Review

Quantum Chemical Methods and Their Applications to Chemical Reactions

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This review is concerned with the impact of quantum chemistry on chemical reactions. Starting from the mid-sixties it focusses on those developments which have enabled us to predict essential features of simple chemical reactions. Thus model theories and computational methods are presented which provide the tools for these predictions. Then procedures to characterize potential surfaces and search methods for reaction paths are described. It is also attempted to relate these features to the terminology of the experimentalist. Finally a systematic survey of the main types of reaction (rearrangement, addition, elimination, substitution) is given.

Key words: Chemical reactions.

1. Introduction

The past decade has seen the advent of powerful quantum chemical methods with the ambitious goal to complement or even substitute the experimentalist's work on chemical reactions. How far these goals have been reached we want to describe in the following. Looking back, there have been two driving forces to advance the development. The first and in the short run the more successful one is the creation of model theories, best known by the work of Woodward and Hoffmann starting 1965 and well documented in their book [1]. Here the knowledge of the experimentalist and the theoretician were combined to achieve sufficient simplification, but retain the essential features of chemical reactions. The almost instantaneous success of their approach has prompted others [2, 3] to seriously pursue and extend their line of work. A careful evaluation of the situation shows, however, that credit was given to them more by the experimentalists than by the theoreticians. Whereas the experimentalists were fascinated in the tool and got more interested in theory, the theoreticians tended at first to little or no appreciation. For them the method

was an oversimplification with all its pitfalls and qualitative answers only. It could be classified as an extension of the well-known MO correlation diagrams. The attitude is not surprising considering that theoreticians were more engaged in the controversy of the relative merits of *ab initio* and semiempirical methods. Ten years ago, there was a tendency to judge methods according to the accuracy of numbers rather than their chemical content. At that time, *ab initio* methods had achieved superiority in calculations of molecular equilibria for small and medium systems. Much credit should be given to Michael Dewar and his collaborators who worked hard at developing semiempirical methods for chemical use. Not counting the many mistakes during the various stages and in the detailed examples of application, they have finally demonstrated that there is and will be a need for reliable semi-empirical MO methods. We are now at a time where the need for diversification, for interaction between experimentalists and theoreticians as well as among theoreticians themselves is recognized. Therefore this article deals in the second section with a brief survey of all these existing MO methods which have been ap-plied to questions of chemical reactions. The third section contains a description of the properties of potential surfaces, the questions involving transition states and intermediates, diradical and concerted reactions. We present the alternatives for reaction pathways and the various search procedures for relevant portions of potential hypersurfaces. Also the question of alternative products from one reactant is discussed. In the fourth section applications are given to a variety of reactions classified according to the chemist's standard scheme: We will see that rearrange-ment reactions have been most extensively pursued because they are of the simplest type. Addition and elimination reactions are complementary, but reveal differences when pursued in both directions. The least explored are substitution reactions, where symmetric substitutions were given preference.

In this article the following topics are not covered: Reactivity, conformational stability, rotation and inversion barriers, protonation and charge transfer reactions, hydrogen bonding. These topics constitute a vast field of application which have been covered by reviews already. Mostly articles on these topics lack the essential features of the focus of this review, namely the influence of the shape of the potential surface on the chemical reaction. Finally, with very minor exceptions, we have not reached the level to study extensively on real potential surfaces the kinetic motion including translation, rotation and vibration. So remarks on these topics, including trajectories, will be of preliminary and qualitative nature only.

2. Methods

Quantum chemical methods to describe patterns of chemical reactions fall into two categories: quantitative or qualitative. The former are capable of generating potential surfaces with significant accuracy and determining minima for reactants, products or intermediates, and saddle points for transition states. The latter use symmetry and topology to distinguish between various postulated pathways of diagram nature. Quantitative methods are called *ab initio* when the energy integrals from an approximate wavefunction and a usually non-relativistic Born–Oppen-heimer Hamiltonian are calculated; they are called semiempirical when fixed

experimental data, e.g. atomic ionization potentials, are used in approximate expressions for some energy integrals or adjustable parameters are varied to achieve best agreement between a calculated and experimental energy value, e.g. heats of formation for a number of reference compounds.

2.1. Ab initio Methods

Approximations. Most methods are based on the single-particle approximation which is popularly known as the MO picture. The MO's are in turn approximated as LCAO combinations. Atomic orbitals are given as Slater orbitals in a minimal basis set. Extension of the basis set leads to double zeta (DZ) orbitals where each atomic orbital of a minimal set is replaced by two orbitals of the same symmetry type with different exponents. Polarization functions (P) can be added to account for charge redistribution in molecules, e.g. *p*-orbitals on hydrogen and *d*-orbitals on carbon. The standard Slater type AO's can be in turn approximated by three or more Gaussians (G) (STO-3G) in a contracted (CG) basis set [4]. When an identification with Slater MO's is not intended and the Gaussian coefficients are varied independently we call the Gaussian basis set uncontracted (UG) [5]. Often AO's are composed as a linear combination of Gaussian lobe (GL) orbitals. The MO's are determined by the SCF or MCSCF procedure. The former wavefunction consists of one configuration which in turn consists of one or several determinants depending on the spin state. The SCF wavefunction can be improved by configuration interaction (CI). The additional configurations are obtained by replacing occupied by virtual orbitals. These orbitals can be orthogonal or non-orthogonal to the occupied orbitals. The correlation energy, i.e. the energy needed to correct the single particle picture, can be approximated by the independent (IEPA) or coupled electron pair approximation (CEPA) [6]. Also a generalized valence bond (GVB) method can be used.

Features. Ab initio methods can in principle solve the Schrödinger equation with any desired accuracy. The main obstacle is the limitation of size of basis sets and number of configurations by the computer time consumed. Geometries of molecules can be systematically improved. Studies on STO-3G, 4-31G, 6-31G by Pople and coworkers [7, 8] on AH_n systems demonstrate a need to go beyond the STO-3G level. In another article [9] it is claimed that heats of formation for organic compounds can be obtained with an error of 5 kcal/mole even on the STO-3G level. One objects to this comparison on the ground that experimental values were not corrected for zero point vibrational energy contributions. In other papers zero point energy corrections are taken into account for a few compounds [10] or the relative energies of isomers are compared with the relative heats of formation at 298°K [11]. The agreement is good for the level 4-31G and 6-31G.

Failures. STO-3G calculations often fail to produce acceptable binding energies and are hence unsuitable for chemical reactions.

2.2. Semiempirical Methods

The extended Hückel method was developed by Hoffmann [12] in the days of quantum mechanics when electronic interaction was difficult to calculate for larger

systems. The lack of explicit inclusion of this interaction leads to serious errors in energies and charge dependent quantities. The method is now obsolete and we will not discuss it further. The next step was the introduction of neglect of overlap methods (CNDO, INDO, NDDO), methods by Pople and coworkers [13–15]. Although the original version had rather large errors in the binding energies up to several hundred per cent, the principles of rotational invariance and the subsequent reduction of the number of energy integrals had a great impact on the further development of semiempirical methods. It eventually leads to Dewar's MINDO and MNDO and our SINDO modifications of Pople's scheme. We will not consider the PCILO [16] and Xα [17] methods here, because of insufficient data on the use for chemical reactions.

2.2.1. MINDO and MNDO Methods

Approximations. The framework is the SCF method with a minimal Slater type AO basis set. Only the valence electrons are treated explicitly. The rotational invariance requirements are the same as in the INDO method for MINDO and the same as in NDDO for MNDO. There exist three levels of the MINDO method the latest of which is MINDO/3. MINDO/1 [18] was abandoned because of poor accuracy in geometries and force constants in favor of MINDO/2 [19], the main features of which are described in the following. Here the two-center repulsion integrals are given as

$$\gamma_{AB} = \frac{1}{\sqrt{r_{AB}^2 + \frac{1}{4}(\gamma_{AA} + \gamma_{BB})^2}}$$

a term which was suggested by Ohno [20] and also by Klopman [21]. The resonance integral is given as

$$H_{ab} = \beta_{AB} S_{ab}(I_a + I_b)$$

β_{AB} is a parameter used to minimize the errors in heats of formation of a few reference compounds. Different from MINDO/2 where the Slater exponents had been used, in MINDO/3 [22] the exponents were varied in order to reduce the overestimate of CH bond lengths. The core-core repulsion was postulated as

$$E_{CC} = Z_A Z_B \left[\gamma_{AB} + \left(\frac{1}{r_{AB}} - \gamma_{AB} \right) e^{-\alpha_{AB} r_{AB}} \right].$$

Finally, in MINDO/3 the one-center integrals were calculated by a method due to Oleari *et al.* [23].

MINDO/3 needs an extensive number of atomic and molecular bond parameters. For first-row elements and hydrogen a total number of 102 adjustable parameters (15 core integrals U, 15 orbital exponents ζ, 36 resonance integrals β, and 36 corecore repulsion exponents α) is needed. MNDO [24] has reduced this number to 41 (15 core integrals U, 8 orbital exponents ζ, 10 resonance integrals β and 8 core-core repulsion exponents α) and added certain diatomic integrals neglected in the INDO approximation.

Features. MINDO/3 yields on the average good results for bond lengths, heats of formation of hydrocarbons, ionization potentials and dipole moments [25]. In chemical reactions activation energies are presented which are often good from either the reactant side or the product side. It is difficult to appreciate though that heats of formation are adjusted to values at 25°C, thus including vibrational contributions implicitly. MNDO properties have been tested for over 200 molecules [26–27]. An average improvement for all properties is documented. However rather unexpected failures in single molecules, e.g. CH_2 geometry, are to be taken seriously [28].

Failures. MINDO/3 bond angles are off by an average of 6 degrees. However, in some cases like OF_2 errors can be as large as 68° [29]. Heats of formation of fluorine compounds are in error by an average of 25 kcal/mole [27]. Hydrogen bonding cannot be described, because MINDO/3 fails to get binding [30, 31]. The method has also been criticized for its integral approximation at non-nearest neighbor distances [32]. This casts doubt on the reliability of MINDO/3 calculations of chemical reactions, e.g. transition state geometries. MNDO results for reactions have so far not been presented in the literature. No direct accuracy tests of force constants have been given in the literature, indirectly through vibration frequencies [33, 197] with acceptable accuracy.

2.2.2. SINDO Method

Approximations. We developed SINDO on the basis of symmetrically orthogonalized orbitals and commutator relations [34]. The invariance requirements are the same as in INDO. We have now abolished the CNDO/2 approximation of penetration and modified the method in the following way [35] keeping the spirit of CNDO/1. The diagonal core integrals are given as

$$H_{aa} = W_a + \sum_{B \neq A} U_{AB} + \sum_{B \neq A} S_{a,1S_B} F_B - \sum_{B \neq A} S_{ab} t_{ab}.$$

The third term is a pseudopotential term and the fourth term an orthogonalization correction given below. The resonance integrals are

$$H_{ab} = \tfrac{1}{4} S_{ab}(K_A + K_B)(f_A \alpha_a + f_B \alpha_b) + t_{ab}$$

$$f = 1 - e^{-\kappa r_{AB}}$$

$$t_{ab} = -\frac{\zeta_a^2 + \zeta_b^2}{2} \frac{S_{ab}(1 - S_{ab})}{1 + \rho_{ab}}.$$

The first term corrects the effect of truncation of the infinite expansion of a commutator equation [36]. The second term is a kinetic energy correction also due to the commutator equation.

SINDO 1 needs less than one half of the number of adjustable parameters of MINDO/3 and about the same as MNDO, in its present form 43 (8 orbital exponents ζ, 15 resonance integral coefficients K and 20 antipenetration factor exponents κ).

Features. SINDO 1 has been tested for over 200 molecules. It yields reliable ground state properties: bond lengths, bond angles and dihedral angles, heats of formation, ionization potentials and dipole moments are well reproduced with an average accuracy mostly better than with MINDO/3. In particular it reproduces qualitatively the H_2O_2 and N_2H_4 dihedral angles whereas MNDO fails to predict the right conformation. Heat of formation is for 0°K and comparison with experimental values can be made after zero point energy correction for vibration.

Failures. The original SINDO leads to results similar to MINDO/2. Bond lengths were overestimated by 10% and relative binding energies by 20%. SINDO 1 has reduced these errors considerably. The testing showed larger errors only for force constants where deviations from experimental data are 40-50%

2.3. Model Theories

Whereas *ab initio* and semiempirical MO methods produce data which can be compared with experimental results, model theories are incapable of doing this. On the other hand, they are much more appealing to experimental chemists, because they aim at a simplification of complicated detailed facts to reveal the essential features. The gross structure or the key elements of a reaction can be described through orbital or wavefunction behaviour, energy or force considerations. Topology and symmetry are used to construct continuous pathways on a qualitative energy surface. Alternatively data of computational methods are analyzed in a systematic, but to some extent arbitrary partitioning of total energy and force on the reacting system.

2.3.1. Topological Orbital Approach

Approximations. The best-known representative of this type are the Woodward–Hoffmann rules [1]. They establish model reaction pathways between reactants and products by considering those occupied and unoccupied molecular orbitals which are involved in the reaction. Most important are highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. The consideration is limited to those atoms undergoing changes in bonding during the course of the reaction. The picture is localized and has topological character. The rules are based on a non-relativistic Born–Oppenheimer Hamiltonian.

Features. The rules are applicable to concerted chemical reactions.
The use of orbital symmetry stresses the essential features of the reaction. The introduction of rotatory and disrotatory pathways for electrocyclic reactions and the supra-antara formalism of cycloaddition reactions is appealing because of its simplicity. It reduces the complicated energy hypersurface to qualitative two-dimensional cuts along an undefined reaction coordinate. The answers are yes or no for the occurrence of a reaction. Data of activation energies or geometries cannot be obtained.

Other work includes the orbital phase continuity principle by Goddard [37]. Selection rules can be obtained for reactions with less symmetry than the Woodward–Hoffmann rules need. The rules for low activation energy are: 1) bonding pairs of orbitals should remain strongly overlapping during reactions, 2) when bonding and non-bonding orbitals must delocalize over the same region, they will tend to become orthogonal at the transition state and hence will exhibit opposite phase-change characteristics, 3) the phase relations among the orbitals change continuously during the reaction. Dewar and collaborators [38, 39] have emphasized orbital isomerism as a controlling factor in chemical reactivity. They distinguish between homomers and lumomers depending on whether one considers isomers which can or cannot be converted into each other without HOMO-LUMO crossing. A topological orbital approach is also the mapping analysis proposed by Trindle [40]. It is based on the hypothesis that nuclear motion may stretch, bend and twist molecular orbitals, but will not introduce new nodes into the orbitals. An allowed reaction is characterized by a mapping which produces the orbitals of B from the orbitals of A in the reaction A → B by a topological identity. The overlap between the mapped function and the ground state function of B is equal or close to unity if the process is allowed, zero or close to zero if forbidden. The mapped function is the one which is obtained from A by subjecting A to the transformation operation reflecting stretches, bends and twists.

Failures. The Woodward–Hoffmann rules are unable to predict whether a reaction pathway is concerted or not. An electronic factor favoring concertedness in Woodward–Hoffmann forbidden reactions was discovered by Berson and Salem [41] stressing subjacent orbital control. The authors advocate that stabilization of a forbidden transition state by an orbital below the highest occupied MO could become important when steric factors are unfavorable to the Woodward–Hoffmann control. This is demonstrated for non-polar 1,3 sigmatropic shifts. Epiotis and coworkers [42] expect that subjacent orbital control is not important in highly polar 1,3 sigmatropic shifts. The Woodward–Hoffmann rules may fail in strained systems where nuclear repulsion exerts a dominating influence. More generally they fail when the coupling terms which have been neglected in the Hamiltonian are important for the reaction. Various possibilities are discussed by Ross and George [43] and Silver [44]. A hierarchy of symmetry rules can be applied when 1) the Born–Oppenheimer approximation holds, 2) nuclear, electronic spin and electronic orbital momenta are separately conserved, 3) electron spin interactions and nuclear dynamic effects are negligible, 4) symmetry elements exist among the nuclear positions along the course of the reaction paths. Van der Lugt and Oosterhoff [45] observed that the breakdown of the Born–Oppenheimer approximation causes the breakdown of the Woodward–Hoffman rules for photochemical cyclization of butadiene to cyclobutene. Conservation of orbital symmetry is violated even though the rules predict the stereochemical course of the photoinduced reaction. When *cis*-butadiene is irradiated with UV light it is excited to an antisymmetric state. During ring closure nuclear vibrations enable the molecule to pass adiabatically into the symmetric state which then goes to the product through perhaps a radiationless transition.

2.3.2. Topological State Approach

The alternative to the orbital picture pursued by Woodward and Hoffmann is the state picture. The initial idea was presented in a note by Longuet–Higgins and Abrahamson [46] but not rigorously applied. The state approach becomes more attractive when different answers from orbital and state approach are to be expected. Salem and coworkers used state correlation diagrams [47, 193] to discover surface crossings in photochemistry and explain the behavior of several families of photochemical reactions [194]. Avoided crossings were classified [195, 196] and criteria established for photochemical reactions which are forbidden by orbital symmetry but allowed by state symmetry. If the interaction element H_{AB} between two configurations A and B is large compared to the energy difference $E_A - E_B$ between the configurations, substantial reduction of a barrier along a reaction pathway can occur. Devaquet and coworkers [48] distinguish between two types of potential energy barriers in photochemical reactions, both of which result from avoided crossings involving a) states of the same symmetry [47] and b) orbitals of the same symmetry. Both result in barriers smaller than 20 kcal/mol. The construction of qualitative potential energy surfaces by the linear combination of fragment configurations approach is pursued by Epiotis and Shaik [49]. Applications to cycloadditions, spin inversion and aromatic substitution are given. Interesting is the discussion of effects of polarity between two reacting molecules. A donor-acceptor pair should yield a dipolar intermediate during the reaction.

2.3.3. Energy and Force Partitioning

In a paper on the MO theoretical interpretation of the nature of chemical reactions, Fukui and Fujimoto [50] partitioned the interaction energy into Coulomb exchange, delocalization and polarization terms. It was pointed out that in ionic reactions Coulomb and delocalization terms dominate. Later these authors [51] stressed the importance of charge transfer for chemical reactions. Charge transfer will cause the bond interchange which lowers the LUMO and elevates the HOMO. With the reaction progressing charge transfer between HOMO and LUMO will be dominant and deformations take place to foster it. In the same spirit Nakatsuji [52] developed the electrostatic force theory for interacting molecules. An atomic dipole force (AD), exchange force (EC) and gross charge force (GC) are defined. The AD force represents attraction between a nucleus and its polarized electron distribution. The EC force originates between a nucleus and the electron distribution in the bonding region between another atom. The GC force represents the interaction between a nucleus and the gross charge on another nucleus. The magnitude is AD > EC (triple > double > single) > GC. An orbital following of the local electron distribution to the motion of the nuclei causes forces that restrain this motion. An orbital preceding of the local electron distribution promotes motion of the nuclei. Later Nakatsuji [53] elaborates that the orbital preceding of electron clouds plays an important role in chemical reactions because it serves to accelerate the reaction. The concept is applied to the $NH_2 + H \rightarrow NH_3$ reaction [54]. An alternative decomposition is given by Joshi and Morokuma [55]. The total force in the direction of the reaction coordinate is decomposed in electrostatic, polariza-

tion, exchange, charge transfer, coupling term and intramolecular deformation force. The model is applied to the H^- + CH_4 exchange reaction. It is found that the primary source of the transition state barrier is the intramolecular deformation force which dominates in the vicinity of the transition state. At large separation of the fragments the interaction force on the monomers, which is the sum of all the rest forces, outweighs the intramolecular deformation force.

3. Properties

In order to use quantum chemical methods for meaningful calculations of chemical reactions, we must set up a scheme and define our goals. Most often it is understood that a potential surface is constructed in the Born–Oppenheimer approximation by use of the variation principle. This energy hypersurface has $3n - 6$ dimensions when n atoms are involved. Less ambitious and often prejudicial is the consideration of one or many-dimensional cuts through the energy surface to simplify the computational task. These regions should include important portions of a static or dynamic pathway relating reactant and products which are local minima on the hypersurface. Various definitions of reaction pathways are given in the subsections. Finally, information can be gathered by taking into account the symmetry group of reactants and products. Forces on the atoms of a reacting system can be computed along a reaction pathway or at any point on the surface to obtain information about the motion of the system.

3.1. Potential Surfaces

In the theory of chemical bonding the structure of ground states of molecules is determined. This is a rather simple problem compared to the investigation of chemical reactions. In the former case a local minimum on the potential surface has to be calculated, in the latter the whole potential surface has to be investigated. Equilibrium structures as local minima belong to stationary points on the energy surface, they are characterized by vanishing first derivatives and positive second derivatives of the energy with respect to all internal coordinates. The matrix of all second derivatives is the force constant matrix. Other stationary points include saddle points, turning points and maxima. All have vanishing first derivatives of the energy, but differ in the second derivatives. Saddle points are characterized by one or more negative roots of the force constant matrix. Turning points may have one or more vanishing second derivatives and maxima have all positive second derivatives. Chemically important are the saddle points with one negative second derivative because they are the lowest barriers connecting equilibrium structures [56]. These are the transition states of chemical reactions. Hammond [57] has postulated that the structure of the transition state will resemble the product more closely than the reactant for endothermic processes whereas the converse is true for exothermic reactions. If there exist several transition states between the two equilibria of reactant and product several possibilities exist. The transition states are sequential or parallel depending on whether reactant and product can be connected by one or two pathways. In the first case a local minimum with a small barrier of a few

kcal/mol exists between the transition states. We call it an intermediate. But whole regions of the hypersurface can have characteristic features: valleys are characterized by one almost vanishing derivative along one internal coordinate with other second derivatives being positive and ridges are regions with one almost vanishing second derivative and at least one negative second derivative. In a certain sense valleys are the generalization of minima and ridges of saddle points of maxima. More complicated features include forking points [58] where three valleys meet at a point with two vanishing eigenvalues of the force constant matrix. A closer look may reveal the existence of a forking region with monkey saddles.

The question in which the chemist is interested is twofold: 1) Which are the possible products from a given reactant, 2) Which specific product is obtained under certain conditions in a particular reaction. The first question is relatively easy to answer. One has to determine all the possible minima on the hypersurface including all isomers and fragments. Chemical intuition will reduce the number of mathematical possibilities usually to a few. Their equilibrium structures and total energies have to be determined. The second question is the real difficult one. Apart from *thermodynamic* control of a reaction in which the product with the lowest total energy is considered, there is a *kinetic* control which is governed by the activation barriers between reactant and products and which favors the product with the lowest barrier. So the initial step is the determination of all minima and lowest-order saddle points on the hypersurface. Mathematicians have solved this problem in principle long ago. But in practice there are differences in the various procedures as far as convergence or computer time is concerned. A comprehensive discussion of search techniques has been given by Himmelblau [59]. Some of them have been taken up and modified for use in molecular calculations. The most efficient ones need the first and some the second derivative of the energy with respect to the atomic or molecular coordinates. The use of these search techniques was much advanced by the work of McIver and Kormonicki. In a paper on rapid geometry optimization [60] they advocated the use of a variable metric minimization method by Davidon [69] and Fletcher and Powell [62]. This method is of the form

$$q^{n+1} = q^n - \alpha_n A^n g^n$$

where q are the coordinates, g the first derivatives of the energy. α_n and A^n depend on the particular method. Davidon, Fletcher and Powell chose

$$\alpha_n = \lambda \quad \text{with} \quad \partial E(q^n - \lambda A^n g^n)/\partial \lambda = 0$$

$$A^n = A^{n-1} + z^n z^{n+}/c^n \quad \text{with} \quad z^n = -A^{n-1}[g^n - (1 - \alpha_{n-1})g^{n-1}]$$

$$\text{and} \quad c^n = (g^n - g^{n-1})^+ z^n \qquad A^0 = 1$$

The less efficient steepest descent method uses $A^n = 1$ throughout. In a generalized Newton–Raphson method which we have used successfully [63] we chose

$$\alpha_n = \tfrac{2}{3}$$

$$A_{ij} = \frac{\partial g_i}{\partial q_j} = \frac{\partial^2 E}{\partial q_i \partial q_j}$$

Here also the second derivative is needed. First derivatives can be calculated analytically, using the Hellmann–Feynman theorem and neglecting the variation of the LCAO coefficients in the vicinity of stationary points, or numerically. Second derivatives should be obtained only numerically because the variation of the LCAO coefficients cannot be neglected. Much progress was made with the paper of McIver and Kormonicki [64] which recognized the need and special problems of a transition state determination. Whereas the convergence for minima is easily achieved, transition state saddle points need more care. Instead of minimizing the energy, the minimization of the norm σ of the gradient g was suggested

$$\sigma = \sum_i g_i^2$$

This puts transition states on the same footing as equilibria. It can be reduced to the Newton–Raphson scheme when a point near the transition state is known. From our experience we can say that this is the crucial point. We have found cases in which there was a huge change in the energy accompanied by a minor change in the norm. This means slow convergence which can be a major obstacle in a multidimensional hypersurface.

3.2. Reaction Coordinates

To use the norm efficiently for the determination of transition states, their approximate location must be known. This problem is intimately connected with the definition of reaction coordinates. McIver and Kormonicki [64] had suggested the use of a bond which is broken or a bond angle or dihedral angle as a guiding coordinate. Then the energy should be calculated along this coordinate for appropriate increments by minimization with respect to all other internal coordinates. This is the so-called *minimal energy pathway*. There are several problems connected with it. First one has to avoid discontinuities of the SCF surface by proper inclusion of CI, because the transition state is usually accompanied by MO crossing or avoided crossing. Even if one accounts for this point, there is no guarantee that the energy is a single-valued function of this particular coordinate. If one reduces the search to the two-dimensional problem there is a two valley structure of the reaction. The forward pathway is different from the reverse pathway. Dewar [65] has coined this fact hysteresis and attached initially physical significance to it. There is however one remarkable truth in this, namely that a reaction will not follow such a mathematical construction of a minimal energy reaction pathway, in particular not as far as the ascent to the transition state is concerned. A better way is the linear internal coordinate path method which was used by McIver and Kormonicki [66] and by us [67] independently. Such a path would be defined as

$$q(\lambda) = q^R + \lambda(q^P - q^R)$$

One can now search the energy along this path for maxima and minima or illuminate the hypersurface through representative two-dimensional cuts [67]. To search further for stationary points one can then use a gradient method and a new quadratic interpolation pathway between reactant, displaced maximum and product [68].

The idea of a linear internal coordinate path was modified and refined by Lipscomb and coworkers [69, 70]. They attempt the calculation of transition states by the use of Cartesian coordinates and without gradients. To summarize their criticism of the minimal energy pathway: 1) It is expensive because all of the remaining coordinates at each increment of the guiding coordinate have to be reoptimized, 2) Different choices of guiding coordinates produce different reaction pathways, 3) Even the same reaction coordinate can produce different reaction pathways depending on whether the starting point is the reactant or product. They search as McIver and Kormonicki for the energy maximum along a linear interpolation path between reactant and product. This maximization is followed by a minimization of the energy under the constraint of fixed distance of the linear interpolation maximum from reactant or product. To implement this constraint a quadratic interpolation between reactant, maximum and product is again used. Although this scheme can be iterated it is not clear how the convergence works or even whether the transition state can be really reached.

Shortcomings in the minimal energy pathway (MEP) and the linear interpolation pathway (LIP) have prompted others to seek alternatives. The problem with the minimal energy pathway is the fact that even in generalized coordinates it constitutes a minimal ascent up to the saddle point and this path is different from the steepest descent, if the path is reversed. The portion from transition to product however is unique because one can imagine the reaction proceeding along a steepest descent path. The transition vector seems to define a unique initial direction for the reaction to continue after the saddle point. However, things are more complicated and one has to distinguish between mathematical construction of pathways on a hypersurface and physical realization in chemical dynamics. In this sense the *steepest descent path* by Ratner and coworkers [71] is a mathematical construction, even though it defines a general orthogonal curvilinear coordinate by a canonical point transformation. The definition breaks down in many cases because it is not true that it will always reach the transition state, rather it may get sidetracked in a dead end valley with no reaction. The situation is even worse when several transition states exist between reactant and product. It is impossible to predict the one with the lowest barrier starting from the reactant. The same problem suffers the definition of an *intrinsic reaction coordinate* by Fukui and coworkers [72]. However, contrary to the previous definition it is put on more physical footing. The authors elegantly define a unique trajectory by infinitely slow motion as an initial condition for the reaction coordinate. This definition is fruitful when the motion from transition state to product is considered. The potential of the method was recognized by Morokuma and coworkers [73]. They suggest that consideration for a reaction should start from the transition state. In both directions steepest descent paths can be conveniently defined and they amount to the intrinsic reaction coordinates of Fukui. More recently Tachibana and Fukui [74] have defined a geometric shell structure of chemically reacting systems and introduced an intrinsic reaction and accumulation time. Another pseudo-kinetic definition of a reaction coordinate is the *least motion path* in unimolecular decomposition by Ehrenson [75]. It is suggested that the distance between the centers of gravity of the fragments is

taken as the reaction coordinate, rather than the local bond displacement of the breaking bond. The latter are useful in the theory of small vibrations, consequently good for reaction initiation. None of these definitions is really satisfactory for the initial part of the reaction, namely how to get to the transition state. But it may very well be that a purely mathematical idea cannot prove pertinent. The best that can be suggested is to calculate the steepest descent path from transition state to reactant. This defines a unique initial direction at the reactant towards the transition state[1]. One can then search the potential surface by trajectories which are obtained by small increments alternatively in all coordinates around this initial direction. This procedure will yield a spread of pathways starting all at the reactant and passing in the vicinity of the transition state. This spread will give information about the activation entropy.

After completion of this manuscript a paper by K. Müller and L. D. Brown [198] appeared with an interesting alternative for the location of saddle points. The authors document the capabilities of their constrained simplex optimization procedure convincingly in small systems. Unfortunately, the procedure is hampered in larger systems by a quadratic increase in computer time with increasing internal degrees of freedom. It appears that only a fraction of the internal coordinates can be subjected to variation in this method with present computer facilities.

3.3. Symmetry

Symmetry considerations can be made for the electronic part and the nuclear part of a reacting system. Fukutome [76] has developed the unrestricted Hartree–Fock theory for chemical reactions. He observes that instabilities will occur in the restricted Hartree–Fock theory in the course of a chemical reaction. There is a triplet instability when crossing of unoccupied and occupied levels takes place. The energy gap between singlet and triplet is expected to become small at the transition state of such reactions. Fukutome and coworkers [77] give an MO classification of reactions of singlet ground state molecules with triplet instability and phase continuity of the highest occupied MO. For the nuclear part Pearson [78] was the first to establish guidelines through the following postulates: 1) All reaction coordinates belong to the totally symmetric representation, 2) Along a particular reaction path there is no change in point group until an energy minimum or maximum is reached. 3) For a chemical reaction to occur with reasonable activation energy there must be low-lying excited states for the reacting system of the same symmetry as the ground state. Ross and coworkers [79] show that a reaction coordinate need not be a normal coordinate. They demonstrate that contrary to Pearson's rules the motion along the reaction coordinate is not totally symmetric, nor is the symmetry of the nuclear configuration necessarily conserved during a reaction. A fresh look at the symmetry of transition states is presented by McIver [80]. He asks the questions whether the structure of transition states is symmetric. The following rules are given: 1) The irreducible representation of the transition vector must be

symmetric under symmetry operations of the transition state which leave reactant and product unchanged, 2) The irreducible representation of the transition vector must be antisymmetric under symmetry operations of the transition state which convert reactant into product, 3) The transition vector cannot belong to a degenerate representation of the transition state's point group. He concludes that the transition state of the Diels–Alder reaction cannot be symmetric. Stanton and McIver [58] give group theoretical selection rules for the transition states of chemical reactions. They discuss symmetry-forbidden transition states, i.e. those with two negative roots of the force constant matrix. These transition states cannot be the lowest ones connecting reactants and products. Bouman and coworkers [81] put the Stanton and McIver concepts on a more rigorous group theoretical basis. They make applications to pseudorotation modes in $C_2H_5^+$ and $C_5H_5^+$ rearrangements. An important contribution to the symmetry problem is given by Pechukas [82]. He finds that a simple saddle point linked directly to reactants and products is limited to the joint symmetry of both of them. A reaction intermediate cannot have symmetries not shared by reactant and product. Nuclear symmetry cannot change along a path of steepest descent and cannot decrease at the end points. However, if reactant and product are physically indistinguishable and themselves related by symmetry, the transition state connecting them may have extra symmetries, namely those that interchange reactant and product. Silver and Karplus [83] discuss the conservation of symmetry in concerted reactions in the valence bond approach. They postulate that a concerted reaction is allowed if the primitive symmetry classification of the principle reactant structure is the same as that of principle product structure.

4. Reactions

Chemical reactions have been the domain of the organic chemist and this is why a classification of the surveyed reactions is given by their standard scheme. The following subsections will treat rearrangement reactions, addition reactions, elimination reactions and substitution reactions. Before we can go into their details, it would be useful to clarify a few terms which are common to all of them. Reactions can be collision induced or photochemically induced. In the first case the reaction moving on the ground state potential surface and vibrational excitation is often a very minor factor in its occurrence. In the second case an excited state of the molecule is prepared by a light source and this state might couple with highly excited vibrational levels of the ground state or another excited state to give rise to radiationless transitions and relaxation. As we shall see, the majority of calculations are of the first type, i.e. they treat thermal reactions on a ground state potential surface. Two key terms for the description of a reaction are transition state and intermediate. As we have already pointed out we will use transition state as a term describing a lowest-order saddle point on the potential surface and intermediate as a term for a small local minimum between reactant and product. Whereas a transition state is a transient configuration of the atoms determining the option for an activation energy, the intermediate has a finite lifetime and can in principle be
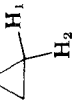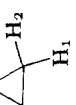
intercepted. How do the terms diradical and zwitterion fit into the developed scheme? A rather comprehensive answer has been given by Salem and Rowland [84]. They point out that the answer is different for a localized or delocalized picture of the electrons in molecules. The localized picture, mostly used by experimental chemists, would define a diradical as a species with lone electrons described by AO's of similar energy and interacting weakly. The delocalized MO picture searches for degenerate or quasi-degenerate MO's for the lone electrons. In this picture a pair of singlet and triplet states with a small or zero separation has to exist. A distinction between diradical and zwitterionic states can be given as follows. Diradicals are composed mainly of the covalent parts of the wavefunction, zwitterions mainly of the ionic part of the wavefunction. Zwitterionic states have a dominating intramolecular charge separation. Their energy is usually higher than that of diradical states. In the terminology of the organic chemist a diradical represents a situation in which one bond is broken before another one is formed. The term diradical is used in the context of loss or retention of configuration during a reaction. Often a diradical pathway is contrasted with a concerted pathway. This is due to the frequent belief that diradicals are small minima, i.e. intermediates, on the potential surface. This can by no means be generally substantiated by calculations. How much this may depend on the special situation is discussed by Huisgen [85]. After it became clear that ethylene dimerization does not involve intermediates, Huisgen thought of a way to construct zwitterionic intermediates by polarizing the CC bond by introducing a pair of electron rich and electron poor olefins to reduce the activation energy. He has raised the question of how to intercept intermediates and proposed to conduct the experiment at lower temperature to avoid the unfavorable negative activation entropy of any bimolecular trapping reaction. As an example of how much the scope of quantum chemistry has broadened we mention two papers by Thorn and Hoffmann [86] and Clementi and coworkers [87]. Thorn and Hoffmann develop a model to facilitate an olefin insertion reaction by the introduction of a metal atom, e.g. platinum. Clementi and coworkers make a preliminary attempt to follow the enthalpy of an enzymatic reaction by *ab initio* computations on the catalytic action of papain. The real systems that have been treated explicitly are more modest but we can hope that the following material provides stimulation for further work.

4.1. Rearrangement Reactions

The majority of chemical reactions covered by quantum chemical methods belongs to the simplest type, namely rearrangement reactions [66, 88–127, 174, 176, 182, 186]. More than fifty representative reactions are covered in Table 1. They are calculated by methods discussed in Sect. 2 and the abbreviations are given there. The general features will be discussed first. Among the reactions 80% involve hydrocarbons with up to 10 carbon atoms. These are mainly three- to seven-membered rings. The remaining 20% are nitrogen- and oxygen-containing compounds. In one case a chlorine atom is involved as a substituent of hydrogen in a benzene ring. A glance at the numbers, namely heats of reaction and activation energies, reveals the remarkable fact that despite the computational activity very
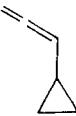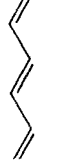
Table 1. Rearrangement reactions
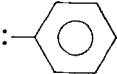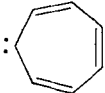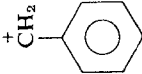
	Reactant	Product	Heat of reaction[a]	Activation energy[a]	Transition state	Saddle points[b]	Method	Author
1.	H–O=O⁺–H (with H)	H–C=C–H⁺ (cyclic)	5.4	5.7	partial	—	DZ + P	[88]
			0.01	1.6	partial	—	+CI	[89]
2.	CH₃CH	=	−72.3	0	none	no	MINDO/2	[90]
				20.9	partial	—	DZ	
3.	△ (=)	△ (·)	0	0.5 (0.57)	full	yes	MINDO/3	[91]
4.	△ (·)	·/= (allyl)	24.8	42.3	partial	—	DZ + P + CI	[92]
5.	+△	= = ⁺		74	2 variables	—	INDO	[93]
6.	+△	+∧	−48.8	8	disrot.	—	MINDO/2	[94]
			−47.7	38	conrot.	—	MINDO/2	
				4.7	disrot.	—	SCF	[95]
				4.4	disrot.	—	CI	
				86.3	conrot.	—	SCF	
				78.5	conrot.	—	CI	
			−6	20	disrot.	—	SINDO	[96]
				55	conrot.	—	+CI	
7.	△ (·)	∧ (·)		25	disrot.	—	MINDO/2	[94]
				57	conrot.	—	MINDO/2	
			−52	35	disrot.	—	Koopmans	[95]
8.	△ (⁻)	∧ (⁻)		31	conrot.	—	MINDO/2	[94]
				57	disrot.	—	MINDO/2	
			−31	97	disrot.	—	Koopmans	[95]
				31	conrot.	—	MINDO/2	[94]
				57	disrot.	—	MINDO/2	
			−31	97	disrot.	—	Koopmans	[95]

#							Method	Ref.
9.			0	111.7 93.1	1 constraint	yes	4 − 31G + 3 × 3CI	[97]
10.			−7.8 (−7.8)	46 (65)	full	yes	SINDO + CI	[98]
11.		(H₂, H₁)	0	52.6 (64.2) 60.5	full partial	indirect —	Min. STO + 3 × 3CI GVB	[99] [100]
12.			−2 −15.3	50.3 97.7	full from MINDO/3	yes	MINDO/3 STO-3G	[101]
13.			−16 −30.4	42.9 56	full from MINDO/3	yes	MINDO/3 STO-3G	[101]
14.			−36.0 −66.6	42.9 56.0	full from MINDO/3	yes	MINDO/3 STO-3G	
15.				55 90 49 (36) 55.6	conrot. disrot. conrot. disrot.	— — — —	MINDO/2 MINDO/2 MINDO/3 MINDO/3	[94] [102]
16.				90 40.3 (40.6)	— via intermediate	—	MINDO/3 + 2 × 2CI	[103]
17.			0	44.7 (40.4) 35.9	partial intermediate	—	STO-3G, 4-31G	[104]
18.			0	0.1 (0.14)	full	yes	MINDO/3	[91]
19.	(+)	(+)	0	38 (15) 47 20 32	bisected eclipsed bisected eclipsed	— — — —	STO-3G STO-3G 4-31G 4-31G	[105]
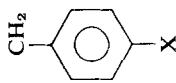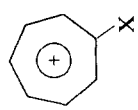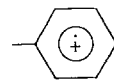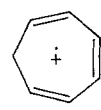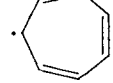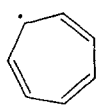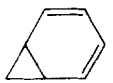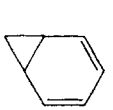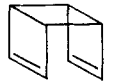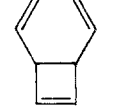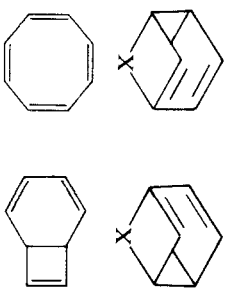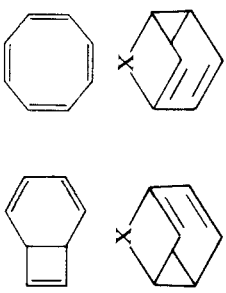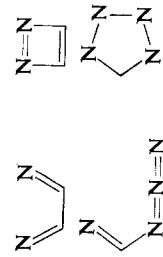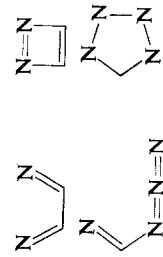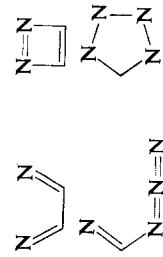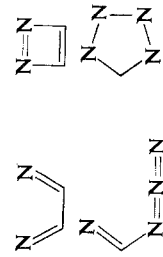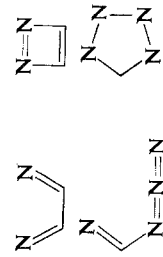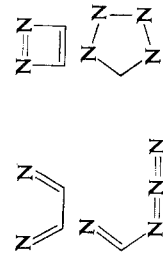
Table 1. *Continued.*

Reactant	Product	Heat of reaction[a]	Activation energy[a]	Transition state	Saddle points[b]	Method	Author
20.		0	69.5 73.5	suprafac. ret. suprafac. inv.		MINDO/2 + 3 × 3CI	[106]
21.		0	3.1	partial		MINDO/2 + 3 × 3CI	[107]
22.			48.4 (49.7)	full		MINDO/3 + 2 × 2CI	[108]
23.		0	64.7 62.0	full	yes	4-31G + 3 × 3CI	[97]
24.		−70	30	—	—	MINDO/3	[109]
25.		−85	21.5	given	—	MINDO/3 + 2 × 2CI	[186]
26.			44.6 (50.2)	full	—	MINDO/3 + 2 × 2CI	[108]
27.		−31.9 (−17.4)	24.6 (29.6)	full	yes	MINDO/2	[66]
28.			0	none	no	MINDO/2	[89]

No.	ΔE	Value	Description	Symmetry	Method	Ref.
29.	0	24 (35.5)	chair	—	MINDO/2	[110]
		30.6	boat	—	MINDO/2	[111]
		22.3	chair	yes	MINDO/2	
		20.1	intermediate		MINDO/2	
		30.3	boat	yes	MINDO/2	
		29.9	intermediate		MINDO/2	
		42.3 (45.9)	full (boat)	yes, 2	MINDO/3	[112]
			1 intermediate			
30.	−26.8	36	full (chair)	yes, 2	MINDO/3	[112]
			1 intermediate			
31.	−8.1	6.3	full	yes, 2	MINDO/3	[113]
			1 intermediate			
		18.5	full	yes	MINDO/3	
32.	0	61	eclipsed	—	STO-3G	[105]
		67	bisected	—	STO-3G	
		43	eclipsed	—	4-31G	
		52	bisected	—	4-31G	
33.	−24.8	32.7	full	yes, 3	MINDO/3	[114]
			2 intermediates			

Table 1. *Continued*

Reactant	Product	Heat of reaction[a]	Activation energy[a]	Transition state	Saddle points[b]	Method	Author
34. X = OH; X = NO₂; X = Cl		− 15.6 − 14.7 − 21.0	44.5 33.4 37.0	full 2 intermediates	yes, 3	MINDO/3	[115]
35.		− 5.6	34.2 33.6	full 2 intermediates full 2 intermediates	yes, 3 yes, 3	MINDO/3 MINDO/3	[116]
36.		0	0.0 (0.0)	full	yes	MINDO/3	[91]
37.		0	70.4 71.8	suprafac. inv. suprafac. ret.		MINDO/2 + 3 × 3CI	[106]
38.			57.7	—	—	MINDO/3	[117]

No.	Structure	E_a	E_r	Path	Type	Method	Ref.
39.	(structure)	22.8 (18.7)		—	—	MINDO/3	[117]
40.	$X = \text{—}$; $X = \text{—}CH_2\text{—}$; $X = \text{—}CH\text{=}CH\text{—}$	2.3 / 5.9 (8.6) / 11.3 (11.8, 12.8)	-19.3 / -9.5 / -9.5 (-14.7)	constrained / constrained / constrained		MINDO/2 / MINDO/2 / MINDO/2	[118]
41.	HNC / HCN	49.9 / 57.6		full / full	yes / yes	STO-3G / 4-31G	[191]
42.	CH_3NC / CH_3CN	34.8 (38.4)		constrained / artificial	2 / intermediate	MINDO/2	[119]
43.	(structure)	60.4 (38.4)	-17.3 / $-(14.7, -16.8)$	partial	indirect	DZ	[120]
44.	(structure)	32.0	-69	linear pathway		STO-3G + CI	[121]
45.	(structure)	12.3 / 5.0	-66.1 / -47.7	partial / partial	— / —	STO-3G / 7s3p	[122]
46.	(structure)	19.1 / 11.8		partial / intermediate		DZ	[123]
47.	(structure)	5.7	-74.3	partial	—	CG	[124]
48.	(structure)	84.6 / 94.1	-11.5 / -12.0	1 constraint	yes	4-31G / +3 × 3Cl	[97]
	(structure)	92 (57)		partial	—	STO-3G + CI	[182]

(continued)

Table 1. *Continued*

	Reactant	Product	Heat of reaction[a]	Activation energy[a]	Transition state	Saddle points[b]	Method	Author
49.			7.2	25	partial	—	DZ	[176]
50.							DZ + DIFF + CI	[190]
51.			38 5	73 34	2 variables	—	STO-3G +CI	[174]
52.			0	61.1 63.0	full	yes	4-31G +3 × 3CI	[97]
53.			−49.4	34.1	full		MINDO/3	[125]
54.			0	11.5 6.6	partial partial spurious intermediate	— yes, 2	CG STO-3G	[126] [127]
				10.3 9.8	full	yes	4-31G +3 × 3CI	[97]

[a] kcal/mol with experimental values in parentheses.
[b] Determination of one or more negative roots of the force constant matrix.

little comparison with experimental data has been done. If we would like to understand this as a lack of experimental data because of difficulty or no specific interest on the side of the experimentalist in this type of reaction, we would classify the calculated number as a prediction. Consequently we would have to make an assessment of the predictive power of the method used. Here MINDO/3 appears the best giving heats of reaction and activation energies within a few kcal/mol, whereas STO-3G [105] and DZ [120] may fail by more than 20 kcal/mol in certain cases. Even minimal STO with CI [99] has errors over 10 kcal/mol. The question of comparison is made more difficult by the ambiguity of comparison of calculated and experimental numbers. Experimental numbers would have to be corrected by zero point vibrational contributions to the heats of reactions if comparison with minima and saddle points of the calculated energy hypersurface is to be made. Dewar has adjusted his parameters in the various MINDO and MNDO methods to reproduce experimental heats of reaction at 25°C. This is an advantage only if reactions are experimentally investigated at room temperature and their zero point vibrational energies differ by a few kcal/mol only, the present limit of accuracy in all methods. Regardless of the accuracy of numbers the determination of transition states is more troublesome. McIver and Kormonicki were the first [64] who recognized the need for calculation of the force constant matrix and to check whether one root is negative. For this purpose it is immaterial that they used MINDO/2 which did not always give reliable results. Only semiempirical methods with a relative ease of calculation of first and second derivatives have been used consequently for transition state determination: MINDO/2 since 1974 [66], MINDO/3 since 1975 [108] and SINDO since 1976 [98]. For this purpose all internal or Cartesian coordinates have to be varied. The full variation has been achieved by semiempirical methods, whereas in *ab initio* methods transition states were constrained to two or few variables. At this time the early impact of the Woodward–Hoffmann rules where conrotatory or disrotatory pathways were calculated has vanished, because their model character has been recognized as an inappropriate simplification for transition states. Another point to mention that it is now well established that at least 3 × 3 CI has to be used to cover regions with diradical character adequately. Dewar and coworkers [103, 186] used initially a 2 × 2 CI in such cases.

Let us now go into details of specific reactions. One of the initial reactions considered was the cyclopropyl cation to allyl cation isomerization [94–96]. The problem was reduced to two variables: the CCC bond angle and the rotation angle of the CH_2 groups. It was proven that the disrotatory path was allowed and the conrotatory path forbidden in agreement with the Woodward–Hoffmann rules. For the radical the disrotatory path was favored, a result which the Woodward–Hoffmann rules cannot predict. They classify both pathways as forbidden. The anion favors the conrotatory pathway again in agreement with the qualitative rules. Later Schöller [106] showed in the walk rearrangement of bicyclo [4.1.0] hepta-2,4-diene that the Woodward–Hoffmann forbidden pathway is stabilized over the allowed one by hyperconjugation. Interest in these model pathways faded when problems of a more general nature showed up. In the $CH_3NC \rightarrow CH_3CN$ isomerization Dewar and Kohn [119] obtained an artificial intermediate when they used a

different reaction coordinate starting the pathway from reactant or product. This result was correctly criticized by Schaefer and coworkers [120], but their *ab initio* method had a large error in the activation energy and no attempt for full optimization had been made. The problems become repeatedly apparent in the conversion of cyclopropylidene to allene in an INDO study [93], where only two variables were used. The statement that the forward and reverse pathway are different is true for many calculations which follow a minimal energy pathway starting from both reactant and product. They are not true in an absolute sense because these pathways depend on the choice of the reaction coordinate. In addition these pathways [88, 121, 122, 124] are often only partially optimized and transition states are not determined according to rigorous criteria. It is certainly worse to postulate transition state structures [90, 105], because these are isolated and guessed points on the hypersurface, and seems a dangerous procedure in general. The search for intermediates continued. In reactions of small systems like the geometrical isomerization of cyclopropane [99, 100] and the cyclopropane–propene isomerization [98], no intermediates were found. Diradical character of the transition states could not be established either. In methylencyclopropane an orthogonal diradical was described by Salem and coworkers [104], but it is not clear whether this intermediate shows singlet–triplet degeneracy. Real intermediates occur in rearrangements of larger systems. In the Cope rearrangement various transition states and intermediates are found [111, 112]. These reactions cannot be classified as concerted pericyclic processes. Kinetic studies are used [192] to suggest that the transition state is a biradicaloid akin to the 1,4-cyclohexylene biradical. Intermediates are also found in the reaction of benzyl cations to tropylium [114, 115] and toluene cation to cycloheptratriene [116]. It often is necessary to achieve a very high accuracy when several paths with similar activation energy are competing [116]. Influences of singlet-triplet crossing on the activation energy have been discussed in the rearrangement of Dewar benzenes [109] and cyclobutadiene dimers [117]. Finally conclusions are subject to failures when information is incomplete. Dewar and coworkers [108] attributed the difference in rate constants of various substituted cyclopropanes to the difference in activation energies. From the three compounds one was not calculated and for a second the authors had no experimental data. Andrews and Baldwin [187] disproved their conclusion by producing the experimental data for the second compound. They also criticized Dewar's conclusion of almost complete loss of configuration in the vinylcyclopropane rearrangement as contradictory to the experimental facts.

4.2. Addition Reactions

Addition reactions and elimination reactions are complementary viewpoints of forward and reverse pathways of certain reactions. We will follow the emphasis of the author when we collect more than 20 addition reactions [96, 128–144] in Table 2. Here hydrocarbons and oxygen-containing compounds constitute 50% each of the total number of reactions. Three exceptions contain fluorine and chlorine, among them is the early calculation by Clementi [144] on $NH_3 + HCl$. Much attention has been paid to the ethylene dimerization [96, 133, 134] and the

Table 2. Addition reactions

Reactants	Product	Heat of reaction[a]	Activation energy[a]	Transition state	Saddle points[b]	Method	Author
1. $^1CH_2 + H_2$	CH_4	−125.2	26.7	least motion	—	DZ + CI	[128]
			0	non motion	—	DZ + CI	[129]
2. $CH_2 + CH_2$	C_2H_4	−176.9	14.8	partial		G + MCSCF	[130]
3. ‖ + $^1CH_2$	△		0	2 variables	no	EHT	[131]
			0	unsymmetrical	—	MINDO/2	[132]
4. ‖ + $^3CH_2$	(structure)		5	constrained	—	MINDO/2	[132]
5. ‖ + ‖	□	−43.5 (−18)	18.5 (44.5)	—	—	MINDO/3	[133]
		−24	21.0	$2_s + 2_s$	—	SINDO + CI	[96]
			31.5	$2_s + 2_a$	—	SINDO	
		−22	54.5	full	yes	SINDO + CI	[134]
6. (butadiene + ethylene)	⬡	−37.3 (−39.4)	28.2 (27.5)	full	—	MINDO/3	[135]
			42.6	concerted		STO-3G + 3 × 3CI	[136]
			46	two-step			
		−106.4	20.8	partial		STO-3G, 7s3p	[137]
		−38.5	10.4	full	yes	SINDO + CI	[134]
7. (butadiene + ethylene)	(vinylcyclobutane)		31.8	full		MINDO/3	[135]
8. (ring + alkyne)	(bicyclic structure)		4.7	full		MINDO/3	[135]
9. (ring + alkene)	(bicyclic structure)		1.7	full		MINDO/3	[135]

Table 2. *Continued*

Reactants	Product	Heat of reaction[a]	Activation energy[a]	Transition state	Saddle points[b]	Method	Author
10. $\|$ + N=N (structure)	N$^-$=N$^+$ (ethyl structure)	−38 −10	39.7 45.3	partial partial		STO-3G 4-31G	[181]
11. H_2CO + H^-	H_3CO^-	−48.3	19.5	partial		G	[138]
12. HCNO + $\equiv$	(isoxazole structure)	−80.9	30.4	partial		STO-3G, 4-31G	[139]
13. HCNO + $\|$	(structure)	−50.1	28.8	partial		STO-3G, 4-31G	[139]
14. HCNO + OH^-	$HC(OH)NO^-$	−91.4	−32.0	partial 1 intermediate		4-31G	[180]
15. $\|$ + $^1O_2$	(dioxetane structure)	−65.5	48.2 18.0 −16.1	full full 1 intermediate	yes yes, 2	MINDO/3	[140]
16. (structure) + $^1O_2$	(dioxetane structure)	−62.6	18.3 11.4	full 1 intermediate full 2 intermediates	yes, 2 yes, 3	MINDO/3	[140]
17. (structure) + $^1O_2$	(dioxane structure)		75.3 66.1	full full 1 intermediate	yes yes, 2	MINDO/3	[141]
18. $2CH_2CO$	(β-lactone structure)	−36 (−23)	6 (11) 31	$2_s + 2_s$ $2_s + 2_a$		SINDO	[142]

No.	Reaction	[a]			[b]	Method	Ref.
19.	(azetidine-dione) + $^1O_2$	−53.9	8.8	full / 1 intermediate	yes, 2	MINDO/3	[140]
20.	$H_2O + CO_2$ → H_2CO_3	−6.9 / −0.5	57.1 / 55.2	partial	—	DZ / +CI	[143]
21.	(pyran) + $^1O_2$	−57.1	13.4	full / 1 intermediate	yes, 2	MINDO/3	[140]
22.	(pyran) + $^1O_2$ → OOH	−46	13.4	full / 3 intermediates	yes, 4	MINDO/3	[140]
23.	$2 \, \overset{+}{O}=\overset{-}{O}$ + ‖ (ethylene) → 2 epoxide + O	98.1	8.6	full	yes	MINDO/3	[125]
24.	epoxide + HF → F–CH₂–CH₂–O	−49.4 (−25) / −43.1	99.4 / 84 / 67	retention	—	STO-3G / 4-31G / STO-3G + CI	[173]
25.	$NH_3 + HCl$ → NH_4Cl / Cl	−19	0	none	no	CG	[144]
26.	Cl_2 + ‖ → Cl–CH₂–CH₂–Cl	−50	128.7	constrained	—	4-31G	[178]

[a] kcal/mol with experimental values in parentheses.
[b] Determination of one or more negative roots of the force constant matrix.

Diels–Alder reaction [134–137]. It seems suggestive now that the ethylene dimerization is a concerted reaction, because it forms no intermediates during the reaction. But it seems equally clear that diradical character is important for the reactions. Most recent calculations with SINDO 1 [188] including 3×3 CI reach the same conclusion as our earlier investigations. In particular we find for the transition state an almost planar carbon framework with dihedral angle close to 8°. This result is at variance a calculation of Segal [147] on the thermolysis of cyclobutane where one intermediate is found together with two transition states. The dihedral angle was close to 65°. Segal used an STO-3G basis plus CI. It is not clear that such a basis will yield sufficient accuracy for this difficult question. In the case of the Diels–Alder reaction it is agreed that the reaction is concerted, but the controversy remains whether the reaction proceeds via a diradical and whether the transition state is symmetric with respect to the two forming bonds. Dewar [135] found a diradical transition state whereas Jug and Krüger [134], Salem [136] and Leroy [137] did not. Also Dewar found a highly unsymmetrical transition state whereas the others find more symmetry for the transition state. In the meantime we have repeated the SINDO calculations with SINDO 1 [188] and support Dewar's conclusion that a highly unsymmetrical transition state with important diradical character exists on the energy hypersurface. We do not agree with Houk [189] that *ab initio* methods will yield symmetric transition states and semiempirical methods of INDO type unsymmetrical ones. His argument is in contrast to the symmetry investigations by McIver [80]. An important new aspect was brought in by Dewar in a paper on the retro Diels–Alder reaction [148], in which he claims that two transition states and one intermediate exist on the surface. The symmetrical transition state of Salem and Leroy is dismissed by him as a higher saddle point with two negative roots of the force constant matrix. The overall accuracy of these calculations is unfortunately not high enough to accept this as the final answer. From the reactions in Table 2 there is only the ketene dimerization [142] besides the two discussed above, for which experimental information is available. Although the agreement with experimental data is fair to good, the only conclusion which is of practical interest is that the forbidden pathway in the Woodward–Hoffmann terminology is more favorable than the allowed pathway. A whole series of reactions calculated by Dewar and coworkers is concerned with the addition of singlet oxygen to carbon–carbon double bonds [140]. In all these cases one or more intermediates are found. Peroxirane or zwitterions play an important part in the ring formation. Dewar explains this by the lack of symmetric transition states in non-polar reactions. He expects them to occur only in polar reactions. *Ab initio* calculations have covered extensively the simplest insertion reaction $^1CH_2 + H_2 \rightarrow CH_4$. Least-motion [128] and non-least motion [129] pathways are compared and significant differences are found. The latter pathway has no activation energy. Also no barriers have been found in MINDO/2 calculations on the singlet carbene reactions with methane or ethylene to form two methyl or cyclopropane [132]. Most *ab initio* calculations again suffer from the lack of calculation of the force constant matrix. But really critical one has to be with a paper by Ažman *et al.* [183] in which the mechanism for oxidation of imines with peroxy acids is investigated by STO-2G and STO-4G calculations with a choice of postulated transition states none of which can in any way be assessed in its importance on the potential surface.

4.3. Elimination Reactions
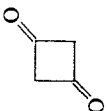
More than twenty elimination reactions [145–157, 175, 182, 184] are described in Table 3. Only 20% are on hydrocarbons, more on oxygen and nitrogen containing compounds. One reaction contains sulphur and one chlorine. The fragmentation of cyclobutane to two ethylenes and the retro Diels–Alder reaction were discussed together with the same cycloaddition reactions in the previous subsection. Most calculations are again by the MINDO/3 method. These are the only ones for which full transition state determination has been achieved. Among the MINDO/3 calculations the most ambitious one is the investigation of the photochemical Norrish type II reaction of butanal [156]. One needs the S_0, S_1 and T_1 surfaces. For this reason Dewar uses a 9 × 9 CI. The triplet reaction is predicted to take place via a stable biradical intermediate. The singlet reaction can bypass the biradical by a mechanism involving direct conversion to the product via a narrowly avoided S_0-S_1 crossing. Agreement with photochemical and pyrolytic studies is claimed. Earlier but less comprehensive are Norrish type II *ab initio* calculations by Salem [193]. Our own studies on the fragmentation of various ketene dimers [154] were hampered by the flat region containing the transition states on the CI surface which made the exact location very difficult. Entropy arguments were used when the reverse reactions, namely the formation of the dimers, were considered to explain the preference for diketene formation. Questionable are the calculations on the direct pathways for cleavage of 1,2-dioxetane [152, 153]. It seems that the disagreement of calculated and experimental activation energies is due to the possibility of circumventing the direct pathway by the formation of peroxiranes as has been suggested by Dewar in other papers [140].

4.4. Substitution Reactions

Twenty substitution reactions [125, 132, 158–172, 177, 179] are covered in Table 4. The majority concerns H, H⁻, F or F⁻ exchange reactions with closed-shell molecules. Included are Li and Si containing molecules. In these small systems *ab initio calculations* dominate. It is easily demonstrated in the case of $F^- + CH_3F$ that simple STO-3G calculations are totally misleading because they yield a stable intermediate instead of a transition state [169]. Even 4-31G cannot describe the situation correctly because the transition state as a local maximum is still by 14 kcal/mol lower than the reactants. The relative error is in the order of over 20 kcal/mol. More sophisticated extended Gaussian [162, 167] and CEPA [158] calculations are, however, in agreement with each other. Most regrettably, little basis for comparison with experimental data is given here again. Even in a simple reaction like $H + F_2 \rightarrow HF + F$ the error in the heat of formation is 14.6 kcal/mol [168]. From the three activation energies compared the one with MIN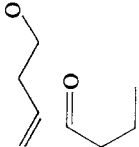DO/2 is the poorest [163, 166, 168]. Force constant matrices have not been calculated, except for only two of the reactions [125], although transition states can be determined with certainty in certain symmetrical cases. We would call several reactions involving ethylene oxide done by MINDO/3 [125, 164] as most advanced as far as consideration of alternatives including intermediates are concerned. The emphasis has to be reduced by the fact that any conclusion involving OO single bonds calculated

Table 3. Elimination reactions

	Reactant	Products	Heat of reaction[a]	Activation energy[a]	Transition state	Saddle point[b]	Method	Author
1.	$C_2H_5^+$	$C_2H_3^+ + H_2$	42.8 (47.8, 46.9)	47 (55, 67)	full	yes	MINDO/3	[145]
2.	$C_2H_6^+$	$C_2H_4^+ + H_2$	11.9 (8.5)	16.8 (13)	full	yes	MINDO/3	[145]
3.	□	∥ + ∥	28 (18.0) / 35.3	156 (62.5) / 77.7	$2_s + 2_s$ partial / 1 intermediate	2	Min. STO / STO-3G + CI	[146] / [147]
4.	⬡	⟍ + ∥	62	94.0 (64.0) / 84	full / 1 intermediate	yes, 2	MINDO/3	[148]
5.	$H_2CN^+H_2$	$HCN^+H + H_2$	67.4 (75)	180.5	partial	—	CG	[149]
6.	CH_5N^+	$CH_3N^+ + H_2$	28.5	81	full	yes	MINDO/3	[145]
7.	△N	$HCN + {}^1CH_2$		104	partial	—	STO-3G + CI	[185]
8.	⬠ N=N	△ + N_2		39.3	constrained	—	STO-3G	[184]
9.	CH_3O^+	$CHO^+ + H_2$	28 (26.9) / 55.6	83.3 (80) / 164.1	full / partial	yes / —	MINDO/3 / CG	[145] / [150]
10.	CH_2CO	${}^1CH_2 + CO$	58	74	linear	—	GL + CI	[151]
11.	[structure]	$CH_3 + CHO^+$	55 (63.7)	58.5 (65)	full	yes	MINDO/3	[175]
12.	[structure]	$CH_3CO^+ + H$	11.7 (32.4)	16 (33.7)	full	yes	MINDO/3	[175]
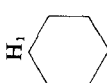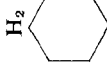
No.	Reaction					Method	Ref.
13.	H$_2$C=O + CH$_2$		140	partial	—	STO-3G + CI	[182]
14.	2H$_2$CO	−32 (−55)	65 (25) 45 47	partial	—	MINDO/3 +2 × 2CI Sem. MCSCF	[152] [153]
15.	2CH$_2$CO	36	45	partial	indirect	SINDO + CI	[154]
16.	2CH$_2$CO	30	39	partial	indirect	SINDO + CI	[154]
17.	2CH$_2$CO	48	54	partial	indirect	SINDO + CI	[154]
18.	+ CO$_2$	−6.8 (−6.8)	46.3 (39.3)	full	yes	MINDO/3	[155]
19.	+		11.7 triplet 9.1 singlet	full 1 intermediate full 1 intermediate	yes, 2 yes	MINDO/3 +9 × 9CI	[156]
20.	CHS$^+$ + H$_2$	33.3	45.8	full	yes	MINDO/3	[145]
24.	+ HCl	59.8 (15) 21.3	113 (60) 69.6	partial partial	— —	STO-3G 4-31G	[157]

[a] kcal/mol with experimental values in parentheses.
[b] Determination of one or more negative roots of the force constant matrix.

Table 4. Substitution reactions

Reactants	Products	Heat of reaction[a]	Activation energy[a]	Transition state	Saddle point[b]	Method	Author
1. $H^- + H_2$	$H_2 + H^-$	0	14.75 9.73			SCF CEPA	[158]
2. $^3CH_2 + H_2$	$CH_3 + H$	-5.4 (4.5) -3.8	15.5 25.5	partial partial	— —	DZ + CI DZ + P	[159] [160]
3. $H^- + CH_4$	$CH_4 + H^-$	0	69 60.2 63.6 56.3	full full full	—	DZ G SCF CEPA	[161] [162] [158]
4. $CH_4 + {}^1CH_2$	$2CH_3$		0	none	no	MINDO/2	[132]
5. $CH_4 + {}^3CH_2$	$2CH_3$	-2	3.8 0.5	constrained 1 intermediate	2	MINDO/2	[132]
6. $CH_3 + CH_4$	$CH_4 + CH_3$	0.5 (-5.0) 0	33.3 4.1(14.1, 14.9) 26.1 29.9	partial partial partial partial	— — — —	DZ + P MINDO/2 STO-3G 4-31G	[159] [163]
7. $\triangle O + C$	$\| + CO$		0 63.0 41.2	none via oxetane via oxetane	no	MINDO/3	[164]
8. $H_2NCHO + OH^-$	$NH_3 + HCOO^-$	-99.5	-68.5	partial 2 intermediates		STO-3G	[165]
9. $\overset{+}{O}-\overset{-}{O}\triangle + {}^1O_2$	$\triangle O + O_3$	36.2	29.2	full	yes	MINDO/3	[125]

No.	Reaction	[a]	[a]	Geometry	Force constants[b]	Method	Ref.
10.	$F + H_2 \rightarrow FH + H$	-35.1 (32.4)	1.7 (1.7)	full	—	DZ + P + CI	[166]
11.	$H^- + CH_3F \rightarrow CH_3F + H^-$	0	60.5	full	—	G	[162]
12.	$H^- + CH_3F \rightarrow CH_4 + F^-$	-68	3.8	partial	—	G	[162]
13.	H_1⬡ + $H_2F \rightarrow$ H_2⬡ + H_1F	0	185	2 variables	—	STO-3G	[177]
			123.2	6 variables			
14.	$F^- + CH_3CN \rightarrow CH_3F + CN^-$	-5.2	17.3	partial	—	G	[167]
15.	$H + F_2 \rightarrow HF + F$	90 (104.6)	1.0 (2.4)	full	—	DZ + P + CI	[168]
16.	$F^- + CH_3F \rightarrow CH_3F + F^-$	0	4.2	full	indirect	SCF	[158]
			8.9	full		CEPA	
			7.9	full		G	[162]
			7.1	full		G	[167]
			-33.4	minimum	no	STO-3G	[169]
			-14.6	full	indirect	4-31G	
			-26.3	intermediate		4-31G	
17.	$H + Li_2 \rightarrow LiH + H$	-32.7	-55.1	minimum	no	CI	[170]
18.	$F + Li_2 \rightarrow LiF + Li$		-4.1	intermediate			[171]
			-8.3	intermediate			
19.	$Li + F_2 \rightarrow LiF + F$	-94 (-100)	0	none	no	VB	[172]
20.	$SiH_4 + H^- \rightarrow H^- + SiH_4$	0	-13.8			CG	[179]
			-20.3			CI	

[a] kcal/mol with experimental values in parentheses.
[b] Determination of one or more negative roots of the force constant matrix.

by MINDO/3 is to be considered with caution because of the large error in this bond length. The overall impression of this subsection as well as the previous is, however, encouraging. The issues have been recognized.

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