

Review Article

How Can Quantum Chemical Calculations Contribute to the Elucidation of Chemical Reactions? Some Theory and Examples

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The aim of the present review article is to introduce some of the methods used in theoretical studies of molecular potential surfaces for chemical reactions. Some of the basic equations relevant to studies of this kind are presented, and applications to some thermal unimolecular reactions are discussed. Three degenerate rearrangements are included: the conversion of methylenecyclobutane into itself, the analogous rearrangement of methylenecyclopropane, and the Cope rearrangement of 1,5-hexadiene. Results are also presented from studies of dimerization and insertion reactions of silylenes. Furthermore, possible species resulting from the reaction between F^- and acylsilanes are presented. Finally, some of the computational and methodical problems met in studies of chemical reactions are discussed.

During the last two decades *ab initio* molecular orbital calculations have been gradually recognized as a useful tool in research related to elucidation of molecular structures and discussions of chemical properties associated with molecular ground states. Extensive bibliographies and data bases containing an enormous number of theoretically derived geometrical structures are available.^{1–3} Today widely distributed program systems^{4–6} that are designed for this kind of computation are used as ordinary tools also by scientists who are primarily experimentally oriented. It is especially worth mentioning the Gaussian series of programs developed by Pople and coworkers.⁴

The success of theoretical calculations in this context is to a large extent due to the fact that the geometry of ground states of stable molecules may be reasonably well described within the independent particle model which constitutes the foundation of the Hartree–Fock approximation. For reactive species, such as very short-lived intermediates that are encountered in chemical reactions, the situation is significantly more complicated, and usually requires theoretical models at a more advanced level, including a proper treatment of electron correlation. The same applies to highly transient species such as transition states. Because of this, the application of theoretical calculations to the study of chemical reactions developed at a later stage, and still faces great computational challenges.

The increased and steadily growing quantitative and qualitative contributions of quantum theory to the eluci-

dation of molecular structures and reactions are also due to the dramatic development of computing technology. Today a variety of advanced program packages for handling computations at a high level of sophistication to a reasonable cost are available. The program packages^{4–6} mentioned above include options needed for adequate calculations of chemical reactions.

The purpose of the present article is to give an introduction to some of the computational methods applied in calculations of potential surfaces for chemical reactions. The presentation will not include all techniques available and in use, but will deal with some of the widely applied standard approaches. Furthermore, some examples on application of these approaches to studies of chemical reactions will be discussed. They will illustrate some of the computational problems encountered in studies of this kind, and hopefully give an indication of the potential and the limitation of different computational methods. The choice of examples has been dictated by the authors' personal interests at the time of writing, and does not imply that the cases presented have an exclusive importance. The reference list is far from exhaustive, but is a result of the choices made of illustrating examples.

The scope of the article is limited to gas-phase reactions. This is a practical limitation, and not an indirect evaluation of some extensive and very interesting theoretical approaches to reactions in solutions.^{7–14} Theoretical models for reactions at solid-state surfaces, important for information on heterogenous catalysis, have been

developed to a high degree of sophistication. This field requires special computational techniques for handling molecule–surface interactions.

An excellent book treating the application of theoretical methods to problems in molecular structure and reactivity has recently been published.¹⁵ The book gives carefully presented evaluations of the limitation of different theoretical approaches.

Theoretical models

Molecular potential surfaces do not exist in nature. Such surfaces are a consequence of the Born–Oppenheimer approximation,¹⁶ which permits a study of the dynamics of the atomic nuclei in a field generated by a time-averaged distribution of the electrons. Within this approximation the energetics of molecular deformations and rearrangements can be mapped and evaluated by a study of the topology of the surface. A general theory for predicting topological properties of such surfaces has been developed.¹⁷ Hypersurfaces of this kind for a system consisting of N atoms will normally be extremely complex, as they are described by $3N - 6$ internal coordinates. Therefore a complete mapping is usually unfeasible, but normally also not required. The chemically interesting parts of such a surface are regions in the vicinity of minima and cols which are associated with equilibrium structures and transition states, respectively. These regions are usually described within the quadratic approximation. In special cases when different potential surfaces cross each other, or come very close, the Born–Oppenheimer approximation breaks down. In such cases non-adiabatic effects have to be invoked, and the concept of classical chemical structures becomes more diffuse. Such effects will not be discussed in the present context.

A prerequisite for the estimate of the effective potential in which the nuclei move is a satisfactory solution to the electronic Schrödinger equation. This is still a great challenge in most molecular calculations if moderately accurate results are aimed at.

Gradient methods. One of the most important single achievements in the field of geometry optimizations and potential surface computations is the introduction of analytically calculated gradients of the molecular energy. The first algorithm for retrieving analytically calculated gradients was developed by Pulay in the late 1960s,^{18–20} although the idea had been alluded to earlier.²¹ In the present context we will outline briefly some of the computational aspects of the gradient method. For an introduction to its extended use and further development we refer to recent excellent review articles by Pulay,²² Schlegel²³ and Bernardi and Robb.²⁴

In the Hartree–Fock approximation the electronic energy for a closed-shell molecule may be written as eqn. (1), where h_1 is the one-electron core Hamiltonian

$$E = 2 \sum_i (\varphi_i | h_1 | \varphi_i) + \sum_i \sum_j [2(\varphi_i \varphi_j | \varphi_j \varphi_i) - (\varphi_i \varphi_j | \varphi_i \varphi_j)] \quad (1)$$

for electron one (chosen as dummy), defined by eqn. (2) in atomic units. In eqn. (2) Z_A is the nominal charge of

$$h_1 = -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \quad (2)$$

nucleus A and r_{1A} is the distance between this nucleus and electron one.

The two-electron integral $(\varphi_i \varphi_j | \varphi_k \varphi_l)$ is defined by eqn. (3), where $\varphi_i(n)$ is the spatial part of the molecular

$$(\varphi_i \varphi_j | \varphi_k \varphi_l) = \iint dv_1 dv_2 \varphi_i^*(1) \varphi_j(1) r_{12}^{-1} \varphi_k^*(2) \varphi_l(2) \quad (3)$$

orbital as a function of the coordinates of electron n ($n = 1$ or 2), and r_{12} is the interelectronic distance. The one-electron integrals in eqn. (1) are defined in an analogous manner.

The molecular orbitals φ_i may be expanded in terms of a chosen set of basis functions χ [eqn. (4)]. Usually the

$$\varphi_i = \sum_{\mu} c_{\mu i} \chi_{\mu} \quad (4)$$

basis functions χ_{μ} are assumed to be atomic orbitals centered on the atoms in the molecule.

The total electronic energy given in eqn. (1) may alternatively be expressed in terms of the chosen basis functions χ [eqn. (5)],

$$E = \sum_{\mu} \sum_{\nu} P_{\mu\nu} (\mu | h | \nu) + \frac{1}{2} \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\mu\nu} P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma)] \quad (5)$$

where the definition of integrals is the same as given in eqn. (3).

The elements of the one-particle density matrix, $P_{\mu\nu}$, are defined by eqn. (6),

$$P_{\mu\nu} = 2 \sum_i c_{\mu i}^* c_{\nu i} \quad (6)$$

where the coefficients are given by eqn. (4) and where the summation extends over the doubly occupied molecular orbitals.

Minimization of the electronic part of the Hartree–Fock energy given by eqn. (5) with respect to the linear coefficients defined by eqn. (4) leads to the matrix form of the Hartree–Fock equations, i.e. the Roothaan–Hall equations^{25,26} [eqn. (7)], when the minimization is

$$\sum_{\nu} [F_{\mu\nu} - \varepsilon_i S_{\mu\nu}] c_{\nu i} = 0 \quad (7)$$

made subject to the orthonormality conditions of eqn. (8). In eqn. (7) $F_{\mu\nu}$ are the elements of the Fock

$$\sum_{\mu} \sum_{\nu} c_{\mu i}^* S_{\mu\nu} c_{\nu j} = \delta_{ij} \quad (8)$$

matrix, defined by eqn. (9), and $S_{\mu\nu}$ are the elements of

$$F_{\mu\nu} = (\mu | h | \nu) + \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma)] \quad (9)$$

the overlap matrix in the atomic orbital representation [eqn. (10)].

$$S_{\mu\nu} = (\mu | \nu) \quad (10)$$

The basis functions used in molecular calculations today are almost exclusively atomic orbitals expanded in terms of Gaussian functions centered on the different atoms.

Analytical gradients, which are the first derivatives of the energy with respect to atomic coordinates, offer a significant improvement in the efficiency of the optimizing routines for equilibrium structures and in the methods used in the search for transition states.

By differentiating the electronic energy given by eqn. (5) with respect to a nuclear coordinate q , we obtain eqn. (11),^{27,28} where $Q_{\mu\nu}$ is given by eqn. (12).

$$\begin{aligned} \frac{\partial E}{\partial q} = & \sum_{\mu} \sum_{\nu} P_{\mu\nu} \frac{\partial}{\partial q} (\mu | h | \nu) \\ & + \frac{1}{2} \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} \left\{ \frac{\partial}{\partial q} (\mu\nu | \lambda\sigma) - \frac{1}{2} \frac{\partial}{\partial q} (\mu\lambda | \nu\sigma) \right\} \\ & \times P_{\mu\nu} P_{\lambda\sigma} - \sum_{\mu} \sum_{\nu} Q_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial q} \end{aligned} \quad (11)$$

$$Q_{\mu\nu} = \sum_i \epsilon_i c_{\mu i}^* c_{\nu i} \quad (12)$$

Thus the first derivative of the energy does not require explicit differentiation of the wavefunction itself. The differentiation of the integrals in eqn. (11) is particularly simple, as these are evaluated in closed forms when Gaussian basis functions are used.

Also, in multiconfigurational SCF (MCSCF) calculations differentiation of the wavefunction itself may be avoided, as all the expansion coefficients in this function are determined variationally, i.e. by minimizing the expectation value of the energy. This implies that, provided the molecular orbitals remain orthonormal and the CI expansion coefficients remain normalized, the derivative of the energy with respect to any change in these coefficients is zero. First derivatives of the MCSCF energy have been derived by several groups.²⁹⁻³³

In geometry optimizations, force constant matrices are also needed. This requires second derivatives of the energy, and analytical expressions for second derivatives have also been developed. They imply the first derivative of the MOs and are accordingly more demanding from a computational point of view. The standard technique for evaluation of these is to solve the coupled perturbed Hartree-Fock equations or the coupled perturbed MCSCF equations.^{27,34} An efficient method for solving the coupled perturbed Hartree-Fock equations has

been devised by Pople *et al.*²⁷ By this method second derivatives of the energy for restricted and unrestricted Hartree-Fock wavefunctions have been made available. Coupled perturbed MCSCF equations have also been formulated,^{33,35-38} and second derivatives of energies obtained by this method have been developed.³⁸⁻⁴²

Intrinsic reaction coordinate (IRC). Minima and cols are well defined points on a molecular potential surface. However, the predicted reaction path bringing us from reactants, through a transition state to products, depends on the coordinate system chosen. Cartesian coordinates would lead to a path different from that obtained using internal coordinates. In addition, alternative sets of internal coordinates may be defined. Hence for a particular chemical reaction the reaction coordinate, which is normally a very complicated mixture of all the more or less simultaneous changes of bond distances and valence angles that take place during the reaction, requires a special definition in order to be unique. The concept of intrinsic reaction coordinate (IRC), introduced by Fukui,⁴³⁻⁴⁵ satisfies this requirement. By analogy with the motion of a classical particle it may be defined as the path traced by such a particle moving with infinitesimal velocity from a col to each of the minima. Since the classical equations of motion can be defined for any coordinate system, and since they must yield the same trajectory, this definition of the IRC is unique. The classical equations of motion have the simplest form in mass-weighted Cartesian coordinates, as the effective mass for each coordinate in such a system is the same. Only in this coordinate system will the IRC coincide with the path of steepest descent. The IRC, which is uniquely determined by a differential equation called the IRC equation,⁴³⁻⁴⁶ has proved to be a very important tool for following a reaction from a stationary point having one imaginary frequency to local minima on each side of this point, i.e. to reactants and products. This is particularly so in cases where the vibrational mode associated with the imaginary frequency of the transition state is difficult to interpret. Following the IRC also gives a clear picture of whether individual geometry changes in a process occur simultaneously, giving a synchronous reaction, or whether one or more of the deformations are delayed relative to the remaining ones, giving an asynchronous reaction.

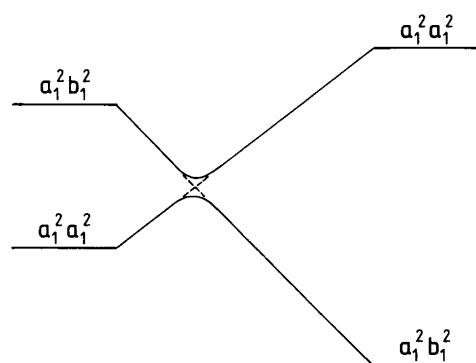
The IRC has some interesting properties. It always belongs to the totally symmetric representation of the point group of the nuclear configuration. This implies that symmetries which may be present in the nuclear arrangement are conserved along the reaction coordinate. The symmetry requirements of a wavefunction for a molecular system result in a conservation of the symmetries of the MOs during a reaction. Thus the principle of conservation of orbital symmetry may be deduced from the IRC equation.

Symmetry rules. Chemical reactions cannot take place without breaking and/or forming chemical bonds.

Through these processes the active molecular orbitals are usually the highest filled one (HOMO) and the lowest vacant one (LUMO) of the reacting system. These orbitals, coined frontier orbitals by Fukui,^{47,48} have to satisfy the symmetry requirements imposed on the reaction by the geometry constraints of the species taking part. These symmetry requirements have been systematized and organized in a brilliant way through the famous Woodward–Hoffmann symmetry correlation rules.^{49–52} These rules serve as a basis for classification of chemical reactions, and may furthermore predict relative probabilities for alternative reaction mechanisms if several channels are available. They have led to the classification of allowed and forbidden reactions, the latter ones normally having significantly higher activation energies.

One of the most famous examples of the application of the Woodward–Hoffmann rules is the reaction between two ethene molecules to form cyclobutane. In this case the π -systems of the two ethene molecules interact to form two new σ -bonds in the product cyclobutane. If the ethene molecules approach each other under C_{2v} symmetry their π -systems span the symmetry representation A_1 . By the smooth transition to cyclobutane these two orbitals are transformed to two σ -bonding orbitals that span the representations A_1 and B_1 .

The π -electron systems of two ethene molecules in their ground state give the electron configuration $(a_1)^2(a_2)^2$. This configuration gives rise to an 1A_1 state. A configuration such as $(a_1)^2(b_1)^2$ is an excited-state configuration. However, it also gives rise to an 1A_1 state. In cyclobutane the situation is reversed. The ground-state configuration, considering only the newly formed σ -orbitals, is $(a_1)^2(b_1)^2$, and $(1a)^2(2a_1)^2$ is an excited-state configuration, although both generate 1A_1 states. The appropriate state correlation diagram is given below. It shows a reaction barrier as a result of an avoided crossing of the energy curves for reactants and products, and exemplifies a symmetry-forbidden reaction.



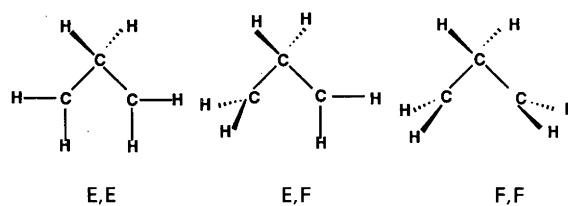
In more complex reactions these simple symmetry-based correlation diagrams are very useful for qualitative estimates of reaction probabilities, and in prediction of possible reaction products.

Another symmetry rule that has an important computational aspect in searches for transition states is

concerned with the possible symmetries of such a state given the symmetries of reactant and product. It has been shown by Pechukas⁵³ that for a non-degenerate reaction the symmetry group of the transition structure in a one-step reaction is either the largest common subgroup of the symmetry groups of reactant and product, or any subgroup of that. This rule has been extended by Schaad to cover degenerate reactions.⁵⁴ Schaad has shown that for a degenerate reaction the allowed symmetry groups of the transition structure are as for the non-degenerate case (set 1), and in addition groups of twice the order with the groups of set 1 as subgroups and operations that interconvert reactant and product as cosets.

Computational aspects of bond forming and bond breaking.

As mentioned above, it is impossible to bring about a chemical reaction without breaking and/or forming a chemical bond. A bond cleavage may be homolytic or heterolytic. In the first case an electron pair is decoupled, and a proper theoretical description of such a process has to invoke open-shell states. If the decoupled electrons are more or less located in different regions of the fragmented species, we have a diradical. A satisfactory treatment of diradicals requires a multiconfigurational wavefunction. Depending on the space symmetry of the diradical, unrestricted Hartree–Fock calculations may be used as a first approximation. However, in many cases space symmetry as well as spin symmetry of the wavefunction has to be broken. This may be illustrated by a simple example. A thermal breaking of one carbon–carbon bond in cyclopropane will lead to the diradical trimethylene, $H_2C-HCH-CH_2$. If we want to describe this species as a diradical with one uncoupled spin at each of the terminal carbon atoms, we have to consider the following different nuclear arrangements:



The E,E and F,F forms belong to the space group C_{2v} , whereas the E,F form belongs to C_s . A Hartree–Fock wavefunction built up of molecular orbitals belonging to irreducible representations of C_{2v} will not be able to describe an electron distribution in the E,E and F,F forms having one electron located on each of the terminal carbons. In order to obtain such a description the space symmetry of the wavefunction has to be broken. As a result it will retain only C_s symmetry in this case. To obtain a proper treatment of diradicals, and other open-shell states, multiconfigurational wavefunctions have to be invoked. For simple descriptions at a low level, two or three configurations often suffice to take care of the symmetry requirements. In this context it is important to

notice that such a multiconfigurational wavefunction does not account for electron correlation in the dynamic sense. It only secures a proper incorporation of the symmetry requirements imposed by the chosen nuclear configuration.

Potential surfaces for excited states. Computational techniques for studies of potential surfaces for electronically excited molecules have not been developed to the same degree as for ground-state systems. The requirements imposed on excited-state solutions often introduce strong limitations on the applicability of techniques developed for obtaining ground-state solutions. This is especially true for excited states of the same symmetry as the ground state.

The basis sets normally used in *ab initio* calculations are optimized for handling molecular ground-state properties, and are not necessarily adequate ones for describing excited states.

General requirements for a satisfactory theoretical model are applicability to molecules of chemical interest, size consistency and variational solutions.⁵⁵ For excited states there is the additional requirement of mutual orthogonality between the excited states and between these and the ground state. If the state of interest has the same space symmetry and the same spin multiplicity as a lower state, techniques for preventing this state from collapsing into the lower state must be developed.

In a very recent paper Pople *et al.*⁵⁶ have initiated systematic studies of the problems addressed above. Their paper also gives a valuable review of the present status within this field. Their strategy has been to develop methods that can be applied to large molecular systems, that are adapted to the use of analytic gradients, and which include effects of electron correlation.

Algorithms and numerical calculation in searches on potential surfaces. From a mathematical point of view the search for a stationary point on a potential surface (a maximum, a minimum or a saddle point) is a problem in numerical analysis. There is a vast literature in numerical analysis focused on the search for extrema on multidimensional surfaces. The methods used may be divided into two main groups. One class contains the algorithms that are based on the evaluation of the energy function only, and not its derivative. These methods are described in standard books on numerical analysis.⁵⁷⁻⁶⁰ As derivatives of the energy function are not available at all levels of theory, these methods may be widely used. However, they normally have a very slow convergence. The other class is characterized by making use of the first derivative of the energy function. If analytical derivatives are available, these methods are very efficient and have improved convergence properties as compared to the function-only methods. Some of the many algorithms available in this class are: Fletcher-Powell,⁶¹ Davidon-Fletcher-Powell,⁶¹ Murtagh-Sargent⁶² and Broyden-Fletcher-Goldfarb-Shanno.⁶³⁻⁶⁶ For a more extensive list with

comments on the merits and limitations of each of the algorithms, see Ref. 23.

In the case of a surface described by n independent variables, the Taylor expansion permits an exploration in the neighborhood of the reference point \mathbf{x}_i [eqn. (13)], in

$$E(\mathbf{x}) = E(\mathbf{x}_i) + \mathbf{g}_i(\mathbf{x} - \mathbf{x}_i) + \frac{1}{2}(\mathbf{x} - \mathbf{x}_i) \mathbf{B}_i(\mathbf{x} - \mathbf{x}_i) + \dots \quad (13)$$

which $\mathbf{x} - \mathbf{x}_i$ is the step vector which gives the displacement away from \mathbf{x}_i , \mathbf{g}_i is the gradient vector in the same point, and \mathbf{B}_i is an estimate of the Hessian, which contains elements of the first and second derivatives of the energy with respect to the components of \mathbf{x}_i . In gradient-type optimizations the energy surface is approximated by a quadratic expansion. This implies that only the two terms explicitly written in eqn. (13) are retained. By minimizing the energy predicted by the model surface [eqn. (14)]

$$dE/d\mathbf{x} = \mathbf{g}(\mathbf{x}) = \mathbf{g}_i(\mathbf{x}_i) + \mathbf{B}_i(\mathbf{x} - \mathbf{x}_i) = 0 \quad (14)$$

we obtain eqn. (15),

$$\mathbf{p}_i = (\mathbf{x} - \mathbf{x}_i) = -\mathbf{B}_i^{-1} \mathbf{g}_i = -\mathbf{H}_i \mathbf{g}_i \quad (15)$$

where \mathbf{p}_i is the step vector leading to the next reference point on the surface, and \mathbf{H}_i is the inverse of the Hessian developed in point \mathbf{x}_i . If the gradient \mathbf{g}_i is smaller than a chosen threshold value, and the predicted change in the geometry, given by \mathbf{p}_i , is sufficiently small, the optimization is considered completed.

Refined algorithms based on the concept presented here have been developed. We mention especially one by Schlegel,⁶⁷ which has been implemented in the Gaussian series of molecular orbital programs.

Applications and illustration of calculational possibilities

In this section we will present and discuss some examples of theoretical calculations applied to chemical reactions in the gas phase. We have chosen chemically simple systems that undergo thermally induced processes. The intention is to illustrate the important interplay between experimental and theoretical efforts in the elucidation of such reactions. We hope to show how theory may contribute significantly to unravelling of reaction mechanisms in cases which are experimentally unfeasible or at least very unattractive. A particular strength of computational methods is their ability to give a detailed account of geometries and relative energies of species that are not attainable experimentally, such as transition states and very short-lived reaction intermediates.

First we will discuss some hydrocarbon reactions, viz. the degenerate rearrangement of methylenecyclobutane and methylenecyclopropane, and the famous Cope rearrangement of 1,5-hexadiene. These are all seemingly simple reactions, and experimental studies of these processes have provided information on their activation energies and reaction orders. However, only recently

have the mechanisms for the methylenecyclobutane and -propane reactions been uncovered by theoretical calculations.

The Cope rearrangement we discuss in some detail, as it gives a good illustration of the power of calculational methods in handling reaction mechanisms, and at the same time shows the limitations of such methods in giving a quantitative insight into the finer details of the potential surface for the reaction. It is sobering to realize that this reaction, discovered more than 50 years ago, still resists a full and definite elucidation of its potential surface, and thus represents a challenge to modern computational chemistry.

Next we discuss some reactions related to silicon and silicon-organic chemistry. In this important and fast developing area of chemistry theoretical calculations have shown to be of great importance, as many of the compounds involved are not sufficiently stable for experimental investigations.

Thermal unimolecular rearrangements of some hydrocarbons. It has been known for some 30 years that methylenecyclobutane is able to undergo a thermally induced degenerate rearrangement:^{68,69}



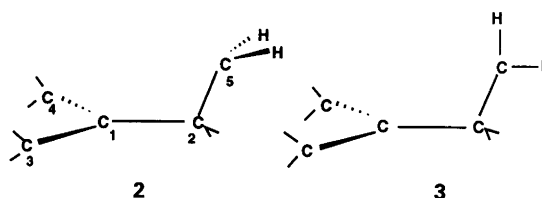
This intramolecular isomerization was uncovered by observation of changes in IR and NMR spectra. It was further confirmed by an unaltered mass spectrum of dideuteriomethylenecyclobutane upon heating at 342°C for 47 h.⁶⁹ The conversion was determined to be a first-order reaction having an activation energy of 49.5 kcal mol⁻¹. As this value is larger than the binding energy for the C₂-C₃ bond in the ring, around 42 kcal mol⁻¹,⁷⁰ it is reason to assume that diradicals may be present in the isomerization process. This in turn implies that the autoisomerization may be a two-step process with a diradical intermediate.

The complexity of the experimental attempts to determine the kinetics and mechanism of this degenerate rearrangement is demonstrated by a series of beautiful studies by Baldwin and Fleming.⁷¹⁻⁷⁴ They measured deuterium scrambling and racemization in the optically active α -d-1-ethylidene-2-methylenecyclobutane. On the basis of the observations made they suggested one particular mechanism for the participation of the allylic moiety in the 1,3-sigmatropic rearrangement. A re-evaluation of the rate constants for racemization and deuterium scrambling in α -d-1-ethylidene-2-methyl-*trans*-3,4,4-trideuteriocyclobutane by Gajewski⁷⁵ led to an alternative assessment of the mechanism. He concluded that the adjusted rate constants could be accounted for by this alternative mechanism for the allylic participation in the reaction. According to Gajewski the major part of the product was formed through a ring closure with random orientation of the migrating CH₂ group. The experimen-

tal observations made have not enabled a determination of the structure and the properties of the biradical suggested to be of importance in this reaction.

Theoretical calculations represent a very powerful tool for scrutinizing reactions of this kind. With the program packages available for studies of molecular potential surfaces the critical points on such surfaces can be located and characterized. This will often lead to an unequivocal assessment of the elementary steps involved in such reactions, and furthermore, activation energies and rate-determining steps may be determined with fair accuracy.

The rearrangement described above has been studied by theoretical calculations,⁷⁶ and we will report on the main findings in this study. By doing this we offer an illustration on how studies of this kind are able to help experiment in elucidation of reaction mechanisms. The ring-opening reaction of 1 is a [1,3] sigmatropic rearrangement. The degenerate process 1 \rightarrow 1' can either proceed with retention at the migrating center, leading to a transient species 2, or it can proceed with inversion at this center, leading to a corresponding species 3:



For symmetry reasons 2 and 3, both having C_s symmetry, are stationary points on the potential surface. Thus they will be transition states in one-step processes, and intermediates in two-step reactions. In the latter case there have to be transition states of C₁ symmetry between 1 and 2, 1 and 3, and 2 and 3, respectively.

As these species result from breaking bonds, they have an open-shell electronic structure. Accordingly their geometries were optimized using⁷⁶ the unrestricted Hartree-Fock (UHF) procedure. Owing to extensive spin contaminations the structures were optimized also using the restricted Hartree-Fock (RHF) approximation. The different approaches led to virtually the same geometries. Analytically calculated vibrational frequencies in the UHF approximation at the C_s-constrained optimized geometries gave one imaginary frequency for each of the species, 32*i* cm⁻¹ and 112*i* cm⁻¹ for 2 and 3, respectively. These frequencies were both associated with a vibrational mode of *a*'' symmetry. The potential surface turned out to be very complex in the vicinity of the stationary points represented by 2 and 3. A cumbersome and complex analysis of the modes associated with the imaginary frequencies demonstrated that 3 is not a transition state for the ring-closure reaction. A symmetry-breaking optimization of 3 revealed a very flat surface around the C_s symmetry and lead to a shallow minimum 3a for a dihedral angle of around 78°. Furthermore, species 3 was found to be a transition state for a process linking 3a to its enantiomer. The energy difference between 2 and 3a

was found to be very small, viz. $0.8 \text{ kcal mol}^{-1}$. This indicates that the migrating CH_2 group has virtually free rotation around the bond $\text{C}_2\text{-C}_5$.

The search for the transition state for the ring-opening reaction in the sigmatropic rearrangement of **1** led to the fully optimized species **4**, given in Fig. 1.

As mentioned above, the UHF approximation was found to be reasonably accurate for the prediction of geometries even if spin contamination of the singlet wavefunction was rather large. However, it is imperative to invoke electron correlation in estimates of energies for transition structures. As a closed-shell ground-state molecule is broken up by a homolytic reaction, transient species having unpaired electrons appear. This implies that the number of coupled electron pairs varies along the reaction path. This will in turn have a great influence on the correlation energy of the system as it moves along this path.

In the calculations⁷⁶ correlation energies were estimated by two different methods, i.e. Møller-Plesset perturbations⁷⁷ up to order four (MP4) and Complete Active Space SCF (CASSCF)⁷⁸⁻⁸⁰ calculations. In CASSCF calculations the assignment of an appropriate active space is decisive for the outcome of the calculations. As such calculations are computationally very expensive, the choice of active space has to represent a delicate balance between the need for exactness and cost of calculation. In the case discussed here, the active space was limited to six electrons and six orbitals. The choice of orbitals made was the following: in **1** the two *exo* π -orbitals, the two σ -orbitals associated with the ring bond to be broken, and their counterparts generated under C_s symmetry; in **2** and **3** also having C_s symmetry,

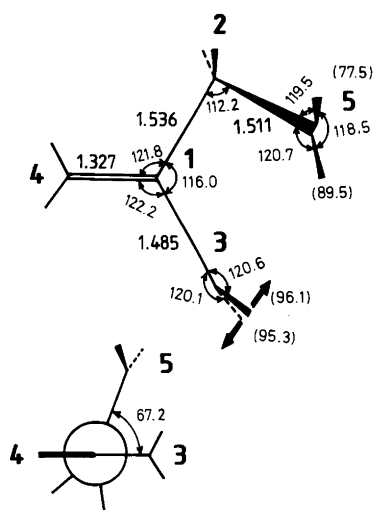


Fig. 1. Optimized geometry (in Å and degrees) of the transition state **4** at the UHF/3-21G level. Values in parentheses are dihedral angles $\text{H-C}(5)\text{-C}(2)\text{-C}(1)$ and $\text{H-C}(3)\text{-C}(1)\text{-C}(4)$. Arrows are the reaction coordinate vector at the transition state. Reprinted with permission from *J. Am. Chem. Soc.* 111 (1989) 1561. © (1989) American Chemical Society.⁷⁶

the three π -orbitals of the allylic moiety, the orbital accommodating the lone electron on the migrating group, and the two σ -orbitals for the C-C bond between the migrating carbon and its neighbour; and in the transition structure **4** the two π -orbitals in the double bond, the two terminal orbitals holding each one electron, and the σ -orbitals related to the same C-C bond as in **2** and **3**. A qualitative picture of the active orbitals chosen in the different species is given in Fig. 2.

For **1** the CASSCF calculations confirmed the closed-shell ground state, the configuration $\dots(13a')^2(6a'')^2$ having the coefficient 0.98. For the species **2-4** these calculations confirmed open-shell structures. In the case of **2** two natural orbitals⁸¹ (NOs), $7a''$ and $13a'$, were found to have unpaired electrons with the occupation number of 1.000 each. Here $7a''$ is the non-bonding π -orbital of the allylic unit and $13a'$ is exclusively located on the migrating carbon. For **3** two NOs, $6a''$ and $7a''$, have an occupation number of 1.153 and 0.847, respectively, where $6a''$ and $7a''$ are in-phase and out-of-phase combinations of the nonbonding allylic π and the pure p function on the migrating carbon, respectively. It is worth mentioning that the NOs of the CASCF wavefunctions for **2** and **3** lead to a localized description of the former and a delocalized description of the latter, which implies that there is an interaction between the allylic moiety and the migrating center in **3**.

The predicted relative energy values for the transition state **4** obtained at different levels of calculation are presented in Table 1. These data support the general experience that energy estimates based on unrestricted SCF and MP calculations may suffer from serious defects owing to spin contamination of the wavefunction. Different schemes for projecting out spin contamination have been published.⁸²⁻⁸⁶ In this case the UHF wavefunction of **4** has a large contribution of the lowest triplet, but also a significant quintet coupling between the three electrons in the allylic unit and the one on the migrating center. By projecting out these contributions the estimated relative energy of **4** changes by amounts ranging from 15 to 20 kcal mol^{-1} depending on the calculational level

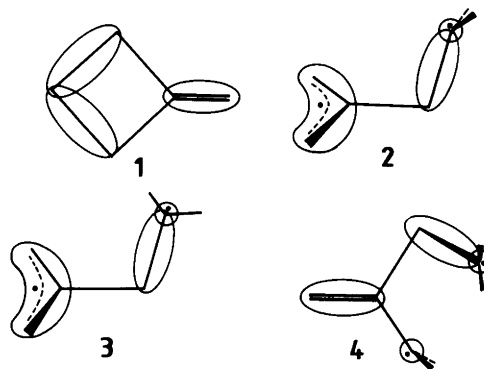


Fig. 2. Outline of orbitals chosen for the active space in CASSCF calculations on the species **1**, **2**, **3** and **4**. Reproduced with permission from *J. Am. Chem. Soc.* 111 (1989) 1561. © (1989) American Chemical Society.⁷⁶

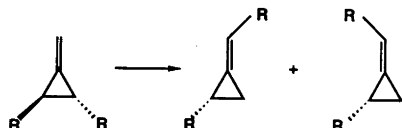
Table 1. Energies (in kcal mol⁻¹) relative to methylenecyclobutane (**1**) for the transition state **4** at different levels of calculation. Geometries optimized by UHF using 3-21G basis.

	3-21G		6-31G			
	UHF	UMP2	UHF	UMP2	UMP3	UMP4
Unprojected	38.0	65.7	34.9	63.4	60.6	59.7
Projected	23.1	46.9	19.3	43.5	41.2	40.1

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applied. The highest level of MP calculation, corrected for spin contamination, predicts an energy barrier of 40 kcal mol⁻¹. This is around 10 kcal mol⁻¹ below the experimental value reported.⁶⁹

Another related thermal degenerate rearrangement of theoretical interest is that of methylenecyclopropane. This rearrangement has been confirmed experimentally by pyrolysis of the substituted molecule, leading to an interchange of ring and *exo*-methylene carbon at temperatures above 150°C.⁷⁰ Stereochemical investigations of optically active derivatives like Feist's ester⁸⁷ and *trans*-2,3-dimethylmethylenecyclopropane^{88,89} have shown that the migrating carbon group undergoes an inversion of configuration as illustrated in the following scheme, where R is CO₂CH₃ or CH₃.

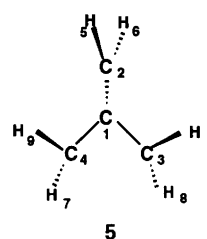


A corresponding mechanism has later been confirmed in a detailed experimental study of the optically active 2-(methoxymethyl)-2,3-dideuterio-1-(dideuteriomethylene)cyclopropane.⁹⁰

According to the experimental results referred to above, the major pathway for this rearrangement has to involve either a chiral intermediate in a nonconcerted reaction or a chiral transition structure in a concerted reaction. Theoretical studies of both of these possible mechanisms have been carried out for the unsubstituted molecule, for which experimental information is not obtainable. Two of these studies^{91,92} have been concerned with the nonconcerted pathway, and have concluded that the intermediate along this reaction path is a singlet diradical in which one of the methylene groups is orthogonal to the plane through the remaining atoms. The transition state between this intermediate and methylenecyclopropane has also been characterized.⁹² It was found that the transition state connecting methylenecyclopropane and the intermediate along a conrotatory path was slightly favoured, its energy being around 2 kcal mol⁻¹ lower than for the disrotatory counterpart. These results were obtained using geometries optimized by a 4-electron/

4-orbital MCSCF wavefunction, and a single and double CI calculation with corrections for quadruple excitations.

In a more recent paper the concerted pathway has been studied.⁹³ Owing to the degeneracy of the rearrangement the transition structure of this path has to be symmetrically located between the carbon atoms breaking and forming bonds in the process. This implies that the migrating carbon must be located in a plane of symmetry of the transition structure. In order to account for the observed stereochemistry of the rearrangement the transition structure for the concerted process also has to comply with the requirement of chirality when appropriately substituted. Such a transition structure having C_s symmetry was located (**5**) and its geometry was optimized using restricted SCF and MP2 calculations. The optimized



geometry parameters are given in Table 2. The energy found for this structure relative to the one for methylenecyclopropane, 55 kcal mol⁻¹, is somewhat higher than the experimental activation energy of 40.4 kcal mol⁻¹ reported for 2-methylmethylenecyclopropane.⁹⁴

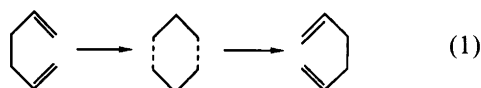
Table 2. Optimized geometry of the ¹A'(C_s) transition structure for the concerted methylenecyclopropane rearrangement (bond distances in Å and angles in degrees).

Parameter	Computation	
	SCF/6-31G*	MP2/6-31G**
Bond distances		
C ₁ C ₂	1.440	1.466
C ₁ C ₃	1.367	1.384
C ₂ H ₅	1.079	1.089
C ₂ H ₆	1.071	1.085
C ₃ H ₈	1.079	1.089
C ₃ H ₁₀	1.073	1.086
Angles		
C ₂ C ₁ C ₃	108.9	114.0
C ₃ C ₁ C ₄	135.3	127.2
C ₁ C ₂ H ₅	126.5	125.8
C ₁ C ₂ H ₆	116.6	116.0
H ₅ C ₂ H ₆	116.9	118.2
C ₁ C ₃ H ₈	123.5	122.6
C ₁ C ₃ H ₁₀	119.2	119.4
H ₈ C ₃ H ₁₀	117.2	117.7
H ₇ C ₄ C ₁ C ₂	137.7	142.0
α ^b	31.8	23.8

* Complete MP2 with full-core. ^b The angle between the C₁C₂ bond and the C₁C₃C₄ plane. Reprinted with permission from *J. Am. Chem. Soc.* 110 (1988) 5315. © (1988) American Chemical Society.⁹³

The Cope rearrangement. Several decades ago Cope and coworkers⁹⁵⁻⁹⁷ discovered a thermal rearrangement of doubly unsaturated systems of the bis-allylic type. The reaction occurred in an uncatalysed process, with a rate that was roughly the same in vapour and condensed phase. The kinetics were observed to be of first order.^{97,98} The polarity of the solvent did not influence the reaction rate to any significant extent. These observations were in line with characteristics for homolytic processes, and led to the early suggestion of a two-step reaction involving diradicals as earlier proposed for the diene synthesis.⁹⁹ However, the reaction also displayed features typical for heterolytic processes, and polar, rather than diradical, intermediates were suggested as an alternative.¹⁰⁰ Unfortunately neither of these two reaction pathways accounted satisfactorily for the observed regio- and stereo-selectivity of the reactions. So a concerted mechanism, earlier proposed for the Diels-Alder reaction^{101,102} involving a cyclic, planar transition state resembling a six-electron aromatic ring, was suggested. Further details, including a survey of early literature on this arrangement, may be found in a text by Badaea.¹⁰³

The prototype Cope rearrangement is that of 1,5-hexadiene, reaction (1). In terms of the Woodward-Hoffmann symmetry rules⁵² the rearrangement is a [3,3]



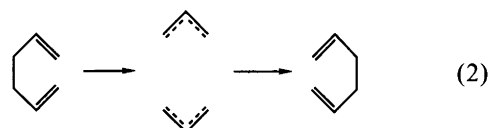
sigmatropic reaction. The nature of its transition state is still an issue of debate. This reaction thus illustrates the importance of interplay between theory and experiment, which is a central theme in the present article. Firstly, the mechanism of this seemingly simple degenerate reaction cannot be determined solely on an experimental basis. Secondly, predictions based on theoretical calculations have shown to be critically dependent on the degree of sophistication of the calculations. As the 1,5-hexadiene Cope rearrangement thus gives a very good illustration of how demanding quantitative predictions related to chemical reactions can be, it will be discussed in some detail.

There are two concepts that are of central importance for the discussion of the mechanism for this reaction. One is the concept of concertedness.¹⁰⁴ There is today a general agreement that this is to be associated with a one-step mechanism with no stable intermediate. A non-concerted reaction implies a multiple-step reaction path with at least one stable intermediate. This intermediate may be a diradical. The other concept is the one of synchronicity.¹⁰⁴ If all the geometrical parameters that contribute to the reaction coordinate in a concerted reaction change to roughly the same extent, we have a synchronous reaction. If, on the other hand, some of the parameters have reached a complete change before others have started to change, the process is described as asynchronous or non-synchronous. In a non-concerted

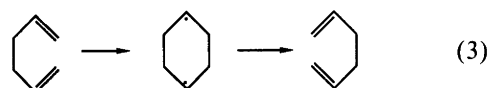
reaction the concept of synchronicity may be applied to each step. These two concepts have recently been applied and discussed in a review article on the transition states in the Cope rearrangement.¹⁰⁵

Referring to the concepts discussed above the following possible reaction channels may be considered:

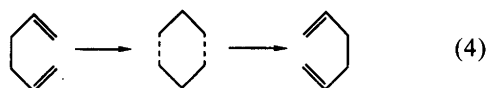
(a) The allylic moieties split apart and lead to a diradical consisting of two allylic radicals that are too wide apart to interact significantly. This gives a non-concerted reaction, reaction (2).



(b) The formation of the new σ -bond in the product is more or less completed before the σ -bond in the reactant starts breaking. This gives a concerted, but very asynchronous reaction. This would lead to a transient species resembling cyclohexane-1,4-diyl, reaction (3).

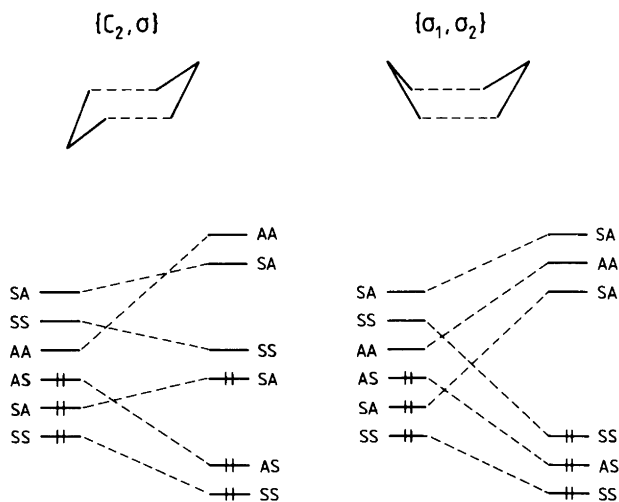


(c) The breaking and formation of the implied σ -bonds take place in a synchronous manner. This leads to a concerted reaction having a highly symmetrical transition state, reaction (4)



In an attempt at revealing the gross structure of the transition state in this sigmatropic rearrangement Doering *et al.*¹⁰⁶ carried out an ingenious experiment. They found that *threo*-3,4-dimethyl-1,5-hexadiene gives a 9 : 1 mixture of *trans,trans*- and *cis,cis*-2,6-octadiene, respectively, upon heating at 180°C for 18 h. Virtually nothing of the *cis,trans* isomer was formed. Heating of the *meso*-3,4-dimethyl-1,5-hexadiene led almost exclusively to *cis,trans*-2,6-octadiene, and only traces of the *trans,trans* isomer were detected. On the basis of these observations it was concluded that a chair form of the transition state was preferred rather than a boat form. For further details see the text by Gajewski.⁷⁰ This conclusion is in accordance with the Woodward-Hoffmann symmetry rules for these two reaction channels having transition states of C_{2h} and C_{2v} symmetry, respectively. In the former case we have the symmetry elements C_2 and σ , and in the latter case we have the two symmetry elements σ_1 and

σ_2 . The orbital correlation diagrams for these two alternatives are as follows:



From these diagrams it may be seen that the chair approach is preferred, as a non-bonding pair in the boat approach correlates with an antibonding pair in the product. This also is in accordance with the results of the experimental study by Doering *et al.*¹⁰⁶

In conformity with the Woodward–Hoffmann symmetry rules for [3,3] sigmatropic reactions, transition states having a twist form and a planar form are also allowed.⁹⁸ However, there is a general agreement that the chair rearrangement goes through a species having C_{2h} symmetry.⁷⁰

In a later study Doering *et al.* focused on the fact that the observed activation energy for this rearrangement was consistent with a mechanism where the new C–C bond is formed before the old one starts breaking.¹⁰⁷ This leads to a symmetrical intermediate having a biradicaloid character rather than being an aromatic non-classical species. Such a two-step mechanism has been supported by more recent experimental studies of several Cope rearrangements.¹⁰⁸ This conclusion was also supported by semi-empirical molecular orbital calculations. The MINDO/2 calculations by Komornicki *et al.*¹⁰⁹ and MINDO/3 calculations by Dewar *et al.*¹¹⁰ both suggested an intermediate having C_{2h} symmetry and an interallylic distance of 1.61 Å. More recent AM1 calculations^{111,112} have suggested the existence of a non- C_{2h} transition state that is very close to the intermediate having a chair form. On this basis it was suggested that the Cope rearrangement could be a concerted reaction having a transition state of C_{2h} symmetry. Regarding the calculated distance of 1.646 Å between the allylic units it could be argued that the process is asynchronous,¹¹³ with bond forming preceding bond cleavage.

More recent *ab initio* calculations have demonstrated that rather advanced calculational levels are required in order to give an adequate description of the electron distribution and relative energies in species relevant for this process.^{114–118} It has been shown that a closed-shell SCF

approach¹¹⁶ combined with perturbation calculations is not adequate for a quantitative evaluation of the relative energies of biradicaloid and aromatic structures. This is not surprising in view of the fact that the wavefunction should be able to account for bond-breaking and bond-forming processes. Osamura *et al.*¹¹⁴ found that the lowest-energy chair species, having C_{2h} symmetry, was a transition state for a concerted pericyclic process. In order to reach this conclusion, which was in contrast to the MINDO results obtained previously,¹¹⁰ it was necessary to use a flexible basis set and to treat electron correlation properly. Unfortunately a full MCSCF calculation using an active space of six electrons and six orbitals was not possible to carry out using a split-valence basis. Consequently such a calculation was simulated by optimizing the orbitals in an MCSCF wavefunction composed of the 12 most important configurations. These orbitals were then used in a full six-electron six-orbital configuration interaction calculation. The minimum energy using the MCSCF wavefunction was found for an inter-allylic distance of 2.062 Å. The corresponding activation energy was estimated to be 29.4 kcal mol⁻¹ above the all-transoid conformation of 1,5-hexadiene, i.e. a value in good agreement with the experimental one¹⁰⁷ of 33.5 kcal mol⁻¹. The final MCSCF wavefunction gave strong evidence against a diradical nature of the transient species. Thus the second largest coefficient in the wavefunction expansion was only 0.18. This result led to the conclusion that the transition state is one in a concerted pericyclic reaction.

A more recent study¹¹⁵ employing full geometry optimization with a 3-21G basis and a six-electron, six-orbital MCSCF wavefunction for the chair and boat conformations led to results that were roughly in agreement with those described above. The inter-allylic bond distances obtained were 2.068 Å for the chair and 2.316 Å for the boat, respectively. A natural orbital analysis of the CASSCF wavefunction showed that the numbers of electrons in antibonding molecular orbitals were 0.29 and 0.36 for the chair and boat forms, respectively. These numbers confirm the earlier conclusion¹¹⁴ of a predominant closed-shell nature of these species. The relative energies obtained at the highest level of calculation were 40.7 and 47.3 kcal mol⁻¹ for the chair and boat form, respectively. Inclusion of a correction for vibrational energy differences led to the final value of 37.7 kcal mol⁻¹ for the chair form.

In a very recent calculation¹¹⁸ a larger basis set, containing polarization functions, was used in an MCSCF treatment. As the active space in this study is the same as in the ones presented above,^{114,115} a comparison between these calculations will give a clear picture of the possible importance of extended basis sets in studies of this kind. The calculations revealed seven stationary points on the potential surface for the degenerate rearrangement, two of which had not been characterized previously. These points were: (a) a diallyl supermolecule, the energy of which is the sum of the energies for two allyl monomers,

(b) 1,5-hexadiene as a reactant and a product, (c) a 'loose' boat transition state having an inter-allylic distance of 2.615 Å, (d) a 'loose' chair transition state having an inter-allylic distance of 2.189 Å, (e) a 'tight' chair stable intermediate of *endo* form with an inter-allylic distance of 1.641 Å, (f) a 'tight' chair stable intermediate of *exo* form with an inter-allylic distance of 1.568 Å, and (g) an unsymmetrical transition state having inter-allylic distances of 1.830 and 1.669 Å. The nature of these stationary points was determined by analytically calculated vibrational frequencies and IRC following.

Five of the structures are presented in Fig. 3, where also some structural parameters are given. A scheme connecting stationary points on the potential surface is given in Fig. 4.

The relative energies of these stationary points were modified as compared with those obtained by previous *ab initio* calculations. As the potential surface for this reaction is rather smooth in the transition state area, these differences are of qualitative importance, as they might suggest alternative reaction channels, and thereby lead to different mechanisms. In Table 3 the total energy of the diallyl supermolecule obtained at different calculational levels is presented along with the relative energies of the other stationary points on the potential surface at the

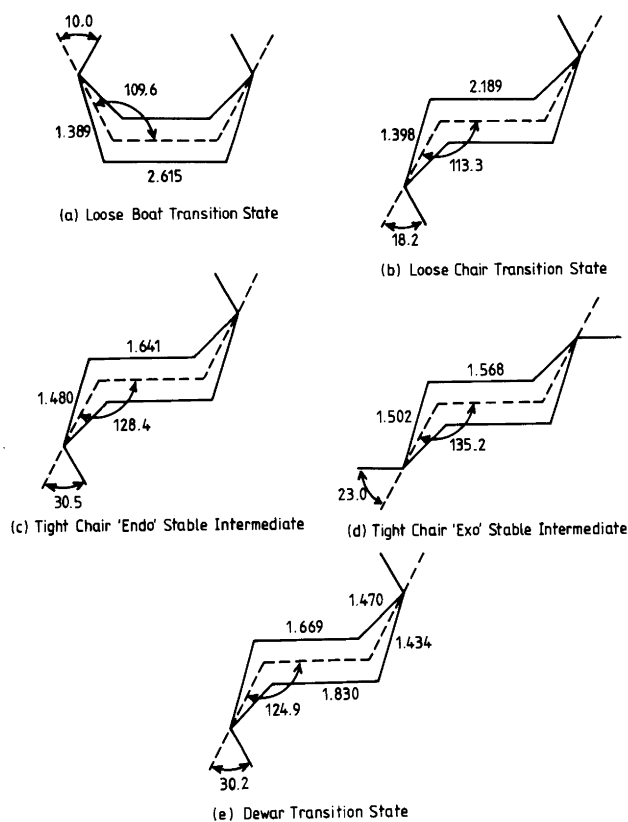


Fig. 3. Stationary points for the Cope rearrangement from a CASSCF calculation with a 6-31G* basis set. Reprinted with permission from *J. Am. Chem. Soc.* 113 (1991) 9757. © (1991) American Chemical Society.¹¹⁸

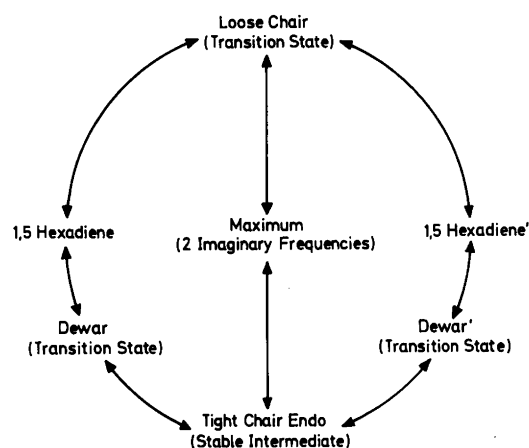


Fig. 4. Paths connecting stationary points for the Cope rearrangement. Reprinted with permission from *J. Am. Chem. Soc.* 113 (1991) 9757. © (1991) American Chemical Society.¹¹⁸

corresponding levels. The values in the table illustrate the sensitivity of the predicted relative energies to refinements in the computational approach.

The main conclusion from this study is that the Cope rearrangement is a concerted synchronous reaction. The transition state along this path is a symmetrical chair (C_{2h}) having aromatic, rather than biradicaloid character. In addition, a non-concerted path, going through a symmetrical biradicaloid intermediate and having an unsymmetric transition state, was found.

The energy differences between the competing reaction paths are found to be very small, as indicated in Table 3. This implies that even an advanced calculation including MCSCF wavefunctions and a basis set having polarization functions is not sufficient for an unequivocal conclusion regarding reaction mechanism. To quote the authors:¹¹⁸ 'At the same time, the present results are certainly still not converged either with respect to basis set or description of electron correlation. The potential energy surface reported here is very flat along the critical inter-allylic distance coordinate connecting C_{2h} structures. The total energy varies by only 3 kcal mol⁻¹ over the range of R (interallylic distance) from 1.64 to 2.19 Å, while the wavefunction changes from biradicaloid to benzenoid. Because of the large change in the nature of the wavefunction, relative energies along this path are uncertain by more than 3 kcal mol⁻¹.'

Silylene dimerization and insertion reactions. One of the major differences between the elements carbon and silicon is related to their ability to form stable unsaturated compounds. Whereas stable organic compounds exhibiting double and triple bonds have been known for a long time, the first syntheses of stable compounds containing multiple bonds to silicon are of a very new date.¹¹⁹⁻¹²² The problems encountered in synthesizing such compounds have made this field a challenging one also from a theoretical point of view, and the interplay between

Table 3. Energies of structures important in the Cope rearrangement.^a

Structure	MCSCF energy	Six-electron CI energy (extrap.)	Six-electron QDVARPT ^a (extrap.)	34-electron CI energy (extrap.)	34-electron QDVARPT (extrap.)
Diallyl supermol.	-232.96716	-232.98457 (-232.9864)	-232.98743 (-232.9864)	-233.50535 (-233.7552)	-233.61650 (-233.7376)
Tight chair <i>exo</i>	-4.8	-8.6 (-9)	-8.7 (-9)	-7.8 (5)	-3.9 (3)
Loose chair	-6.3	-12.4 (-13)	-12.6 (-13)	-20.6 (-32)	-31.1 (-32)
Loose boat	-1.7	-5.2 (-6)	-5.3 (-6)	-5.4 (-36)	-13.8 (-31)
Tight chair <i>endo</i>	-8.2	-13.9 (-14)	-14 (-14)	2.2 (1)	7.6 (3)
Hexadiene	-54.0	-56.9 (-58)	-56.9 (-58)		
Dewar structure	-6.9	-12.6 (-14)	-12.8 (-14)		
2-(allyl monomer)	0.00 (-0.5)	-1.5 (-0.5)	-1.4 (27)	-83.3 (10)	-57.6

^aThe absolute energy for the diallyl supermolecule is in hartrees, the energies relative to diallyl are in kcal mol⁻¹. Values in parentheses are extrapolated values. Basis set 6-31G*. ^bQuasidegenerate variational perturbation theory. Reprinted with permission from *J. Am. Chem. Soc.* 113 (1991) 9759. © (1991) American Chemical Society.¹¹⁸

experimental efforts and theoretical calculations has been very important for the recent development of this area. Extensive reviews of the chemistry of multiply bonded silicon compounds, covering both experimental and theoretical contributions, are available.¹²³⁻¹²⁵ A more general, and very extensive, review on theoretical aspects of organosilicon compounds has also been published.¹²⁶

The purpose of the present article is to present and comment on the results of some of the publications discussing the reactions of silylenes, which are reactive intermediates analogous to the carbenes. We will focus on two types of silylene reactions, viz. addition reactions and insertion reactions. An important class of the first-mentioned category is the dimerization reaction producing disilene, reaction (I).



The prototype insertion reaction is the insertion of silylene into molecular hydrogen, reaction (II).



A very important aspect of this reaction is that its reverse is the primary step in the thermal decomposition of silane to silylene and molecular hydrogen.

Reaction paths for combination of the CH₂: and SiH₂: fragments leading to ethene, disilene and silaethene have been studied thoroughly by theoretical calculations.^{127,128} In the studies MCSCF and multireference CI (MRCI) procedures were applied, as a single determinant wavefunction is not sufficient for a proper description of the electronic structures and rearrangements in these reactions. Basis sets containing polarization functions were used. A comparative study of this kind is very interesting as the ground states of methylene and silylene have

different multiplicities, the state parameters being ³B₁ and ¹A₁, respectively.

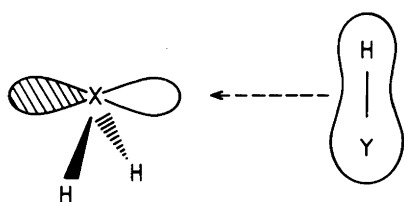
The ground-state dimerization of methylene is symmetry-allowed along the path of least motion,¹²⁹ maintaining D_{2h} symmetry, and is found to give ethene in its ground state without a barrier.¹²⁸ This is in agreement with results from earlier MCSCF calculations.¹³⁰⁻¹³⁴ The lowest singlet state of methylene, ¹A₁, on the other hand, does not dimerize along this path, which is symmetry forbidden for this excited state. The path correlates with a Rydberg excited state ¹A_g of ethene in this case.¹³³ The reaction was found to proceed along a non-least-motion path¹²⁹ starting with C_s symmetry. The ground state of the silylene fragment undergoes a dimerization to ground-state disilene with a substantial barrier along the least-motion path. This barrier is due to an avoided crossing between two different electronic configurations. The calculations confirm that there is no barrier along the non-least-motion path for the combination of two ground-state silylenes.

In the cross-coupling reactions between the ¹A₁ excited-state methylene and the ground-state ¹A₁ silylene a repulsive path that passes over a substantial barrier along the least-motion channel was predicted. The same states of the fragments were found to combine to ground-state silaethene without a barrier along the non-least-motion path. On the other hand, the ground-state ³B₁ methylene and the ³B₁ excited-state silylene were found to combine to a ground-state silaethene along the least-motion path without a barrier.

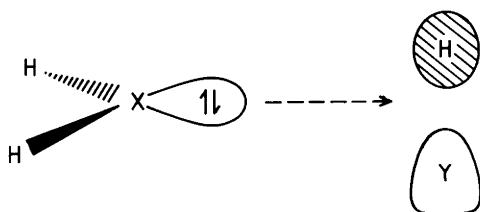
The insertion reaction of silylene into H₂ has been studied by several different theoretical methods.¹³⁵⁻¹⁴¹ Also in this case a comparison with the methylene insertion reaction^{145,146} is interesting, as the spin multiplicities

of the methylene and silylene ground states are different, and comparative studies have been performed.^{136,139} Systematic theoretical studies of the influence of substituents on these reactions have also been published,^{139,142} and so has the insertion into other σ -bonds. Here we mention the insertion of H_2Si and H_2C into methane and silane,^{137,143} and the insertion of H_2Si into SiH_3F to give $\text{H}_3\text{SiSiH}_2\text{F}$.¹⁴⁴

The insertion reactions referred to above may all be interpreted qualitatively in terms of a mechanism that implies a concerted non-least-motion process. It has been suggested^{137,140} that the reactions take place in two different stages. Initially there is an electrophilic phase in which the vacant p-orbital on the methylene carbon or the silicon atom (X) attacks the σ bond H–Y to form a three-center bond.



This phase is followed by a nucleophilic step where the lone pair on X interacts with the antibonding sigma orbital in H–Y.



It is well established that insertion of H_2C in its $^1\text{A}_1$ state into H_2 occurs without any barrier.¹³⁶ However, for the corresponding silylene reaction there is definitely a barrier. The estimated magnitude of this barrier, and the predicted geometry of the transition state for the reaction, appear to be rather dependent on the calculational level applied. In an SCF geometry-optimized study using the 6-31G* basis set, and with energies calculated at the MP2 level, the insertion barrier was found to be

8.6 kcal mol⁻¹.¹³⁶ By use of an augmented basis set, 6-31G**, at the MP3 level the barrier was modified to 5.5 kcal mol⁻¹.¹³⁷ When zero-point vibrational corrections were added to these values, they were changed to 10.6 and 7.5 kcal mol⁻¹, respectively. A study based on a two-configuration MCSCF wavefunction using a double-zeta basis augmented with polarization functions, and invoking second-order configuration interaction, led to an insertion barrier of 6.8 kcal mol⁻¹.¹³⁸

By expanding this wavefunction to include the four active orbitals in the insertion process, and using a 6-31G* basis set, the activation energy was estimated to be 10.4 kcal mol⁻¹,¹³⁸ i.e. somewhat higher. This value was reduced to 8.0 kcal mol⁻¹ after correcting for lack of polarization functions on the H atoms.

In a systematic study using two different basis sets and MP calculations up to fourth order¹³⁹ it was found that a reliable predicted insertion barrier can only be obtained by going beyond the SCF level. Values obtained in this study are given in Table 4.

The values in the table show that the one obtained at the highest calculational level, MP4, corrected for differences in ZPE is 12.2 kcal mol⁻¹, in reasonable agreement with the MCSCF values mentioned above. It is worth noticing that irrespective of chosen basis set the SCF approximation predicts activation energies that are far too high.

In an advanced study¹⁴¹ based on IRC following at the MP2 level using the McLean–Chandler (MC) basis¹⁴⁷ for Si combined with a 311G** basis¹⁴⁸ for H, and with single-point calculations at the MP4(SDTQ) level using the MC-311++G(3df,3pd) basis set,¹⁴⁹ led to an insertion barrier that is only 1.7 kcal mol⁻¹ above the separated fragments. However, at a certain level of calculation a long-range potential well describing a silylene–hydrogen complex is found.^{139,141} Relative to the minimum of this well an activation energy of 4.8 kcal mol⁻¹ is predicted. The major part of this energy comes from the ZPE correction. A diagram of the energetics for this reaction obtained in this work is given in Fig. 5.

Fig. 6 reproduces optimized geometries of the transition state for the insertion reaction obtained at different levels of calculation. As seen from the figure the geometries are quantitatively dependent on the calcula-

Table 4. Calculated activation energies (in kcal mol⁻¹) for the insertion reactions indicated by column headings as a function of basis set and level of perturbation. Zero-point energy corrections for the reactions are also included.

	$\text{CH}_2 + \text{H}_2$	$\text{CHF} + \text{H}_2$	$\text{CF}_2 + \text{H}_2$	$\text{SiH}_2 + \text{H}_2$	$\text{SiHF} + \text{H}_2$	$\text{SiF}_2 + \text{H}_2$
HF/3-21G	0.3	18.2	52.6	27.5	44.3	75.8
HF/6-31G*	0.7	18.4	53.6	18.4	36.6	68.7
MP2/6-31G*	-3.1	9.3	43.1	8.4	28.2	64.4
MP3/6-31G*	-2.6	9.3	41.9	8.4	27.5	62.7
MP4/6-31G*	-2.4	10.8	43.5	9.1	28.5	63.4
DZPE/3-21G	4.3	4.5	3.6	3.1	2.6	1.9

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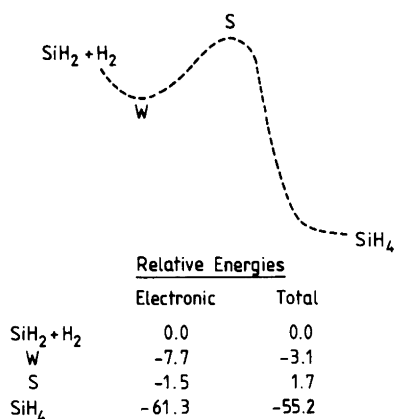


Fig. 5. Energetics for the insertion of SiH₂ into H₂. Energies in kcal mol⁻¹ calculated at the level MP4(SDTQ)/MC-311 + G(3df,3pd)//MP2/MC-311G(2d,2p). Total energy refers to the sum of the electronic energy and zero-point correction. Reprinted with permission from *J. Am. Chem. Soc.* 108 (1986) 2195. © (1986) American Chemical Society.¹⁴¹

tional approximation applied, but they all show a transition state that is in the nucleophilic stage of the reaction.

A systematic study of the possible influence of substituents on the silylene insertion into H₂ has been published in a paper¹³⁹ including the series H₂Si:, HFSi: and F₂Si:. The paper also included the same reaction of the corresponding methylene series. The geometry optimizations were carried through using both the extended 3-21G and the 6-31G* basis sets at the Hartree-Fock level. Energies were corrected for electron correlation by MP4 calculations including single, double and quadruple excitations. The optimized geometries of the transition states, given in Fig. 6, show some interesting trends. Increasing the number of F atoms leaves the silylene-H₂ distance approximately unchanged, but increases the HX₁Si angle (where X₁ is the midpoint of the H-H bond) and also the X₁SiX₂ angle (where X₂ is on the silylene valence angle bisector). These structural trends are interpreted in the following way.¹³⁹ The transition structure occurs progressively later along the reaction path for insertion as the fluorine substitution is increased. This is found to be in accordance with Hammond's rule, as fluorine substitution also is found to decrease the exothermicity of the insertion reactions.

The calculated barrier heights, reproduced in Table 4, show a large increase as a result of fluorine substitution at all levels of calculation. The first F atom increases the barrier by about 20 kcal mol⁻¹, and the second one by an additional 30 kcal mol⁻¹. By introducing correlation corrections the predicted barriers are lowered by 8-10 kcal mol⁻¹. These corrections do not change the main conclusion that increased fluorine substitution leads to markedly higher transition barriers.

Pentacoordinated silicon anions. One of the noticeable differences between carbon and silicon is the ability

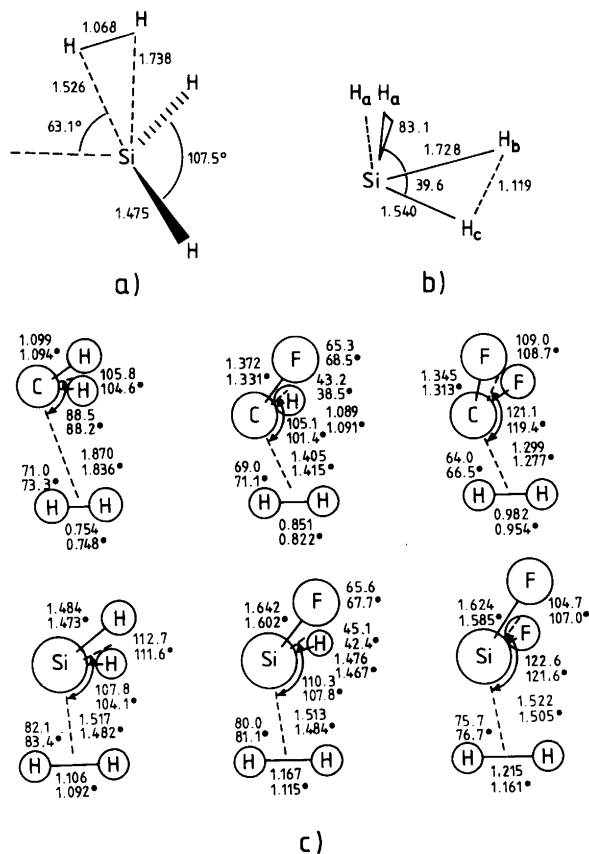
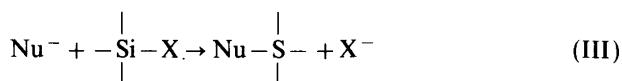


Fig. 6. (a) and (b) Optimized transition structures (in Å and degrees) for the insertion of SiH₂ into H₂: (a) at the TCSCF/(dz + p) level of theory, reproduced with permission from the Royal Society of Chemistry from Ref. 138; (b) at the MCSCF/6-31G* level of theory, $R(\text{CH}_a) = 1.483$, $H_a\text{SiH}_c$ angle = 105.8; reproduced with permission from *J. Am. Chem. Soc.* 108 (1986) 2192. © (1986) American Chemical Society.¹⁴¹ (c) Transition structures for carbene and silylene insertion into H₂, optimized at HF/3-21G (no superscript) and HF/6-31G* (filled circles). For CHF, the F-C-X-H₂ dihedral angle is 98.9°, 99.4°, where X is a dummy atom in the CHF and C-H₂ planes. Similarly for SiHF, F-Si-X-H₂ is 101.7°, 102.4°. Reproduced with permission from *J. Am. Chem. Soc.* 106 (1984) 5848. © (1984) American Chemical Society.¹³⁹

of Si to form stable pentacoordinated compounds. Several pentacoordinated silicon anions have been detected and studied in the gas phase,¹⁵⁰⁻¹⁵² using the flowing afterglow¹⁵³⁻¹⁵⁵ and ion cyclotron resonance¹⁵⁶ techniques. Gas-phase experiments of this kind are very important as a reference for theoretical calculations on ion stabilities and reactivities. On the other hand, accurate *ab initio* calculations may contribute to suggesting new species that could be looked for in gas-phase investigations under low pressure, where solvent effects are absent. In a recent combined investigation using the flowing afterglow technique and molecular orbital calculations substitution reactions of the kind shown in reaction (III)



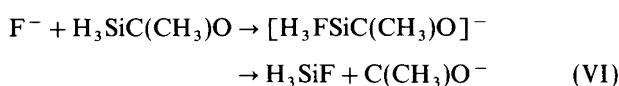
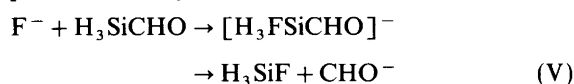
have been systematically studied.¹⁵³ It was found that exothermic reactions occurred at the collision rate, whereas analogous endothermic reactions were not observed in the experiment. In the cases where no substitutions occurred a series of pentacoordinate silicon anions were detected.

A series of studies of anionic pentacoordinated silicon species have been made.¹⁵⁷⁻¹⁶² The most extensive calculations have been performed on the prototype SiH_5^- , although products arising from the insertion reaction (IV),



where $\text{X} = \text{H}, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}, \text{SiH}_3, \text{PH}_2, \text{SH}$ and Cl , have also been studied.¹⁶³ The stability of the pentacoordinated anion relative to departure of HX has also been evaluated by theoretical calculations. The major problems addressed in these studies are related to the stereochemistry of the substitution, and the question as to whether the anion is an intermediate or a transition state for the reaction.

Very recently a similar theoretical study of the more complex reaction systems (V) and (VI) has been per-



formed.¹⁶⁴ The calculations were spurred by the experimental observation¹⁶⁵ that when F^- ions collide with $(\text{CH}_3)_3\text{SiC}(\text{C}_3\text{H}_7)\text{O}$ in the gas phase, acetyl anions, $\text{C}(\text{CH}_3)\text{O}^-$, are detected. For computational reasons the methyl groups attached to silicon in the experiment were replaced by hydrogens in the calculations. Geometry optimizations for all the species involved were performed within the RHF approximation using a 6-31++G** basis.¹⁶⁶ The diffuse functions were included in the basis, as they are known to be important for an appropriate description of the electron distribution in anions. Energies were estimated using perturbation calculations up to fourth order, MP4(SDTQ). All energies were corrected for zero-point energy (ZPE) contributions calculated analytically, and using the same basis.

One group of problems addressed in these calculations may be summarized by the following questions: Do the pentacoordinated Si anions exist as stable species in the gas phase, or are they transition states in one-step reactions? If the anions represent local minima on the potential surface, does the F^- ion fall into the acylsilane without a barrier, or is there an activation energy for the process? What is the shape of the energy surface for the escape of the leaving ion in the displacement reaction? Are the displacement reactions endothermic or exothermic, and how do the predicted energies agree with qualitative estimates based on experimental information?

The pentacoordinated anions resulting from a nucleophilic attack on Si by F^- have a trigonal bipyramidal

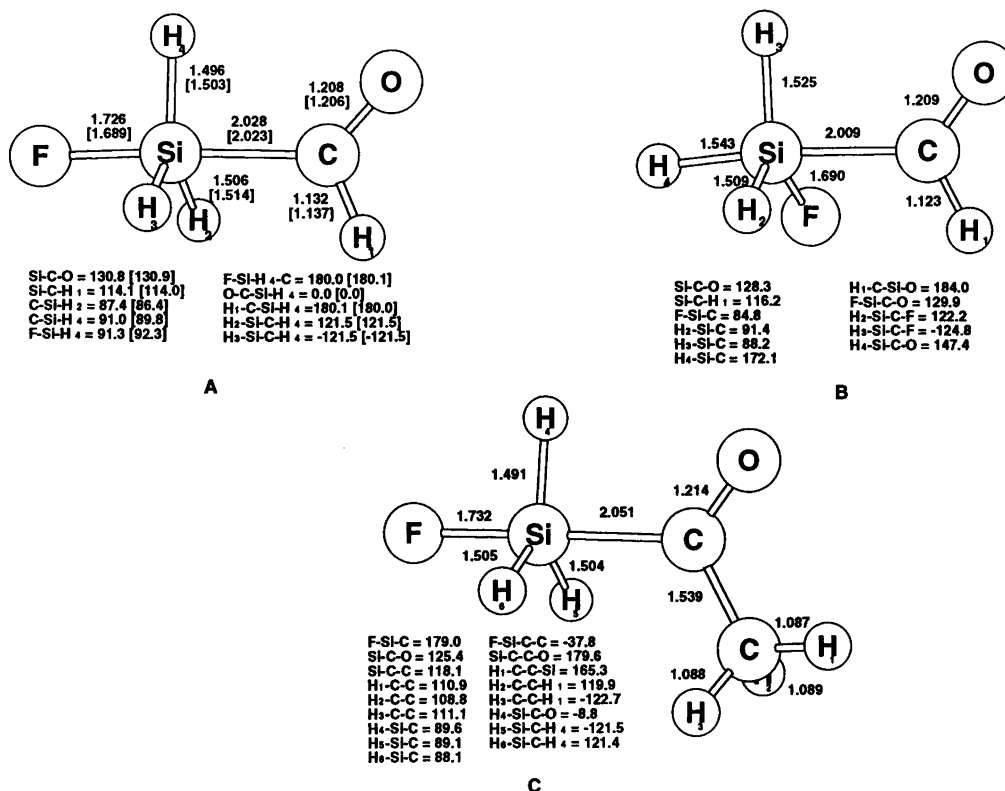


Fig. 7. Optimized geometries of pentacoordinated anions. Adducts of F^- with formylsilane (A and B), and with acetylsilane (C). Optimizations at HF/6-31++G**. Values in parentheses on A are optimizations at HF/6-31G**.

structure as shown in Fig. 7. Depending on the mode of attack the F atom may be in an axial or equatorial position. In the case of formylsilane both forms were studied and their equilibrium geometries are given in Fig. 7. The global energy minimum is for the axial form. The energy associated with the loss of F^- from this form is predicted to be $50.5 \text{ kcal mol}^{-1}$, which means that the pentacoordinated anion has a large stabilization energy relative to the reactants. The energy of the anion relative to the sum of the energies for $FSiH_3$ and CHO^- was predicted to be even lower, viz. $-56.8 \text{ kcal mol}^{-1}$. This implies (1) that the pentacoordinated anion is situated in a deep energy minimum along the displacement reaction path, and (2) that the displacement reaction is endothermic by $6.3 \text{ kcal mol}^{-1}$.

For the acetylsilane only the pentacoordinated anion having F in an axial position was optimized. Its geometry, presented in Fig. 7, shows a trigonal bipyramidal arrangement around Si that is very similar to the formylsilane system. The energetics for this reaction also parallels the formyl case. The adduct was found to have an energy of $-47.6 \text{ kcal mol}^{-1}$ relative to the reactants, and an endothermicity of $3.6 \text{ kcal mol}^{-1}$. Considering the fact that this displacement reaction is observed in the gas phase [with $(CH_3)_3Si-$], and that the energetics for the formyl reaction is very similar, the latter reaction should not be excluded on the basis of thermodynamics.

In order to search for a possible energy barrier along the reaction path leading to the pentacoordinated formylsilane anion, the geometry of the anion was fully optimized for a series of fixed values of the F–Si distance. The results of these calculations indicated that the F^- ion approaches silicon along an extension of the Si–C bond, and that during the approach the H atoms bound to Si monotonically move from a nearly tetrahedral Si arrangement to a plane orthogonal to the F–Si–C axis, i.e. a trigonal bipyramidal arrangement around Si. The energy curve for this approach did not reveal any barrier to the reaction. The same approach was used to analyse the

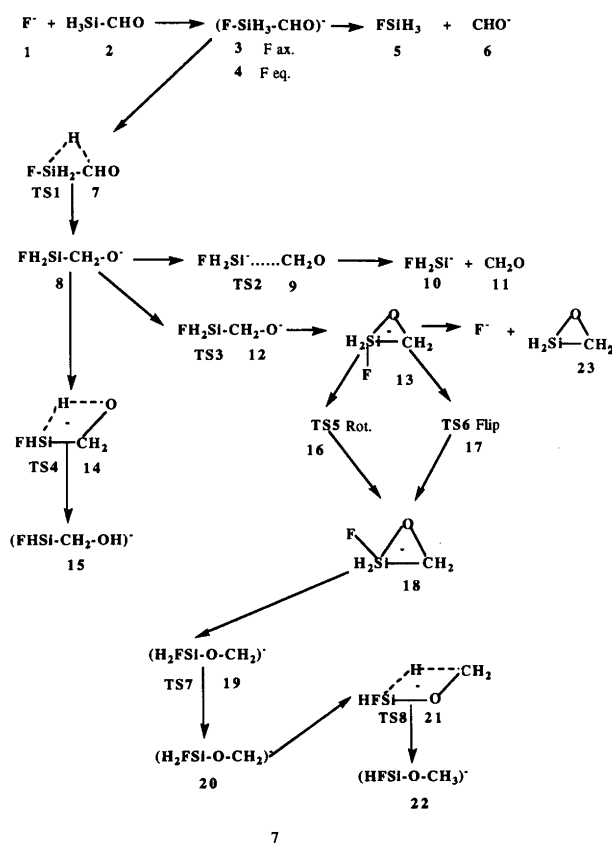


Fig. 8. Chart of possible reaction channels emanating from the adduct between F^- and formylsilane. From Ref. 164.

energetics and geometry changes associated with a departure of the CHO^- ion as leaving group. In this process we found a smooth change to a tetrahedral geometry around Si as CHO^- departed. The energy change for this process demonstrated a monotonic increase until reaching the sum of the energies for $FSiH_3$ and CHO^- . This implies that the leaving group departs along a smooth energy curve without any local hump.

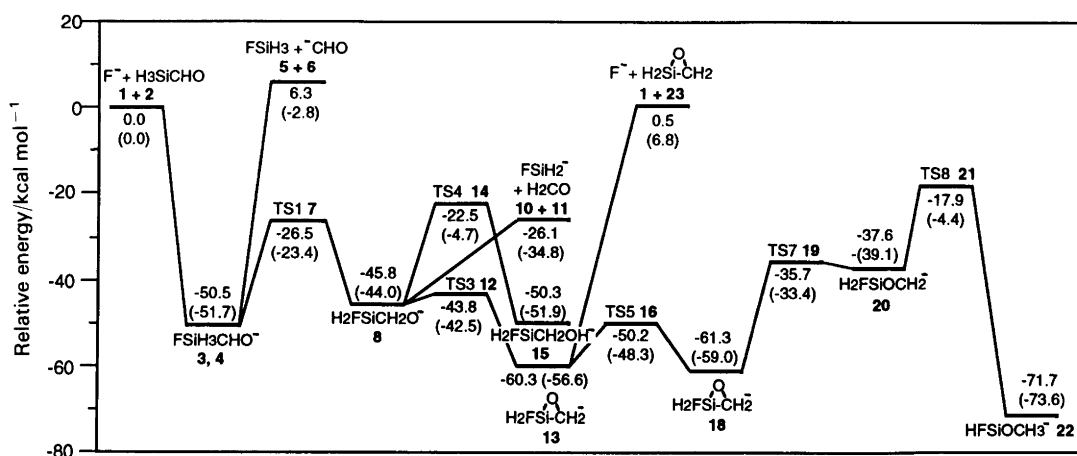


Fig. 9. Theoretical estimates of relative energies in kcal mol^{-1} . Upper values refer to MP4(SDTQ) + ZPE. Lower values (in parentheses) refer to HF + ZPE. From Ref. 164.

A second aim of the calculations was to obtain accurate information on thermodynamic and kinetic stabilities of species that are conceivable as products by further reactions of the initially formed formylsilane adduct. The species included and the different reaction channels considered in this study are shown in Fig. 8.

All the species included in the study were fully optimized at the SCF level using a 6-31++G** basis, and energies were calculated up to the MP4(SDTQ) level. Relative energies were also corrected for differences in ZPE. The energy diagram displayed in Fig. 9 does reveal some interesting features. Firstly it shows that the initially formed adduct may rearrange unimolecularly to several other low-energy species, notably an ether HFSiOCH_3^- and two three-membered rings having pentacoordinated Si atoms. Secondly the majority of the barriers to these unimolecular rearrangements are small, indicating that many of these species should be accessible in thermal reactions. The largest barrier between the initially formed adduct and the multitude of rearranged species is around 25 kcal mol^{-1} . This implies that many of them could be possible targets for experimental observations in the gas phase.

Some problems and challenges met in theoretical studies of chemical reactions

As mentioned in the Introduction, and illustrated in other paragraphs of this article, the computation of a potential surface for a chemical reaction is far more complicated and demanding than describing a well behaved closed shell molecule in its electronic ground state. In the latter case restricted SCF calculations using a split valence basis set will as a rule give an adequate description of its ground-state properties.

In a chemical reaction this is no longer valid. During a reaction chemical bonds are broken and/or formed. This may bring about a significant redistribution of electrons, as pairs of electrons are decoupled and reunited in new arrangements as the system moves along the reaction path. A realistic description of such a process requires calculations that go beyond the SCF approach. This is especially important for locating and characterizing transition states, which are often weakly bonded structures having only partial bonding. In many cases bond rupture is almost completed in the transition state, and its structure is accordingly properly described only by a wavefunction that also incorporates diradical and ionic states. In many-step reactions there are short-lived and unstable reaction intermediates that represent very shallow minima on the potential surface. The location and characterization of such intermediates often requires advanced calculational techniques.

In a study of a chemical reaction it is also important to realize that the finding of one transition structure does not exclude the possibility of alternative reaction paths having other transition structures. In order to discriminate between alternative reaction channels a quantitative

assessment of the energies of each of the located transition structures is essential. This may require energy calculations at a very high level.

In choosing a theoretical model adequate for describing a chemical reaction there are often several options available, but also pitfalls and problems are encountered. In spite of the fact that each reaction system has to be treated individually, there are some common problems and challenges that are met in calculations on chemical reactions. Here we mention a couple of the more important problems that have to be considered and tackled in calculations of this kind.

First we will focus on the size-consistency problem. When a molecule undergoes a reaction that splits it up in several fragments it is required of the method chosen that the energy predicted for the assembly of the non-interacting fragments equals the sum of the energies for each of the fragments. Unless this requirement is met, a comparison of energies and other properties of molecules of different size will not give quantitatively meaningful results. Unfortunately truncated CI methods like CID and CISD, which are computationally attractive for incorporation of electron correlation, do not meet this requirement. A correction to energies predicted by CI in order to compensate for this shortcoming has been developed, and is in use.^{167,168} Recently an alternative CI method, called quadratic CI (QCI), has been developed.¹⁶⁹ This method is size-consistent at all levels, and QCI approximations including both single and double excitations with estimates of the effect of triple excitations have been implemented in the Gaussian program package.⁴

An alternative way of including electron correlation is to apply perturbation methods. One type of approximation along this line is the Møller–Plesset (MP)⁷⁷ perturbation, which is closely related to many-body perturbation theory. Perturbation expansions of this kind to any order satisfy the size-consistency requirement, and are in this respect more satisfactory than the CID and CISD methods. However, contrary to the CI methods, perturbation expansions do not give a variationally determined energy, as they are not derived as expectation values of the Hamiltonian. This implies that energies predicted by such expansions to any order are not upper bounds to the exact energy for the system under consideration.

Another problem often encountered in calculations on chemical reactions is related to symmetry breaking and spin contamination. As mentioned above (pp. 632 and 634), a description of bond-breaking and bond-forming processes requires open-shell approaches, as spin pairs may be decoupled and reunited in new arrangements along such reaction paths. From a computational point of view spin-unrestricted approximations are very attractive for treating such cases, but as they give wavefunctions that are not eigenfunctions of the S^2 operator, severe spin contamination of the wavefunction may occur. In such cases both optimized geometries and calculated

energies may be influenced by the contribution of higher spin states to the wavefunction. A systematic study of geometries obtained by UHF calculations on open-shell cases show that for small basis sets the results are very poor, whereas for larger basis sets they improve.¹⁵ A proper treatment of spin contamination implies single or multiple projections in order to correct for the unwanted contributions to the wavefunction. The rearrangement reaction discussed on pp. 634–636 shows that the energy corrections resulting from projections may be very large.⁷⁶ In a recent study of the dimerization of HNO it was found that the energy of the transition state relative to the *trans*-form of the dimer calculated at the UMP4(SDTQ) level changed from 44.8 to 24.9 kcal mol⁻¹ after projecting out states from *s* + 1 to *s* + 4.¹⁷⁰ Another important consequence of spin contamination is the fact that significant spin contamination may give a very slow convergence of perturbation expansions. This means that reliable energy predictions would require expansions to a very high order.¹⁷¹ For open-shell species belonging to a certain symmetry group the lowest energy UHF solution often give molecular orbitals that belong to a point group of lower symmetry. By imposing a symmetry-constrained solution, geometries that are in better agreement with experiment will often be obtained, and the spin contamination will be significantly reduced.¹⁵

Today powerful algorithms implemented in advanced program systems combined with high-speed supercomputers have provided an important new tool for high level theoretical studies of chemical reactions. If chemists using this tool are able to take advantage of its versatility and at the same time avoid the pitfalls and meet the challenges it presents, they may gain detailed insight into the fascinating world of chemical reactions.

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References

- Richards, W. G., Walker, T. E. H. and Hinkley, R. K. *A Bibliography of ab initio Molecular Wavefunctions*, Oxford University Press, Oxford 1971, and supplements for 1970–73, 1974–77 and 1978–80.
- Ohno, K. and Morokuma, K. *Quantum Chemistry Literature Data Base*, Elsevier, Amsterdam 1982; annually appearing supplements available on magnetic tapes and published in special issues of *THEOCHEM*.
- BROWSE* Quantum Chemistry Database System, Gaussian Inc., Pittsburgh, PA.
- Frisch, M. J., Head-Gordon, M., Trucks, G. W., Foresman, J. B., Schlegel, H. B., Raghavachari, K., Robb, M., Binkley, J. S., Gonzales, C., Defrees, D. J., Fox, D. J., Whiteside, R. A., Seeger, R., Melius, C. F., Baker, J., Martin, R. L., Kahn, L. R., Stewart, J. J. P., Topiol, S. and Pople, J. A. *GAUSSIAN 90*, Gaussian Inc., Pittsburgh, Pennsylvania 1990, and a series of forerunners to this program developed within the same group.
- Guest, M. F. *GAMESS* SERC Daresbury Laboratory, 1990, and previous releases of the same program.
- Peterson, M. R. and Poirier, R. A. *MONSTERGAUSS*, University of Toronto, Toronto, Ontario.
- Miertus, S., Scrocco, E. and Tomasi, J. *Chem. Phys.* 55 (1980) 117.
- Rivail, J. L., Terryn, B., Rinaldi, D. and Ruiz-Lopez, M. F. *J. Mol. Struct. (THEOCHEM)* 120 (1985) 387.
- Karlström, G. *J. Phys. Chem.* 92 (1988) 1315.
- Hoshi, H., Sakurai, M., Inoue, Y. and Chujo, R. *J. Chem. Phys.* 87 (1987) 1107.
- Ågren, H., Medina-Llanos, C. and Mikkelsen, K. V. *Chem. Phys.* 115 (1987) 43.
- Alagona, G., Ghio, C., Igual, J. and Tomasi, J. *J. Mol. Struct. (THEOCHEM)* 204 (1990) 253.
- Montagnani, R. and Tomasi, J. *Int. J. Quant. Chem.* 39 (1991) 851.
- Bonaccorsi, R., Cammi, R. and Tomasi, J. *J. Comput. Chem.* 12 (1991) 301.
- Hehre, W. J., Radom, L., Schleyer, P. v. R. and Pople, J. A. *Ab Initio Molecular Orbital Theory*, J. Wiley, New York 1986.
- Born, M. and Oppenheimer, R. *Ann. Phys.* 84 (1927) 457.
- Mezey, P. G. *Potential Energy Hypersurfaces*, Elsevier, Amsterdam 1987.
- Pulay, P. *Mol. Phys.* 17 (1969) 197.
- Pulay, P. *Mol. Phys.* 18 (1970) 473.
- Pulay, P. *Mol. Phys.* 36 (1971) 2470.
- Bratoz, S. and Allavena, M. *J. Chem. Phys.* 37 (1962) 2138.
- Pulay, P. *Adv. Chem. Phys.* 69 (1987) 241.
- Schlegel, H. B. *Adv. Chem. Phys.* 67 (1987) 249.
- Bernardi, F. and Robb, M. A. *Adv. Chem. Phys.* 67 (1987) 155.
- Roothaan, C. C. J. *Rev. Mod. Phys.* 23 (1951) 69.
- Hall, G. G. *Proc. R. Soc. London, Ser. A* 205 (1951) 541.
- Pople, J. A., Krishnan, R., Schlegel, H. B. and Binkley, J. S. *Int. J. Quantum Chem., Quantum Chem. Symp.* 13 (1979) 225.
- Schlegel, H. B. and Frisch, M. J. In: Formosinho, S. J., Csizmadia, I. G. and Arnaut, L. G., Eds., *Theoretical and Computational Models for Organic Chemistry*, Kluwer Academic Publications, New York 1991.
- Kato, S. and Morokuma, K. *Chem. Phys. Lett.* 65 (1979) 19.
- Goddard, J., Handy, N. C. and Schaefer, III, H. F. *J. Chem. Phys.* 71 (1979) 1525.
- Dupuis, M. *J. Chem. Phys.* 74 (1981) 5758.
- Schlegel, H. B. and Robb, M. *Chem. Phys. Lett.* 93 (1982) 43.
- Osamura, Y., Yamaguchi, Y. and Schaefer, III, H. F. *J. Chem. Phys.* 77 (1982) 385.
- Gerratt, J. and Mills, I. J. *Chem. Phys.* 49 (1968) 1719.
- Pulay, P. *J. Chem. Phys.* 78 (1983) 5043.
- Jørgensen, P. and Simons, J. *J. Chem. Phys.* 79 (1983) 334.
- Almløf, J. and Taylor, P. R. *Int. J. Quantum Chem.* 27 (1985) 743.
- Yamaguchi, Y., Osamura, Y., Fitzgerald, G. and Schaefer, H. F., III. *J. Chem. Phys.* 78 (1983) 1607.
- Camp, R. N., King, H. F., McIver, Jr., J. W. and Mullally, D. J. *J. Chem. Phys.* 79 (1983) 1089.
- Hoffmann, M. R., Fox, D. J., Gaw, J. F., Osamura, Y., Yamaguchi, Y., Grev, R. S., Fitzgerald, G., Schaefer, H. F., III, Knowles, P. J. and Handy, N. C. *J. Chem. Phys.* 80 (1984) 2660.
- Page, M., Saxe, P., Adams, G. F. and Lengsfeld, B. H., III. *J. Chem. Phys.* 81 (1984) 434.
- Banerjee, A., Jensen, J. O., Simons, J. and Shepard, R. *Chem. Phys.* 81 (1984) 203.
- Fukui, K. *J. Phys. Chem.* 74 (1970) 4161.
- Fukui, K. *Acc. Chem. Res.* 14 (1981) 363.
- Fukui, K., Kato, S. and Fujimoto, H. *J. Am. Chem. Soc.* 97 (1975) 1.

46. Baldrige, K. K., Gordon, M. S., Steckler, R. and Truhlar, D. G. *J. Phys. Chem.* 93 (1989) 5107.
47. Fukui, K., Yonezawa, T. and Shingu, H. *J. Chem. Phys.* 20 (1952) 722.
48. Fukui, K. *Theory of Orientation and Stereoselection*, Springer-Verlag, Berlin 1975.
49. Woodward, R. B. and Hoffmann, R. *J. Am. Chem. Soc.* 87 (1965) 395.
50. Hoffmann, R. and Woodward, R. B. *J. Am. Chem. Soc.* 87 (1965) 2046.
51. Woodward, R. B. and Hoffmann, R. *J. Am. Chem. Soc.* 87 (1965) 2511.
52. Woodward, R. B. and Hoffmann, R. *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim 1971.
53. Pechukas, P. *J. Chem. Phys.* 64 (1976) 1516.
54. Schaad, L. J. and Hu, J. *Personal communication*.
55. Pople, J. A., Binkley, J. S. and Seeger, R. *Int. J. Quantum Chem. Symp.* 10 (1976) 1.
56. Forsman, J. B., Head-Gordon, M., Pople, J. A. and Frisch, M. J. *J. Phys. Chem.* 96 (1992) 135.
57. Fletcher, R. *Practical Methods of Optimization*, Wiley, Chichester 1981.
58. Gill, P. E., Murray, W. and Wright, M. H. *Practical Optimization*, Academic Press, New York 1981.
59. Powell, M. J. D., ed., *Non-linear Optimization*, Academic Press, New York 1982.
60. Scales, L. E. *Introduction to Non-linear Optimization*, Macmillan, Basingstoke 1985.
61. Fletcher, R. and Powell, M. J. D. *Comput. J.* 6 (1963) 163.
62. Murtagh, B. A. and Sargent, R. W. H. *Comput. J.* 13 (1972) 185.
63. Broyden, C. G. *J. Inst. Math. Appl.* 6 (1970) 76.
64. Fletcher, R. *Comput. J.* 13 (1970) 317.
65. Goldfarb, D. *Math. Comput.* 24 (1970) 23.
66. Shanno, D. F. *Math. Comput.* 24 (1970) 647.
67. Schlegel, H. B. *J. Comput. Chem.* 3 (1982) 214.
68. Chesick, J. P. *J. Phys. Chem.* 65 (1961) 2170.
69. Doering, W. von E. and Gilbert, J. C. *Tetrahedron. Suppl.* 7 (1966) 397.
70. Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*, Academic Press, New York 1981.
71. Baldwin, J. E. and Flemming, R. H. *J. Am. Chem. Soc.* 94 (1972) 2140.
72. Baldwin, J. E. and Fleming, R. H. *J. Am. Chem. Soc.* 95 (1973) 5249.
73. Baldwin, J. E. and Fleming, R. H. *J. Am. Chem. Soc.* 95 (1973) 5256.
74. Baldwin, J. E. and Fleming, R. H. *J. Am. Chem. Soc.* 95 (1973) 5261.
75. Gajewski, J. J. *J. Am. Chem. Soc.* 98 (1976) 5254.
76. Skancke, P. N., Koga, N. and Morokuma, K. *J. Am. Chem. Soc.* 111 (1989) 1559.
77. Møller, C. and Plesset, M. S. *Phys. Rev.* 46 (1934) 618.
78. Roos, B. O., Taylor, P. R. and Siegbahn, P. E. M. *Chem. Phys.* 48 (1980) 157.
79. Siegbahn, P. E. M., Almløf, J., Heiberg, A. and Roos, B. O. *J. Chem. Phys.* 74 (1981) 2384.
80. Roos, B. O. *Int. J. Quantum Chem. Symp.* 14 (1980) 175.
81. Løwdin, P.-O. *Phys. Rev.* 97 (1955) 1474.
82. Gill, P. M. W. and Radom, L. *Chem. Phys. Lett.* 132 (1986) 16.
83. Sosa, C. and Schlegel, H. B. *Int. J. Quantum Chem.* 29 (1986) 1001.
84. Schlegel, H. B. *J. Chem. Phys.* 84 (1986) 4530.
85. Knowles, P. J. and Handy, N. C. *J. Chem. Phys.* 88 (1988) 6991.
86. Yamaguchi, K., Takahara, Y., Fueno, T. and Houk, K. N. *Theor. Chim. Acta* 73 (1988) 337.
87. Doering, W. v. E. and Roth, H. D. *Tetrahedron* 26 (1970) 2825.
88. Gajewski, J. J. *J. Am. Chem. Soc.* 93 (1971) 4450.
89. Gajewski, J. J. and Chou, S. K. *J. Am. Chem. Soc.* 99 (1977) 5696.
90. Baldwin, J. E. and Chang, G. E. C. *Tetrahedron* 32 (1982) 825.
91. Hehre, W. J., Salem, L. and Willcott, M. R. *J. Am. Chem. Soc.* 96 (1974) 4328.
92. Feller, D., Tanaka, K., Davidson, E. R. and Borden, W. T. *J. Am. Chem. Soc.* 104 (1982) 967.
93. Skancke, A., Schaad, L. J. and Hess, B. A., Jr. *J. Am. Chem. Soc.* 110 (1988) 5315.
94. Chesick, J. P. *J. Am. Chem. Soc.* 85 (1963) 2720.
95. Cope, A. C. and Hardy, E. M. *J. Am. Chem. Soc.* 62 (1940) 441.
96. Levy, H. and Cope, A. C. *J. Am. Chem. Soc.* 66 (1944) 1684.
97. Foster, E. G., Cope, A. C. and Daniels, F. *J. Am. Chem. Soc.* 69 (1947) 1893.
98. Aldridge, G. R. and Murphy, G. W. *J. Am. Chem. Soc.* 73 (1951) 1158.
99. Kistiakowsky, G. B. and Ransom, W. W. *J. Chem. Phys.* 7 (1938) 725.
100. Gompper, R. *Angew. Chem.* 81 (1969) 348.
101. Evans, M. G. and Warhurst, E. *Trans. Faraday Soc.* 34 (1938) 614.
102. Evans, M. G. *Trans. Faraday Soc.* 35 (1939) 824.
103. Badea, F. *Reaction Mechanisms in Organic Chemistry*, Abacus Press, Turnbridge Wells, Kent 1977.
104. Dewar, M. J. S. *J. Am. Chem. Soc.* 106 (1984) 209.
105. Borden, W. T., Loncharich, R. J. and Houk, K. N. *Annu. Rev. Phys. Chem.* 39 (1988) 213.
106. Doering, W. v. E. and Roth, W. R. *Tetrahedron* 18 (1962) 67.
107. Doering, W. v. E., Toscano, V. G. and Beasley, G. H. *Tetrahedron* 27 (1971) 299.
108. Dewar, M. J. S. and Wade, L. E. Jr. *J. Am. Chem. Soc.* 99 (1977) 4417.
109. Komornicki, A. and McIver, J. W. *J. Am. Chem. Soc.* 98 (1976) 4553.
110. Dewar, M. J. S., Ford, G. P., McKee, M. L., Rzepa, H. S. and Wade, L. E. Jr. *J. Am. Chem. Soc.* 99 (1977) 5069.
111. Dewar, M. J. S. and Jie, C. *J. Am. Chem. Soc.* 109 (1987) 5893.
112. Dewar, M. J. S. and Jie, C. *J. Chem. Soc., Chem. Commun.* (1987) 1451.
113. Dewar, M. J. S. *J. Am. Chem. Soc.* 106 (1984) 209.
114. Osamura, Y., Kato, S., Morokuma, K., Feller, D., Davidson, E. R. and Borden, W. T. *J. Am. Chem. Soc.* 106 (1984) 3362.
115. Morokuma, K., Borden, W. T. and Hrovat, D. A. *J. Am. Chem. Soc.* 110 (1988) 4474.
116. Dewar, M. S. J. and Healy, E. F. *Chem. Phys. Lett.* 141 (1987) 521.
117. Hrovat, D. A., Borden, W. T., Vance, R. L., Rondan, N. G., Houk, K. N. and Morokuma, K. *J. Am. Chem. Soc.* 112 (1990) 2018.
118. Dupuis, M., Murray, C. and Davidson, E. R. *J. Am. Chem. Soc.* 113 (1991) 9756.
119. Brook, A. G., Abdesaken, F., Gutekunst, B., Gutekunst, G. and Kallury, R. K. *J. Chem. Soc., Chem. Commun.* (1981) 191.
120. West, R., Fink, M. J. and Michl, J. *Science (Washington, D. C.)* 214 (1981) 1343.
121. Wiberg, N., Schurz, K., Reber, G. and Muller, G. *J. Chem. Soc., Chem. Commun.* (1986) 591.
122. Hesse, M. and Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* 25 (1986) 649.
123. Raabe, G. and Michl, J. *Chem. Rev.* 85 (1985) 419.
124. Gordon, M. S. In: Liebman, J. F. and Greenberg, A., Eds., *Molecular Structure and Energetics*, Vol. 1, Chap. 4, p. 101, VCH Publishers, Deerfield Beach, FL 1986.

125. Raabe, G. and Michl, J. In: Patai, S. and Rappoport, Z., Eds., *The Chemistry of Silicon Compounds*, Part 2, Chap. 17, p. 1015, Wiley, New York 1986.
126. Apeloig, Y., in Patai, S. and Rappoport, Z., Eds., *The Chemistry of Organic Silicon Compounds*, Part 1, Chap. 2, p. 57, Wiley, New York 1986.
127. Morokuma, K., Ohta, K., Koga, N., Obara, S. and Davidson, E. R. *Faraday Symp. Chem. Soc.* 19 (1984) 49.
128. Ohta, K., Davidson, E. R. and Morokuma, K. *J. Am. Chem. Soc.* 108 (1985) 3466.
129. Hoffmann, R., Gleiter, R. and Mallory, F. B. *J. Am. Chem. Soc.* 92 (1970) 1460.
130. Basch, H. *J. Chem. Phys.* 55 (1971) 1700.
131. Cheung, L. M., Sundberg, K. R. and Ruedenberg, K. *Int. J. Quantum Chem.* 16 (1979) 1103.
132. Ruedenberg, K., Schmidt, M. W., Gilbert, M. M. and Elbert, S. T. *Chem. Phys.* 71 (1982) 41.
133. Feller, D. and Davidson, E. R. *J. Phys. Chem.* 87 (1983) 2721.
134. Bernardi, F. and Robb, M. A. *Mol. Phys.* 48 (1983) 1345.
135. Viswanathan, R., Thompson, D. L. and Raff, L. M. *J. Chem. Phys.* 80 (1984) 4230.
136. Gordon, M. S. *J. Chem. Soc., Chem. Commun.* (1981) 890.
137. Gordon, M. S. and Gano, D. R. *J. Am. Chem. Soc.* 106 (1984) 5421.
138. Grev, R. S. and Schaefer, H. F., III, *J. Chem. Soc., Chem. Commun.* (1983) 785.
139. Sosa, C. and Schlegel, H. B. *J. Am. Chem. Soc.* 106 (1984) 5847.
140. Sax, A. and Olbrich, G. *J. Am. Chem. Soc.* 107 (1985) 4868.
141. Gordon, M. S., Gano, D. R., Binkley, J. S. and Frisch, M. *J. Am. Chem. Soc.* 108 (1986) 2191.
142. Gordon, M. S. and Truong, T. N. *Chem. Phys. Lett.* 142 (1987) 110.
143. Gordon, M. S., Truong, N. T. and Bonderson, E. K. *J. Am. Chem. Soc.* 108 (1986) 1421.
144. Schlegel, H. B. and Sosa, C. *J. Phys. Chem.* 89 (1985) 537.
145. Kollmar, H. *J. Am. Chem. Soc.* 100 (1978) 2660.
146. Jeziorek, D. and Zurawski, B. *Int. J. Quantum Chem.* 16 (1979) 277.
147. McLean, A. D. and Chandler, G. S. *J. Chem. Phys.* 72 (1980) 5639.
148. Krishnan, R., Binkley, J. S., Seeger, R. and Pople, J. A. *J. Chem. Phys.* 72 (1980) 650.
149. Frisch, M. J., Pople, J. A. and Binkley, J. S. *J. Chem. Phys.* 80 (1984) 3265.
150. Damrauer, R., Burggraf, L. W., Davis, L. P. and Gordon, M. S. *J. Am. Chem. Soc.* 110 (1988) 6601.
151. Sheldon, J. C., Hayes, R. N. and Bowie, J. H. *J. Am. Chem. Soc.* 106 (1984) 7711.
152. DePuy, C. H., Bierbaum, V. M., Flippin, L. A., Grabowski, J. J., King, G. K., Schmitt, R. J. and Sullivan, S. A. *J. Am. Chem. Soc.* 102 (1980) 5012.
153. DePuy, C. H. and Bierbaum, V. M. *Acc. Chem. Res.* 14 (1981) 146.
154. Bierbaum, V. M., DePuy, C. H., Shapiro, R. H. and Stewart, J. H. *J. Am. Chem. Soc.* 98 (1976) 4229.
155. DePuy, C. H., Grabowski, J. J. and Bierbaum, V. M. *Science* 218 (1982) 955.
156. Bowie, J. H. *Acc. Chem. Res.* 13 (1980) 76.
157. Kutzelnigg, W., Wallmeier, H. and Wasilewski, J. *Theor. Chim. Acta* 51 (1979) 261.
158. Kutzelnigg, W. and Wasilewski, J. *J. Am. Chem. Soc.* 104 (1982) 953.
159. Shih, S. K., Peyerimhoff, S. D. and Buenker, R. J. *J. Chem. Soc., Faraday Trans. 2* (1986) 261.
160. Brandemark, U. and Siegbahn, P. E. M. *Theor. Chim. Acta* 66 (1984) 233.
161. Reed, A. E. and Schleyer, P. v. R. *Chem. Phys. Lett.* 133 (1982) 553.
162. Gordon, M. S., Davis, L. P., Burggraf, L. W. and Damrauer, R. *J. Am. Chem. Soc.* 108 (1986) 7889.
163. Davis, L. P., Burggraf, L. W., Gordon, M. S. and Baldrige, K. K. *J. Am. Chem. Soc.* 107 (1985) 4415.
164. Schlegel, H. B. and Skancke, P. N. *J. Am. Chem. Soc.* *In press.*
165. DePuy, C. H., Bierbaum, V. M., Damrauer, R. and Soderquist, J. A. *J. Am. Chem. Soc.* 107 (1985) 3385.
166. Clark, T., Chandrasekhar, J., Spitznagel, G. W. and Schleyer, P. v. R. *J. Comput. Chem.* 4 (1983) 294.
167. Langhoff, S. R. and Davidson, E. R. *Int. J. Quantum Chem.* 8 (1974) 61.
168. Pople, J. A., Seeger, R. and Krishnab, R. *Int. J. Quantum Chem. Symp.* 11 (1977) 149.
169. Pople, J. A., Head-Gordon, M. and Raghavachari, K. *J. Chem. Phys.* 87 (1987) 5968.
170. Luttke, W., Skancke, P. N. and Traetteberg, M. *Theor. Chim. Acta.* *In press.*
171. Handy, N. C., Knowles, P. J. and Somasundram, K. *Theor. Chim. Acta* 68 (1985) 87.

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