosine potential is known to be a good model of large amplitude (high temperature) torsional vibrations in ethane. If the

barrier is very small or non-existent, the free rotor model may be appropriate. The free rotor (FR) partition is shown below:

$$q_{FR} = \frac{\sqrt{2\pi I k_B T}}{h\sigma} \quad (34)$$

where I is the (reduced) internal mode moment of inertia and σ the symmetry of the potential. The problem of accurately modelling internal rotation vibrational modes is very much temperature dependant. For example, the internal rotation mode in ethane is actually adequately modeled by the harmonic oscillator framework at $T \sim 300$ K and lower; at higher temperatures, however, the amplitude of the vibration explores more and more of the vibrational potential and eventually one must abandon the parabola and use a cosine curve. This can be seen in the figure below where the curves nearly match at the bottom of the potential but clearly do not for large deviations from it.

Figure 3: Parabola versus cosine curve: A View of $y=x^2$ and $y = 2(1-\cos(x))$:

The practical problem presented by internal rotation modes is that the vibrational partition function may be in great error if the harmonic oscillator is used when one should be using an internal rotation or free rotor model.

For internal rotation modes, the partition function for the harmonic oscillator converges to the accurate result from below as the barrier increases, underestimates q_{vib} as the barrier becomes smaller, and then at some critical small barrier becomes larger and then shoots up and becomes far too large as the barrier is decreased further (**Ayala98**).

Therefore, the harmonic oscillator approximation tends to produce vibrational partition functions slightly too small but for internal rotation vibrational modes with small barriers it can greatly overestimate q_{vib} .

Many authors have noted this potential problem with internal rotation vibrational modes and there is a substantial literature dealing with the subject (**Ayala98, Truhlar91, Pitzer42, Chuang00a**). Pitzer and Gwinn in 1942 (**Pitzer42**) produced one of the first important works in the area by calculating accurate partition functions for internal rotation modes with a variety of barrier heights and cosine PES curves.

A major contribution by D. G. Truhlar in 1991 (**Truhlar91**) was to derive a partition function model for internal rotation that interpolates between the limiting cases of the harmonic oscillator and the free rotor. It was shown that the following very simple hyperbolic tangent model prevents the “blow up” of q_{vib} for low barrier internal rotation modes:

$$q_{vib,Truh} = q_{HOQ} \tanh(q_{FR} / q_{HOCl}) \quad (35)$$

where q_{HOQ} is the quantum harmonic oscillator partition function and the classical harmonic oscillator partition function is:

$$q_{HOCl} = \frac{k_B T}{h\nu} \quad (36)$$

Therefore, the Truhlar interpolating function has the correct qualitative behaviour for all frequencies, unlike q_{FR} or q_{HOQ} and approaches q_{HOQ} for large internal rotation barriers and q_{FR} for small barriers.

However, for most of the range of the harmonic oscillator partition function the Truhlar internal rotation “correction” actually makes the partition function even smaller than q_{HOQ} (which usually underestimates the accurate partition function) and thus slightly less accurate. Therefore, the value of the Truhlar interpolation function is only to prevent q_{vib} infinite divergence for very small barriers to internal rotation.

Chuang and Truhlar in 2000 (**Chuang00a**) wrote an article that effectively summarized the procedures for calculating corrections to internal rotation vibrational modes and shows five different approaches for calculating parameters needed for the available corrections. One of the five approaches presented is called “scheme ω -W” because from the harmonic frequency (ω) and barrier height (W) it is possible to determine the reduced moment of inertia for the vibrational mode.

A FORTRAN 90 program has been written for this thesis that uses scheme ω -W to determine the reduced moment of inertia for an internal rotation from rotational mode

frequency and barrier height; internal rotation corrections may then be calculated by any of the common approaches. This program is included in **Appendix A** of the thesis.

We have shown now how one may obtain all of the components needed for computing theoretical kinetics of chemical reactions using the framework of transition state theory.

(ix) Transition State Theory:

(a) The Arrhenius Equation:

From basic chemistry it is known that many elementary chemical reaction rates obey the phenomenological Arrhenius equation:

$$k_{Arrh} = Ae^{\frac{-E_a}{RT}} \quad (37)$$

where k_{Arrh} is the reaction rate, E_a is the reaction's activation energy and A is the Arrhenius pre-exponential factor or simply A-factor.

This model is of course very simple but nevertheless is successful to such an extent that it is considered the basic theory of experimental chemical kinetics and represents the “picture” chemists carry in their minds.

(b) Conventional Transition State Theory:

Firstly, it is important to be able to visualize a simplified reaction pathway illustrating relevant features used in transition state theory. These are shown below:

Figure 4: A simple picture of a pathway for an exothermic reaction:

The theory of chemical equilibrium is what inspired the development of transition state theory in the mid 1930s (Eyring35). From standard physical chemistry textbooks it is known that for a general gas phase addition reaction (Atkins98):

the equilibrium constant K can be written in terms of the molecular partition functions and quantum energy difference between reactants and products as follows:

$$K = \frac{Q_C}{Q_A Q_B} e^{\frac{-E_0}{RT}} = \frac{[C]}{[A][B]} \quad (39)$$

where $[X]$ is the concentration of species X and E_0 is the “quantum” energy difference (i.e. energy difference corrected for zero-point contributions) between reactants and products.

If we assume the reaction in equation 38 has a barrier to activation we can define the conventional transition state (CTS) separating products and reactants as being the highest energy point along the minimum energy pathway (MEP) separating reactants and products (**Quapp84**). Since the CTS is the highest point along a multi-dimensional reaction valley, it is defined as a saddle point of order 1 separating reactants and products along the MEP. Because dynamically the reactants may pass *by* the saddle point along the MEP from reactants to product without actually crossing over the saddle point itself, the *transition state* (TS) is practically taken to define a “dividing surface” that contains the saddle point and that is orthogonal to the MEP at the saddle point. This dividing surface therefore represents a “generalized” transition state that must be crossed for the reactants to form products.

Figure 5: An example of a three dimensional (order 1) saddle point and its surrounding area:

The brilliant insight of transition state theory is to assume that the reactants are in equilibrium with the transition state:

And therefore the equilibrium equation with the transition state as product is a simple corollary of equation 39.

$$K_{TS} = \frac{Q_{TS}}{Q_A Q_B} e^{\frac{-E_0}{RT}} = \frac{[TS]}{[A][B]} \quad (41)$$

Now the rate constant equation of kinetics is derived (**Laidler87**).

First, the imaginary frequency vibrational mode of the transition state must be treated specially because it represents motion along the reaction pathway and not a true vibration. Since this mode has no restoring force, it can be well approximated as a vibration with frequency of zero at the CTS. Therefore, we obtain the following result for the partition function of this vibration:

$$\lim_{\nu \rightarrow 0} \frac{1}{1 - e^{\frac{-h\nu}{k_B T}}} = \frac{k_B T}{h\nu} \quad (42)$$

The term $\frac{k_B T}{h\nu}$ is actually the equation for the classical harmonic oscillator. Recalling that the partition function for the TS is the product of partition functions from each contributing mode we obtain a new modified partition function:

$$Q_{TS} = Q'_{TS} \frac{k_B T}{h\nu} \quad (43)$$

which when substituted into equation 41 and algebraically rearranged yields:

$$v[TS] = [A][B] \frac{k_B T}{h} \frac{Q'_{TS}}{Q_A Q_B} e^{\frac{-E_0}{RT}} \quad (44)$$

where the left hand side of equation 44, the product of concentration of activation complexes with their frequency of conversion into products, is the rate of reaction, ν . Since the rate constant k of a bimolecular reaction $= \nu[A][B]$ we thus have the very important equation:

$$k_{CTST} = \frac{k_B T}{h} \frac{Q_{TS}}{Q_A Q_B} e^{\frac{-E_0}{RT}} \quad (45)$$

which is *the* conventional transition state theory (CTST) equation for chemical kinetics (we now refer to Q'_{TS} as simply Q_{TS}) where E_0 is the quantum barrier to reaction ($E_0 = E_c + \Delta E_{ZPE}$ where E_c is the classical barrier to reaction) and k_{CTST} is the CTST rate constant for a bimolecular reaction. Therefore, given the molecular partition functions of the reactants and the TS and the quantum reaction barrier it is then possible to calculate a first principles rate constant for any bimolecular reaction. It is interesting to note that in the CTST framework one calculates a bimolecular rate constant from only information of the two reactants and the CTS; one need know nothing about the product of the reaction. CTST has been used extensively and successfully for calculating chemical reaction rate constants (**Laidler87, Pechukas81, Truhlar96, Laidler83**). It is very useful to know the important underlying assumptions of this simple kinetics theory. There are four such major assumptions of CTST (**Laidler87**) :

(i) No Recrossing of saddle point:

It is assumed that if the reactants pass through the TS (dividing surface) along the MEP in the direction of the products that they do not recross the surface and form reactants again. This is why in CTST one need know nothing specific about the reaction products; it is assumed that anything that crosses in the direction of the products does not come back! Realistically chemical systems do recross the dividing surface to some extent, and this effect is well known in the theory of molecular reaction dynamics. Therefore, CTST, even with a perfect PES will tend to overestimate the rate of reaction slightly due to recrossing of the dividing surface.

(ii) Maxwell-Boltzmann statistics should be valid:

The energy distribution of the reactant molecules and the TS should be adequately described by Maxwell-Boltzmann (classical) statistics since one uses classical statistics in the equilibrium theory derivation. The concentration of activated complexes should therefore be obtainable from equilibrium theory.

(iii) Motion along MEP should be separable:

To separate out the reaction progress coordinate from the activation complex's q_{vib} as in equations 42 and 43 this mode of motion should be separable from the others.

(iv) Classical Motion along MEP should be valid:

Since the theoretical framework of the dividing surface, minimum energy reaction pathway, potential energy saddle point, etc. are all inherently classical, it should be a valid approximation that motion along the reaction pathway can be well approximated ignoring quantum effects such as tunnelling. This condition is the basis for rate calculations from the molecular dynamics viewpoint as well.

A fifth assumption is that all of the components of the CTST rate equation (equation 45) such as partition functions and energy differences are themselves accurately determined. Also, all derivation of CTST and the partition functions and energies up to this point have ignored effects of other non-reacting molecules and thus the theoretical framework specifically pertains to the conditions of an ideal gas.

(c) The Connection between CTST and Arrhenius Theory:

It is important to realize the connection between conventional transition state theory and Arrhenius theory. For example, most theoretical kinetics results are published with the terminology of "quantum barrier" whereas experimental kinetics results would report "activation energies". Below is a comparison of these two closely related theories.

If we differentiate equation 37 with respect to temperature and assume that A is independent of temperature we obtain:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad (46)$$

but if we differentiate with respect to T the equilibrium equation we obtain:

$$\frac{d \ln K}{dT} = \frac{E_c + \Delta E_{therm} + \Delta E_{ZPE}}{RT^2} \quad (47)$$

where E_c is the classical energy difference between products and reactants, ΔE_{therm} is the thermal correction to energy and excludes the ΔE_{ZPE} . If we compare the equation 45 with 39 we also obtain the important relationship:

$$k = \frac{k_B T}{h} K \quad (48)$$

therefore,

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K}{dT} \quad (49)$$

and thus,

$$\frac{d \ln k}{dT} = \frac{E_c + \Delta E_{therm} + \Delta E_{ZPE} + RT}{RT^2} \quad (50)$$

which leads directly to,

$$E_a = E_c + \Delta E_{therm} + \Delta E_{ZPE} + RT \quad (51)$$

Equation 51 is very important because it allows direct comparison of the experimental and phenomenological activation energy with quantum mechanical (e.g. classical barrier) calculations. The CTST pre-exponential factor (A_{CTST}) is now compared with the A-factor as follows. Assume that the CTST rate constant is the same as the Arrhenius theory rate constant. Then, by simple comparison of equations 45 and 37 we find the equation to theoretical determine an Arrhenius A-factor using CTST:

$$A - factor = \frac{k_B T}{h} \frac{Q_{TS}}{Q_A Q_B} e^{\frac{E_a - E_0}{RT}} = A_{CTST} e^{\frac{E_a - E_0}{RT}} \quad (52)$$

(d) Conformational Analysis:

Many small molecules such as methane, water, and ethane exist in only one possible minimum geometric shape or conformation. However, may larger molecules have more than one possible minimum energy geometry. Specifically, there may be local energy minimum conformations but of course only one or several degenerate global minima. An example of a simple molecule with more than one possible conformation is 1,2-dichloroethane with one global minimum (if the two Cl atoms are most far apart) and two degenerate local minima.

At any finite temperature a collection of molecules with several possible conformations will exist as a mixture of such conformations. Since all conformers exist in a state of equilibrium with each other (e.g. for conformers "n" and "m"):

the relative populations at any temperature can be determined for any two conformers using the equilibrium equation:

$$K = \frac{Q_{conf,n}}{Q_{conf,m}} e^{\frac{-E_0}{RT}} = \frac{[conf,n]}{[conf,m]} \quad (54)$$

Therefore, the relative populations depend on both energy and molecular partition function differences.

(e) Canonical Variational Transition State Theory:

Variational transition state theory is a generalization of conventional transition state theory. The idea is that one can generalize the location of the TS dividing surface such that it is not required to pass through the MEP saddle point. Instead, the only requirement of the dividing surface is that it be perpendicular to the MEP valley.

The goal of generalizing the transition state is to minimize TS dividing surface recrossing effects in the TST formalism. So the idea is to iteratively examine the reaction MEP with

generalized transition states and variationally find the TS location that minimizes the resulting rate constant (and hence recrossing effects). There are several theoretical frameworks for finding the optimal TS.

Out of all the variational TST models the canonical variational transition state theory (CVTST) framework most closely resembles conventional transition state theory. The CVTST equation is exactly the same as the CTST equation except that the TS dividing surface is variationally chosen to find a minimum rate. Thus, only the reaction barrier and molecular partition function of the now generalized TS species change from the CTST equation 45:

$$k_{CVTST} = \frac{k_B T}{h} \frac{Q_{TS,CVTST}}{Q_A Q_B} e^{\frac{-E_{0,CVTST}}{RT}} \quad (55)$$

The drawback of variational TS models is of course that a substantial portion of the MEP must be explored instead of only the saddle point.

(f) Transition State Theory in the liquid phase:

Up to this point, all theory has implicitly assumed that there are no intermolecular interactions occurring; namely, all theory has assumed ideal gas behaviour.

Most of chemistry of course occurs in the liquid phase and so it would be good to have a method for directly comparing theoretical kinetics with experimental liquid phase kinetics. Unfortunately, it is difficult computationally to account for solvation effects.

There are two different types of theoretical solvation models. Implicit solvation models attempt to account for solvation effects without actually including discrete solvent molecules in the calculation. Often such models use bulk solvation properties such as relative permittivity to try to include solvent dissipation of electric field. Additionally, solvent effects between strongly interacting solute and solvent (e.g. dipole-dipole interactions) can be included by having a solvent model with optimizable classical charge distributions; such self-consistent reaction field models have found some success in the literature for predicting quantities such as enthalpies of solvation. Explicit solvation models include a finite number of discrete solvent molecules in the calculation. Often the outer boundary of the explicit solvent molecules is surrounded by an implicit solvent. These models are capable of much better describing solute-solvent interactions since real solvent molecules are used. However, it is very difficult to adequately survey the vast solvation conformational space required to simulate the dynamical nature of a liquid solvent. Explicit solvation models therefore increase the cost of calculation greatly and tend to be impractical if one includes quantum mechanical treatment of more than several solvent molecules.

Due to computational cost we do not implement solvation models in this project but instead consider how solvent can be expected to affect chemical reaction rates.

The presence of high-pressure gas or liquid solvent of course can be a very important theoretical effect and can change the rates of chemical reactions from the gas phase significantly. Unfortunately, there is no general way to define “solvent” since different solvent environments can differ greatly from each other and there is no straightforward

formal way to compare theoretical gas phase kinetics with experimental liquid phase kinetics (**Fischer01**).

We assume that the solute and solvent are not interacting strongly (i.e. the solvent and solute molecules are non-polar) because for our experimental systems considered in the results and discussion this is the case.

Since many of the chemical systems investigated in this thesis are so large that modest gas phase quantum mechanical calculations can take days or weeks on supercomputers, we are not at liberty to use a complicated solvation theory to correct our gas phase rates for solvation effects.

There are, however, well known simple models that have shown that rates in gas phase and liquid solution should be similar if the reactants and solvent do not interact very strongly.

A classic work by Rabinowitch and Wood (**Rabinowitch36**) has shown that the number of reactive collisions should be roughly the same regardless of whether a reaction is occurring in the gas phase or solution. In the gas phase, reactive collisions occur individually with fairly periodic intervals between successive collisions. In the liquid phase, there tends to be even longer intervals between reactive collisions since the reacting molecules are separated by solvent. However, once the reactant molecules happen upon each other, it is likely that they may collide with each other several times. Hence, the overall number of collisions in the gas phase and liquid phase per unit time should be roughly equivalent. The solvent is said to have a cage effect on the reaction; reactants come together in solution less frequently but when they do come together they stay in close proximity for a greater period of time.

Somewhat more rigorously, Benson (**Benson60**) has shown that the ratio of rate constant in solution to rate constant in gas phase can be approximated as:

$$R_n = 10^{2n-2}/n e^{n-1} \quad (56)$$

where n is the number of molecules involved in the reaction. For bimolecular reactions $n = 2$ and thus $R_n \sim 20$; we therefore expect bimolecular reactions in solution to be somewhat faster than in the gas phase.

Ultimately, however, all current methods of correction to gas phase theoretical kinetics are somewhat arbitrary and much more work must be done in this area of research (**Cramer99**).

(x) Laser-Flash Photolysis and Experimental Kinetics in the liquid phase:

The technique used in this project for experimentally studying kinetics is *laser-flash photolysis* (LFP) (**Hadel89**). In the LFP method, a pulse of laser light is directed at a solution and the rate of a photochemical or photochemically-induced reaction is subsequently measured.

In the present work the laser pulse is generated by first forming an excited complex or exciplex between xenon and chlorine atoms through electric discharge through a gas containing xenon, neon, and HCl. The excited complex decays after a few nanoseconds and emits photons of 308 nm wavelength.

Photons with wavelength of ~ 300 nm are ideal for dissociating peroxide bonds and a peroxide is in fact used to induce a photochemical chain reaction.

The reaction sequence is as follows. Di-tert-butyl peroxide in liquid solution is homolytically dissociated at the O-O bond by a pulse of 308 nm laser light. The liquid solution contains 1,1-diphenylethylene (DPE), isooctane as bulk solvent, and either tris(trimethylsilyl)silane (TTMSS, or H-Si(SiMe₃)₃) or triethylsilane (TES, or H-SiEt₃). The tert-butyl oxyl radicals that are generated by the laser pulse are very reactive and quickly generate silicon-centered radicals by abstracting the hydrogen from the Si-H bond of either of the silane compounds. These silicon-centered radical compounds then react with the olefin compound DPE at the terminal –CH₂ group and form a reaction adduct which strongly absorbs light in the range of 320-360 nm.

The rate of addition of the silyl radical with DPE can then be measured if one records the change in optical density of the solution as a function of time. This method of kinetics measurement assumes that the changes in solution optical density are due entirely to growth of the silyl-DPE adduct.

The following laser probe method was pioneered in the work **Chatgililoglu81**.

Quantitatively, the rate of addition of the silicon radical with DPE is measured as follows.

The concentrations of all species but 1,1-diphenylethylene are held constant. Then, measurement of the observed reaction rate with several concentrations of DPE obeys the linear equation (**Ballestri91, Chatgililoglu81**):

$$k_{obs} = k_{DPE}[DPE] + k_0 \quad (57)$$

where k_{obs} is the observed rate, k_{DPE} is the rate constant for the addition of the silicon radical with 1,1-diphenylethylene, $[DPE]$ is the concentration of 1,1-diphenylethylene and k_0 is the lifetime of the silicon radical in the absence of DPE.

Since the silyl-DPE adduct is ideal for change in optical density measurements we can use the reaction of silicon radicals and DPE as a kinetically competitive probe to indirectly measure the rates of addition of silicon radicals with olefins that do not form optically measurable adducts. Specifically, if there is another olefin present in solution in addition to DPE, equation 57 becomes modified (**Ballestri91, Chatgililoglu81**):

$$k_{obs} = k_{DPE}[DPE] + k_{olefin}[olefin] + k_0 \quad (58)$$

However, if the concentration of DPE is held constant and only the concentration of the other olefin is varied equation 58 becomes:

$$k_{obs} = k_{olefin}[olefin] + C \quad (59)$$

which is completely analogous to equation 57; the concentration of the olefin of interest is varied while holding the concentration of the probe DPE constant. A plot of the observed rate versus the concentration of the olefin then gives the rate constant of the reaction as the slope of the line (**Ballestri91, Chatgililoglu81**).

Using these LFP techniques, the rate constants of the reactions of $\text{Si}(\text{SiMe}_3)_3$ and SiEt_3 silicon centered radicals with 1-hexene, 1-decene, 1-pentadecene, styrene and 1,1-diphenylethylene are reported in this thesis.

Experimental:

(i) Theory:

All electronic structure calculations were performed with the *Gaussian* suite of programs (**Gaussian98**). Reactant molecules were geometry optimized using the “Opt” keyword and with the tight convergence criteria when possible (i.e. the calculations would never finish in some cases if the tight convergence criteria were used). Normal mode frequency analyses were performed on the optimized structures to determine molecular partition functions and to ensure that no undesired imaginary modes were present. The *Gaussian*-based molecular viewer *Gaussview* was used to build nonoptimized geometry structures, to visually assess the quality of optimized geometries and to animate vibrational modes. Transition state structures were checked by visualizing whether the imaginary mode led to reaction product formation.

For reaction pathway calculations where not all PES first derivatives are zero, geometry optimizations were conducted with the *modredundant* option. This keyword allows one to modify internal (redundant) coordinates before the structure is submitted to calculation. One can also freeze these coordinates so that bond lengths, angles and dihedral angles may be kept frozen. Using such *partial optimization* techniques it is quite simple to explore an addition reaction pathway by freezing the bond length of the atoms between which the incipient bond forms and geometry optimizing the rest of the geometry coordinates. PES derivative information is printed for each of the internal coordinates of the molecule and the derivatives are useful for deciding how close a partially optimized

structure is to the TS. This was the approach used to find good guesses at TS structures in this project. Transition state structures were then found using the *TS* keyword which searches for a saddle point of order one and the *CalcFC* keyword which calculates force constants of the input geometry. One needs an adequate TS guess and calculated force constants because it is difficult for the *TS* routine to find the saddle point otherwise. Of course if the reaction path derivative was found to be zero with the *modredundant* partial optimization then no further calculation is required as one is already at the TS structure; this is how some of the bigger TS structures were found in this project because the automated *TS* procedure tends to fail frequently for large systems and the calculation of force constants is computationally expensive.

Frequency scale factor corrections (**Scott96**) were not used in this project. A preliminary study found that the corrections were unnecessary complications with very little if any improvement on frequency estimations of DFT methods. This is illustrated by the fact that the “optimum” scale factors reported (**Scott96**) for many DFT methods are in the range of 0.98 to 1.02 and there is therefore very little effect on the default scale factor of “1”. Also, there are no scale factors published for most modern methods.

Geometry optimization calculations are generally much more expensive than a *single-point energy* calculation but it is well known that geometries tend to change little for a method if a basis set is increased from “medium-sized” (e.g. 6-31G(d)) to the infinite basis set limit. Relative energies of a set of geometries are much more sensitive to basis set and converge slowly with increasing basis set size. Therefore, in this thesis the “{energy method}/{geometry method}” approach is often used to improve on the relative energies of sets of geometries. For example, if one has all the geometry

structures needed to analyse the reaction path of a reaction at the QCISD/6-31G(d) level of theory and desires accurate relative energies of these geometries, one might run QCISD/aug-cc-pVTZ single point calculations on these geometries. Therefore, the method would be described as QCISD/aug-cc-pVTZ//QCISD/6-31G(d). Many such calculations are included in the results of this project.

(ii) Laser-Flash Photolysis:

The procedure used to obtain the kinetics for all reactions considered has been established in the literature (**Ballestri91, Chatgililoglu81**) and is used in this project.

The laser used for the LFP experiments is a *Lumonics Excimer 500*, which emits laser light at 308 nm. The light source for monitoring change in optical density of the reaction solutions was a *PTi Model A 1010* xenon arc lamp with pulser. The photomultiplier that acquired the raw optical density data is a *Digikrom 240*. A *Tektronix 7912 AD Programmable Digitizer* converted the raw analog data to digital form for computer analysis. All transient spectra were analysed and plotted using custom software on the PC that operated the LFP equipment.

All reagents were purchased from manufacturers and therefore no synthesis was required. Tris(trimethylsilyl)silane (purity 97+ %) was purchased from *Fluka*. Isooctane (GC quality) was purchased from *EM Science*. Triethylsilane (97 %), di-tert-butyl peroxide (98 %), 1,1-diphenylethylene (97 %), styrene (99+ %), 1-hexene (99+ %), 1-decene (94 %), and 1-pentadecene (98 %) were all purchased from *Aldrich*. Reagents were not purified.

Quartz cuvettes with optical path length of 0.7 cm were used to hold the reaction contents.

The $\text{Si}(\text{SiMe}_3)_3$ and SiEt_3 + DPE reaction solutions were prepared with 1.3 mL isooctane, 0.6 mL of $\text{H-Si}(\text{SiMe}_3)_3$ or H-SiEt_3 , 0.1 mL of di-tert-butyl peroxide and either 5, 10, 25 or 50 μL of DPE. It is assumed that the volume of addition of the various liquids is completely *additive* and that the inclusion of microliter quantities of DPE is a minor perturbation on the total volume; therefore total volume should be 2.0 mL.

The $\text{Si}(\text{SiMe}_3)_3$ and SiEt_3 + styrene reaction solutions were prepared with 1.3 mL isooctane, 0.6 mL of $\text{H-Si}(\text{SiMe}_3)_3$ or H-SiEt_3 , 0.1 mL of di-tert-butyl peroxide, 10 μL of DPE as the probe, and 10, 25 or 50 μL of styrene for 2.0 mL total volume.

The $\text{Si}(\text{SiMe}_3)_3$ and SiEt_3 + 1-hexene, 1-decene and 1-pentadecene reactions solutions each contained 0.6 mL of $\text{H-Si}(\text{SiMe}_3)_3$ or H-SiEt_3 , 0.1 mL of di-tert-butyl peroxide and 10 μL of DPE. Three different concentrations of the olefin (1-hexene, 1-decene or 1-pentadecene) were included by then adding either 0.1 mL olefin + 1.2 mL isooctane, 0.6 mL olefin + 0.7 mL isooctane, or 1.3 mL olefin and no isooctane. Therefore, all solutions again were approximately 2.0 mL total volume.

All solutions were mixed and allowed to equilibrate before use. To eliminate potentially reactive dissolved gases from the solutions, N_2 gas was bubbled through them for approximately 10 minutes.

During the LFP experiments, the growth adduct of $\text{Si}(\text{SiMe}_3)_3$ radical and DPE was monitored at 330 nm and the SiEt_3 + DPE adduct was monitored at 345 nm. Before the wavelength for monitoring was chosen it was ensured that no undesired significant

changes in optical density were occurring from sources other than the addition of the silicon radicals to DPE by preparing *blank samples*.

Analysis of the raw kinetic data was performed on with the program *KAP* (kinetics analysis plotter).

A *Cary 3 UV-VIS* spectrophotometer was used to measure solution absorbances before laser use; this was done to ensure that the majority of the 308 nm laser pulse would be absorbed by di-tert-butyl peroxide and not other compounds present in solution.

Results and Discussion:

The following sections will be considered in the results and discussion: (i) the reaction between SiH_3 radical and ethene, (ii) the reaction between CH_3 radical and ethene, (iii) the reaction between SiMe_3 radical and ethene, (iv) the reaction of SiEt_3 radical and ethene, (v) the reaction of CMe_3 radical and ethene, (vi) experimental gas versus liquid phase kinetics for some small systems, (vii) theoretical gas phase kinetics for large reacting systems, (viii) experimental liquid phase kinetics for large reacting systems, (ix) a comparison of theoretical gas versus experimental liquid phase kinetics for large systems and an assessment of using gas phase CTST to predict liquid phase experimental kinetics for large systems, and (x) summarizing remarks.

(i) System 1: SiH_3 radical + ethene addition reaction:

In this section, the following aspects of the SiH₃ radical + ethene reaction are considered:

(a) minimum energy path, (b), basis set effects, (c) kinetics, (d) internal rotation effects in the TS, and (e) a comparison of CTST versus CVTST. Additional data may be found in Appendix C.

(a) Minimum Energy Path

The conventional transition state for the reaction of SiH₃ radical with ethene has been investigated only once in the literature (**Bottoni97**) where it has been reported that E_c and E_a are, at QCISD(T)/6-311G(d,p)//MP2/6-31G* level of theory, respectively equal to 4.31 and 6.46 kcal/mol. We decided to see if these results were insensitive to changes in theory and therefore we calculate E_c and E_a (and E₀) with a wide variety of *ab initio* and DFT approaches. Because the classical barrier only gives information about the reaction saddle point we also decided to investigate a substantial portion of the minimum energy path of the reaction; specifically the Si---C bond formation region of 2.50 to 2.90 Å. A view of the transition state at BHandHLYP/6-31G(d) level of theory is given below:

Figure 6: A view of the BHandHLYP/6-31G(d) transition state of the reaction of

SiH₃ radical with ethene:

There is only one possible conformation for the transition state but the conformation is 12-fold degenerate.

Since to the best of our knowledge there is no literature data available for comparison of the MEP of SiH₃ radical + ethene reaction we have decided to compare our theoretical results with the high-level energy method QCISD(T)/aug-cc-pVTZ; this method is therefore treated as our standard because it is well known for being a very accurate energy method with use limited mostly by the expensive cost of calculation (Lynch02, Lynch03, Chuang00b)! It is worth noting that QCISD(T) performed almost identically to the slightly more expensive CCSD(T) method for MEP test calculations and so QCISD(T)/aug-cc-pVTZ was chosen because it is less expensive. It is impossible to do geometry optimizations with the QCISD(T) method with the Gaussian package of

programs, however, so we investigated MEP single point energies of QCISD(T)/aug-cc-pVTZ at the following “high” levels of geometry: QCISD/aug-cc-pVDZ and QCISD/6-311+G(d,p). The classical PES of these two curves plus those of a couple of others are shown below; the reacting Si-C bond length is frozen and all other geometry parameters are minimized:

Figure 7: A portion of the MEP of reaction of SiH_3 radical + ethene at QCISD(T)/aug-cc-pVTZ level of energy:

The single point energies are not very sensitive to the four geometry methods and the classical barrier is predicted to be between 1.60 to 1.75 kcal/mol and the Si-C CTST bond length is between 2.60 and 2.65 Angstroms. Of the four geometry methods, we choose QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ as the level of theory to which all others

will be compared for quality because both the geometries and energies should be of high quality. The data points of our target method QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ will henceforth be shown with a spline fit to better illustrate how other methods compare with it. The energies based on the DFT method BHandHLYP/6-31G(d) geometries are included to show that DFT methods are suitable for determining geometries along the reaction pathway.

We now compare the MEPs of some less computationally expensive methods to our target method, QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ:

Figure 8: How do other methods compare to QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ for the MEP of SiH₃ radical adding to ethene?

Many important facts are discernible from figure 8. Noting that our target MEP is QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ, it is obvious that the QCISD method seriously overestimates the classical barrier with smaller basis sets (especially 6-31G(d) and 6-311+G(d,p)). MP2/6-31G(d) is an extreme failure; it predicts a barrier of almost 10 kcal/mol when the target shows it should be approximately 1.65 kcal/mol! The DFT method B3P86/6-31G(d) seriously underestimates energies all along the MEP and does not even predict a true barrier since the relative energies are below 0 kcal/mol for the entire MEP! Fortunately, some of the methods do well approximate the target MEP. In particular we see that BHandHLYP/6-31G(d) and B1LYP/6-31G(d) are close to the target for both barrier height and “shape” of the curve (Si-C bond length of TS). The most commonly used DFT method in existence, B3LYP/6-31G(d), performs fairly well too. We now examine the successful approaches from figure 8 in greater detail.

Figure 9: A close up of the better quality MEP methods of figure 8:

It is now apparent that BHandHLYP/6-31G(d) predicts a classical reaction barrier almost identical to QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ (~1.65 kcal/mol) with a slightly longer bond length. B1LYP/6-31G(d) underestimates E_c by approximately 0.4 kcal/mol and B3LYP/6-31G(d) underestimates E_c more seriously, by about 1 kcal/mol. Such small barrier differences may sound trivial, but they are not because of the exponential dependence of rate constant on barrier height.

Therefore, MP2/6-31G(d), QCISD/6-31G(d) and B3P86/6-31G(d) are inappropriate for use in MEP energies because their barrier predictions are in great error of the target result.

The MEPs of some poorly performing DFT methods are shown below:

Figure 10: SiH_3 radical + ethene reaction MEP for some very poorly performing methods

None of these methods predict barriers to reaction since the relative energies never cross 0 kcal/mol. More interestingly, the BHandH/6-31G(d), PBEPBE/6-31G(d), and PW91PW91/6-31G(d) methods do not even predict a saddle point on the MEP! The energies along the MEP for these three methods are decreasing for the whole MEP as the reacting fragments come together. Clearly, none of these DFT methods are appropriate for use in the MEP of SiH₃ radical + ethene. It is also interesting to note that the PBEPBE and PW91PW91 methods have been cited as candidates for usefully describing intermolecular interactions (van der Waal forces) (Tsuzuki01, Adamo02) yet they fail so terribly for the MEP of a simple chemical reaction!

Based on figure 9, we conclude that the BHandHLYP/6-31G(d) method is, as compared to our target method QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ, by far the best method for energies along the MEP. It is indeed fortunate that the best method is a DFT method with the 6-31G(d) basis set; such an approach is very computationally inexpensive and can be applied to large molecular systems.

(b) Basis Set Effects along the Minimum Energy Path

The 6-31G(d) basis set is not all that big and it is worthwhile to see if MEP of BHandHLYP and the other methods are very sensitive to changes in basis set.

We first show the basis set dependence of the QCISD and QCISD(T) method for predicting the MEP of SiH₃ radical + ethene.

Figure 11: Basis set effects for QCISD and QCISD(T) MEP of SiH₃ radical + ethene

Figure 11 shows plainly that as one increases the basis set for QCISD or QCISD(T) (with 6-31G(d) < 6-311+G(d,p) < aug-cc-pVDZ < aug-cc-pVTZ) the energies along the reaction pathway decrease systematically to our target QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ. This decrease in MEP energy is indeed very significant and so one must be careful to use a large basis set with either the QCISD or QCISD(T) methods or relative energies along the reaction MEP will be seriously overestimated. It is interesting to note, however, that the transition state Si-C bond length does not seem to change much with changing basis set. In other words, the shapes of the curves do not change much with changing basis set; it is the height of the curves that does change significantly.

This basis set dependence is of relevance to the conclusions of the 1997 Bottoni paper (Bottoni97) where the QCISD(T)/6-311G(d,p)//MP2/6-31G(d) approach predicted a classical barrier to reaction of SiH₃ radical + ethene of 4.31 kcal/mol. We expect the QCISD(T) method with such a small basis set to seriously overestimate the MEP energies. This appears to be the case as a value for E_c of 4.31 kcal/mol is clearly too high since our target method QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ indicates that the barrier is roughly 1.65 kcal/mol.

We now show basis set effects of the DFT method BHandHLYP for the MEP.

Figure 12: Basis Set effects along the SiH₃ radical + ethene reaction MEP for the BHandHLYP method:

What is striking from figure 12 is that as one increases the basis set of this DFT method, the relative energies along the MEP increase systematically. This is opposite to the effect that was seen with the correlated *ab initio* methods where the relative energies decreased with increasing basis set size. Also, the shapes of the curves can be seen to be constant with the three basis sets shown; the curves appear different only in that they are translated along the relative energy axis away from each other. These trends are seen for all tested DFT methods (Appendix C).

Therefore, the BHandHLYP MEP energies are not improved in going beyond the medium-sized 6-31G(d) basis set. Using the BHandHLYP/6-311+G(d,p) method for E_c would result in an overestimation of approximately 1.5 kcal/mol as is clearly visible in figure 12.

We conclude that the BHandHLYP/6-31G(d) method is by far the best compromise of accuracy and efficiency for determining energies along the MEP of the reaction of SiH₃ radical with ethene. The MEP of the BHandHLYP/6-31G(d) method gives a classical barrier height of approximately 1.63 kcal/mol which is almost identical to our target method (QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ) with a Si-C bond length saddle point roughly 0.06 Å longer (2.69 Å versus approximately 2.63 Å).

Following is a summary table of the various measures of reaction barrier at various levels of theory. The data for QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ, QCISD/aug-cc-pVDZ, and QCISD/6-311+G(d,p) levels of theory was obtained from a spline fit of 0.05 Å resolution MEP data with the program Microcal Origin.

Table 1: Summary of Transition State Data for reaction of SiH₃ radical with ethene

at 298.15 K:

Method	Classical Barrier, E _c (kcal/mol)	Quantum Barrier, E ₀ (kcal/mol)	Activation Energy, E _a (kcal/mol)	Si-C TS Bond Length (Angstroms)
QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ	1.65	2.97	3.34	2.63
QCISD/aug-cc-pVDZ	2.76	4.08	4.45	2.63
QCISD/6-311+G(d,p)	4.50	5.78	6.22	2.62
QCISD/6-31G(d)	5.21	6.61	6.94	2.59
BHandHLYP/6-31G(d)	1.63	2.88	3.28	2.69
B1LYP/6-31G(d)	1.30	2.54	2.99	2.72
B3LYP/6-31G(d)	0.83	2.07	2.54	2.73
B3P86/6-31G(d)	-0.63	0.71	1.21	2.82

BHandHLYP/6-31G(d) is by far the best DFT method in comparison to our target

QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ.

(c) *Kinetics of the SiH₃ radical + ethene addition reaction:*

Up to this point we have been interested only in the classical relative energies along the MEP because from these it is possible to assess whether a method predicts good energies and curve shapes in the vicinity of the saddle point. It is of course impossible to measure MEP energies experimentally and since there is no MEP data in the literature (apart from Bottoni's QCISD(T)/6-311G(d,p)//MP2/6-31G(d) classical barrier) we have virtually no literature data for MEP comparison.

However, there is literature data on the kinetics of the reaction of SiH₃ radical with ethene (Loh90). Loh et al. found that the gas phase rate of addition is $= 1.81 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. From this rate constant it was assumed that an A-factor of $6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ was reasonable and if this is the case Loh et al. determined that the Arrhenius activation energy, E_a , of the reaction must be approximately 6 kcal/mol.

We now turn our theoretical approaches to kinetics from MEPs to see if these data from (Loh90) are reasonable.

Our target MEP method QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ will again be used as our theoretical standard; this time for the kinetics of this system.

Using conventional transition state theory (equation 45) and equations 51 and 52 to convert to Arrhenius parameters we obtained the following kinetics data. A_{CTST} denotes "CTST pre-exponential factor".

Table 2: Kinetics data for the reaction of SiH₃ radical with ethene at 298.15 K:

Method	Rate Constant, $k \text{ M}^{-1}\text{s}^{-1}$	$A_{\text{CTST}} \text{ M}^{-1}\text{s}^{-1}$	Quantum Barrier, $E_0 \text{ (kcal/mol)}$	A-factor $\text{M}^{-1}\text{s}^{-1}$	Activation Energy, E_a (kcal/mol)
QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ	1.41×10^6	2.04×10^8	2.97	3.81×10^8	3.34
BHandHLYP/6-31G*	2.01×10^6	2.57×10^8	2.88	5.06×10^8	3.28
B1LYP/6-31G*	4.08×10^6	2.96×10^8	2.54	6.34×10^8	2.99
B3LYP/6-31G*	9.51×10^6	3.13×10^8	2.07	6.91×10^8	2.54
B3P86/6-31G*	1.07×10^8	3.52×10^8	0.71	8.30×10^8	1.21
Experimental (Loh90)	1.81×10^6			6.00×10^{10}	6

In table 2 we see that BHandHLYP/6-31G(d) gives the rate constant in best agreement with the experimental results of Loh et al. followed by our “target” theoretical method QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ; note that the quantum barrier and activation energies are virtually identical for both methods so all difference in rate can be attributed to the CTST pre-exponential factor or A-factor. Because the activation energies of all other methods are underestimated in comparison to QCISD/aug-cc-pVTZ//QCISD/aug-cc-pVDZ, their rates are too high. Thus, BHandHLYP/6-31G(d) is by far the best DFT method for determining rates for this reaction. We note that the “guesses” of $6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ and 6 kcal/mol for A-factor and E_a by Loh et al. appear to be in significant error in light of the results in table 2! Had the guess of A-factor been closer to $6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ then the A-factor and E_a would have been in much better agreement with QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ and BHandHLYP/6-31G* because the rate constants agree to within 30 % of each other. It is not clear why Loh et al. guessed $6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ for the A-factor because for the analogous reaction CH_3 radical + ethene the A-factor is much smaller, on the order of $10^8 \text{ M}^{-1}\text{s}^{-1}$ (as it seems the A-factor for SiH_3 radical + ethene is too).

The CTST pre-exponential factors (A_{CTST}) and A-factors are seen to be fairly invariant to method with QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ giving the lowest values and B3P86/6-31G(d) giving the highest values which are approximately a factor of 2 higher. This is not a major difference and it can be attributed to the rigidity or floppiness of the transitional vibrational modes.

When two reactants or fragments come together in an addition reaction and the fragment geometries in the transition state are qualitatively the same (no geometric rearrangement,

same symmetry, etc.) then the vibrational modes of the TS are made up of the $3N-12$ modes of each separated reactant (the conserved modes) and 5 new transitional modes (corresponding to 5 translations and rotations of the fragments with respect to each other) resulting in a total of $3N-7$ vibrational modes in the TS. These 5 transitional modes are often the lowest frequency modes due to higher reduced mass of the vibrating components and lower force constants. Note that conserved modes do not have the same frequencies in the TS (due to different fragment reduced masses) as in the reactants but they simply have the same atoms vibrating in the same directions.

We show now the frequencies of the five conserved modes for each of the methods in table 2 and evaluate the vibrational partition function of those five modes (i.e. the product of the partition function of each mode):

Table 3: Transitional Vibration Modes Frequencies and Transitional Mode

Partition Functions for the H_3Si ---ethene transition state at 298.15 K:

Method	Transitional Frequency 1 (cm^{-1})	Transitional Frequency 2 (cm^{-1})	Transitional Frequency 3 (cm^{-1})	Transitional Frequency 4 (cm^{-1})	Transitional Frequency 5 (cm^{-1})	Transitional Modes q_{vib}	Conserved Modes q_{vib}
QCISD/aug-cc-pVDZ	108.68	150.69	267.98	364.21	431.03	9.02	1.11
BHandHLYP/6-31G*	100.00	141.12	269.89	346.41	423.30	10.28	1.09
B1LYP/6-31G*	92.21	136.29	257.90	325.65	400.96	11.97	1.10
B3LYP/6-31G*	89.86	134.97	254.12	317.88	391.45	12.62	1.10
B3P86/6-31G*	91.26	132.02	245.48	295.20	358.84	13.73	1.10

Since the ratio of conserved modes is nearly constant, most of the variation of the CTST pre-exponential factor and A-factor comes from contributions from the transitional

modes' q_{vib} . This is because errors in treatment in the partition functions are not cancelled out as is the case with the conserved modes (because the contributions from the conserved modes appear on top and bottom of the partition function ratio in the CTST rate equation). Also because the transitional modes typically are of the smallest frequency, errors in their contribution to the CTST rate constant are in general larger than the errors in the contribution from the conserved modes in the first place.

(d) Internal Rotation Effects on the Rate of SiH_3 radical addition to ethene:

We present the following analysis of internal rotation on the rate of reaction. The internal rotation vibrational mode represents rotation between the SiH_3 and ethene moieties (about the bonding Si-C atom axis). Note that because q_{vib} directly scales the rate constant, any scaling corrections in table 4 scale the rate constant directly by the amount shown.

Table 4: Internal Rotation Scaling Corrections on Internal Rotation Vibrational Mode of H_3Si ---ethene TS at 298.15 K:

Method	Classical Rotation Barrier (kcal/mol)	Truhlar Scale Correction to q_{vib}	Pitzer and Gwinn Scale Correction to q_{vib}
BHandHLYP/6-31G(d)	1.049	0.982	1.173
B3LYP/6-31G(d)	0.978	0.979	1.175

The Truhlar correction (**Truhlar91**) is scaling down the partition function of the internal rotation mode whereas the Pitzer and Gwinn correction (**Pitzer42**) is scaling up the partition function. This discrepancy is easy to explain. The Pitzer and Gwinn correction is generally more accurate and is based on tables of data generated using cosine curves to simulate the PES of internal rotation. The harmonic oscillator partition function tends to slightly underestimate the “true” partition function as the vibrational frequency decreases; this underestimating error reaches a maximum of 15-20 % at a fairly low frequency and then quickly shoots up and diverges towards infinity (**Ayala98**). The Truhlar correction, however, is not very accurate and is of value only to prevent the divergence towards infinity; if the partition function is not diverging the Truhlar correction actually makes the partition function slightly worse! We therefore certainly do not need to employ the Truhlar correction and for the amount of work required to obtain a Pitzer and Gwinn correction (i.e. to calculate an internal rotation barrier) of 1.17 we conclude that the harmonic oscillator partition function is adequate for the internal mode of vibration without further correction for the reaction of SiH_3 radical with ethene.

(e) Comparison of Conventional Transition State Theory and Canonical Variational Transition State Theory for SiH_3 radical reaction with ethene:

In this section, the rate constant of SiH_3 radical with ethene is calculated with CVTST at the BHandHLYP/6-31G(d), B3LYP/6-31G(d), and B3P86/6-31G(d) levels of theory and the results compared with the simpler CTST.

The CVTST transition state is defined as being the part of the MEP that minimizes the rate when the CV transition state E_0 and partition functions are put into the standard CTST rate equation. The MEPs are investigated to only a resolution of 0.05 Å but this is sufficient to get a good approximation of the canonical variational transition state. The additional effort of CVTST is not necessary because the CVTST rates are virtually identical to the CTST rates and hence the conventional transition state (saddle point) is a good location of the MEP to put the TS dividing surface. We therefore expect little dividing surface recrossing at the conventional transition state. We do not use the CVTST approach in later sections.

The CTST and CVTST comparison is summarized in the following table.

Table 5: Comparison of CTST and CVTST kinetics for SiH₃ radical reaction with ethene

Quantity	BHandHLYP/6-31G(d)	B3LYP/6-31G(d)	B3P86/6-31G(d)
$k_{\text{CVTST}} \text{ M}^{-1} \text{ s}^{-1}$	2.01×10^6	9.67×10^6	1.03×10^8
$k_{\text{CTST}} \text{ M}^{-1} \text{ s}^{-1}$	2.01×10^6	9.51×10^6	1.07×10^8
CVTST Quantum Barrier (kcal/mol)	2.89	2.08	0.70
CTST Quantum Barrier (kcal/mol)	2.88	2.07	0.71
CVTST Pre-exponential factor $\text{M}^{-1} \text{ s}^{-1}$	2.64×10^8	3.23×10^8	3.37×10^8
CTST Pre-exponential factor $\text{M}^{-1} \text{ s}^{-1}$	2.57×10^8	3.13×10^8	3.52×10^8
CVTST Si-C bond length (Angstroms)	2.70	2.75	2.80
CTST Si-C bond length (Angstroms)	2.69	2.73	2.82

In summary, it has been found that the BHandHLYP/6-31G(d) is by far the best DFT method for following the reaction MEP of SiH₃ radical with ethene as compared to our

target high level of theory QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ. The literature classical barrier and activation energy (4.31 and 6.46 kcal/mol respectively (**Bottoni97**)) are serious overestimations of what our highest level method QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ predicts to 1.63 and 3.34 kcal/mol respectively. The literature kinetics rate constant appears reasonable but the A-factor and activation energy ($6 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ and 6 kcal/mol) were guesses (**Loh90**) that appear largely incorrect by comparison to the A-factor and activation energy predicted by QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ to be $3.81 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and 3.34 kcal/mol (or in comparison to the BHandHLYP/6-31G(d) results). The harmonic oscillator model has been shown to be appropriate for description of the internal rotational mode of the H_3Si ---ethene at $T = 298.15 \text{ K}$. Canonical variational transition state theory was shown to not significantly improve the conventional transition state rates and so conventional transition state theory appears to be an appropriate model for the reaction of SiH_3 radical with ethene.

(ii) **System 2: CH_3 radical addition to ethene reaction**

In this section, the following are considered: (a) minimum energy path, (b) basis set effects, and (c) kinetics.

The transition state of this system is geometrically very similar to the SiH_3 radical + ethene TS. The shape of the TS is shown below (at the BHandHLYP/6-31G(d) level of theory):

Figure 13: The CH₃ radical + ethene conventional transition state:

This transition state is 24-fold degenerate (instead of 12-fold like SiH₃ radical + ethene TS) because the CH₃ reacting fragment is actually a planar radical instead of trigonal pyramidal like the SiH₃ radical. The angle of approach of ethene to the CH₃ radical is slightly different than it was for the SiH₃ radical.

(a) Minimum Energy Path:

To the best of our knowledge, the minimum energy path of this system has not been published in the literature either; however it is reported that the experimental activation energy is 7.36 kcal/mol (**Fischer01**) and the highest level of theory available for the activation energy is QCISD(T)/6-311+G(d,p)//B3LYP/6-31G(d) (**Fischer01**) which predicts an activation energy of 7.17 kcal/mol. We use the high level “target” method for studying the SiH₃ radical + ethene reaction path, QCISD(T)/aug-cc-pVTZ//QCISD/aug-

cc-pVDZ, to investigate the CH_3 radical + ethene MEP and to test whether the literature theoretical and experimental activation energies are reasonable.

Figure 14: The CH_3 radical + ethene MEP at QCISD(T)/aug-cc-pVTZ energies with various geometries:

There is some difference in the QCISD(T)/aug-cc-pVTZ relative energies depending on which geometry method is used. The QCISD geometries with the larger basis sets, aug-cc-pVDZ and 6-311+G(d,p), produce nearly identical QCISD(T)/aug-cc-pVTZ energies whereas the QCISD/6-31G(d) and BHandHLYP/6-31G(d) geometries result in somewhat lower single point energies along the MEP. We now plot QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ energies versus some lower levels of theory to try and find a cheap method for computing energies along the CH_3 radical + ethene MEP. Our “target”

classical barrier is therefore roughly 6 kcal/mol and is between 2.25 and 2.30 Angstroms of frozen C(methyl)–C(ethene) bond length.

Figure 15: CH₃ radical + ethene MEP for various levels of theory.

In figure 15 it is apparent that many of the trends observed for the SiH₃ + ethene MEP occur as well for the CH₃ + ethene MEP. For example, BHandHLYP/6-31G(d) follows the MEP very closely to the target and appears to be a very good method for this reaction. B1LYP/6-31G(d), B3LYP/6-31G(d), and B3P86/6-31G(d) underestimate energies along the MEP with B3P86/6-31G(d) seriously underestimating the energies. Also, QCISD methods overestimate the MEP energies with overestimation increasing as basis set decreases in size. Other DFT and correlated *ab initio* methods that were tested were in significant error as compared to our target QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ. Therefore, as was the case for SiH₃ radical + ethene, the DFT method

BHandHLYP/6-31G(d) is a low cost and high accuracy method for predicting energies along the CH_3 radical + ethene MEP.

(b) Basis Set effects along the MEP:

The basis set effects are very similar for the CH_3 radical + ethene system as for the SiH_3 + ethene system. Correlated *ab initio* MEP energies become lower with increasing basis set whereas DFT MEP energies increase with increasing basis set size. The increase in MEP energies for correlated *ab initio* can be seen for the QCISD method in figure 15 and below for the BHandHLYP DFT method.

Figure 16: Basis set effects (kcal/mol) along the CH_3 radical + ethene MEP.:

Increasing the BHandHLYP basis set raises the MEP energy for the CH₃ radical + ethene reaction; this effect is seen for all tested DFT methods (Appendix C). Therefore, the quality of the MEP as compared to our target decreases if one increases the BHandHLYP basis set size from 6-31G(d) because the energies become overestimated. However, for a DFT method that underestimates the MEP energies such as B3P86/6-31G(d), the quality of the MEP energies improve for larger basis sets. It is fortunate that the BHandHLYP/6-31G(d) method gives the best DFT energies along the MEP since the method is very computationally efficient and can therefore be applied to much larger systems. It has been previously found (**Barone95, Durant96, Truong94, Truong95**) that the BHandHLYP/6-31G(d) method is excellent for the CH₃ radical + ethene transition state classical energy and for some other reacting systems (**Knyazev03, Li04a, Li04b, Nguyen04**); however, the authors of **Barone95** instead recommended B3LYP with larger basis sets (since this raises the MEP energies) because they were unsure whether the BHandHLYP/6-31G(d) method would be robust with its medium-sized basis set. Because we are interested in calculating transition state energies for large systems, we instead will recommend BHandHLYP/6-31G(d) as the method appears to be robust along the reaction MEP and because it will be efficient for large system calculations. Following is a summary table of reaction barrier data for the CH₃ radical + ethene addition reaction. The data for QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ, QCISD/aug-cc-pVDZ, and QCISD/6-311+G(d,p) levels of theory was obtained from a spline fit of 0.05 Å resolution MEP data with the program Microcal Origin.

Table 6: Summary of Transition State Data for reaction of CH₃ radical with ethene

at 298.15 K:

Method	Classical Barrier, E _c (kcal/mol)	Quantum Barrier, E ₀ (kcal/mol)	Activation Energy, E _a (kcal/mol)	C(methyl- C(ethene) TS Bond Length (Angstroms)
QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ	5.97	8.25	8.25	2.29
QCISD/aug-cc-pVDZ	6.84	9.12	9.12	2.29
QCISD/6-311+G(d,p)	8.48	10.91	10.90	2.28
QCISD/6-31G(d)	8.82	11.35	11.29	2.27
BHandHLYP/6-31G(d)	5.94	8.26	8.23	2.31
B1LYP/6-31G(d)	5.01	7.28	7.31	2.35
B3LYP/6-31G(d)	4.38	6.61	6.67	2.36
B3P86/6-31G(d)	3.19	5.27	5.40	2.40

BHandHLYP/6-31G(d) data is by far the best in comparison to our target method

QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ.

(c) Kinetics of the CH₃ radical + ethene addition reaction:

We now compare our theoretical kinetics with the most recent gas phase experimental kinetics. Fischer and Radom (**Fischer01**) recommend the following kinetic parameters for T = 298.15 K: $k = 8.50 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, A-factor = $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and $E_a = 7.36 \text{ kcal/mol}$.

We will use the method QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ as our theoretical target and to assess the quality of the parameters of Fischer and Radom.

Table 7: Kinetics data for the reaction of CH₃ radical with ethene at 298.15 K:

Method	Rate Constant, $k \text{ M}^{-1}\text{s}^{-1}$	$A_{\text{CTST}} \text{ M}^{-1}\text{s}^{-1}$	Quantum Barrier, $E_0 \text{ (kcal/mol)}$	A-factor $\text{M}^{-1}\text{s}^{-1}$	Activation Energy, E_a (kcal/mol)
QCISD(T)/aug-cc- pVTZ//QCISD/aug-cc- pVDZ	5.12×10^2	5.68×10^8	8.25	5.68×10^8	8.25
BHandHLYP/6-31G*	5.75×10^2	6.52×10^8	8.26	6.20×10^8	8.23
B1LYP/6-31G*	3.37×10^3	7.30×10^8	7.28	7.70×10^8	7.31
B3LYP/6-31G*	1.10×10^4	7.73×10^8	6.61	8.53×10^8	6.67
B3P86/6-31G*	1.23×10^5	8.95×10^8	5.27	1.10×10^9	5.40
Experimental (Fischer01)	8.50×10^2			2×10^8	7.36

BHandHLYP/6-31G(d) is the method that gives the best rate, A-factor, and activation energy in comparison to our theoretical target and the data are in very good agreement.

BHandHLYP/6-31G(d) gives also the best rate in comparison to experiment but

B1LYP/6-31G(d) gives the best activation energy, according to table 7. However,

Fischer and Radom (**Fischer01**) speculate that the experimental activation energy in table

7 is slightly too low and in fact offer a revision of *8.01 kcal/mol* as being in their opinion

a better estimate of E_a . If we accept their revision of 8.01 kcal/mol then BHandHLYP/6-

31G(d) is also the DFT method in best agreement with experiment for activation energy.

For the theoretical methods, one may notice that the A-factors decrease somewhat as

activation energy (or quantum barrier) increases. This is mostly due to the fact that for

methods that more significantly underestimate the activation energy, the “flatter” the

energy valley will be in the transition state region. This flatter MEP results in lower

frequencies for the five TS transitional vibrational modes and this in turn causes the vibrational partition function and consequently the A-factor to increase somewhat.

Since BHandHLYP/6-31G(d) is in such good agreement with our target theory method and experiment for the CH₃ radical + ethene reaction we again recommend it as the best DFT approach for studying this reacting system.

The internal rotation transitional mode for the TS has an internal rotation barrier of approximately 3 kcal/mol which is much higher than the barrier for SiH₃ radical + ethene (approximately 1 kcal/mol). Therefore, at 298.15 K, the internal rotation mode is well described by the harmonic oscillator model and no internal rotation treatment is needed; this was verified by running a few test calculations which resulted in a Truhlar model scale correction of 0.932 and a Pitzer and Gwinn correction of 1.125 at the BHandHLYP/6-31G(d) level of theory and T = 298.15 K.

(iii) **System 3: SiMe₃ radical addition to ethene reaction:**

In this section we present data on (a) the minimum energy path and (b) kinetics.

There is no known literature source for theoretical barriers or kinetics for this system; however there is a recent experimental gas phase work (Arthur02) which in fact laments the lack of theoretical data available. We first calculate the MEP for the system and then theoretical kinetics for comparison to Arthur and Potzinger's experimental data (Arthur02). A view of the transition state is provided at BHandHLYP/6-31G(d) level of theory; there is one conformer which is 12-fold degenerate.

Figure 17: The Me₃Si radical + ethene transition state:

(a) Minimum Energy Path:

This system is too large to apply our target computational method of the previous systems, QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ. In fact, the QCISD method and medium-sized basis set 6-31G(d) is about the limit of what can be practically applied to this slightly larger chemical system. The QCISD method seriously overestimates MEP energies if the basis set is not very large and so there will not be a “target” computational method for the Me₃Si radical + ethene system. QCISD/6-31G(d) is expected to provide an upper bound to the true MEP energies.

Figure 18: MEP of Me₃Si radical + ethene reaction:

In figure 18 there are trends similar to those observed for the H₃Si radical and H₃C radical + ethene MEPs; specifically, B3P86/6-31G(d) gives low MEP energies, QCISD/6-31G(d) gives high MEP energies and B3LYP/6-31G(d), B1LYP/6-31G(d), and BHandHLYP/6-31G(d) MEPs are not far separated with BHandHLYP/6-31G(d) giving the highest energies and B3LYP/6-31G(d) energies the lowest of the three. However, there is no method that one should have confidence in given that there is no “target” high level of theory and so we compare the methods of figure 18 with the available experimental kinetics data shown in the following subsection. Barrier data of the SiMe₃ radical + ethene reaction MEP for DFT methods is shown in table 8.

Table 8: MEP Data for the SiMe₃ radical + ethene reaction:

Method	Classical Barrier, E _c (kcal/mol)	Quantum Barrier, E ₀ (kcal/mol)	Activation Energy, E _a (kcal/mol)	Si-C TS Bond Length (Angstroms)
BHandHLYP/6-31G(d)	2.98	3.50	4.33	2.76
B1LYP/6-31G(d)	2.76	3.16	4.11	2.78
B3LYP/6-31G(d)	2.27	2.69	3.65	2.80
B3P86/6-31G(d)	0.75	1.25	2.23	2.86

(b) Kinetics of the SiMe₃ radical + ethene addition reaction:

There are literature kinetics data available for this system in the gas phase (**Arthur02**).

The paper gives upper and lower bounds for both the A-factor and activation energy as,

respectively (at T = 298.15 K): A-factor = $4.27 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ to $1.14 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; E_a =

2.77 to 3.37 kcal/mol. Using these data with the Arrhenius equation, the rate constant

must be in the range of $1.46 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ to $1.07 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. A comparison of this data

with theoretical kinetics data is shown below:

Table 9: Kinetics data for the reaction of SiMe₃ radical with ethene at 298.15 K:

Method	Rate Constant, k $M^{-1}s^{-1}$	$A_{CTST} M^{-1}s^{-1}$	Quantum Barrier, E_0 (kcal/mol)	A-factor $M^{-1}s^{-1}$	Activation Energy, E_a (kcal/mol)
BHandHLYP/6-31G*	1.32×10^5	4.84×10^7	3.50	1.97×10^8	4.33
B1LYP/6-31G*	5.20×10^5	1.08×10^8	3.16	5.38×10^8	4.11
B3LYP/6-31G*	1.18×10^6	1.10×10^8	2.69	5.59×10^8	3.65
B3P86/6-31G*	4.39×10^7	3.62×10^8	1.25	1.90×10^9	2.33
Experimental (Arthur02)	4×10^6			4.27×10^8 - 1.14×10^9	2.77 – 3.37

The experimental rate constant is significantly larger than that of our best method for SiH₃ radical and CH₃ radical + ethene reactions, BHandHLYP/6-31G(d). This is due mostly to BHandHLYP/6-31G(d) predicting a significantly larger activation energy of 4.33 kcal/mol versus 2.77 – 3.37 kcal/mol for the experimental kinetics. This is not a severe overestimation but it is significant. Therefore, BHandHLYP/6-31G(d) is not excellent for the kinetics of this reaction but is adequate. In fact, both B1LYP/6-31G(d) and B3LYP/6-31G(d) overestimate the barrier to reaction for this reaction as well and consequently underestimate the rate constant. Only B3P86/6-31G(d) underestimates the barrier and consequently overestimates the rate.

The MEP for SiMe₃ radical + ethene reaction cannot be evaluated with QCISD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ to provide a better assessment of the quality of the DFT MEPs. It is possible that the activation energy overestimation of the DFTs is a result of poor accounting of intermolecular non-bonding interactions such as those of the methyl groups on SiMe₃ and the ethene fragment. There is some evidence of this given that the change in classical barrier height in going from SiH₃ radical to SiMe₃ radical + ethene is

greater for the DFT methods than for the correlated *ab initio* method QCISD/6-31G(d); some DFT methods are known to overestimate non-bonded repulsions whereas correlated *ab initio* methods are usually significantly more accurate (Tsuzuki01, Johnson04). The changes in classical barrier (ΔE_c) from SiH₃ radical to SiMe₃ radical + ethene are summarized in the following table.

Table 10: Change in classical barrier height from SiH₃ radical to SiMe₃ radical + ethene reacting systems:

Method	Change in classical barrier height (kcal/mol)
QCISD/6-31G*	0.01
BHandHLYP/6-31G*	1.35
B1LYP/6-31G*	1.46
B3LYP/6-31G*	1.44
B3P86/6-31G*	1.38

It is very interesting that the energy hardly changes for QCISD/6-31G(d) yet increases by approximately 1.4 kcal/mol for the DFT methods. If we assume that the change in the QCISD/6-31G(d) is correct and then subtract off 1.34 kcal/mol off of E_a for BHandHLYP/6-31G(d) we end up with an activation energy of 2.99 kcal/mol which would result in a revised rate constant of $1.26 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ which is in much better agreement with experiment.

However, with an effect of only approximately 1 to 1.5 kcal/mol (assuming that the literature activation energy is correct) it would be difficult to determine if the DFT methods (BHandHLYP/6-31G(d) in particular) are really in significant error for the MEP.

We therefore accept that the DFT methods (except B3P86/6-31G(d)) are likely slightly overestimating the activation energy of the reaction of SiMe₃ radical with ethene in the gas phase which causes an underestimation of rate constant of up to 1 order of magnitude.

The internal rotation transitional vibrational mode is not in need of refinement from the harmonic oscillator model for SiMe₃ radical + ethene TS; the internal rotation barrier is ~ 0.8 kcal/mol by BHandHLYP/6-31G(d) and so at 298.15 K the vibration is well approximated by a parabolic PES.

(iv) **System 4: SiEt₃ radical addition to ethene reaction:**

In this section the theoretical kinetics of the two systems SiMe₃ and SiEt₃ radical + ethene are compared using BHandHLYP/6-31G(d).

The SiEt₃ reacting system is significantly more complicated than the SiMe₃ radical + ethene reaction because the SiEt₃ radical has 27 possible conformations. However, out of the 27 conformers there are only 7 nondegenerate forms. Still, computing rates for seven conformers is obviously much more complicated than calculating rates for one conformer as in the SiMe₃ radical case. We therefore investigate the rates on these seven conformers with only BHandHLYP/6-31G(d) and if the rates turn out similar to the SiMe₃ case we will use the simpler SiMe₃ radical as a model for rate calculations of larger olefins for comparison to SiEt₃ + olefin LFP data generated in this thesis' work. We do not expect the kinetics to be significantly different for SiEt₃ radical + ethene case compared to the SiMe₃ case because the same chemical reaction is occurring with

essentially the same substituent effects on the silicon radical and the ethyl groups do not sterically interfere with the reactive approach of ethene to the silicon radical site. For simplicity we assume that SiEt_3 conformers do not change on the timescale of the reactive approach of ethene, therefore any reactant conformer will be the same conformer in the TS. Also, not all of the paths of approach of the ethene radical are identical for some of the SiEt_3 radical conformers, this is illustrated in the following diagram (at BHandHLYP/6-31G(d) level of theory).

Figure 19: One of the seven TS conformers for SiEt_3 radical + ethene reaction.

In figure 19 it can be seen that if the dihedral angle of ethene addition was changed by ± 120 degrees the reaction path would be slightly different than for the illustrated path. However, for simplicity it is assumed that each path of approach is identical and with this

assumption we set the TS degeneracy equal to 12 for each of the seven SiEt₃ radical conformer fragments. Below are the kinetics results for T = 298.15 K for the seven conformers of the SiEt₃ radical + ethene addition; the SiMe₃ radical + ethene system is included for comparison.

Table 11: Kinetics of the SiEt₃ radical + ethene system for T = 298.15 K. Level of theory is BHandHLYP/6-31G(d). SiMe₃ radical + ethene results are included in last row of the table.

Conformer #	k _{CTST} M ⁻¹ s ⁻¹	A _{CTST} M ⁻¹ s ⁻¹	Quantum barrier, E _o (kcal/mol)
1	8.13 x 10 ⁴	4.00 x 10 ⁷	3.67
2	6.30 x 10 ⁴	4.29 x 10 ⁷	3.87
3	2.38 x 10 ⁵	7.14 x 10 ⁷	3.38
4	7.41 x 10 ⁴	3.40 x 10 ⁷	3.63
5	1.16 x 10 ⁵	3.94 x 10 ⁷	3.45
6	1.09 x 10 ⁵	3.61 x 10 ⁷	3.44
7	9.94 x 10 ⁴	3.20 x 10 ⁷	3.42
SiMe ₃ + ethene	1.32 x 10 ⁵	4.84 x 10 ⁷	3.50

The rates, pre-exponential factors and quantum barriers for the seven conformers do not vary seriously and it is apparent that these quantities for SiMe₃ radical + ethene lie somewhere in the middle of the results of the seven SiEt₃ radical conformers. There are two conclusions: (i) The SiEt₃ radical reacting fragment can be replaced with the single conformer SiMe₃ radical fragment for this reaction. (ii) The range of rates for each of the seven conformers spans less than an order of magnitude with the lowest 6.30 x 10⁴ and the highest 2.38 x 10⁵ M⁻¹s⁻¹. Since this range is fairly small we avoid the apparently

unnneeded complexities of doing a conformational analysis on the rates of the SiEt₃ radical + ethene system as could be accomplished with equation 54.

(v) **System 5: CMe₃ radical addition to ethene reaction:**

In this section the theoretical gas phase kinetics are compared to experimental data.

We noticed in our investigation of the SiMe₃ radical + ethene system that the MEP energies with the BHandHLYP/6-31G(d) method, which were so accurate for the small systems SiH₃ and CH₃ radical + ethene addition reactions, appeared to overestimate the MEP energies somewhat. This overestimation is hypothesized to be a result of overestimation of non-bonding steric interactions between the methyl groups of the silyl radical and the ethene fragment.

There are gas phase kinetics data available for the analogous CMe₃ radical + ethene addition reaction (**Fischer01**) and so kinetics calculations were performed on this system as well to see if the BHandHLYP/6-31G(d) activation energy appeared to overestimate the experimental activation energy as well and hence provide further evidence of incorrect treatment of sterics between methyl groups and the ethene fragment.

First we present a figure of the TS of CMe₃ radical + ethene reacting system.

Figure 20: A view of the BHandHLYP/6-31G(d) transition state for CMe₃ radical + ethene addition reaction.

This transition state has only one possible conformer which is 12-fold degenerate. Below is a comparison between the theoretical approaches and the available literature gas phase kinetics data:

Table 12: Theoretical and Experimental kinetics results for the CMe₃ radical + ethene reacting system. Temperature = 298.15 K.

Method	Rate Constant, $k \text{ M}^{-1}\text{s}^{-1}$	$A_{\text{CTST}} \text{ M}^{-1}\text{s}^{-1}$	Quantum Barrier, E_0 (kcal/mol)	A-factor $\text{M}^{-1}\text{s}^{-1}$	Activation Energy, E_a (kcal/mol)
BHandHLYP/6-31G*	2.35	5.16×10^6	8.65	7.36×10^6	8.88
B1LYP/6-31G*	3.05	5.20×10^6	8.50	7.96×10^6	8.75
B3LYP/6-31G*	8.74	5.20×10^6	7.88	8.03×10^6	8.14
B3P86/6-31G*	411	6.09×10^6	5.69	1.02×10^7	6.00
Experimental (Fischer01)	30			2×10^7	7.98

In table 12 we see that indeed the BHandHLYP/6-31G(d) method overestimates the experimental activation energy by approximately 1 kcal/mol and thus the rate constant is approximately 1 order of magnitude too small. The B1LYP/6-31G(d) and B3LYP/6-31G(d) methods also overestimate the activation energies somewhat and thus underestimate the rate constant as well. B3P86/6-31G(d) seriously underestimates the activation energy and overestimates the rate constant. Therefore there is further evidence (in addition to the SiMe₃ radical + ethene case) that the DFT approaches overestimate non-bonded interactions between methyl groups and the ethene fragment in the TS species (Johnson04).

Therefore, we presume that in fact BHandHLYP/6-31G(d) does indeed overestimate MEP energies and consequently the activation energies of the CMe₃ radical + ethene system by approximately 1 kcal/mol. This results in rate constant underestimation of approximately 1 order of magnitude for temperature = 298.15 K.

(vi) A Comparison of Experimental Gas-Phase versus Liquid-Phase kinetics for some small olefins adding to carbon-centered radicals.

We are about to move on to comparison and analysis of theoretical gas-phase kinetics and LFP liquid-phase kinetics for large (20-90 atoms in TS) silyl radical + olefin reacting systems. Before doing so, it may be useful to illustrate typical differences in experimental kinetics for analogous smaller systems involving carbon-centered radicals and olefins (no gas-phase experimental kinetics data is available for large systems due partly to difficulty in making large molecules leave the condensed phase for temperatures ~ 300 K). The following data is from Fischer and Radom's review article (**Fischer01**):

Table 13: Gas-Phase versus Liquid-Phase kinetics for small carbon-centered radicals adding to small olefins. Temperature is 298.15 K.. Data is from (Fischer01).

Reaction	$k_{\text{gas}} \text{ M}^{-1}\text{s}^{-1}$	$k_{\text{liquid}} \text{ M}^{-1}\text{s}^{-1}$	$k_{\text{liquid}}/k_{\text{gas}}$
CH ₃ radical + ethene	850	7000	8.2
CH ₃ radical + 1-propene	500	4300	8.6
CH ₃ radical + 1-butene	530	7600	14.0
CH ₃ radical + isobutene	1400	8500	6.1
CH ₃ radical + fluoroethene	560	4600	8.2
CMe ₃ radical + ethene	30	2500	83.0

In table 13 the rate constants in liquid solution are always higher than the rate constants in the gas phase, typically by approximately 1 order of magnitude. The rate is much faster

in liquid solution than gas phase for the CMe_3 radical adding to ethene and the ratio for this reaction is closer to two orders of magnitude. These ratios are fairly consistent with our ratio prediction of approximately 20 from equation 56 of the theory section. Armed with this rate ratio intuition, we move on to analysis of kinetics of larger systems in the gas (theoretical kinetics) and liquid (experimental kinetics) phases.

(vii) Theoretical Gas Phase Kinetics for larger silicon radicals and olefins using DFT approaches.

The systems considered in this section include every combination of the silicon radicals SiH_3 , SiMe_3 , and $\text{Si}(\text{SiMe}_3)_3$ reacting with the olefins ethene, 1-hexene, 1-decene, 1-pentadecene, styrene, and 1,1-diphenylethylene at the BHandHLYP/6-31G(d) level of theory. All of the silicon centered radicals exist in only one possible conformer. A picture of the $\text{Si}(\text{SiMe}_3)_3$ radical is shown below for BHandHLYP/6-31G(d) geometry; the symmetry point group is C_3 .

Figure 21: The $\text{Si}(\text{SiMe}_3)_3$ radical at BHandHLYP/6-31G(d) level of theory.

The olefins ethene, styrene, and 1,1-diphenylethylene only exist in one possible conformer as well. However, the olefins 1-hexene, 1-decene, and 1-pentadecene exist in many possible conformers due to their long hydrocarbon chain tails. We do not expect the kinetics of these various conformers to be significantly different than that of the most stable “straight chain” conformer since the conformers of the tail portion are unlikely to sterically hinder the reaction appreciably at the $\text{C}=\text{C}$ site at one end of the molecule.

Therefore, for simplicity we assume a single conformer for 1-hexene, 1-decene, and 1-pentadecene and the straight-chain conformer is chosen for the geometries. A picture of the straight-chain conformer of 1-pentadecene is shown below.

Figure 22: The “straight chain” pentadecene conformer at BHandHLYP/6-31G(d) level of theory.

and in the next figure it is shown how the transition state of the $\text{Si}(\text{SiMe}_3)$ radical + pentadecene reaction appears.

Figure 23: The transition state of the $\text{Si}(\text{SiMe}_3)_3$ radical + “straight chain” pentadecene conformer at BHandHLYP/6-31G(d) level of theory.

The kinetics of all reactions are presented in the following table.

Table 14: Theoretical kinetics data for silyl radical addition reactions to olefins at**BHandHLYP/6-31G(d) level of theory. Temperature is 298.15 K.**

System	$k_{\text{CTST}} (1/(M \cdot s))$	$A_{\text{CTST}} M^{-1} s^{-1}$	Quantum barrier, E_o , (kcal/mol)	A-factor $M^{-1} s^{-1}$	Activation Energy, E_a , (kcal/mol)
H ₃ Si. + ethene	1.02×10^6	2.57×10^8	2.88	5.05×10^8	3.27
H ₃ Si. + 1-hexene	3.28×10^5	7.83×10^7	3.24	2.32×10^8	3.89
H ₃ Si. + 1-decene	3.96×10^5	8.54×10^7	3.18	2.64×10^8	3.85
H ₃ Si. + 1-pentadecene	4.24×10^5	8.54×10^7	3.14	2.72×10^8	3.83
H ₃ Si. + styrene	3.33×10^6	1.41×10^7	0.86	5.06×10^7	1.61
H ₃ Si. + 1,1-diphenylethylene	1.02×10^7	6.69×10^7	1.11	3.22×10^8	2.04
Me ₃ Si. + ethene	1.38×10^5	4.96×10^7	3.49	2.04×10^8	4.33
Me ₃ Si. + 1-hexene	3.85×10^4	1.50×10^7	3.53	1.22×10^8	4.78
Me ₃ Si. + 1-decene	5.08×10^4	1.73×10^7	3.46	1.52×10^8	4.74
Me ₃ Si. + 1-pentadecene	2.06×10^4	6.77×10^6	3.43	5.73×10^7	4.70
Me ₃ Si. + styrene	6.18×10^5	5.00×10^6	1.24	3.79×10^7	2.44
Me ₃ Si. + 1,1-diphenylethylene	1.06×10^6	9.81×10^6	1.32	1.01×10^8	2.70
(Me ₃ Si) ₃ Si. + ethene	3.34×10^2	5.50×10^6	5.75	2.29×10^7	6.60
(Me ₃ Si) ₃ Si. + 1-hexene	55.8	9.38×10^5	5.76	8.06×10^6	7.04
(Me ₃ Si) ₃ Si. + 1-decene	27.7	4.89×10^5	5.79	4.19×10^6	7.07
(Me ₃ Si) ₃ Si. + 1-pentadecene	9.17	1.64×10^5	5.80	1.26×10^6	7.01
(Me ₃ Si) ₃ Si. + styrene	1.49×10^3	1.24×10^5	2.62	9.79×10^5	3.85
(Me ₃ Si) ₃ Si. + 1,1-diphenylethylene	1.13×10^3	8.63×10^4	2.57	7.86×10^5	3.88

For any particular olefin, the activation energy and quantum barrier increase as the size of the silicon radical increases; the increase is close to 1 kcal/mol for going from SiH₃ to SiMe₃ radical and roughly 3 kcal/mol for going from SiH₃ to Si(SiMe₃)₃ radical.

Therefore the rates are expected to slow down significantly for the larger silicon radicals and this is in fact what occurs.

There are interesting trends that are apparent if one instead considers how the activation energy changes with olefin for a particular silicon radical.

For any silicon radical, the activation energies (and quantum barriers) of 1-hexene, 1-decene, and 1-pentadecene are the largest and almost equal to each other.

The ethene activation energies and quantum barriers are somewhat lower than the other 1-ene olefins presumably due to lowered steric interaction between the fragments in the TS; this lowering is on the order of 0.3-0.5 kcal/mol for each silicon radical (closer to 0.3 for $\text{Si}(\text{SiMe}_3)_3$ radical and closer to 0.5 kcal/mol for SiH_3 radical).

The olefins with the lowest activation energies are styrene and 1,1-diphenylethylene; these data are 2-4 kcal/mol lower than the other olefins and hence we expect and find the fastest rates with these olefins. The transition states of these systems are stabilized by the presence of the conjugating ring(s) and hence the lower activation energies and faster rates.

There is also a trend with the magnitudes of A_{CTST} and A-factors. These decrease with increasing system size and therefore the values near the bottom of table 14 (the larger systems) are a full 2 to 3 orders of magnitude smaller than those at the top of the table (the smaller systems). The potential reasons for this are considered in section ix. Clearly, one cannot assume an A_{CTST} or A-factor for a family of reactions such as silicon-centered radicals adding to olefins to remain constant with increasing system size.

There are no experimental gas phase kinetics data for any of the larger systems, however, and we therefore have no data available for direct comparison and cannot check our DFT results with a higher level theory method.

We therefore resort to the only practical method for evaluating the rates of the larger systems in table 14: experimental kinetics with the laser flash photolysis technique.

(viii) Experimental Liquid Phase Kinetics for larger silyl radicals and olefins using laser flash photolysis.

Equations 57 and 59 were used to obtain the linear relationship between concentration of olefin and observed rate for reactions between SiEt_3 or $\text{Si}(\text{SiMe}_3)_3$ radicals and 1,1-diphenylethylene (DPE), styrene, 1-hexene, 1-decene, or 1-pentadecene. We use the SiEt_3 radical instead of SiMe_3 because SiMe_3 is too volatile and because there are more available literature liquid phase kinetics data involving the SiEt_3 radical for comparison purposes. Least squares analysis was performed on the raw kinetics data with the standard Microsoft Excel "LINEST" routine to obtain the rates and statistical analysis presented in table 15.

Table 15: Experimental kinetics results obtained from laser flash photolysis

experiments with T equal to approximately 298 K. (a) data is from reference

Chatgililoglu83, (b) data is from Ballestri91.

Reacting System	Rate Constant, k $M^{-1} s^{-1}$	Standard Error of k , $M^{-1} s^{-1}$	R-squared of slope (k)	Literature k $M^{-1} s^{-1}$
SiEt ₃ radical and 1-hexene	8.23×10^5	4.09×10^4	0.998	$(4.8 \pm 0.5)^a \times 10^6$
SiEt ₃ radical and 1-decene	1.11×10^6	5.02×10^4	0.998	
SiEt ₃ radical and 1-pentadecene	2.00×10^6	8.33×10^4	0.998	
SiEt ₃ radical and styrene	1.98×10^7	4.34×10^5	1	$(2.2 \pm 0.2)^a \times 10^8$
SiEt ₃ radical and DPE	6.22×10^7	1.17×10^7	0.934	
Si(SiMe ₃) ₃ radical and 1-hexene	2.83×10^5	2.92×10^4	0.989	
Si(SiMe ₃) ₃ radical and 1-decene	3.76×10^5	6.31×10^3	1	
Si(SiMe ₃) ₃ radical and 1-pentadecene	5.31×10^5	1.26×10^5	0.946	
Si(SiMe ₃) ₃ radical and styrene	3.15×10^7	3.05×10^6	0.991	$(5.93 \pm 0.28)^b \times 10^7$
Si(SiMe ₃) ₃ radical and DPE	2.96×10^7	2.57×10^6	0.985	$(1.04 \pm 0.14)^b \times 10^8$

The data in table 15 was obtained in solutions containing 65 % isooctane/hydrocarbon solution and 30 % silane solution by volume; therefore we expect intermolecular interactions to be fairly weak in these solutions since all components are fairly non-polar. So, the chemical environment of the reactants and TS in the liquid phase should be somewhat analogous to a very dense gas.

Keeping this in mind, it is immediately obvious that the experimental LFP liquid phase rates are very different from the gas phase theoretical rates of table 14; they are very much faster! Not surprisingly, for either of the silicon radicals the reactions with the conjugated ring systems 1,1-diphenylethylene or styrene are the fastest and the reactions

with the 1-enes are slower by 1-2 orders of magnitude. However, the rates of the 1-enes show a different trend in the liquid than the theoretical gas phase. The rates increase with increasing size of 1-ene; therefore the rates are faster with 1-pentadecene than 1-decene and faster for 1-decene than with 1-hexene. The opposite is true for the gas phase results of table 14.

The following table lists the ratio of liquid phase experimental kinetics of table 15 to the theoretical gas phase kinetics of table 14, assuming that the rates with SiMe_3 and SiEt_3 radicals should be roughly the same.

Table 16: The ratio of experimental liquid phase kinetics to theoretical gas phase kinetics using the data of tables 15 and 14. BHandHLYP/6-31G(d) was chosen as the theory method and SiMe_3 gas phase kinetics are used for comparison to SiEt_3 liquid phase kinetics.

Reacting System	$k_{\text{liquid}}/k_{\text{gas}}$
SiEt_3 radical and 1-hexene	21
SiEt_3 radical and 1-decene	22
SiEt_3 radical and 1-pentadecene	97
SiEt_3 radical and styrene	32
SiEt_3 radical and DPE	59
$\text{Si}(\text{SiMe}_3)_3$ radical and 1-hexene	5072
$\text{Si}(\text{SiMe}_3)_3$ radical and 1-decene	13574
$\text{Si}(\text{SiMe}_3)_3$ radical and 1-pentadecene	57906
$\text{Si}(\text{SiMe}_3)_3$ radical and styrene	21141
$\text{Si}(\text{SiMe}_3)_3$ radical and DPE	26195

In liquid solution the rates are approximately 1.5 orders of magnitude faster for the SiEt_3 radical reactions and 4.5 orders of magnitude faster for the $\text{Si}(\text{SiMe}_3)_3$ radical reactions. One might be inclined to attribute this great difference in rates to systematic experimental error, but the experimental rates actually agree fairly well with the available literature data.

These ratios of $k_{\text{liquid}}/k_{\text{gas}}$ in table 16 are much greater (especially for the $\text{Si}(\text{SiMe}_3)_3$ radical) than the literature data ratios examined in table 13 for some smaller systems (which ranged mostly from 6 to 14 with the biggest system, CMe_3 radical + ethene having a ratio of 83) and are also much larger than the estimate of 20 from equation 56 of the theory section. We now attempt to explain these differences.

(ix) Analysis of trends in rate data for large systems from theoretical gas phase and experimental liquid phase data.

It is very clear that the theoretical gas phase rate constants are much smaller than the experimental liquid phase rate constants for our larger silicon radical + olefin reacting systems; in fact, the difference in rates seems to increase with increasing system size. We now investigate possible sources of this trend, which is shown graphically for the 1-ene olefins and $\text{Si}(\text{SiMe}_3)_3$ radical below.

Figure 24: Plot of experimental liquid phase kinetics for the reactions of $\text{Si}(\text{SiMe}_3)_3$ radical with 1-hexene, 1-decene, and 1-pentadecene as a function of number of carbon atoms in the olefin (temperature = 298.15 K).

It is apparent that the trend is linear for the three data that are available. We expect and have calculated the activation energies for these three systems to be similar and so the rate differences must be due to differences in A-factors.

Figure 25: Plot of theoretical gas phase kinetics for the reactions of Si(SiMe₃)₃ radical with 1-hexene, 1-decene, and 1-pentadecene as a function of number of carbon atoms in the olefin at BHandHLYP/6-31G(d) level of theory and temperature = 298.15 K.

The trend in figure 25 is not linear if ethene is included but excluding ethene it is almost linear; the ethene point likely does not fit in due to the reaction having a much smaller activation energy (~ 6.60 kcal/mol) than the larger olefins (~ 7.0 to 7.1 kcal/mol).

Firstly, it may be possible that the theoretical gas phase rates underestimate the liquid phase rates due to activation energy overestimation. It was indeed noticed that the best theoretical method for predicting the kinetics of SiH₃ and CH₃ radicals adding to ethene, BHandHLYP/6-31G(d), suffered from a slight overestimation (~ 1 kcal/mol) in the activation energy of the larger systems SiMe₃ and CMe₃ radicals adding to ethene. It was hypothesized that this slight overestimation for the larger systems must be due to

overestimation of the steric repulsions of the methyl groups of SiMe_3 and CMe_3 radicals in the transition state because this is all that has changed between the larger and smaller systems. Also, the correlated *ab initio* method QCISD/6-31G(d) predicted *better relative activation energies* for the two smaller and two larger systems. Because it is known that correlated *ab initio* methods tend to account for steric interactions better than many DFT methods (Tsuzuki01,Johnson04) it therefore seems very reasonable that the DFT methods BHandHLYP/6-31G(d), B3LYP/6-31G(d), B1LYP/6-31G(d), and B3P86/6-31G(d) may indeed be overestimating the steric interactions in the SiMe_3 and CMe_3 radical + ethene systems.

For even larger systems such as $\text{Si}(\text{SiMe}_3)_3$ radical adding to olefins, it is therefore possible that there are even greater steric interaction overestimations predicted by the DFT methods BHandHLYP/6-31G(d), B3LYP/6-31G(d), B3P86/6-31G(d) and it certainly would not be presumptuous to assume that the activation energy of BHandHLYP/6-31G(d) is overestimated by at least the ~ 1 kcal/mol as in the case of SiMe_3 radical + ethene reaction. Therefore, it is likely that the rate constants ratios between liquid and gas phase are so large partly due to *overestimated activation energies by BHandHLYP/6-31G(d)*. However, we would like to know if this is the only factor.

We now examine the transition state theory framework in some detail.

The CTST and Arrhenius theory rate equations shows that the rate constant is really equal to the Boltzmann factor of the activation energy (for the Arrhenius equation) or the quantum barrier (for the CTST equation) multiplied by some constant. We can, however, view this from the alternative perspective that the rate constant is equal to the pre-exponential factor (CTST) or the A-factor (Arrhenius theory) multiplied by a scaling

Boltzmann factor which has the limiting forms of 0 (for a very large barrier) and 1 (for a very small barrier). Therefore, *the CTST rate constant can never be larger than the pre-exponential factor and the Arrhenius rate constant can never be larger than the A-factor.*

The forms of the CTST pre-exponential factor and A-factor are shown below:

$$A_{CTST} = \frac{k_B T}{h} \frac{Q_{TS}}{Q_A Q_B} \quad (60)$$

$$A - factor = A_{CTST} e^{\frac{E_a - E_0}{RT}} \quad (52)$$

and we can see that the CTST pre-exponential factor is made up of only three variables: the partition functions of the transition state and the two reactants. Therefore, if the partition function ratio in equation 60 is too large, then the rate constant will be too large by a similar amount (assuming the Boltzmann factor to be roughly correct). If this partition function ratio is too small, then similarly the rate constant will be too small. It is important to notice that if the theoretical A_{CTST} (or A-factor) of a reaction is smaller than the experimental rate constant, then the theoretical rate will by necessity be underestimated because the Boltzmann factor (which ranges from 0 to 1) can only scale the pre-exponential factor (or A-factor) down in size and therefore the rate constant is always $\leq A_{CTST}$ (or A-factor).

We now compare theoretical A-factors and CTST pre-exponential factors with the experimental liquid phase kinetics of our larger systems to see if *the partition function ratio may be contributing to the large disparity between gas phase and liquid phase kinetics.*

Table 17: A comparison of experimental liquid phase kinetics and theoretical gas phase A-factors at BHandHLYP/6-31G(d) level of theory. The A-factors were obtained for the reaction SiMe₃ radical adding to olefins instead of the SiEt₃ radical.

Reacting System	$k_{\text{liquid}} \text{ M}^{-1}\text{s}^{-1}$	A-factor (gas) $\text{M}^{-1}\text{s}^{-1}$
SiEt ₃ radical and DPE	6.22×10^7	1.01×10^8
SiEt ₃ radical and styrene	1.98×10^7	3.79×10^7
SiEt ₃ radical and 1-hexene	8.23×10^5	1.22×10^8
SiEt ₃ radical and 1-decene	1.11×10^6	1.52×10^8
SiEt ₃ radical and 1-pentadecene	2.00×10^6	5.73×10^7
Si(SiMe ₃) ₃ radical and DPE	2.96×10^7	7.86×10^5
Si(SiMe ₃) ₃ radical and styrene	3.15×10^7	9.79×10^5
Si(SiMe ₃) ₃ radical and 1-hexene	2.83×10^5	8.06×10^6
Si(SiMe ₃) ₃ radical and 1-decene	3.76×10^5	4.19×10^6
Si(SiMe ₃) ₃ radical and 1-pentadecene	5.31×10^5	1.26×10^6

The A-factors are equal to the reaction rates if the activation energy equals zero. In table 17 it is therefore clear, especially for the Si(SiMe₃)₃ radical systems reacting with DPE and styrene, that the theoretical A-factors are too small to possibly account for the experimental liquid phase rate constant; it is also clear that the A-factor generally decreases with increasing system size. This is a contradiction to the “chemical intuition” offered in some of the standard review articles of addition reactions (**Fischer01**) where it is assumed that the A-factors stay fairly constant for “families” of reactions (e.g. CH₃ radical adding to 1-enes).

Instead of being only a result of activation energy overestimation, the great difference in gas phase and liquid phase rates for the larger systems (i.e. the Si(SiMe₃)₃ reactions)

must also be largely due to calculated gas phase A-factors being smaller than liquid phase A-factors.

(a) Analysis of the partition function ratios in A_{CTST} .

We now consider the CTST pre-exponential factor in detail to explore causes of the trends in the gas phase and liquid phase data. The following table illustrates the trends in *partition function ratios (i.e. $Q_{TS}/(Q_{reactant1}Q_{reactant2})$ of the theoretical gas phase reactions already presented in table 14.* The translational partition function ratio has not included the volume element in the determination (see equation 30).

Table 18: Partition function ratios (BHandHLYP/6-31G(d)) of the theoretical reactions considered in table 14. Temperature is 298.15 K.

System	Total Ratio M^{-1}	Vibrational Ratio	Rotational Ratio	Translational Ratio M^{-1}
H ₃ Si. + ethene	1.41×10^{-7}	10.3	3.03×10^{-2}	4.50×10^{-7}
H ₃ Si. + 1-hexene	8.58×10^{-8}	76.2	4.77×10^{-3}	2.36×10^{-7}
H ₃ Si. + 1-decene	9.36×10^{-8}	1.27×10^2	3.72×10^{-3}	1.99×10^{-7}
H ₃ Si. + 1-pentadecene	9.36×10^{-8}	1.54×10^2	3.35×10^{-3}	1.81×10^{-7}
H ₃ Si. + styrene	1.55×10^{-8}	15.5	4.60×10^{-3}	2.18×10^{-7}
H ₃ Si. + 1,1-diphenylethylene	7.34×10^{-8}	1.42×10^2	2.76×10^{-3}	1.87×10^{-7}
Me ₃ Si. + ethene	2.72×10^{-8}	68.7	1.42×10^{-3}	2.79×10^{-7}
Me ₃ Si. + 1-hexene	1.64×10^{-8}	1.53×10^3	1.03×10^{-4}	1.04×10^{-7}
Me ₃ Si. + 1-decene	1.90×10^{-8}	4.36×10^3	5.70×10^{-5}	7.65×10^{-8}
Me ₃ Si. + 1-pentadecene	7.43×10^{-9}	2.85×10^3	4.09×10^{-5}	6.37×10^{-8}
Me ₃ Si. + styrene	5.48×10^{-9}	7.71×10^2	7.86×10^{-5}	9.05×10^{-8}
Me ₃ Si. + 1,1-diphenylethylene	1.08×10^{-8}	4.45×10^3	3.56×10^{-5}	6.79×10^{-8}
(Me ₃ Si) ₃ Si. + ethene	3.01×10^{-9}	30.7	4.87×10^{-4}	2.01×10^{-7}
(Me ₃ Si) ₃ Si. + 1-hexene	1.03×10^{-9}	1.30×10^3	1.55×10^{-5}	5.12×10^{-8}
(Me ₃ Si) ₃ Si. + 1-pentadecene	1.79×10^{-10}	2.26×10^3	3.78×10^{-6}	2.10×10^{-8}
(Me ₃ Si) ₃ Si. + styrene	1.36×10^{-10}	3.16×10^2	1.06×10^{-5}	4.06×10^{-8}
(Me ₃ Si) ₃ Si. + 1,1-diphenylethylene	9.47×10^{-11}	1.43×10^3	2.76×10^{-6}	2.39×10^{-8}

In table 18, the partition function ratios from each type of contribution (except for the electronic partition function ratio which is trivially equal to 1 at temperature of 298.15 K) are considered along with the total partition function ratio.

(i) The total partition function ratio:

The *total partition function ratio* decreases by three orders of magnitude from roughly $1.4 \times 10^{-7} \text{ M}^{-1}$ for the smallest system (SiH_3 radical adding to ethene) to roughly $9.5 \times 10^{-11} \text{ M}^{-1}$ for the largest system ($\text{Si}(\text{SiMe}_3)_3$ radical adding to 1,1-diphenylethylene).

(ii) The vibrational partition function ratio:

The vibrational partition function ratios increase slightly from approximately 1.0×10^1 for SiH_3 radical adding to ethene to 1.4×10^3 for $\text{Si}(\text{SiMe}_3)_3$ radical adding to 1,1-diphenylethylene. This increase can be attributed to the fact that the five transitional vibrational modes in the transition state tend to be low in energy and therefore the partition function of the transition state has five additional low modes increasing it compared to the reactant portion of the ratio (the conserved modes). It is worth mentioning that it can be extremely difficult and even impossible in some cases to find the five transitional modes in the transition state with a molecular viewer such as Gaussview (**Gaussian98**), however, and this appears to be due to mode-mode mixing in the normal mode analysis. Specifically, for the small system SiH_3 radical adding to ethene, it is easy to pick out the five transitional modes of the transition state because they are clearly visible but for a large system such as $\text{Si}(\text{SiMe}_3)_3$ radical adding to 1-pentadecene it is very difficult to specifically determine which five modes are transitional, partly because none of them look to be of “pure” transitional source. Had it been possible to separate the transitional and conserved modes in the transition state it

would have been interesting to have shown how the product of the five transitional modes partition functions increased with increasing system size and how the ratio of the 3N-12 conserved mode partition functions changed with increasing molecular size.

(iii) The translational partition function ratio:

The equation for the translational partition function of an ideal gas is the following:

$$q_{trans} = \left[\frac{2\pi(\sum_i m_i)k_B T}{h^2} \right]^{3/2} V \quad (30)$$

It is easy to show for a bimolecular reacting system where one fragment has mass x and the other mass y that the translational partition function ratio is per unit volume (i.e. with volume element scaled out):

$$\frac{q_{trans,TS}}{q_{trans,fragment1}q_{trans,fragment2}} = \frac{(x+y)^{\frac{3}{2}}}{(xy)^{\frac{3}{2}}} \left(\frac{h^2}{2\pi k_B T} \right)^{\frac{3}{2}} \quad (61)$$

and the important thing to notice from equation 61 is that this ratio decreases with increasing system size (specifically mass, since the product of masses x and y increases more quickly than their sum), as we see in the ratio data of table 18.

(iv) The rotational partition function ratio:

The equation for the rotational partition function is:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 I_A k_B T}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_B k_B T}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_C k_B T}{h^2} \right)^{1/2} \quad (31)$$

The rotational partition function ratio decreases the most with increasing system size for the data in table 18. Rotational partition functions are not as simple to compare as translational partition functions because they depend on the mass *and shape* of the molecule since they depend on the principal moments of inertia I_A , I_B , and I_C , of the molecule. However, the moments of inertia along any principal axis tend to behave as follows:

$$I = \xi m L^2 \quad (62)$$

where I is the moment of inertia along the axis, ξ is a proportionality, m is mass for a system with approximately evenly distributed mass, and L is the length of the system along the axis. We can now rationalize why the ratio of rotational partition functions decrease with increasing system size by picking a convenient geometric shape case. A mathematically convenient case is the attachment of solid cylinders at their ends (e.g. approximating a bimolecular reaction between two straight chain hydrocarbon molecules).

Imagine two cylinders of identical shape and mass “reacting” by attaching such that the transition state is a single cylinder with the same radius but twice the length of the two reactants.

The ratio of partition functions of this hypothetical system is:

$$\frac{q_{rot,TS}}{q_{rot,fragment1}q_{rot,fragment2}} = \frac{h^3 \sigma}{\pi^2 (8k_B T)^{\frac{3}{2}}} * \frac{(I_{A,TS} I_{B,TS} I_{C,TS})^{\frac{1}{2}}}{I_{A,fragment1} I_{B,fragment1} I_{C,fragment1}} \quad (63)$$

A cylinder of mass m, radius R, and length L has the following moments of inertia:

$$I_A = \frac{1}{2} m R^2 \quad ; \quad I_B = I_C = \frac{1}{12} m L^2 \quad (64)$$

and, substituting equation 64 into 63:

$$\frac{q_{rot,TS}}{q_{rot,fragment1}q_{rot,fragment2}} = \frac{h^3 \sigma}{\pi^2 (8k_B T)^{\frac{3}{2}}} * \frac{1}{432 m^{\frac{3}{2}} R L^2} \quad (65)$$

and so for our cylinder attachment example, the rotational partition function ratio becomes smaller if m, R, or L increase. For this specific example and for any examples of *shapes of non-linear reacting molecules reacting* in the gas phase, the rotational partition function ratio will tend to decrease with increasing system size. This is consistent with the results of table 18 where there is a decrease in rotational partition

function ratio of four orders of magnitude from the TS of SiH_3 radical reacting with ethene to $\text{Si}(\text{SiMe}_3)_3$ radical adding to 1,1-diphenylethylene.

There is a serious problem with experimentally verifying that gas phase rotational partition function ratios decrease with increasing system size and that is the larger the system becomes, the more difficult it is to perform gas phase kinetics experiments due to the large systems becoming non-volatile. It is worth noting that rotational partition function ratios are not expected to decrease with increasing system size for unimolecular reactions, only for bimolecular reactions.

To summarize this section, it has been shown that the rates for larger systems follow differing trends with increasing molecular sizes depending whether the system is a theoretical gas phase (figure 25) or experimental liquid phase (figure 24). This is mostly due to differences in A-factors in the gas or liquid phases; the theoretical gas phase A-factors can not possibly account for the experimental rates in solution (table 17).

(v) Why are the liquid phase kinetics so much faster than the gas phase kinetics, especially for the larger systems?

A major reason why the theoretical gas phase rates are significantly smaller than the experimental liquid phase rates has been shown to be due to the fact that A-factors appear to be smaller in the gas phase for large reacting systems than in the liquid phase. It is a good assumption that the electronic and vibrational partition functions are almost unchanged in going from the gas phase to liquid phase (**Canepa01**) so we consider the rotational and translational partition functions. It is not straightforward to evaluate

translational and rotational partition functions in solution, unfortunately. Below are *rationalizations* for the surprising trend that A-factors are larger in liquid solutions than in the gas phase for our larger reaction systems (especially the $\text{Si}(\text{SiMe}_3)_3$ radical reactions). To prove the rationalizations is beyond the scope of this thesis.

(a) The Translational Partition Function in the Liquid Phase:

It has been hypothesized that the form of the translational partition function in liquid solution is very similar to that in the gas phase (**Canepa01**):

$$q_{trans} = \left[\frac{2\pi(\sum_i m_i)k_B T}{h^2} \right]^{3/2} v' \quad (66)$$

where the only difference for q_{trans} in liquid is that the volume of the container from the gas phase equation, V , is now not a large box (e.g. 24.4 L/mol for an ideal gas) but is instead replaced by a configurational integral, v' , because now the particle does not translate freely but instead feels the electronic potential of the surrounding solvent and is surrounded by a "cage" of solvent molecules.

The general form of a configurational integral for a single molecule interacting with its environment is (**Hill86, McQuarrie00, Davidson62**):

$$v' = \int_V e^{-\frac{U}{k_B T}} dV \quad (67)$$

where U is the potential of interaction between the molecule and its surroundings. For an ideal gas, $U = 0$ so the Boltzmann factor $e^{-\frac{U}{k_B T}}$ is equal to 1 and the configuration integral is therefore equal to the system volume. If U is not known, equation 67 is impossible to solve but approximations such as the Lennard-Jones-Devonshire (LJD) approximation simplify matters somewhat (Canepa01,Hill86).

In the LJD approximation, the configurational integral equation 67 is simplified to (Canepa01):

$$v' = 4\pi \int_0^g r^2 e^{-\frac{U}{k_B T}} dr \quad (68)$$

where U is now the potential of the molecule in a LJD solution cavity of radius g at a distance r from its equilibrium position. For large reacting molecules in non-polar solvent we expect U and r to not differ greatly and we therefore expect the configurational integral to not change greatly for the two reactants or the TS for our larger systems.

For a reaction in solution, the translational partition function ratios should each be multiplied by a configurational integral to make them dimensionless and then divided by the appropriate volume to ensure that they are reported per unit volume. Thus for a reacting system in liquid solution where one reacting fragment has mass x and the other mass y :

$$\frac{q_{trans,TS}}{q_{trans,fragment1} * q_{trans,fragment2}} = \frac{(x+y)^{\frac{3}{2}}}{(xy)^{\frac{3}{2}}} * \left(\frac{h^2}{2\pi k_B T} \right)^{\frac{3}{2}} * \frac{v_{TS}}{ev_A v_B} * \frac{V_{m,A} V_{m,B}}{V_{m,TS}} \quad (69)$$

where the part of equation (69) in red illustrates what is not in the gas phase ratio.

Based on the argument following equation 68 we expect the configurational integral ratio

in equation 69 to be equal to approximately $\frac{1}{4\pi e}$ ($\sim \frac{1}{34}$). The molar volume ratio in

equation 69 can be approximated simply as well. If one of the reacting fragments is much

smaller than the other, the molar volume of the TS is approximately equal to that of the

larger reactant and the molar volume ratio of equation 69 will be approximately equal to

the inverse molar volume of the small reactant. If the two reacting fragments are of

similar sizes, then the molar volume ratio in equation 69 will be somewhat larger.

However, in both limiting cases, the molar volume ratio will be much smaller than 24.4

M⁻¹ as was the case for an ideal gas, because the molar volumes of liquids are 2-3 orders

of magnitude smaller.

Therefore, the translational partition function ratio should be significantly smaller in the

liquid phase than the gas phase. From equation 69 it is apparent that the configurational

integral ratio should lower the gas phase translational partition function ratio by

approximately $\frac{1}{4\pi e}$ and the molar volume ratio should be substantially (2-3 orders of

magnitude) smaller than the gas phase value of 24.4 M⁻¹.

The liquid phase corrections to the translational partition function therefore cannot

explain why A-factors and rates in solution are larger than calculated in the gas phase.

(b) The Rotational Partition Function in the Liquid Phase:

The rotational partition function in the liquid phase is likely to be smaller for big, bulky molecules than in the gas phase due to solvent friction significantly reducing the number of rotational states available to the molecule. In fact, it has been postulated (**Canepa01**, **McLaughlin66**) that the rotational partition function in a liquid is equal to the following:

$$q_{rot,liquid} = q_{rot,gas} e^{\frac{-U_l}{k_B T}} + q_{rot,hin} (1 - e^{\frac{-U_l}{k_B T}}) \quad (70)$$

where $q_{rot,gas}$ is the usual gas phase “free” rotational partition function (equation 31), $q_{rot,hin}$ is the partition function of a hindered rotor which may be represented as libration (“vibration”, with respect to solvent, around the molecule’s three principle axes of rotation) in a harmonic potential (**Canepa01** equation 23) and U_l represents the barrier to rotation of the molecule in its liquid cavity. Therefore, in its limiting forms, the rotational partition function of a liquid approaches that of the gas phase if U_l is small and approaches that of a librating harmonic oscillator if U_l is large. It is very difficult to determine barriers to rotation of a molecule about its principal axes in solution (**Canepa01**) and this has not been attempted in this work.

It is useful, however, to investigate the implications of the limiting forms of equation 70 on the rotational partition function ratios in table 18, especially as a function of molecular “size”. For example, small and symmetric molecules such as methane or ethene are

unlikely to experience significant barrier to rotation in solution and therefore their rotational partition functions likely are of the form $q_{rot,liquid} \cong q_{rot,gas}$. A large cylindrical molecule like 1-pentadecene is more interesting. In its straight chain form conformer it is well approximated by the geometry of a long solid cylinder. This molecule can likely rotate freely along the axis passing through the circles along the end of the cylinder and so for that principal moment of inertia, $q_{rot,liquid} \cong q_{rot,gas}$. However, the two other axes of rotation (with 1-pentadecene “tumbling”) are bound to be hindered by a large barrier and so for these two axes, $q_{rot,liquid} \cong q_{rot,hin}$. Therefore, the rotational partition function of the 1-pentadecene molecule is likely to be *greatly reduced in the liquid phase as compared to gas phase because two free rotations have effectively become solvent “vibrations” (librations)*. There are many more thermally accessible states for a molecule freely rotating than for a molecule librating in a system exerting significant barrier to movement and this explains why the rotational partition function decreases in solution as compared to the gas phase; there are simply many fewer thermally accessible rotational states available.

The straight chain conformer of 1-pentadecene (or 1-hexene, or 1-decene) was convenient to consider because its symmetry is similar to a cylinder; however, we expect that any larger molecule will experience greater solvent friction (and hence larger barriers to rotation) than smaller molecules of similar shape in solution and so we expect the gas phase free rotation partition function to be a less and less adequate representation of the rotational partition function of a molecule in liquid as the molecular size and solvent friction increases.

If each component of the rotational partition function ratio

$$\frac{q_{rot,TS}}{q_{rot,fragment1}q_{rot,fragment2}} \quad (71)$$

decreases as molecular size increases due to increasing solvent friction then we expect that the ratio itself will not decrease as much (or even necessarily decrease at all) in liquid solution. Therefore, the dramatic lowering of the gas phase rotational partition function ratios in table 18 (and consequently the dramatic lowering of gas phase rates) with increasing system size is not expected to occur in the liquid phase.

It has been shown that the calculated A-factors are much smaller in the gas phase than liquid phase for the reactions of our larger systems. This difference can only be explained by differences in rotational partition functions in the gas versus liquid state.

(x) Summarizing Remarks:

It has been shown in this project that the BHandHLYP/6-31G(d) electronic structure theory method is an efficient and accurate method for determining the minimum energy reaction path and kinetics for SiH₃ and CH₃ radicals adding to ethene. The conventional transition state theory framework was shown to give rates of reaction essentially identical to the more complicated canonical variational transition state theory framework for the SiH₃ radical + ethene system. Hindered internal rotation vibrational modes were shown to be well approximated by the harmonic oscillator model for temperature = 298.15 K.

For the larger systems SiMe_3 and CMe_3 radicals adding to ethene, the BHandHLYP/6-31G(d) method appears to slightly overestimate (~ 1 kcal/mol) the activation energies due to incorrect treatment of steric interactions between the methyl groups and ethene in the transition state. This overestimation is not too serious, however, and the BHandHLYP/6-31G(d) method is therefore adequate for studying these systems.

For larger systems it was found that the gas phase theoretical CTST pre-exponential factors (A_{CTST}), A-factors and rate constants decreased with increasing system size. Little is mentioned in the literature about decreasing theoretical gas phase A-factors with increasing system size, however (except for the trivial cases of diatomic reactions versus bimolecular reactions (**Johnston66, Laidler87**)), and it is possible that this is not a widely known fact because there have been few gas phase theoretical transition state or experimental kinetics studies on systems larger than 15-20 atoms in the literature.

It was shown that the major factor in decreasing the theoretical gas phase A-factors with increasing system size was the rotational partition function ratio.

Due to the lack of available theoretical or experimental literature data for the larger gas phase systems, liquid phase laser flash photolysis kinetics experiments were performed.

Gas phase studies would have been preferable to directly compare with the theoretical gas phase reaction rates but unfortunately such experiments posed serious technical difficulties such as volatilizing large molecules in sufficient quantities to be able to measure a gas phase reaction rate.

The experimental rate constants of larger systems in solution turned out to be much, much faster than the theoretical gas phase rates. In fact, the rates in solution generally

increased with increasing system size which is the opposite trend for the gas phase kinetics.

An attempt to rationalize these trends was made by analysing how partition functions should change from the gas to liquid phase.

Electronic and vibrational partition functions should not differ appreciably in the gas and liquid phases. Rotational and translational partition functions may differ, however.

It was shown that the trend of decreasing rotational partition function ratio with increasing system size in the gas phase does not likely exist in the liquid phase where solvent friction dramatically reduces the abilities of larger molecules to rotate. Therefore, the rotational partition function ratio does not necessarily decrease so dramatically with increasing molecule size in the liquid phase and *may even increase*, offering an explanation as to why the rates of liquid phase systems increase as system size increases.

The translational partition function ratio was shown to decrease in the liquid phase and therefore it cannot account for the fact that A-factors are larger in solution for larger reacting systems.

The goal was to find a theoretical method capable of accurately predicting the rates of reactions between silicon centered radicals and olefins. BHandHLYP/6-31G(d) does in fact appear to be a suitable method for estimating the rates of these systems and due to its accuracy and efficiency for calculations on gas phase kinetics it is the recommended method. We extrapolate that because the BHandHLYP/6-31G(d) method works well for small systems (where there is literature experimental data and high-level theory available for comparison) there is no reason to assume that it does not work well for larger gas

phase systems (where there is no available experimental data or high-level theory for comparison).

As a by-product of this study we have learned that one cannot necessarily run a gas phase rate constant calculation and get a good approximation for a liquid phase rate constant.

With computing power constantly increasing and computational chemists gaining the ability to theoretically study systems of ever increasing size with accurate quantum mechanical methods, it is important that this divergence of theoretical gas phase and experimental liquid phase kinetics has been observed in this work.

Future research will establish why exactly there is a divergence in gas phase and liquid phase rates for larger systems by more rigorously analysing how partition functions differ in the gas and liquid phases.

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Appendix A: A Fortran 90 Program for Evaluating Internal Rotation Corrections to Vibrational Partition

Functions.

```
! Q_hin_zpe.f90 | Written by Owen J. Clarkin, May 31 2003

! This program will use the procedures from Chuang and Truhlar's paper
! (Journal of Chemical Physics, Vol. 112, # 3, pages 1221-1228, 2000.)
! to determine Q_hin_zpe for the torsional mode of several molecules.
! The paper uses the bottom of the PES for determination of Q, not the ZPE.
! My procedure follows "scheme 1" from the paper (see page 1222).

! This code has been checked against the Truhlar model's results in
! JCP 112, 1221-1228, 2000 and gives the same results.

! The method uses scheme #1 (of five possibilities) from the Truhlar paper
! to obtain the value of the reduced moment of inertia and thus Q_fr. Scheme 1
! determines I indirectly from the torsional harmonic frequency and barrier
! height. The other four schemes determine I directly and either Vo or nu
! indirectly.

PROGRAM Q_hin_zpe

IMPLICIT NONE

DOUBLE PRECISION :: h, nu, c, k, T, Qvib_hoq, c_J, Na, pi, Vo, P, M
DOUBLE PRECISION :: Q_hin_truh, Q_fr, Qvib_hocl, I, I_me_ao, I_amu_Ang
DOUBLE PRECISION :: ao, me, amu, Angstrom, p_a, p_b, p_c, p_d, p_e
DOUBLE PRECISION :: p_f, p_g, q_a, q_b, q_c, q_d, q_e, q_f, q_g, q_h, q_i
DOUBLE PRECISION :: bessell_mod, Q_hin_pandg, Q_hin_mcclurg, Q_hin_aands
DOUBLE PRECISION :: exe, why

! Fundamental constants from CODATA 1998 recommended values (NIST)

h=6.62606876E-34      ! J*s
k=1.3806503E-23       ! J/K
c=2.99792458E10       ! cm/s
c_J=4.184             ! J/cal
pi=3.141592653589793 ! from HCP (1st student edition)
Na=6.02214199E23      ! mol-1
ao=5.291772083E-11    ! m/ao (Bohr radius)
me=9.10938188E-31     ! kg/me (electron mass)
amu=1.6605402E-27     ! kg/amu (atomic mass unit)
Angstrom=1E-10        ! m/Ang (Angstrom)

! Modified Bessel function polynomial coefficient terms p's and q's follow:

p_a=1.0                !
p_b=3.5156229          !
p_c=3.0899424          !
p_d=1.2067492          ! the p coefficients pertain to -3.75 < x < 3.75 for Io(x)
p_e=0.2659732          ! with an error in this function quoted as < 1.6E-7
p_f=0.0360768          ! (see Abramowitz and Stegun's classic work "Handbook of
p_g=0.0045813          ! Mathematical Functions" from Dover Publishers)
q_a=0.39894228         !
q_b=0.01328592         !
q_c=0.00225319         !
q_d=(-0.00157565)       ! the q coefficients pertain to 3.75 < x --> infinity
q_e=0.00916281         ! for Io(x) with an error in this function quoted as
q_f=(-0.02057706)       ! < 1.9E-7
```

```

q_g=0.02635537      !
q_h=(-0.01647633)   !
q_i=0.00392377      !

WRITE(*,*) "This program calculates hindered rotor partition functions"
WRITE(*,*) "for several types of PESS. See JCP 112 p. 1221, 2000."
WRITE(*,*)
WRITE(*,*) "Please enter the temperature in Kelvin."

READ(*,*) T

WRITE(*,*) "Please enter the torsional frequency (in cm-1)."
```

$$Q_{\text{vib_hoq}} = \frac{1}{(1 - \exp((-h \cdot \nu \cdot c) / (k \cdot T)))}$$

```

READ(*,*) nu

WRITE(*,*) "The Harmonic Vibrational Partition Function (ZPE) is = "
WRITE(*,*) Q_vib_hoq, "for T = ", T, " K."
WRITE(*,*) "Now on to the treatment of the hindered rotor partition function."

WRITE(*,*) "What is the barrier height (in kcal/mol) to internal rotation of"
WRITE(*,*) "your rotor?"

READ(*,*) Vo

WRITE(*,*) "How many minima are there along the torsional PES? (including"
WRITE(*,*) "degenerate cases; e.g. ethane = 3)"

READ(*,*) M

WRITE(*,*) "How many types of equivalent minima are there on the torsional"
WRITE(*,*) "PES? (e.g. ethane = 1; 1,2 dichloroethane = 2)"

READ(*,*) P

! Here we define our Bessel functions for later use in the Pitzer and Gwinn,
! McClurg et al., or Ayala and Schlegel models. The fomula used is valid to
! within roughly E-7 and is described in "Handbook of Mathematical Functions"
! by Abramowitz and Stegun and also in Numerical Recipes.

IF ((ABS((Vo*1E3*c_J)/(2*Na*k*T))).LE.(3.75)) THEN !use the p coefficients
bessel_mod=p_a+p_b*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**2)+ &
& p_c*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**4)+ &
& p_d*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**6)+ &
& p_e*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**8)+ &
& p_f*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**10)+ &
& p_g*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**12)
ELSE IF (((ABS((Vo*1E3*c_J)/(2*Na*k*T))).GT.(3.75)) THEN ! we use the q's
bessel_mod=(EXP(((Vo*1E3*c_J)/(2*Na*k*T)))/(SQRT(((Vo*1E3*c_J)/(2*Na*k*T))))) &
& *(q_a+ &
& q_b*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**(-1))+ &
& q_c*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**(-2))+ &
& (q_d)*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**(-3))+ &
& q_e*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**(-4))+ &
& (q_f)*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**(-5))+ &
& q_g*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**(-6))+ &
& (q_h)*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**(-7))+ &
& q_i*(((Vo*1E3*c_J)/(3.75*2*Na*k*T))**(-8)))
ELSE
WRITE(*,*) "Your Bessel function definition failed!"
END IF

```

```

! End Bessel Function polynomial approximation definition

I=((Vo*c_J*1E3)/(2*Na))*((M/(c*nu*2*pi))**2) !Units J*(s**2) and/or kg*(m**2)

I_me_ao=(1/me)*((1/ao)**2)*I ! Units are me*(ao**2)

I_amu_Ang=(1/amu)*((1/Angstrom)**2)*I ! Units are amu*(Angstrom**2)

Q_fr=((8*(pi**3)*I*k*T*(P**2))/((h*M)**2))**(0.5))

Qvib_hocl=((k*T)/(h*c*nu))

Q_hin_truh=Qvib_hoq*tanh(Q_fr/Qvib_hocl)

Q_hin_pandg=((Qvib_hoq*Q_fr)/Qvib_hocl)*EXP((-
Vo*1E3*c_J)/(2*Na*k*T))*bessel_mod

Q_hin_mcclurg=EXP((((h*((nu*c)))**2)/((2*h*nu*c)+((16*Vo*c_J*1E3)/Na)))/(k*T))*
Q_hin_pandg

exe=1/Q_fr
why=((Vo*1E3*c_J)/(Na*k*T))

Q_hin_aands=((1+((0.067113)*exe+(0.772485)*(exe**2)-(3.0674131)*(exe**3)+ &
& (4.595051)*(exe**4)-(2.101341)*(exe**5)+(0.015800)*(why**(0.5))+ &
& (0.102119)*(exe)*(why**(0.5))-(0.555270)*(exe**2)*(why**(0.5))- &
& (1.125261)*(exe**3)*(why**(0.5))+(0.071884)*(exe**4)* &
& (why**(0.5))-(0.397330)*(why)+(2.284956)*(exe)*(why)+ &
& (0.850046)*(exe**2)*(why)-(0.174240)*(exe**3)*(why)- &
& (0.451875)*(why**1.5))-(2.136226)*(exe)*(why**1.5))+ &
& (0.303469)*(exe**2)*(why**1.5))+(0.470837)*(why**2)+ &
& (0.675898)*(exe)*(why**2)-(0.226287)*(why**2.5))* &
& EXP((-Vo*1E3*c_J)/(2*Na*k*T)))/(1+((0.003235)* &
& (exe)-(0.026252)*(exe**2)+(0.110460)*(exe**3)-(0.203340)* &
& (exe**4)+(0.130633)*(exe**5)-(0.010112)*(why**(0.5))+(0.650122)* &
& (exe)*(why**(0.5))+(0.067112)*(exe**2)*(why**(0.5))+ &
& (0.088807)*(exe**3)*(why**(0.5))-(0.014290)*(exe**4)* &
& (why**(0.5))-(0.364852)*(why)+(0.913073)*(exe)*(why)- &
& (0.021116)*(exe**2)*(why)-(0.092086)*(exe**3)*(why)-(0.415689)* &
& (why**1.5))-(1.128961)*(exe)*(why**1.5))+(0.233009)*(exe**2)* &
& (why**1.5))+(0.421344)*(why**2)+(0.505139)*(exe)*(why**2)- &
& (0.215088)*(why**2.5))*EXP((-Vo*1E3*c_J)/(2*Na*k*T)))*Q_hin_pandg

WRITE(*,*) "The results for this system are as follows (for T =, ",T,"Kelvin."
WRITE(*,*)
WRITE(*,*) "Effective moment of inertia, I, is given below in several units"
WRITE(*,*) "I = ",I,"J*(s**2) and/or kg*(m**2)."
WRITE(*,*) "      ",I_me_ao,"me*(ao**2)."
WRITE(*,*) "      ",I_amu_Ang,"amu*(Angstrom**2)."
WRITE(*,*)
WRITE(*,*) "Canonical Partition Functions for the torsional mode"
WRITE(*,*) "are given below from the zpe of the PES well (ZPE):"
WRITE(*,*)
WRITE(*,*) "Q =",Qvib_hoq,"(quantum harmonic oscillator, HOQ)"
WRITE(*,*) "Q =",Qvib_hocl,"(classical harmonic oscillator, HOCL)"
WRITE(*,*) "Q =",Q_fr,"(free rotor)"
WRITE(*,*)
WRITE(*,*) "Q =",Q_hin_truh," (Truhlar's hindered rotor);"
WRITE(*,*) "and scaled Q_HOQ by",Q_hin_truh/Qvib_hoq,"."
WRITE(*,*)
WRITE(*,*) "Q =",Q_hin_pandg," (Pitzer and Gwinn's hindered rotor);"

```

```
WRITE(*,*) "and scaled Q_HOQ by",Q_hin_pandg/Qvib_hoq, "."
WRITE(*,*)
WRITE(*,*) "Q =",Q_hin_mcclurg," (McClurg et al.'s hindered rotor);"
WRITE(*,*) "and scaled Q_HOQ by",Q_hin_mcclurg/Qvib_hoq, "."
WRITE(*,*)
WRITE(*,*) "Q =",Q_hin_aands," (Ayala and Schlegel's hindered rotor);"
WRITE(*,*) "and scaled Q_HOQ by",Q_hin_aands/Qvib_hoq, "."

END PROGRAM Q_hin_zpe
```

Appendix B: Laser Flash Photolysis Raw Data.

Table B.1: Raw Rate Data for LFP Reactions of Si(SiMe₃)₃ radical with 1,1-diphenylethylene, styrene, 1-hexene, 1-decene, and 1-pentadecene. Observed rate is shown as a function of olefin concentration.

[1,1-diphenylethylene] (M)	k_{obs} s⁻¹
0.01416	2.56 x 10 ⁶
0.02832	2.89 x 10 ⁶
0.0708	3.80 x 10 ⁶
0.1416	6.34 x 10 ⁶
[styrene] (M)	k_{obs} s⁻¹
0.04364	4.00 x 10 ⁶
0.1091	5.56 x 10 ⁶
0.2182	9.41 x 10 ⁶
[1-hexene] (M)	k_{obs} s⁻¹
0.3998	2.18 x 10 ⁶
2.399	2.87 x 10 ⁶
5.198	3.55 x 10 ⁶
[1-decene] (M)	k_{obs} s⁻¹
0.2642	2.26 x 10 ⁶
1.585	2.78 x 10 ⁶
3.434	3.45 x 10 ⁶
[1-pentadecene] (M)	k_{obs} s⁻¹
0.1842	2.45 x 10 ⁶
1.1050	3.19 x 10 ⁶
2.3940	3.65 x 10 ⁶

Table B.2: Raw Rate Data for LFP Reactions of SiEt₃ radical with 1,1-diphenylethylene, styrene, 1-hexene, 1-decene, and 1-pentadecene. Observed rate is shown as a function of olefin concentration.

[1,1-diphenylethylene] (M)	k_{obs} s⁻¹
0.01416	5.59 x 10 ⁶
0.02832	6.56 x 10 ⁶
0.0708	1.10 x 10 ⁷
0.1416	1.34 x 10 ⁷
[styrene] (M)	k_{obs} s⁻¹
0.04364	8.54 x 10 ⁶
0.1091	9.76 x 10 ⁶
0.2182	1.20 x 10 ⁷
[1-hexene] (M)	k_{obs} s⁻¹
0.3998	6.75 x 10 ⁶
2.399	8.22 x 10 ⁶
5.198	1.07 x 10 ⁷
[1-decene] (M)	k_{obs} s⁻¹
0.2642	6.68 x 10 ⁶
1.585	8.29 x 10 ⁶
3.434	1.02 x 10 ⁷
[1-pentadecene] (M)	k_{obs} s⁻¹
0.1842	6.35 x 10 ⁶
1.1050	8.37 x 10 ⁶
2.3940	1.08 x 10 ⁷

Appendix C: Theoretical Rate Data.

Table C.1: Rate Data for a variety of DFT methods and the standard 6-31G(d) basis set for the SiH₃ radical + ethene addition reaction. The methods BHandH, PBEPBE, and PW91PW91 did not locate saddle points along the MEP.

Method	$k_{\text{CTST}} \text{ M}^{-1}\text{s}^{-1}$	$A_{\text{CTST}} \text{ M}^{-1}\text{s}^{-1}$	quantum barrier, E_o (kcal/mol)	A-factor $\text{M}^{-1}\text{s}^{-1}$	activation energy, E_a (kcal/mol)
G96LYP	1.14×10^6	4.95×10^8	3.60	1.32×10^9	4.18
B1LYP	4.08×10^6	2.96×10^8	2.54	6.34×10^8	2.99
BLYP	3.35×10^7	4.20×10^8	1.50	1.07×10^9	2.05
B3LYP	9.51×10^6	3.13×10^8	2.07	6.91×10^8	2.54
BHandHLYP	2.01×10^6	2.57×10^8	2.88	5.06×10^8	3.28
B3P86	1.07×10^8	3.52×10^8	0.71	8.30×10^8	1.21
B3PW91	1.56×10^7	3.19×10^8	1.79	7.19×10^8	2.27
MPW1PW91	5.58×10^7	3.02×10^8	1.00	6.66×10^8	1.47
MPW1K	3.08×10^7	2.68×10^8	1.28	5.48×10^8	1.71
PBE1PBE	1.52×10^8	3.10×10^8	0.42	6.96×10^8	0.90

Table C.2: Rate Data for a variety of ab initio methods and the standard 6-31G(d) basis set for the SiH₃ radical + ethene addition reaction.

Method	$k_{\text{CTST}} \text{ M}^{-1}\text{s}^{-1}$	$A_{\text{CTST}} \text{ M}^{-1}\text{s}^{-1}$	quantum barrier, E_o (kcal/mol)	A-factor $\text{M}^{-1}\text{s}^{-1}$	activation energy, E_a (kcal/mol)
HF	3.42×10^4	2.65×10^8	5.31	5.34×10^8	5.72
MP2	3.77×10^{-1}	1.55×10^8	11.75	2.31×10^8	11.99
PMP2//MP2	2.81×10^3	2.49×10^8	6.75	4.53×10^8	7.10
QCISD	2.74×10^3	1.92×10^8	6.61	3.38×10^8	6.94

Table C.3: Basis Set Effects on the rate of reaction of SiH₃ radical + ethene with the B3LYP functional.

Basis Set	$k_{CTST} \text{ M}^{-1}\text{s}^{-1}$	$A_{CTST} \text{ M}^{-1}\text{s}^{-1}$	$E_o \text{ (kcal/mol)}$
3-21G(d)	9.30×10^7	2.33×10^8	0.54
3-21+G(d)	1.38×10^7	2.95×10^8	1.81
6-31G(d)	9.51×10^6	3.13×10^8	2.07
6-31+G(d)	1.88×10^6	3.74×10^8	3.14
6-311G(d)	2.79×10^6	3.12×10^8	2.80
6-311+G(d)	1.68×10^6	3.47×10^8	3.16
6-311+G(d,p)	1.14×10^6	3.70×10^8	3.43
6-311+G(3df,2p)	1.19×10^6	3.31×10^8	3.33

Table C.4: Basis Set Effects on the rate of reaction of SiH₃ radical + ethene with the B3P86 functional.

Basis Set	$k_{CTST} \text{ M}^{-1}\text{s}^{-1}$	$A_{CTST} \text{ M}^{-1}\text{s}^{-1}$	$E_o \text{ (kcal/mol)}$
3-21G(d)	neg barrier	4.17×10^8	-1.04
3-21+G(d)	2.73×10^8	3.37×10^8	0.12
6-31G(d)	1.07×10^8	3.52×10^8	0.71
6-31+G(d)	2.91×10^7	3.87×10^8	1.53
6-311G(d)	4.98×10^7	3.66×10^8	1.18
6-311+G(d)	3.49×10^7	3.93×10^8	1.44
6-311+G(d,p)	2.26×10^7	4.12×10^8	1.72
6-311+G(3df,2p)	2.80×10^7	3.78×10^8	1.54

Table C.5: Basis Set Effects on the rate of reaction of SiH₃ radical + ethene with the BHandHLYP functional.

Basis Set	$k_{CTST} \text{ M}^{-1}\text{s}^{-1}$	$A_{CTST} \text{ M}^{-1}\text{s}^{-1}$	$E_o \text{ (kcal/mol)}$
3-21G(d)	3.22×10^7	2.01×10^8	1.08
3-21+G(d)	1.35×10^7	7.16×10^8	2.35
6-31G(d)	2.01×10^6	2.57×10^8	2.88
6-31+G(d)	4.14×10^5	2.91×10^8	3.88
6-311G(d)	6.81×10^5	2.57×10^8	3.51
6-311+G(d)	3.92×10^5	2.78×10^8	3.89
6-311+G(d,p)	2.30×10^5	2.92×10^8	4.23
6-311+G(3df,2p)	2.40×10^5	2.61×10^8	4.14

Table C.6: Rate Data for a variety of DFT methods and the standard 6-31G(d) basis set for the CH₃ radical + ethene addition reaction.

Method	k_{CTST} $M^{-1}s^{-1}$	A_{CTST} $M^{-1}s^{-1}$	quantum barrier, E_o (kcal/mol)	A-factor $M^{-1}s^{-1}$	activation energy, E_a (kcal/mol)
G96LYP	2.88×10^3	9.18×10^8	7.51	1.16×10^9	7.65
B1LYP	3.37×10^3	7.30×10^8	7.28	7.70×10^8	7.31
B3LYP	1.10×10^4	7.73×10^8	6.61	8.53×10^8	6.67
BHandHLYP	5.75×10^2	6.52×10^8	8.26	6.20×10^8	8.23
B3P86	1.23×10^5	8.95×10^8	5.27	1.11×10^9	5.40
PBEPBE	7.02×10^6	1.14×10^9	3.02	1.73×10^9	3.26
PBE1PBE	1.34×10^5	8.62×10^8	5.20	1.05×10^9	5.31

Table C.7: Rate Data for a variety of ab initio methods and the standard 6-31G(d) basis set for the CH₃ radical + ethene addition reaction.

Method	k_{CTST} $M^{-1}s^{-1}$	A_{CTST} $M^{-1}s^{-1}$	quantum barrier, E_o (kcal/mol)	A-factor $M^{-1}s^{-1}$	activation energy, E_a (kcal/mol)
HF	1.58	4.82×10^8	11.58	3.49×10^8	11.38
MP2	1.15×10^{-4}	4.89×10^8	17.23	3.82×10^8	17.08
PMP2//MP2	1.57×10^2	4.89×10^8	8.86	3.82×10^8	8.71
QCISD	2.69	5.64×10^8	11.35	5.09×10^8	11.29

Table C.8 Kinetics Data for the larger silicon radical + olefin reacting systems with the DFT methods BHandHLYP/6-31G(d), B3LYP/6-31G(d), and B3P86/6-31G(d).

System	Method	k_{CTST} $M^{-1}s^{-1}$	A_{CTST} $M^{-1}s^{-1}$	Quantum barrier, E_o (kcal/mol)	A-factor $M^{-1}s^{-1}$	E_a , (kcal/mol)
H ₃ Si radical + ethene	BHandHLYP/6-31G*	1.02×10^6	2.57×10^8	2.88	5.05×10^8	3.27
H ₃ Si radical + ethene	B3LYP/6-31G*	9.51×10^6	3.13×10^8	2.07	6.91×10^8	2.54
H ₃ Si radical + ethene	B3P86/6-31G*	1.07×10^8	3.52×10^8	0.71	8.30×10^8	1.21
H ₃ Si radical + 1-hexene	BHandHLYP/6-31G*	3.28×10^5	7.83×10^7	3.24	2.32×10^8	3.89
H ₃ Si radical + 1-hexene	B3LYP/6-31G*	1.68×10^6	8.97×10^7	2.36	2.95×10^8	3.06
H ₃ Si radical + 1-hexene	B3P86/6-31G*	4.02×10^7	1.65×10^8	0.83	6.20×10^8	1.62
H ₃ Si radical + 1-decene	BHandHLYP/6-31G*	3.96×10^5	8.54×10^7	3.18	2.64×10^8	3.85
H ₃ Si radical + 1-decene	B3LYP/6-31G*	2.20×10^6	1.02×10^8	2.28	3.53×10^8	3.01
H ₃ Si radical + 1-decene	B3P86/6-31G*	2.89×10^7	1.17×10^8	0.83	4.31×10^8	1.60

H ₃ Si radical + 1-pentadecene	BHandHLYP/6-31G*	4.24 x 10 ⁵	8.54 x 10 ⁷	3.14	2.72 x 10 ⁸	3.83
H ₃ Si radical + 1-pentadecene	B3LYP/6-31G*	2.77 x 10 ⁶	1.14 x 10 ⁸	2.20	4.11 x 10 ⁸	2.96
H ₃ Si radical + 1-pentadecene	B3P86/6-31G*	3.67 x 10 ⁷	1.28 x 10 ⁸	0.74	4.93 x 10 ⁸	1.54
H ₃ Si radical + styrene	BHandHLYP/6-31G*	3.33 x 10 ⁶	1.41 x 10 ⁷	0.86	5.06 x 10 ⁷	1.61
H ₃ Si radical + styrene	B3LYP/6-31G*	1.50 x 10 ⁸	1.89 x 10 ⁸	0.14	9.29 x 10 ⁸	1.08
H ₃ Si radical + 1,1-diphenylethylene	BHandHLYP/6-31G*	1.02 x 10 ⁷	6.69 x 10 ⁷	1.11	3.22 x 10 ⁸	2.04
H ₃ Si radical + 1,1-diphenylethylene	B3LYP/6-31G*	7.48 x 10 ⁷	1.29 x 10 ⁸	0.32	7.58 x 10 ⁸	1.37
Me ₃ Si radical + ethene	BHandHLYP/6-31G*	1.38 x 10 ⁵	4.96 x 10 ⁷	3.49	2.04 x 10 ⁸	4.33
Me ₃ Si radical + ethene	B3LYP/6-31G*	1.18 x 10 ⁶	1.10 x 10 ⁸	2.69	5.59 x 10 ⁸	3.65
Me ₃ Si radical + ethene	B3P86/6-31G*	4.39 x 10 ⁷	3.62 x 10 ⁸	1.25	1.90 x 10 ⁹	2.23
Me ₃ Si radical + 1-hexene	BHandHLYP/6-31G*	3.85 x 10 ⁴	1.50 x 10 ⁷	3.53	1.22 x 10 ⁸	4.78
Me ₃ Si radical + 1-hexene	B3LYP/6-31G*	1.15 x 10 ⁵	1.38 x 10 ⁷	2.84	1.15 x 10 ⁸	4.09
Me ₃ Si radical + 1-hexene	B3P86/6-31G*	1.16 x 10 ⁶	1.37 x 10 ⁷	1.46	5.01 x 10 ⁷	2.23
Me ₃ Si radical + 1-decene	BHandHLYP/6-31G*	5.08 x 10 ⁴	1.73 x 10 ⁷	3.46	1.52 x 10 ⁸	4.74
Me ₃ Si radical + 1-decene	B3LYP/6-31G*	1.99 x 10 ⁵	1.98 x 10 ⁷	2.72	1.80 x 10 ⁸	4.03
Me ₃ Si radical + 1-decene	B3P86/6-31G*	8.87 x 10 ⁵	9.54 x 10 ⁶	1.41	7.92 x 10 ⁷	2.66
Me ₃ Si radical + 1-pentadecene	BHandHLYP/6-31G*	2.06 x 10 ⁴	6.77 x 10 ⁶	3.43	5.73 x 10 ⁷	4.70
Me ₃ Si radical + 1-pentadecene	B3LYP/6-31G*	5.32 x 10 ⁴	5.20 x 10 ⁶	2.72	4.42 x 10 ⁷	3.98
Me ₃ Si radical + 1-pentadecene	B3P86/6-31G*	6.13 x 10 ⁵	6.05 x 10 ⁶	1.36	4.95 x 10 ⁷	2.60
Me ₃ Si radical + styrene	BHandHLYP/6-31G*	6.18 x 10 ⁵	5.00 x 10 ⁶	1.24	3.79 x 10 ⁷	2.44
Me ₃ Si radical + styrene	B3LYP/6-31G*	4.99 x 10 ⁶	1.55 x 10 ⁷	0.67	1.29 x 10 ⁸	1.93
Me ₃ Si radical + 1,1-diphenylethylene	BHandHLYP/6-31G*	1.06 x 10 ⁶	9.81 x 10 ⁶	1.32	1.01 x 10 ⁸	2.70
Me ₃ Si radical + 1,1-diphenylethylene	B3LYP/6-31G*	2.31 x 10 ⁶	8.91 x 10 ⁶	0.80	8.74 x 10 ⁷	2.15
Si(SiMe ₃) ₃ radical + ethene	BHandHLYP/6-31G*	3.34 x 10 ²	5.50 x 10 ⁶	5.75	2.29 x 10 ⁷	6.60
Si(SiMe ₃) ₃ radical + ethene	B3LYP/6-31G*	1.38 x 10 ³	9.62 x 10 ⁶	5.24	4.40 x 10 ⁷	6.14
Si(SiMe ₃) ₃ radical + ethene	B3P86/6-31G*	1.12 x 10 ⁵	2.29 x 10 ⁷	3.15	1.31 x 10 ⁸	4.19
Si(SiMe ₃) ₃ radical + 1-hexene	BHandHLYP/6-31G*	5.58 x 10 ¹	9.38 x 10 ⁵	5.76	8.06 x 10 ⁶	7.04
Si(SiMe ₃) ₃ radical + 1-hexene	B3LYP/6-31G*	3.80 x 10 ¹	2.99 x 10 ⁵	5.31	2.11 x 10 ⁶	6.47
Si(SiMe ₃) ₃ radical + 1-hexene	B3P86/6-31G*	1.14 x 10 ⁴	2.31 x 10 ⁶	3.15	2.38 x 10 ⁷	4.53
Si(SiMe ₃) ₃ radical + 1-decene	BHandHLYP/6-31G*	2.77 x 10 ¹	4.89 x 10 ⁵	5.79	4.19 x 10 ⁶	7.07
Si(SiMe ₃) ₃ radical + 1-decene	B3LYP/6-31G*	8.56	7.97 x 10 ⁴	5.41	5.25 x 10 ⁵	6.53
Si(SiMe ₃) ₃ radical + 1-decene	B3P86/6-31G*	6.15 x 10 ²	2.41 x 10 ⁵	3.54	1.79 x 10 ⁶	4.73
Si(SiMe ₃) ₃ radical + 1-pentadecene	BHandHLYP/6-31G*	9.17	1.64 x 10 ⁵	5.80	1.26 x 10 ⁶	7.01
Si(SiMe ₃) ₃ radical + 1-pentadecene	B3LYP/6-31G*	3.93	3.65 x 10 ⁴	5.41	2.18 x 10 ⁵	6.47
Si(SiMe ₃) ₃ radical + 1-pentadecene	B3P86/6-31G*	1.67 x 10 ³	3.73 x 10 ⁵	3.21	3.66 x 10 ⁶	4.56
Si(SiMe ₃) ₃ radical + styrene	BHandHLYP/6-31G*	1.49 x 10 ³	1.24 x 10 ⁵	2.62	9.79 x 10 ⁵	3.85
Si(SiMe ₃) ₃ radical + styrene	B3LYP/6-31G*	2.70 x 10 ³	1.55 x 10 ⁵	2.40	1.06 x 10 ⁶	3.54
Si(SiMe ₃) ₃ radical + styrene	B3P86/6-31G*	5.92 x 10 ⁴	4.26 x 10 ⁵	1.17	3.22 x 10 ⁶	2.37
Si(SiMe ₃) ₃ radical + 1,1-diphenylethylene	BHandHLYP/6-31G*	1.13 x 10 ³	8.63 x 10 ⁴	2.57	7.86 x 10 ⁵	3.88
Si(SiMe ₃) ₃ radical + 1,1-diphenylethylene	B3LYP/6-31G*	1.09 x 10 ³	6.07 x 10 ⁴	2.38	5.23 x 10 ⁵	3.66
Si(SiMe ₃) ₃ radical + 1,1-diphenylethylene	B3P86/6-31G*	1.03 x 10 ⁴	4.20 x 10 ⁴	0.83	3.41 x 10 ⁵	2.07

Appendix D: List of important abbreviations.

AO	Atomic Orbital
CC	Coupled Cluster
CGTF	Contracted Gaussian-Type Function
CI	Configuration Interaction
CTS	Conventional Transition State
CTST	Conventional Transition State Theory
CVTST	Canonical Variational Transition State Theory
DFT	Density Functional Theory
DPE	1,1-diphenylethylene
FR	Free Rotor
GTF	Gaussian-Type Function
HF	Hartree-Fock theory
HO	Harmonic Oscillator
HOCI	Harmonic Oscillator (classical)
HOQ	Harmonic Oscillator (quantum)
LFP	Laser Flash Photolysis
MEP	Minimum Energy (Reaction) Path
MO	Molecular Orbital
MPPT	Moller-Plesset Perturbation Theory
PES	Potential Energy Surface
QCI	Quadratic Configuration Interaction

STO	Slater-Type Orbital
TS	Transition State
TST	Transition State Theory
ZPE	Zero Point Energy