1 Theory of Radical Reactions

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CONTENTS

1.1 Introduction
1.2 Classical Theories of Monomer and Radical Reactivity
  1.2.1 The Q–e Scheme
  1.2.2 Patterns of Reactivity
  1.2.3 Beyond Classical Theories
1.3 Basic Transition State Theory
1.4 Basic Quantum Chemistry
  1.4.1 Ab Initio Molecular Orbital Theory
  1.4.2 “Interactions of the Electrons”
  1.4.3 Treating $\alpha$ and $\beta$ Orbitals in MO Theory
  1.4.4 Alternative Popular Quantum Chemical Procedures
  1.4.5 Pitfalls in Computational Quantum Chemistry
  1.4.6 Practical Computational Quantum Chemistry
1.5 Basic Theory of Reaction Barrier Formation
1.6 Applications in Free-Radical Polymerization
  1.6.1 Radical Addition and Propagation
  1.6.2 Atom Abstraction and Chain Transfer
1.7 Concluding Remarks

1.1 INTRODUCTION

Free-radical polymerization proceeds via a chain mechanism, which basically consists of four different types of reactions involving free radicals: (1) radical generation from nonradical species (initiation), (2) radical addition to a substituted alkene (propagation), (3) atom transfer and atom abstraction reactions (chain transfer and termination by disproportionation), and (4) radical–radical recombination reactions (termination by combination). It is clear that a good process and product
control (design) requires a thorough knowledge of the respective rates of these reactions, and, preferably, a knowledge about the physics governing these rates.

In this chapter, the role that theoretical chemistry has played and can play in further elucidating the physical chemistry of these important radical reactions will be discussed. We often wish to answer questions that cannot be addressed directly through experiments, such as “Why does this reaction follow pathway A instead of pathway B?” or “How will a particular substituent affect the rate of a reaction?” In many cases, the required information needs to be extracted from elaborate experiments that address the question in an indirect way, involving many assumptions and/or simplifications; in other cases, the required information is simply impossible to obtain by current state-of-the-art experimental techniques. In such instances, theoretical chemistry, and in particular computational quantum chemistry, can provide the chemist with the appropriate tools to address the problems directly. This is particularly true for radical reactions (where the reactive intermediates are very short-lived) and for obtaining information about the transition state of a reaction; the importance and difficulties in obtaining information regarding transition structures are evidenced by the award of the 1999 Nobel Prize for Chemistry to Zewail.\(^2\) The advent of increasingly powerful computers and user-friendly computational quantum-chemistry software make computational chemistry more accessible to the nontheoretician, and it is the aim of this chapter to provide the reader with some insight into the theory and applications of theoretical chemistry in radical polymerization. This chapter is not intended to be a rigorous introduction to theoretical chemistry, but rather aims at simple qualitative explanations of fundamental theoretical concepts so as to make the theoretical literature more accessible to the nontheoretician. The reader interested in more rigorous introductions is referred to some excellent textbooks and reviews on the various topics: transition state theory,\(^3\)–\(^9\) statistical mechanics,\(^10\) quantum chemistry,\(^11\)–\(^14\) and organic reactivity.\(^15\)–\(^20\)

First, the framework provided by the pioneers in free-radical polymerization will be discussed, as this framework has been a guide to the polymer scientist for the past decades and has provided us with a working understanding of free-radical polymerization.\(^21\) This discussion will then be followed by an outline of chemical dynamics and quantum-chemical models, which can provide us with a physically more realistic picture of the physics underlying the reactions of concern. With the seemingly ever-increasing computation power, these methods will become increasingly accurate and applicable to the systems of interest to the polymer chemist. Unfortunately, this ready availability may also lead to incorrect uses of theoretical models. With this in mind, the chemical dynamics and quantum-chemical sections were written in such a way to enable the nontheoretician to initiate theoretical studies and interpret their results. Realizing that many quantitative aspects of this chapter may be replaced by more accurate computational data within a few years (months?) after publication of this book, the discussion will focus on general aspects of the different computational procedures and in which situations particular procedures are useful. Several different examples will be discussed where theory has provided us with information that is not directly experimentally accessible and where future opportunities lie for computational studies in free-radical polymerization.
1.2 CLASSICAL THEORIES OF MONOMER AND RADICAL REACTIVITY

Although great progress has been made since the early 1980s in understanding radical reactivity, there seems to be a tendency among polymer chemists to think in models about radical and monomer reactivity which were laid down in the sixties and early 1970s. Since these models have greatly influenced our thinking and the development of polymer science, they will be briefly discussed here.

Traditionally, the reactivities of monomers and radicals have been studied by means of copolymerization data. In a series of monomer pairs \{A, B\} with fixed monomer A, the series of respective \(1/r_A\) values represents a series of relative reactivities of these monomers B toward a radical \(\sim A^*\) (see Scheme 1.1).

These studies and early studies on small radicals have led to the current framework in which we tend to think about radical and monomer reactivities. The factors that govern the reactivity are generally summarized in the following four features: (1) polar effects, (2) steric effects, (3) (resonance) stabilization effects, and (4) thermodynamic effects.

1. Polar Effects. From the numerous observations that nucleophilic radicals readily react with electrophilic monomers (and vice versa), it is concluded that polar effects can be very important in radical reactions. The importance of polar effects has been well established since the early 1980s through both experimental and theoretical studies.

2. Steric Effects. Perhaps the most convincing observations that steric effects play an important role in radical reactions is that the most common propagation reaction is a head-to-tail addition and that head-to-head additions hardly ever occur. Furthermore, several studies to date indicate that 1,2-disubstituted alkenes do not readily homopolymerize (although they might copolymerize quite readily), which could possibly be attributed to steric hindrance.

3. Stabilization Effects. These effects can arise if delocalization of the unpaired electron in the reactant and product radicals is possible. If the reactant radical has a highly delocalized electron, it will be relatively stable and have a relatively low reactivity. On the other hand, if the addition of a monomer will lead to a radical that has a highly delocalized electron, it is said that the monomer is relatively more reactive. In general, the order of reactivity of a range of monomers is the reverse of the order of reactivity of their respective derived radicals.

\[
\begin{align*}
\sim A^* + A & \xrightarrow{k_{AA}} \sim AA^* \\
\sim A^* + B & \xrightarrow{k_{AB}} \sim AB^*
\end{align*}
\]

\[
\frac{r_A}{k_{AA}} = \frac{k_{AB}}{k_{AB}}
\]

Scheme 1.1
4. Thermodynamic Effects. These effects can be ascribed to differences in the relative energies between reactants and products, lowering or increasing the reaction barrier. For many reactions, including propagation and transfer reactions, an approximate linear relationship exists between the activation energy, \( E_{act} \), and reaction enthalpy, \( \Delta H_r \), the so-called Bell–Evans–Polanyi relation: \(^{22,23}\)

\[
E_{act} = \rho \Delta H_r + C
\]

where \( \rho \) and \( C \) are constants.

Attempts have been made to quantify the abovementioned concepts in several semi-empirical schemes. These schemes were developed in order to predict the reaction rate coefficients of propagation and transfer reactions, and particularly to predict monomer reactivity ratios. Here, the two most interesting among these models will be briefly described: the \( Q-e \) scheme of Alfrey and Price \(^{21,24,25}\) and the “patterns of reactivity” scheme of Bamford and co-workers. \(^{21,26–28}\)

1.2.1 The \( Q-e \) Scheme

This scheme was one of the first to appear \(^{21,24,25}\) and is probably still the most widely used for the semiquantitative prediction of monomer reactivity ratios. It is based on the assumptions that a given radical \( \sim A^* \) has an intrinsic reactivity \( P_A \), a monomer \( A \) has an intrinsic reactivity \( Q_A \), and that the polar effects in the transition state can be accounted for by a factor \( e_A \), which is a constant for a given monomer (it is assumed that \( e \) in the radical derived from a particular monomer is the same as \( e \) for that monomer). The reaction rate coefficients of the reactions shown in Scheme 1.1 may then be represented as in Eqs. (1.2a) and (1.2b), which result in the expression of Eq. (1.2c) for the resulting monomer reactivity ratio, \( r_A \):

\[
k_{AA} = P_A Q_A \exp(-e_A^2)
\]

\[
k_{AB} = P_A Q_B \exp(-e_A e_B)
\]

\[
r_A = \frac{k_{AA}}{k_{AB}} = \frac{Q_A}{Q_B} \exp\{-e_A(e_A - e_B)\}
\]

After defining styrene as a reference monomer, with standard \( Q = 1.00 \) and \( e = -0.80,^{29} \) the \( Q \) and \( e \) values for other monomers can be obtained by measuring the monomer reactivity ratios. This leads to a “unique” set of \( Q-e \) parameters for a wide range of monomers (there are major solvent effects on these parameters), which are relatively successful in predicting monomer reactivity ratios of any pair of comonomers. Although the scheme is fundamentally flawed in that reaction rate coefficients are not only composed of individual contributions from the two reactants but also contain a large contribution from specific interactions in the transition state of the reaction, the scheme is very successful in practical applications. The reason for this lies partially in the fact that the transition states for all propagation
reactions are rather similar, and that predictions involve the ratios of two rate coefficients.

1.2.2 Patterns of Reactivity

This approach, which is applicable to both propagation and transfer reactions, is based on Hammett-type relationships between the reaction rate coefficient and certain electronic substituents. As in the case of the $Q-e$ scheme, a general reactivity is assigned to the radical. In this case, however, it is apparently better defined and taken to be the rate coefficient, $k_{tr,T}$, of the $H$ abstraction from toluene by the radical. The contribution by the substrate (i.e., a monomer or chain transfer agent) to the reaction rate in the absence of polar effects is given by a constant $\beta$. Polar effects are taken into account by using two different parameters $\alpha$ and $\sigma_p$ for the substrate and radical, respectively (as compared to the single $e$ for monomer and radical in the $Q-e$ scheme). The rate coefficient can now be expressed by

$$\log k = \log k_{tr,T} + \alpha\sigma_p + \beta$$  \hspace{1cm} (1.3)

Although this scheme does improve on some of the assumptions made in the $Q-e$ scheme, it still suffers from the fundamental shortcoming that a rate coefficient is not just composed of the separate individual contributions of the two reactants, but contains their interactions in the transition state. As in the case of the $Q-e$ scheme, this scheme is rather successful in predicting monomer reactivity ratios, but since the former scheme is much simpler, it seems to be more popular with the general polymer community.

1.2.3 Beyond Classical Theories

It is clear that the “classical” theories have helped us greatly advance our understanding of free-radical polymerization and its development, however, these theories are now too limited to answer our current questions. Many studies in small-radical organic chemistry since the early 1980s have significantly improved our understanding of radical reactions, and together with the use of fundamental theory outlined later in this chapter, some general trends in barrier heights for radical additions have been clearly identified. The interested reader is referred to an excellent recent review article by Fischer and Radom on this topic. After analysis of the available data on radical additions to alkenes to date, they identified the following trends in reactivity:

- Enthalpy effects as given by the Bell–Evans–Polanyi relationship [Eq. (1.1)]; these effects are always present, but may be obscured by the presence of other effects.
- Polar effects, which can decrease the barrier beyond that indicated by the enthalpy effect.
The authors further propose the following relationship between activation energy \( (E_{\text{act}}) \) on the one hand and the reaction enthalpy \( (\Delta H_r) \), nucleophilic polar effects \( (F_n) \), and electrophilic polar effects \( (F_e) \) on the other:

\[
E_{\text{act}} = (50 + 0.22 \Delta H_r)F_nF_e \tag{1.4}
\]

where the part between brackets corresponds to an “unperturbed” Bell–Evans–Polanyi-type relationship, and \( F_n \) and \( F_e \) are multiplicative polar factors with a value between 0 and 1, which are given by

\[
F_n = 1 - \exp\left\{-\left(\frac{I(R) - EA(A) - C_n}{\gamma_n}\right)^2\right\} \tag{1.5a}
\]

and

\[
F_e = 1 - \exp\left\{-\left(\frac{I(A) - EA(R) - C_e}{\gamma_e}\right)^2\right\} \tag{1.5b}
\]

where \( I \) and \( EA \) refer to ionization potential and electron affinity, respectively; \( A \) and \( R \), refer to the alkene and radical, respectively; \( C_n \) and \( \gamma_n \) are the Coulomb and interaction terms for nucleophilic polar effects, respectively; and \( C_e \) and \( \gamma_e \) are the Coulomb and interaction terms for electrophilic polar effects, respectively. Whereas the ionization potential and electron affinity are clearly properties of the individual reactants, the Coulomb and interaction parameters are constants that can be applied to wider ranges of radical–alkene pairs. These relationships describe the experimental observations well and are shown to have some predictive quality. Since this approach is based on very fundamental aspects of reaction barrier formation (see discussion below), it has a firmer theoretical basis than either of the \( Q-e \) and Patterns schemes. However, the actual forms of Eq. (1.4) and of \( F_n \) [Eq. (1.5a)] and \( F_e \) [Eq. (1.5b)] still appear to be of an empirical nature.

It should now be clear that in order to answer some of our more fundamental questions, we will need to resort to theoretical chemistry. In what follows we briefly outline the more fundamental theories and the results obtained with these theories.

### 1.3 BASIC TRANSITION STATE THEORY

In order to introduce some of the concepts in chemical dynamics, it is useful to revisit our ideas about chemical reactions. First, we need to realize that atoms move; that is, they translate and rotate. This occurs even within molecules, where this motion leads to vibrations, rotations, angular distortion, and other activities, of which the characteristic energies can be observed in an infrared spectrum of the molecule. The atomic motions are governed by the potential energy field, which is determined
by the electronic energy of the system. Since the electronic energy will depend on the geometric arrangement of the atoms, the potential energy field in which the atoms move will change with displacement of atoms.\(^*\) Plotting the potential energy as a function of the atomic coordinates yields the potential energy surface, which is one of the most fundamental concepts in chemical dynamics.

Returning to a chemical reaction, we can now say that, simply speaking, a chemical reaction involves the rearrangement of the mutual orientation of a given set of atoms in which certain existing chemical bonds may be broken and new ones formed; thus, we move from one spot on the potential energy surface to another. This is probably best illustrated by a simple example, which is more rigorously, but still very clearly, discussed by Gilbert and Smith.\(^3\)

Let us consider the displacement of atom A by atom C in the diatomic molecule BC:

\[
AB + C \xrightarrow{k} A + BC
\]

(1.6)

To simplify matters, the atoms are aligned in a linear fashion and will not move away from this linear rearrangement. It is simple to see that the electronic energy is determined by two coordinates, namely, the distance between atoms A and B, \(r_{AB}\), and the distance between atoms B and C, \(r_{BC}\). In the reactant configuration (i.e., \(A - B + C\)), \(r_{AB}\) is small and at its equilibrium value, whereas \(r_{BC}\) is rather large (i.e., large enough for C not to be considered as part of the molecule). In the product configuration (i.e., \(B - C + A\)), this situation is obviously reversed. Let us start with the reactant configuration. Any motion of the atoms causes a change in energy; for instance, compression of the A–B bond (i.e., a decrease in \(r_{AB}\)) leads to an increase in energy due to nuclear repulsion, and a stretch in the A–B bond (i.e., an increase in \(r_{AB}\)) will also lead to an increase in energy (i.e., we are trying to break a bond). Any motions of C will not affect the energy of the system until C comes close to B. When B starts to feel the electronic forces caused by the presence of C and bond formation starts, the original A–B bond needs to be stretched. Clearly, this bond-breaking process initially results in an increasing potential energy until the B–C bond-forming process starts to dominate. The net result is a decrease in energy. This process continues until the stable BC molecule is formed and the A–B bond is completely broken. We are now in the product configuration. A further decrease in \(r_{BC}\) would also lead to an increase in the potential energy, due to nuclear repulsion. The potential energy surface for this system is schematically shown in Fig. 1.1.

The potential energy surface shown in Fig. 1.1 reveals that there is a minimum energy pathway that can be followed when going from \{AB + C\} to \{A + BC\}, namely, the “gully” in the figure. This minimum energy pathway, which in this particular case is a combination of \(r_{AB}\) and \(r_{BC}\), is called the reaction coordinate.\(^3, 7, 9\)

In cases in which existing bonds are broken and new bonds are formed, the energy

\(^*\) This representation of atomic motion is based on the Born–Oppenheimer approximation in quantum mechanics, which states that electronic and nuclear motion can be separated.
profile along the reaction will display a maximum. The structure that corresponds to the coordinates at this maximum along the reaction coordinate is commonly known as the transition state (TS). A plot of the potential energy against the reaction coordinate yields the very familiar picture in undergraduate textbooks defining the reaction barrier ($\Delta E^\dagger$) and reaction energy ($\Delta E_{\text{reaction}}$) (see Fig. 1.2).

Before continuing with examples that are more relevant to free-radical polymerization, there is another point that deserves some attention. If we return our attention to Fig. 1.1, it can be seen that the transition state is located on a saddle point, that is, it displays a maximum in energy for only one of the coordinates (i.e., the reaction coordinate), whereas it displays a minimum for the others (in this case a coordinate perpendicular to the reaction coordinate). This is in contrast to the reactant and product configurations, which have minimal energy for all their coordinates.

This simple picture can be extended to any system with $N$ atoms. Instead of the 2 coordinates in the previous example, we will now have $3N - 6$ internal coordinates, and we will now have a $(3N - 5)$-dimensional potential energy surface, which is obviously impossible to draw. However, the energy profile along the reaction coordinate will still be a two-dimensional picture, but it is likely that the reaction coordinate is now composed of several different internal coordinates. Figure 1.3 illustrates this point for a radical addition to an alkene. Although the reaction coordinate largely comprises the forming C–C bond length, it also comprises the out-of-plane bending of the hydrogen atoms attached to the C atoms forming the bond, and to some extent stretching of the C=C bond, which will end up as a C–C bond in the product radical.
Figure 1.2  Schematic representation of the potential energy along the reaction coordinate for a collinear triatomic system AB + C reacting to give A + BC. Clearly indicated are the reactant, product and transition state regions, as are the barrier ($\Delta E^\ddagger$) and reaction energy ($\Delta E_{\text{reaction}}$).

Figure 1.3  Schematic representation of the potential energy profile along the reaction coordinate for a radical addition reaction. Note that the reaction coordinate largely consists of the length of the forming C–C bond, but that it also contains some contributions from the disappearing C≡C bond length and the angles of the hydrogen atoms adjacent to the forming bond.
To summarize, we can state that atoms move in a force field that is determined by the electronic energy, and that if a motion along the reaction coordinate contains sufficient energy to overcome the barrier, a chemical reaction occurs. If the energy is not large enough, then motion is still possible along the reaction coordinate, but it will not lead to a reaction.

We can evaluate the reaction rate coefficient exactly (classically) by solving the classical equations of motion of the atoms on the potential energy surface. This results in the momenta and positions of atoms at any given time, namely, a trajectory. If we calculate a large number of trajectories, we can evaluate how many of these trajectories start in the reactant region of the potential energy surface and end in the product region on the potential energy surface in any given time. This is a lengthy and computationally demanding process, which can be greatly simplified by making the transition state assumption, which states that all trajectories passing through a critical geometry (i.e., the transition state) and have started as reactants will end up as products. Evaluation of the mathematical description of this process leads to a relatively simple expression of the bimolecular rate coefficient, \( k \), which depends only on the properties of the two reactants and the transition state: \( \text{(1.7)} \)

\[
k = \frac{k_B T}{h} \frac{Q^1 Q_2}{Q^{\prime}} \exp \left( -\frac{E_0}{k_B T} \right)
\]

In this equation \( k_B \) is Boltzmann’s constant; \( T \) is the absolute temperature in Kelvin; \( h \) is Planck’s constant; \( Q^1, Q_1, \) and \( Q_2 \) are the molecular partition functions of the transition state, reactant 1, and reactant 2, respectively; and \( E_0 \) is the critical energy to reaction. In what follows, the concepts of partition functions and critical energy will be briefly discussed.

First, we consider the critical energy, \( E_0 \), which is defined as the difference in zero-point energies between reactants and transition state (see Fig. 1.4). Since there is always a motion of the atoms within a molecule, that is, the zero-point vibration, the energy of a molecule should not only be represented by the minimum ground-state energy, but a small additional term due to the vibrations; specifically, the zero-point vibrational energy (ZPVE), needs to be added. The ZPVE contains a contribution from all \( 3N - 6 \) vibrations of the molecule \( (3N - 7 \) in the transition state, i.e., the motion along the reaction coordinate is excluded—the corresponding frequency is imaginary!), and is defined as:

\[
\text{ZPVE} = \frac{1}{2} \sum_{j=n}^{3N-6} h\nu_j
\]

where \( n = 1 \) for a minimum-energy structure (e.g., reactants and products), \( n = 2 \) for a transition state, \( n = m + 1 \) for any \( m \)th order saddlepoint (e.g., a rotational maximum in the TS has \( m = 1 \)), and \( \nu_j \) is the harmonic frequency of the \( j \)th normal mode vibration. It is clear from this definition that the high-frequency modes (e.g., C–H bond stretches) dominate the ZPVE.

We also need to discuss the meaning of a partition function, a concept originating from statistical thermodynamics, which serves as a bridge between the quantum
mechanical energy states of a macroscopic system and its thermodynamic properties. For example, we can express the enthalpy \( H \) and entropy \( S \) of a molecule in terms of molecular partition functions:

\[
S = k_B \ln Q - k_B \frac{\partial \ln Q}{\partial T} \quad (1.9)
\]

\[
H = -k_B \frac{\partial \ln Q}{\partial T} + k_B T \quad (1.10)
\]

If we use these definitions of \( H \) and \( S \) in the TST expression for the rate coefficient, we can relate the empirical parameters in the Arrhenius equation [Eq. (1.11)], namely, the frequency factor \( A \) and the activation energy \( E_{\text{act}} \), to fundamental thermodynamic properties of the system

\[
k = A \exp \left( -\frac{E_{\text{act}}}{k_B T} \right) \quad (1.11)
\]

First, we express \( E_{\text{act}} \) and \( A \) in terms of partition functions:

\[
E_{\text{act}} = -k_B \frac{\partial \ln k}{\partial T} = E_0 - k_B \frac{\partial \ln \left( \frac{Q'}{Q_1 Q_2} \right)}{\partial T} + k_B T \quad (1.12)
\]

\[
\ln A = \ln \left( \frac{e k_B T}{h} \right) - \frac{1}{T} \frac{\partial \ln \left( \frac{Q'}{Q_1 Q_2} \right)}{\partial T} + \ln \left( \frac{Q'}{Q_1 Q_2} \right) \quad (1.13)
\]
If we now define an enthalpy of activation, $\Delta H^\ddagger$, as
\[
\Delta H^\ddagger = H^\ddagger - H_1 - H_2
\]
where $H^\ddagger$ is the enthalpy of the transition state, and $H_1$ and $H_2$ are the enthalpies of reactants 1 and 2, respectively, and we define an entropy of activation, $\Delta S^\ddagger$, as
\[
\Delta S^\ddagger = S^\ddagger - S_1 - S_2
\]
where $S^\ddagger$ is the entropy of the transition state, and $S_1$ and $S_2$ are the entropies of reactants 1 and 2, respectively, then we obtain the following expressions for the Arrhenius parameters:\textsuperscript{3,7,9}

\[
E_{\text{act}} = E_0 + \Delta H^\ddagger + 2k_B T
\]
\[
A = \frac{e k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{k_B}\right)
\]

It is clear from these expressions that the activation energy is mainly determined by enthalpic factors and the frequency factor by entropic factors.

Let us now return to the partition function and its definition. The canonical (i.e., number of particles, volume and temperature constant) partition function $Q$ of a system is given by\textsuperscript{10}
\[
Q = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)
\]
which is a summation over all energy levels, $\varepsilon_i$, all with a number of degenerate states $g_i$. In the TST expression of the rate coefficient the molecular partition function is required, but before considering this, we will first look at the simple example of a harmonic oscillator, which is commonly used to represent a normal-mode vibration. The values for $\varepsilon_i$ can be obtained from solving the Schrödinger equation for a particular problem:
\[
\hat{H}\phi = \varepsilon\phi
\]
where $\hat{H}$ is the Hamiltonian, or energy operator, $\phi$ the eigenfunction, and $\varepsilon$ the corresponding eigenvalue, that is, the energy level. The energy levels $\varepsilon_i$ of a harmonic oscillator with a frequency of $\nu_j$ are given by (see Fig. 1.5)\textsuperscript{10}
\[
\varepsilon_i = \left(i + \frac{1}{2}\right)\hbar \nu_j
\]
Substitution of this expression of the energy levels into Eq. (1.18) then yields the partition function for the harmonic oscillator,

\[ Q_{\text{vib}, j} = \frac{1}{C_0} \exp\left( -\frac{\hbar \nu_j}{k_B T} \right) \]  

(1.21)

Let us now return to the concept of molecular partition functions. It is clear that the energy levels with corresponding energies are much more complex than those for the simple problem of a harmonic oscillator. However, if we assume that the several physical factors contributing to the overall energy—the electronic, translational, rotational and vibrational energies—are independent, the molecular partition function can be expressed as the product of the partition functions of the individual contributions:

\[ Q = Q_{\text{elec}} \times Q_{\text{trans}} \times Q_{\text{rot}} \times Q_{\text{int}} \]  

(1.22)

where \( Q_{\text{elec}}, Q_{\text{trans}}, Q_{\text{rot}}, \) and \( Q_{\text{int}} \) are the electronic, translational, (external) rotational, and internal vibrational partition functions, respectively. These individual partition functions are simple and can be determined in a relatively straightforward manner as shown below. We will consider the partition functions of ideal gas molecules as a model for our current system.

The electronic partition function can be quite complex if more than one electronic pathway of the reaction is possible, for example reactions involving excited
molecules. However, the reactions that we will consider here, namely, “ordinary” radical additions and atom abstractions, do not involve excited molecules, but proceed through so-called ground-state intermediates (see section on quantum chemistry). This means that only a single energy level is accessible, and hence $Q_{\text{elec}} = 1$.

The translational partition function of an ideal gas molecule is given by

$$Q_{\text{trans}} = V \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2}$$

(1.23)

where $V$ is the reference volume and $m$ is the mass of the translating molecule. In the case of radical addition or abstraction reactions, the translational contribution to the frequency factor is then given by

$$\left( \frac{Q^i}{Q_{\text{very long}} Q_{\text{small}}} \right)_{\text{trans}} = \frac{1}{V} \left( \frac{m_1 + m_2}{m_1 m_2} \right)^{3/2} \left( \frac{\hbar^2}{2\pi k_B T} \right)^{3/2}$$

(1.24)

For a reaction between a small molecule, for instance, monomer or chain transfer agent, with mass $m_{\text{small}}$ and a long radical chain with mass $m_{\text{rad}}$, we have in the limit of long chains that the masses of the radical and the transition state ($m^i$) are roughly the same: $m_{\text{rad}} \approx m^i$. Hence Eq. (1.24) will reduce to

$$\left( \frac{Q^i}{Q_{\text{very long}} Q_{\text{small}}} \right)_{\text{trans}} \approx \frac{1}{V} \left( \frac{1}{m_{\text{small}}} \right)^{3/2} \left( \frac{\hbar^2}{2\pi k_B T} \right)^{3/2}$$

(1.25)

All (nonlinear) molecules exhibit an external three-dimensional rotation, for which the partition function is given by

$$Q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \left( \frac{8\pi^2 k_B T}{\hbar^2} \right)^{3/2} \sqrt{I_a I_b I_c}$$

(1.26)

where $\sigma$ is the symmetry number of the molecule and $I_a$, $I_b$, and $I_c$ are the principal moments of inertia, given by $I = \Sigma m_i r_i^2$, where $m_i$ and $r_i$ are the mass and the distance to the appropriate principal axis of rotation, respectively, of atom $i$. The principal moments of inertia can be easily calculated if the geometry of the molecule is known. In the case of a small radical adding to the monomer, the external rotations of both reactants and the TS need to be considered, but in the long-chain limit, it is only the external rotation of the small molecule that is important (since the moments of inertia of the polymeric radical and the TS will not differ significantly and will approximately cancel), leading to

$$\left( \frac{Q^i}{Q_{\text{very long}} Q_{\text{small}}} \right)_{\text{rot}} \approx \left( \frac{1}{Q_{\text{small}}} \right)_{\text{rot}}$$

(1.27)
Except for transition states, the geometry information required for the determination of rotational partition functions can be obtained experimentally. However, as we will discuss later, this information can also be adequately obtained by appropriate quantum-chemical calculations, including the information about the transition state.

Finally, we have to consider the internal vibrational partition function. We have already seen that the vibrational partition function of a single harmonic oscillator—the model we use for an internal vibration—is given by the following equation [\(=\text{Eq. (1.21)}\):]

\[
Q_{\text{vib},j} = \left[1 - \exp\left(-\frac{\hbar \nu_j}{k_B T}\right)\right]^{-1}
\]  

(1.28)

In a polyatomic, non-linear, molecule consisting of \(N\) atoms, we have \(3N - 6\) such vibrations and we can write the overall vibrational partition function \(Q_{\text{vib}}\) as the product of the vibrational partition functions of separate vibrational modes:

\[
Q_{\text{vib}} = \prod_{j=n}^{3N-6} Q_{\text{vib},j}
\]

(1.29)

In this expression \(n\) is defined in the same way as for Eq. (1.8) (e.g., \(n = 1\) for reactants and/or products, and \(n = 2\) for the transition state).

It should be noted here that, in contrast to what we previously saw for the zero-point vibrational energy (i.e., a contribution to the critical energy \(E_0\); see above), the low-frequency vibrations are most important, as can be seen from Eq. (1.28). Vibrational frequencies can be determined experimentally (e.g., infrared measurements) or theoretically. The experimental measurements, however, are very difficult for radicals, and virtually impossible for transition structures, which leaves theory as an important alternative. When applying theoretical methods to determine the vibrational frequencies, two factors need to be considered: (1) experience has shown that the harmonic frequencies calculated by a particular quantum-chemical method (see below) tend to be systematically out (by less than \(\sim 10\%\)) depending on the procedure, and will require scaling by appropriate scale factors;\(^{32,33}\) and (2) the calculated frequencies are obtained by using the harmonic oscillator approximation for all the determined “vibrations.” Although this is indeed an appropriate and relatively accurate description for most internal motions, it may lead to some errors for certain low-frequency modes. The actual motions of some of these low-frequency modes, as indicated by a normal-mode analysis, are better represented as internal rotations, and should be treated either as hindered or unhindered rotors (depending on the barrier to rotation).\(^{3,31}\) As is shown in Fig. 1.6, the potential energy profiles of a harmonic oscillator and a hindered rotor at small displacements can be quite similar, and it is only this part that is calculated automatically by the quantum-chemistry programs.\(^{11}\) These programs then automatically extrapolate with a parabola, which confines the motion to relatively small displacements. However, if the motion is really a hindered rotation, then the true potential energy profile is of a periodic
nature and after overcoming a barrier, a new energy well is reached. Without going into specific details, it should be noted that because of the different potential energy profiles, the two treatments, namely, the harmonic oscillator and the hindered rotor, give different partition functions and hence it is more appropriate to treat the internal rotations as hindered rotors, rather than harmonic oscillators.3

The frequencies of these hindered rotors are then omitted from the vibrational partition function and enter the internal rotational partition function ($Q_{\text{int rot}}$). It is now possible to define the overall partition function of all internal motions ($Q_{\text{int}}$), for a system that contains $r$ internal rotations:3,31

$$Q_{\text{int}} = \prod_{j=n}^{n+r} Q_{\text{int rot},j} \prod_{j=n+r+1}^{3N-6} Q_{\text{vib},j}$$

(1.30)

In this expression $n$ is defined in the same way as for Eq. (1.8) (e.g., $n = 1$ for reactants and/or products, and $n = 2$ for the transition state).

Internal rotations may be described as hindered one-dimensional or two-dimensional rotors, and the corresponding partition functions can be obtained by solving the Schrödinger equation for an appropriate rigid rotor with corresponding rotational potential. Without going into details of these calculations, it should be noted that a higher barrier to rotation lowers the partition function, whereas a higher moment of inertia (mass of rotating moieties) increases the partition function.31,34

To conclude this section on transition state theory we should discuss the very important so-called transitional modes.3,31 We have already seen that the transition
state has one imaginary frequency (which is a characteristic of the transition state), corresponding to a motion along the reaction coordinate, and which is omitted from the vibrational partition function and zero-point vibrational energy. It is clear that this motion along the reaction coordinate, such as the stretching of the forming C–C bond in radical addition, did not exist previously in the reactants (simply because this bond did not exist). A detailed examination of the vibrational modes in the transition state of a bimolecular reaction reveals that there are five more internal motions (with real frequencies) that did not exist previously in the reactants. These six extra modes (with one imaginary and five real frequencies) are the so-called transitional modes and arise because of the loss of three external rotational and three translational degrees of freedom of the reactants when brought together in the transition state (see Fig. 1.7).

All the other modes in the transition state correspond to modes that already existed in the reactants (they will be slightly lower because of the higher mass of the transition state). This implies that the overall contribution of the internal motions to the reaction rate coefficient, namely, $Q_{\text{int}}^{i}/(Q_{1,\text{int}}Q_{2,\text{int}})$, is determined mainly by the frequencies of the five real transitional modes. These frequencies typically lie below 1000 cm$^{-1}$ and the lowest frequencies often correspond to torsional modes. Since the transition states of propagation reactions (or transfer reactions) in different monomer systems will all have similar characteristics, the differences in the overall vibrational contributions will be small.$^{31,35}$ Sterically more crowded

Figure 1.7  Schematic representation of the transformation of 6 external modes into 6 transitional modes when two reactants combine to form a single transition state.
monomers will probably show an increase in the frequency of a particular mode as compared with a similar mode in a less crowded monomer. Although the observed differences between different monomer systems will be significant, it is unlikely that the internal contribution to the frequency factors will show variations exceeding one order of magnitude from system to system; even an extremely large increase in frequency from 200 to 600 cm\(^{-1}\) results in a decrease in the overall vibrational contribution by a factor of only 1.6. It should be kept in mind, however, that all these small changes appear in the frequency factor as a product, so several small changes can quickly become a combined factor of, say, 5.

### 1.4 BASIC QUANTUM CHEMISTRY

In the previous section we saw that we need knowledge of the potential energy surface, or at least of the reactants and transition states in order to determine the reaction rate coefficient. The potential energy surface can be calculated by solving the Schrödinger equation for every possible set of atomic coordinates. The Schrödinger equation [Eq. (1.31)] is a numerical eigenvalue problem for which multiple solutions can be found, each characterised by a certain wavefunction and corresponding energy.\(^{11–14}\)

\[
\hat{H}\psi = E\psi
\]  

(1.31)

In this expression, \(\hat{H}\) is the Hamilton operator (which corresponds to the total energy of the system), \(E\) is the numerical value of the energy (an eigenvalue), and \(\psi\) is the wavefunction (an eigenfunction), which depends on the coordinates of all the particles and the spin coordinates in the system. The solutions of the Schrödinger equation are called *stationary states* and the state with the lowest energy is called the *ground state*. Stationary states with higher energies correspond to so-called excited states. These excited states are, for example, important in photochemical reactions that play a role in photoinitiation processes; in this chapter, we will discuss only the ground states, as the “ordinary” radical addition and transfer reactions involve reactions between molecules in their ground state.

In only a few simple cases do analytic solutions of the Schrödinger equation exist, and in order to solve this equation for systems of interest, certain approximations need to be made, but before we will briefly discuss the most important features of the involved calculational procedures, the actual results of quantum-chemical calculations will be discussed.

As stated before, solution of the Schrödinger equation yields the (ground state) energy and corresponding wavefunction, from which the electronic configuration of the molecule is deduced. With this information it is possible to calculate properties such as ionization energies, electron affinities, charge distributions, and dipole moments.\(^{11}\) If the energy is optimized with respect to all coordinates, one obtains “stable” molecules. “Normal molecules” correspond to minima on the potential energy surface and the transition state of a reaction corresponds to a maximum in
the reaction coordinate and a minimum in all other coordinates, namely, a first-order saddle point (see also Fig. 1.1). From the second derivatives of the energy with respect to all the nuclear coordinates, the force constants of the $3N - 6$ normal-mode vibrations can be obtained for a molecule consisting of $N$ atoms ($3N - 5$ for a linear molecule). The second derivatives, that is, the force constants, are all positive in the case of minima on the potential energy surface, which leads to $3N - 6$ real frequencies for the vibrations. In the case of a transition state of a reaction, which is characterized by a maximum in the reaction coordinate, one of the force constants is negative, and this “molecule” is now characterized by $3N - 7$ real frequencies and 1 imaginary frequency for the motion along the reaction coordinate.

To summarize, a standard quantum-chemical calculation will provide us with all the required input for a TST calculation of the rate coefficient (i.e., geometries, normal-mode vibrations and corresponding frequencies, rotational barriers, and absolute energies) and with information about the electronic structure of a molecule (i.e., important for the study of substituent effects on reaction barriers, e.g., polar effects). Let us now turn our attention to the assumptions and simplifications in the actual computational procedures.

### 1.4.1 Ab Initio Molecular Orbital Theory

Among the procedures for obtaining (approximate) solutions to the Schrödinger equation are the molecular orbital (MO) and valence bond (VB) theories. Whereas both procedures yield the same results in the limiting case, MO theory is much more easily implemented in computational procedures and hence forms the basis of the great majority of theoretical studies. In this section we will focus only on MO theory; we will encounter VB theory again in the section on barrier formation.

In MO theory, the full wavefunction $\Psi$ is approximated by one electron functions, the so-called spin orbitals ($\chi$); the exact nature of this approximation is beyond the scope of this chapter. The spin orbitals are given by the product of molecular orbitals ($\psi$), which depend on the Cartesian coordinates $x$, $y$, and $z$ of a single electron, and a spin function ($\alpha$ or $\beta$):

$$\chi = \psi(x, y, z)\alpha \quad \text{or} \quad \chi = \psi(x, y, z)\beta$$  \hspace{1cm} (1.32)

It is difficult to picture the actual meaning of a molecular orbital (MO), but its square, $|\psi|^2$, can be interpreted as the probability of finding the electron in a particular space. In practice, the MOs are expressed as linear combinations of $M$ one-electron functions, the so-called basis functions ($\phi$). Then, each individual orbital $\psi_i$ can be written in terms of the $M$ basis functions $\phi_\mu$ as follows:

$$\psi_i = \sum_{\mu=1}^{M} c_{i\mu} \phi_\mu$$  \hspace{1cm} (1.33)
where the $c_{ni}$ are the molecular orbital expansion coefficients. The actual form of the
basis functions is based on the form of the atomic orbitals obtained analytically for
the hydrogen atom. The basis functions can then be classified as $s$, $p$, $d$, $f$, . . . -type
orbitals according to their angular momentum properties (see Fig. 1.8).11–14

At this point it is useful to recall what we are trying to achieve. We wish to solve
an eigenvalue problem: the Schrödinger equation. This is basically a problem in a
vector space of infinite dimensions, which we try to approximate by a limited
number of basis functions. It is important to realize that the more basis functions
we use, that is, the better we approximate the real vector space, the more expensive
our calculations will be, and that we are therefore forced to use as few basis
functions as is possible. In what follows, only the Pople–Gaussian basis sets11 and
corresponding nomenclature will be discussed for no other reasons than simplicity
and their frequent usage.

We are used to thinking in such terms as that a hydrogen atom has one $s$ electron,
and a carbon atom has two electrons in its inner-shell $s$ orbitals, two electrons in its
valence $s$ orbitals, and two electrons in its valence $p$ orbitals. This suggests that if we
allow the electrons to occupy these particular orbitals (approximated by basis func-
tions of a similar “shape”), then we should have a fairly good description of the
actual situation (i.e., the approximation of the infinite vector space), and we should
get fairly good results when solving the Schrödinger equation. The so-called mini-
mal basis sets (with names such as STO-3G), and to some extent the slightly better
split-valence basis sets (with names such as 3-21G, 6-31G) are based on this
philosophy.11

Although these minimal and split-valence basis sets do a reasonable job in certain
applications, they have some major shortcomings, of which one will be briefly dis-
cussed here. These basis sets cannot take into account any distortion from atomic
symmetry when placing the atoms in a molecular environment. For example, if
we only allow the electron of hydrogen to occupy an orbital of $s$-type symmetry,
then this description is clearly better for a single hydrogen atom, than when this
hydrogen atom is placed in a molecule in which it forms a $\sigma$ bond. In this case it
is likely that the electron will have a higher probability of being found in the region
of the bond, rather than away from it (which would be a consequence of the fully
spherical symmetry of the $s$ orbital). Hence, a better description would result if we

Figure 1.8  Representation of $s$, $p$, and $d$ atomic orbitals as the boundary surface within
which there is a 90% probability of finding the electron.
allowed the electron to use orbitals of different shape to create a new orbital with a better-suited shape. This process can be accomplished by the addition of polarization functions to the basis set describing a particular atom. The effect of the addition of \( p \)-type functions to \( s \)-type functions, and of \( d \)-type functions to \( p \)-type functions is shown in Fig. 1.9. The much greater flexibility of the orbital is immediately clear from this figure.

Basis sets containing polarization functions are often denoted by symbols such as * or **, or by the addition of extra letters between brackets indicating the symmetry type of the polarization functions, such as, 6-31G(\( d \)) (=6-31G*), 6-311G(\( d,p \)) (=6-311G**), and 6-311G(df,p).

Additional “freedom” to the electrons can be provided by the addition of diffuse functions, which are very important for the description of long range behaviour with energies close to the ionisation limit, such as anions. The terminology employed here is the addition of a “+” or “++” to the basis set, such as 6-311+G**.

To summarize, we can say that the approximate solution to the Schrödinger equation improves when we give a greater flexibility to where the electrons “are allowed to go,” that is, the size of the basis set. However, we need to take into account that the more basis functions we use, the more computationally demanding is our problem. Hence, we will always be trading accuracy against cost. In Table 1.1, the number of basis functions for hydrogen and first-row elements is given for several commonly used basis sets. Generally we can state that the larger the name of the basis set, the larger the basis set itself.

### 1.4.2 “Interactions of the Electrons”

We have already seen that the size of the used basis set affects the obtained results, and in this section we will discuss briefly another factor that can greatly affect the results. This factor is caused by the number of interactions between the electrons that we take into account. For example, are we describing the electrons as each individually experiencing a combined electronic field generated by the others or...
will we also take into account individual interactions? If we consider the research output of a graduate student as an analogy, it is probably very important to consider the student’s interactions with members of the research group in great detail, the interaction with the wider scientific community in some detail, and the student’s night out in town as a “background force field” (using the same analogy, the research group, the wider scientific community and the nightlife can be considered as the size of the basis set). If we wish to describe the student’s personal life accurately, the amount of detail would probably require the reverse. A similar situation exists for the description of electronic interactions; in certain cases, such as the description of geometries of stable molecules, no detailed interactions are required, whereas the description of absolute energies, and properties of transition structures require more detail.

The starting point in the description of electronic interactions is Hartree–Fock (HF) theory.\textsuperscript{11–14} This theory is used to evaluate the orbital expansion coefficients $c_{\mu i}$ in Eq. (1.33), without consideration of detailed interactions between the electrons. The overall result of these calculations is a set of molecular orbitals ($\psi$) to which the electrons are assigned (there will also be unoccupied orbitals!); the resulting many-electron wavefunction ($\Psi$) now represents an electronic configuration of the system.

Although Hartree–Fock theory does a decent job in describing most properties of normal ground-state molecules, the limited interaction between the electrons leads to absolute energies that are too high, and sometimes to incorrect descriptions of more complex molecular systems. In order to take more interactions (i.e., electron correlation) into account, one has to invoke configuration interaction.\textsuperscript{11} Instead of using a single electronic configuration to describe the many-electron wavefunction, we now use several different electronic configurations. These additional electronic configurations can be obtained by distributing the electrons over different molecular orbitals than just the lowest-energy ones as we did to obtain the HF wavefunction. Clearly, the more of these electronic configurations are added, the more accurate the overall wavefunction. However, the cost of the computations will increase dramatically.

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Hydrogen Atom</th>
<th>First-Row Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-21G</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>6-31G* = 6-31G(d)</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>6-31G** = 6-31G(d,p)</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>6-311G** = 6-311G(d,p)</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>6-311G(df,p)</td>
<td>6</td>
<td>25</td>
</tr>
<tr>
<td>6-311 + G(2df,p)</td>
<td>6</td>
<td>34</td>
</tr>
<tr>
<td>6-311 + G(3df,2p)</td>
<td>9</td>
<td>39</td>
</tr>
</tbody>
</table>
We can roughly distinguish two different ways of introducing electron correlation; the first one is exactly the way described above, namely, configuration interaction, and the second way is via perturbation theory. The best configuration interaction method is **full configuration interaction** (FCI), which takes into account all possible electronic configurations. This method, which in practice is possible only for very small systems, would result in an exact solution of the Schrödinger equation if an infinite basis set were used. Since this is in practice not possible, only a limited number of alternative configurations are often used. In general, the more alternative configurations, that is, configurations in which certain molecular orbitals are substituted for others, the better the result. Depending on the exact formulation of the procedure, we distinguish methods such as (1) CIS, CID, and CISD (i.e., configuration interaction with single, double, and single + double substitutions, respectively); (2) CCSD, CCSD(T), and CCSD(T,Q) (i.e., coupled cluster with single and double; single, double and triple; and single, double, triple, and quadruple substitutions, respectively); and (3) QCISD, QCISD(T), and QCISD(T,Q) (i.e., quadratic configuration interaction with single and double; single, double, and triple; and single, double, triple, and quadruple substitutions, respectively). The coupled cluster (CC) and quadratic configuration interaction (QCI) methods are very similar in performance for most problems, and can currently be regarded as the best practical procedures available to describe problems of interest to the polymer chemist.

The alternative method of taking into account electron correlation is Möller–Plesset perturbation theory. It is more difficult to provide a simple picture of the mathematics involved in these procedures, but the outcome is similar to what is achieved in the configuration interaction procedures. Instead of double substitutions, we have now second-order Möller–Plesset theory (MP2); instead of higher substitutions we now have MP3, MP4, . . . . The Möller–Plesset procedures are less expensive than the corresponding CC or QCI procedures, and in many cases yield comparable results. However, we will see below that certain formulations of these theories (e.g., UMP2, UMP3, UMP4, . . .) perform very poorly in radical reactions. We have seen that the quality of a calculation depends on both the size of the basis set and the amount of electron correlation. Depending on the problem we wish to describe, we will have to compromise on one aspect or the other, or both aspects. A clear way of depicting the quality of a calculation is a so-called Pople diagram (see Fig. 1.10), which shows the size (and improvement) of the basis set in the left hand column, and the amount (and improvement) of electron correlation in the top row. The combination of the best basis set (i.e., an infinite size basis set) and full configuration interaction results in an exact solution of the Schrödinger equation. We denote the overall level of theory as the combination of procedure and basis set, for example, HF/3-21G, MP2/6-31G*, and QCISD(T)/6-311G(3df,2p).

### 1.4.3 Treating \( \alpha \) and \( \beta \) Orbitals in MO Theory

So far, when discussing the electrons and molecular orbitals we have not paid much attention to the fact that we have \( \alpha \) (spin up) and \( \beta \) (spin down) electrons. In radicals we have a single unpaired electron, a situation that is characterized by a spin
quantum number $S = \frac{1}{2}$; the wavefunction should be a pure doublet (i.e., $2S + 1 = 2$) and have an spin-squared expectation value $\langle S^2 \rangle = S(S + 1) = 0.75$. We basically have two ways of treating the $\alpha$ and $\beta$ electrons in Hartree–Fock theory: (1) in a restricted (RHF) or (2) in an unrestricted way (UHF). The former procedure, RHF, restricts the $\alpha$ and $\beta$ electrons to the same molecular orbital leading to a single orbital with an unpaired electron and results in a wavefunction that is indeed a pure doublet with $\langle S^2 \rangle = 0.75$. Unrestricted Hartree–Fock allows the $\alpha$ and $\beta$ electrons to occupy different molecular orbitals, thus giving the electrons a bit more freedom, and resulting in a wavefunction with a lower energy. However, because of this additional freedom, the net effect is that more than one electron remains unpaired; the wavefunction is said to be contaminated by states of higher spin multiplicity and the spin-squared expectation value $\langle S^2 \rangle > 0.75$. This effect, which is called spin contamination, is especially severe in radical addition transition states.

Correlated procedures can use both UHF and RHF wavefunctions as a starting point and for methods as quadratic configuration interaction (QCI: denoted as UQCI or RQCI, respectively) and coupled cluster (CC: denoted as UQCI or RQCI, respectively) the final results are generally not significantly different. However, the situation is very different for the Møller–Plesset procedures, which generally show very poor convergence when UHF wavefunctions are used (these Møller–Plesset procedures are denoted as UMP2, UMP3, . . .), and the results are

![Figure 1.10 Pople diagram showing the dependence of the performance of an ab initio method on the basis set and the amount of electron correlation.](image-url)
often erratic when using this procedure, as will be shown in a later section.\textsuperscript{44,45} The results of the UMP procedures can often be significantly improved by so-called spin projection, a procedure that removes the contributions from the unwanted higher spin states (the resulting procedures are denoted as PMP2, PMP3, \ldots).\textsuperscript{44,45} Møller–Plesset procedures using the RHF wavefunction as a starting point (i.e., RMP2, RMP3, \ldots or ROMP2, ROMP3, \ldots)\textsuperscript{48–50} also result in significantly better results than the corresponding UMP procedures.

1.4.4 Alternative Popular Quantum Chemical Procedures

Finally, a short note should be added on two very popular alternatives to the ab initio MO procedures that we have discussed until this point: semiempirical MO procedures\textsuperscript{51} and density functional theory (DFT).\textsuperscript{52}

The molecular properties that can be calculated with semiempirical MO procedures are similar to those that can be calculated using conventional ab initio procedures. However, the semiempirical procedures are less computationally demanding and hence allow, in principle, for larger systems to be studied. The semiempirical methods, for example, CNDO, INDO, MINDO, MNDO, AM1, and PM3, are computationally less demanding because they neglect several difficult integrals that need to be evaluated in the Hartree–Fock procedure;\textsuperscript{51} recall that this was the procedure for determining the orbital coefficient and molecular orbitals. Depending on the procedure, particular interactions between certain orbitals are either completely neglected or replaced by parameters (unique for each atom) obtained by fitting against (experimental) data.\textsuperscript{51} Furthermore, the basis sets employed in these procedures are often minimal basis sets, although some procedures try to correct for some shortcomings by the addition of a few more basis functions.\textsuperscript{51} It is clear that the performances of these procedures will highly depend on the application and that the best results will be obtained for systems and parameters similar to those used for the parametrization and that their performance will be worse for describing more complicated electronic problems. This is not to say that semiempirical methods always lead to results of inferior quality compared to ab initio methods. Indeed, many problems, otherwise inaccessible to study using an initio methods, have been successfully studied using these procedures. However, it is always very important to establish the suitability of a method before using it to study unknown systems. This is especially true for semiempirical procedures, and we will see later on in this chapter that the AM1 procedure, which is probably together with PM3 the best-performing semiempirical procedure to date, dramatically fails in describing radical addition reactions.\textsuperscript{42}

The solution of the Schrödinger equation yields \(N\)-electron wavefunctions \(\Psi\), which contain very detailed information about the electronic structure of the system. However, for many properties of interest, such as the total energy, we do not require this very detailed information, and we can obtain these properties if we know the total electron density of the system, which in principle is much simpler to evaluate.\textsuperscript{52} This realization has led to the development of density functional theory (DFT), which has been quite successful in describing and explaining many-electron systems.
that have been too complicated to treat with conventional ab initio procedures, including crystal structure, metals and polymers. Density functional theory has undergone major developments since the early 1970s, and current procedures are based mostly on solving the so-called Kohn–Sham equations, which can be compared with, and are indeed similar, to the Hartree–Fock equations, which are used to evaluate the MOs in ab initio MO theory. In the case of DFT the equations are solved to obtain the electron density, and certain functionals of the electron density are used to represent electronic interactions. This procedure is in principle exact, but the exact forms of the functionals are not known and hence approximate functionals need to be used. The very similar nature of the Hartree–Fock and Kohn–Sham procedures has led to the development of hybrid methods, which generally show a great improvement over conventional Hartree–Fock procedures, because the DFT procedure contains more electron correlation. Currently popular and successful procedures are B-LYP,53,54 and B3-LYP,54,55 which perform very well in many applications and often produce results of similar or even better quality than several higher level ab initio procedures. Since the computational demands of these procedures are generally less than those of conventional correlated ab initio methods, and they scale more favorably with increasing number of basis functions, it is likely that the popularity of these procedures, including radical reactions, will continue to rise.

1.4.4.1 Summary From the theory outlined in this section, it is obvious that a more accurate description of the system is obtained with a high level of theory and a large and flexible basis set. It is also clear that the choice of basis set and level of theory depend on the nature of the molecular property that needs to be described. Both choices will always involve a compromise between desired accuracy and computational resources (e.g., for nearly all correlated procedures, the required amount of disk space scales as $M^4$, where $M$ is the number of basis functions).

1.4.5 Pitfalls in Computational Quantum Chemistry

It is clear that, in general, the higher the level of theory, the more reliable our results. This is especially true if we wish to obtain accurate absolute energies. However, often we are interested in energy differences or certain trends, and we need not resort to these incredibly high-level and expensive methods. It is often possible to obtain adequate results at much simpler levels of theory, but it is important to establish before using these levels of theory whether they are appropriate. For example, a particular simple level procedure can introduce errors in the absolute energies of the reactants ($\Delta E_{\text{reac}}$), transition state ($\Delta E_{\text{TS}}$) and products ($\Delta E_{\text{prod}}$). This situation is schematically shown in Fig. 1.11, where the calculated energies are indicated by the full lines and the real energies by dashed lines. Also the calculated and real barriers ($E_0$) and reaction energies ($E_r$) are indicated.

The description of the reactants and products is often (but not always!) not too difficult, and although we introduce an error in the absolute energies, the calculated reaction energy will be similar to the real one ($E_{r,\text{real}} \approx E_{r,\text{calc}}$) as long as the absolute error introduced in the product energies is similar to the one introduced in the
reactant energies ($\Delta E_{\text{reac}} \approx \Delta E_{\text{prod}}$). However, the description of the transition state is often much more complicated than the description of the reactants, which will result in different absolute errors for the transition state and reactant energies. In Fig. 1.11 the situation is shown where the error in transition state energy is much larger than that of the reactants and products ($\Delta E_{\text{reac}} \approx \Delta E_{\text{prod}} \ll \Delta E_{\text{TS}}$), and although we found in this example that the calculated reaction energy was relatively close to the real one, the calculated barrier will be significantly too high ($E_{0,\text{calc}} \gg E_{0,\text{real}}$).

A very relevant real example of this problem is shown in Figs. 1.12 and 1.13. The data in these figures originate from an extensive study by Radom and co-workers,\textsuperscript{42,43} who examined the effect of level of theory on the reaction energies and barriers for a range of radical additions. They established that the results for the barriers and reaction energies, respectively, converged at the QCISD(T) level of theory;\textsuperscript{42} hence we plot the data of two different procedures against the QCISD(T) values. If the other procedures are equally good, then the data should lie on the diagonal. What we can see in Fig. 1.12 is that, except for two data points, the generally

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**Figure 1.11** Schematic representation of the effect of computational errors on the calculated potential energy surface: full lines represent calculated energies, dashed lines represent the real energies (i.e., obtained using full CI and an infinite basis set). The situation depicted here reflects the case where the absolute error introduced in the energy of the transition state is much larger than the errors introduced in reactants and products.
popular (and generally accurate) UMP2 reaction energies show a reasonable, but far from perfect, agreement with the QCISD(T) results. However, the also popular semiempirical AM1 procedure gives very erratic results. Since AM1 often gives relatively good results for other types of organic reactions, we may conclude that its parametrization is incapable of providing an adequate description of radical addition reactions. Methods such as PMP2, RMP2, and QCISD showed good agreement with the QCISD(T) results.

When we consider the results for the reaction barriers obtained at the same levels of theory, we observe dramatic failures of both methods (Fig. 1.13). Clearly, the AM1 barriers are all too low and do not show any particular trend. The UMP2 results seem to look better, but all the barriers are significantly higher than those at the QCISD(T) level of theory, and furthermore the trend is quite erratic.

This poor performance of UMP2 can be ascribed to spin contamination (see discussion above). If we have a ground state reaction such as in the reactions of most interest to us, then the electronic state does not change in going from reactants to products; in fact, it is exactly the same everywhere at the potential energy surface. Hence, everywhere on the potential energy surface we should have a single unpaired electron. However, the unrestricted procedures tend to “spread out” this single electron, and whereas this effect need not be really large when we just have a radical

Figure 1.12  Plot of calculated UMP2/6-31G* (●) and AM1 (▲) reaction energies against calculated QCISD(T)/6-31G* reaction energies for the addition of CH$_3$ radical to a range of substituted ethylenes CH$_2$=CHY (Y = OH, F, H, CH$_3$, NH$_2$, SiH$_3$, Cl, CHO, NO$_2$). The erroneous UMP2 results are obtained for Y = CHO and CN, which both have UMP2/6-31G* reaction energies of about −123 kJ/mol, whereas their QCISD(T)/6-31G* reaction energies are about −151 kJ/mol. (Data are taken from the extensive study by Wong and Radom.)
[although several examples with severe spin contamination in simple radicals exist, e.g., cyanovinyl radical has $\langle S^2 \rangle = 1.49$], this effect can be enormous in the electronically more complicated description of the transition state. Hence the effect of spin contamination on the calculated barrier may be huge, whereas it may be small in the case of the reaction energies. The problem of spin contamination does not exist for the restricted procedures.

In summary, it is of utmost importance to establish the suitability of the simpler levels of theory for the calculation of properties one wishes to study. Certain procedures may be cheaper and faster, and larger molecules can potentially be studied; however, one should be aware of the fact that the results may be meaningless if the chosen procedure is not appropriate. For example, the UMP2 procedure yields excellent results for many organic reactions, but we have seen it performs very poorly in radical reactions and its use should be avoided.

1.4.6 Practical Computational Quantum Chemistry

We saw in the previous part that it is essential to choose the appropriate level of theory if reliable results are to be obtained. This does not necessarily mean that one has to perform all calculations at the most expensive level of theory. For example, accurate energies for the calculation of reaction energies or barriers often

![Figure 1.13](image.png)
require high levels of theory, and often we cannot compromise much. However, the first cost-saving lies in geometry optimization. Although the best geometries are generally obtained at the highest levels of theory, the optimum geometries at simpler levels of theory are often very close (this is not always the case, but this can be considered as a general rule of thumb). This means that we can often optimize the geometry at a simple level of theory and then calculate the energy at the high level of theory for this geometry; this is a single-point energy calculation (often denoted as level of theory of single point/level of theory of geometry optimization). Naturally, one has to establish first that the geometries indeed converge with increasing level of theory; this is essential as the potential energy surface obtained at different levels of theory may differ significantly; for instance, spurious minima or transition states may occur at lower levels of theory, or essential features might be absent. This procedure of an energy calculation is shown in Fig. 1.14, in which I have attempted to reduce $N$ atomic coordinates to a single set of coordinates. In this way we can plot the potential energy surface as a two-dimensional plot; the $Y$ axis represents the energy and the $X$ axis, a given set of coordinates. Three potential energy surfaces are shown, each corresponding to a different level of theory. Ultimately, we wish to calculate the energy of the molecule corresponding to the minimum on the high-level potential energy surface. However, we do not know where to start in our geometry optimization.

Figure 1.14  Schematic representation of the use of simple-level geometry optimizations and single-point energy calculation to approximate the energy of a high-level miminum energy conformation. Three different potential energy surfaces are shown, each at a different level of theory.
We start with the simplest level of theory and optimize until we reach the minimum on its potential energy surface, which in this particular case involves five optimization steps. Note that the potential energy surface was deliberately given a different shape than the two higher levels of theory. Since this is the case, it is not likely that the obtained geometry is sufficiently accurate, and indeed if we were to use this geometry to calculate the energy at the high level of theory, we would get a result that is significantly excessive. Hence we need to further optimize at a higher level of theory. In this example, we need only one single optimization step. It should be noted that the obtained geometry is indeed close to the optimum at the high level of theory, but that the energy is significantly higher. Finally, we use this geometry to calculate the energy at the highest level of theory, and it can be seen that the energy is indeed very close to the optimal energy. In this example, we have reduced the costs of a potentially very expensive problem significantly by not optimizing at the high level of theory, which would have involved a high-level calculation for every single optimization step; the geometry optimizations at the lower levels of theory are often only a fraction of the cost of the single-point calculation. Hence, if the same number of optimization steps at the high level of theory had been carried out as at the simpler levels, we would have had a six times more expensive calculation. Naturally, the required number of optimization steps and/or levels of theory will vary significantly from problem to problem, and will depend on the initial geometry guesses. It should be mentioned here that these procedures are often only required for the calculation of accurate energies. For example, the other properties required in a TST calculation, such as moments of inertia, rotational barriers and vibrational frequencies are often sufficiently accurate at relatively simple levels of theory, as was clearly shown for calculation of frequency factors in radical addition\textsuperscript{47} and hydrogen abstraction reactions.\textsuperscript{60}

The practical observations that certain properties can be adequately obtained at simpler levels of theory have led to several different additivity schemes that approximate the properties (especially the energy) at a very high level of theory by combining results obtained at simpler levels of theory. All these additivity schemes (e.g., G1,\textsuperscript{61} G2,\textsuperscript{62} G3,\textsuperscript{63} CBS,\textsuperscript{64,65} CBS-RAD\textsuperscript{58}) have the following assumptions in common:

- Geometry at high level of theory \( \approx \) geometry at simple level of theory
  
  \[ \text{HLG} \approx \text{SLG} \]

- Scaled ZPVE at high level of theory \( \approx \) scaled ZPVE at simple level of theory
  
  \[ \text{ZPVE-HL} \approx \text{ZPVE-SL} \]

- Basis set effect at high level of theory \( \approx \) basis set effect at simpler level of theory
  
  \[ \text{HL/LB} – \text{HL/SB} \approx \text{SL/LB} – \text{SL/SB} \]
where HL = high level of theory, SL = simple level of theory, HLG = high-level geometry, SLG = simple level geometry, LB = large basis set, SB = small basis set, ZPVE-HL = zero-point vibrational energy at high level of theory, and ZPVE-SL = zero-point vibrational energy at simple level of theory.

The energy calculated at a high level of theory of a geometry optimized at the corresponding level of theory is then in general approximated by the following equation:

\[
\frac{\text{HL}}{\text{LB}}/\text{HLG} \approx (\frac{\text{HL}}{\text{SB}}/\text{SLG}) + (\frac{\text{SL}}{\text{LB}}/\text{SLG}) - (\frac{\text{SL}}{\text{SB}}/\text{SLG}) + (\text{ZPVE-SL}) + \Omega \tag{1.34}
\]

where \(\Omega\) contains some empirical corrections.

Pople and co-workers have pioneered these additivity schemes and devised the G1–G2–G3 family of theories,\(^{61-63}\) in order to predict thermochemical properties of molecules within experimental errors. Others have come up with similar schemes such as the complete basis set (CBS) scheme by Petersson et al.\(^{64,65}\) and the infinite basis extrapolation techniques by Martin.\(^{66}\) In particular Radom and co-workers examined and optimized schemes to adequately describe radical thermochemistry and reactions.\(^{42,43,47,56-59}\) Currently recommended procedures for the description of radicals are CBS-RAD and G3(MP2)-RAD.\(^{30,43}\)

1.5 BASIC THEORY OF REACTION BARRIER FORMATION

So far we have discussed ways of predicting rate coefficients via transition state theory from molecular and electronic parameters, which we can calculate using, for example, ab initio molecular orbital theory. We have seen that simple geometric factors and vibrations govern the Arrhenius frequency factors and any temperature corrections to the critical energy (i.e., the barrier at 0 K). However, we have not yet discussed the factors that govern the height of a reaction barrier (and hence the activation energy) or possible ways of predicting it. A powerful theoretical framework for the discussion of reaction barrier formation is the curve-crossing model, also called the valence bond (VB) state correlation model, VB configuration mixing or state correlation diagram. This model, which has been developed by Shaik and Pross, is based on VB theory.\(^{15-20}\)

In VB theory, the focus does not lie on molecular orbitals, but on electron pair bonds between atoms; VB theory assigns electrons to atomic orbitals, even in molecules.\(^{14,17}\) In the limit, both VB and MO theories yield the same result; however because of the greater computational difficulties associated with VB theory, MO theory has become more interesting from a computational point of view. On the other hand, the VB descriptions allow for simple, nonmathematical representations of wavefunctions.\(^{17}\) Electronic configurations described in VB theory correspond in nonmathematical terms just to the commonly used Lewis structures, and a full wavefunction with configuration interaction just corresponds to mixing of simple
resonance structures. We will encounter several examples in the course of this section.

Let us return to the curve-crossing model. We are interested in building up a reaction profile using VB theory, which we have just seen must be described in terms of electronic configurations that assign electrons to given atomic orbitals. It is clear that, in a reaction, we start with the electronic configuration of the reactants. Moving along the reaction coordinate, which involves geometric rearrangements, the electrons will start to feel increasingly uncomfortable in the atomic orbitals to which they have been assigned. The reaction involves the breaking of old and formation of new bonds, so clearly the closer the geometry resembles the product, the more the electrons wish to occupy different atomic orbitals (i.e., those making up the new bonds). Because of this effect, it is clear that the energy associated with the reactant electronic configuration ($\Psi_{\text{reac}}$) will continuously increase along the reaction coordinate. It is clear that the appropriate electronic configuration of the products is the one in which the electrons are assigned to the atomic orbitals making up the new bonds ($\Psi_{\text{prod}}$). If we were now to use the product electronic configuration and move back along the reaction coordinate, we would observe the same as we did previously with the reactant electron configuration; the farther away we move from the product geometry, the worse the description of the electrons becomes if we only use the product electronic configuration (see Fig. 1.15). Hence it is clear that in going from the reactants to the products along the reaction coordinate, we will, at some point, need to "switch" from $\Psi_{\text{reac}}$ to $\Psi_{\text{prod}}$. This will happen in the region where the two curves "cross," and we can see that this happens at an energy that is higher than that of either the reactant or product configuration, and that it happens for a

![Diagram](image-url)

**Figure 1.15** Curve-crossing diagram of reaction barrier formation through the avoided crossing of the reactant and product electronic configuration curves.
conformation between that of the reactants and that of the products.\textsuperscript{17} Indeed, this happens in the region of the transition state.

We know from quantum mechanics [see also the discussion around Eq. (1.31)] that the ground-state wavefunction is always the lowest-energy wavefunction (for any given atomic configuration), and hence that state wavefunctions do not cross. Furthermore, we have seen in the section on configuration interaction that we often need more than a single electronic configuration to describe the state wavefunction; this situation is a very clear example of this need. The two configuration wavefunctions $\Psi_{\text{reac}}$ and $\Psi_{\text{prod}}$ combine to give two state wavefunctions: one for the ground state ($\Psi_{\text{ground}}$) and one for an excited state ($\Psi_{\text{excited}}$).\textsuperscript{17} Since the ground state is of more interest to us, we will now focus our attention to the ground-state wavefunction, which we can express in terms of the two configuration wavefunctions:\textsuperscript{17}

$$\Psi_{\text{ground}} = C_1 \Psi_{\text{reac}} + C_2 \Psi_{\text{prod}}$$  \hspace{1cm} (1.35)

where the coefficients $C_1$ and $C_2$ will depend on the position along the reaction coordinate: $C_1 \gg C_2$ close to the reactant geometry, whereas $C_2 \gg C_1$ close to the product geometry. Considering Fig. 1.15, we can also simply see that the excited-state wavefunction in the reactant geometry is determined mainly by $\Psi_{\text{prod}}$ and in the product geometry by $\Psi_{\text{reac}}$. In the transition region, where we expect the electronic rearrangement to take place and where the energies of the two configurations are similar, we expect $C_1 \approx C_2$ and hence that the wavefunction in the transition state can be described as\textsuperscript{17}

$$\Psi_{\text{TS}} \approx \frac{1}{\sqrt{2}} (\Psi_{\text{reac}} + \Psi_{\text{prod}})$$  \hspace{1cm} (1.36)

We have seen before that configuration interaction leads to a lowering of the energy, and hence the relative energy of the transition state; thus the barrier ($\Delta E^\dagger$) is significantly lowered as compared to the energy at which the two electronic configurations cross. This lowering is indicated by the quantum-mechanical interaction parameter $B$ in Fig. 1.15. From Fig. 1.15, we can also see that the point where the two curves cross is determined by the initial energy gap ($G$) between the energies of $\Psi_{\text{reac}}$ and $\Psi_{\text{prod}}$. In reality, the two configuration curves are not straight lines, and hence their curvature, which is expressed in a factor $f(0 < f < 1)$, will determine the fraction of the initial energy gap that contributes to the barrier height. We can now express the barrier height as a function of these (quantum-mechanical) parameters:\textsuperscript{17}

$$\Delta E^\dagger = f \cdot G - B$$  \hspace{1cm} (1.37)

If we compare the barriers of related reactions, the interaction parameter $B$ is often considered to remain constant, and hence any differences in barrier heights are explained by changes in the parameters $f$ and $G$.\textsuperscript{17}

In general, reaction exothermicity affects $f$; a reaction that is more exothermic has a smaller $f$, and hence a lower barrier. This effect, which leads to
Bell–Evans–Polanyi behavior,\textsuperscript{22,23} is schematically shown in Fig. 1.16; by making the reaction more exothermic, the curves cross at a lower energy, thus lowering the barrier. Furthermore, we see that the location of the transition state has moved closer to the reactant geometry. Generally speaking, the transition state of an exothermic reaction lies closer to the reactant configuration and is said to be early, whereas an endothermic reaction lies closer to the product side and is said to be late.

A second effect on the barrier height is caused by the initial energy gap $G$, and we can see in Fig. 1.16 that an increase in $G$ results in a higher barrier. This effect, which is general, need not be accompanied by a change in reaction exothermicity (see Fig. 1.16). However, in the case of radical reactions, the initial energy gap is closely related to the stability of the products (as we will see later) and hence is highly correlated with the reaction exothermicity.\textsuperscript{17,39} This situation is depicted in Fig. 1.17, and again we expect to see a change in the location of the transition state when $G$ changes.\textsuperscript{17}

To summarize the discussion of the curve-crossing model to this point, we can say that in its simplest formulation, the barrier is considered to arise from an avoided crossing of the electronic configurations that correspond to reactants and products, respectively. However, it is obvious that the valence bond description in terms of single reactant and product electronic configurations will become increasingly poor on moving toward the transition state along the reaction coordinate. In order

\textbf{Figure 1.16}  Effect of reaction exothermicity (expressed through $f$) and initial energy gap ($G$) on barrier height and location of the transition state. For simplicity the configuration wavefunctions are depicted as straight lines. The initial situation, the effect of $f$, and the effect $G$, are characterized by the parameters with subscripts 1, 2, and 3 respectively.
to provide a better description of the transition state region, other configurations (which are, by definition, excited-state configurations at both the reactant and product geometries) are often mixed with the ground-state descriptions of the reactant and product electronic configurations. In the case of radical reactions, possible important configurations are those corresponding to polar charge transfer (CT) configurations, in which an electron has been transferred from the radical to the second reactant or vice versa. If we denote the charge transfer configuration wavefunction by $\Phi_{\text{CT}}$, we can now express the ground state wavefunction as

$$\Psi_{\text{ground}} = C_1 \Psi_{\text{reac}} + C_2 \Psi_{\text{prod}} + C_3 \Phi_{\text{CT}}$$

(1.38)

and assuming that the extent of mixing of $\Phi_{\text{CT}}$ into the state wavefunction does not disturb the equal contributions of $\Psi_{\text{reac}}$ and $\Psi_{\text{prod}}$ to the wavefunction describing the transition state, then $\Psi_{\text{TS}}$ can be written as

$$\Psi_{\text{TS}} \approx N \left\{ \frac{1}{\sqrt{2}} (\Psi_{\text{reac}} + \Psi_{\text{prod}}) + \lambda \Phi_{\text{CT}} \right\}$$

(1.39)

where $N$ is a normalization constant and $\lambda$ is the mixing coefficient of $\Phi_{\text{CT}}$. The parameter $\gamma$ in the model proposed by Fischer and Radom [Eq. (1.5)] is related to the mixing parameter $\lambda$. 

Figure 1.17 Effect of initial gap, $G$, on reaction barrier when $G$ is highly correlated with the reaction exothermicity (or stability of the products). This is often the case in radical reactions, especially in radical addition reactions.
Let us now specifically look at radical addition and abstraction reactions, beginning with radical addition reactions. In Scheme 1.2, the reaction of a radical addition is given with the corresponding electron spin shifts that accompany the reaction.17 These schematic representations of electron pairs and electron spins are at the same time pictorial representations of the VB configurations of the reactant and product. We denote the radical in this reaction as D (donor) and the alkene as A (acceptor). Note that in the reactant configuration DA, the electrons in the π bond are of opposite spin and hence form a bond, whereas the electrons on the radical and the central carbon have the same spin (they form a triplet interaction), and do not form a bond. In the product configuration, however, the electron of the radical and the central carbon atom are paired (and have formed a new bond), whereas the electrons in the original π bond now have the same spin (and the bond is broken). Hence, the electronic configuration in the original alkene has been changed from a singlet in the reactant configuration to a triplet in the product configuration. Since the triplet is an excited state of the initial singlet, we denote the electronic state of the acceptor molecule by \(^3\)A* and the overall product configuration wavefunction by D\(^3\)A*. Hence, in its simplest formulation, the barrier in a radical addition reaction is governed by a DA–D\(^3\)A* avoided crossing,17,38–41 and it is furthermore clear that the initial energy gap can be approximated by the singlet–triplet energy gap (\(\Delta E_{\text{ST}}\)) of the π bond (\(G \approx \Delta E_{\text{ST}} \approx 2.5 - 4.5 \, \text{eV} \approx 240 - 440 \, \text{kJ/mol, depending on the alkene substituents}.\)17,30,39 It can also be understood now that the reaction exothermicity and G are interrelated. If the alkene is monosubstituted, the substituent will be on the carbon with the unpaired electron in the product radical and the unpaired electron in the triplet state of the alkene. Hence, the effect of the substituent on the energies of these two species is expected to be similar, and a near-parallel shift of \(\Psi_{\text{prod}}\) is expected, as shown schematically in Fig. 1.17.

As stated before, the most important additional electronic configurations to radical reactions are the charge transfer configurations, which are shown in Scheme 1.3. The D\(^-\)A\(^+\) configuration is generated by the electron transfer from the alkene to the radical, whereas the D\(^+\)A\(^-\) configuration is generated by the reverse reaction.

In Fig. 1.18, the curve-crossing diagram for a radical addition is shown, including all contributing electronic configurations.

\[
\begin{align*}
\Phi_{\text{CT, 1}} &= \text{D}^-\text{A}^+ \\
\Phi_{\text{CT, 2}} &= \text{D}^+\text{A}^-
\end{align*}
\]
The shape of the two charge transfer configuration curves is explained as follows. Both configurations are excited state configurations which are generated by the electron transfer between the donor and acceptor molecules, which are neutral in the ground state. The relative energies of the charge transfer states as compared to the ground state are determined by the electron affinities \( (EA) \) and the ionization potentials \( (I) \) of the donor and acceptor molecules, which are defined as in Scheme 1.4.\(^{17}\)

Hence the relative energies of \( D^+A^- \) and \( D^-A^+ \) with respect to the ground-state energy of \( DA \) can be given by\(^{17}\)

\[
E(D^+A^-) = I_D - EA_A \tag{1.40}
\]
\[
E(D^-A^+) = I_A - EA_D \tag{1.41}
\]

For the addition of methyl radical, which does not seem to be significantly affected by polar effects, these energies, depending on the alkene substituent, lie roughly

\[
M \rightarrow M^+ + e^- \quad \Delta E = 1
\]
\[
M + e^- \rightarrow M^- \quad \Delta E = -EA
\]

**Scheme 1.4**
between 8 and 12 eV ($\approx$770–1150 kJ/mol) above the ground-state energy.\textsuperscript{39} The lowering of the energy of these configurations in the region of the transition state is caused by the Coulomb interaction ($C = e^2/r$) between the two ionic species when they approach.\textsuperscript{17,30,39} Mixing of a charge transfer configuration into the ground-state configuration becomes important if one or both of these charge transfer configurations is low in energy. Hence it depends on the absolute values of $(I - EA - e^2/r)$ in the region of the transition state (for radical addition reactions $r \approx 2.2$ Å; hence $C \approx 6.5$ eV $\approx 630$ kJ/mol; this value should be considered as an upper limit as delocalization of electrons will lower C).\textsuperscript{30,39} In the extreme case, where $I - EA \approx C$, the barrier is likely to be very low. At this point, we should refer back again to the Fischer–Radom model [Eq. (1.5)],\textsuperscript{30} which accounts for the polar effects using this term in their polar factors $F_p$ and $F_e$. Finally, it should be pointed out that if polar effects are important and $E(D^+A^-) < E(D^-A^+)$, the radical has an electron-donating, that is, a nucleophilic, character, whereas if polar effects are important and $E(D^-A^+) < E(D^+A^-)$, the radical has electron-accepting, or an electrophilic, character.

Let us now consider radical abstraction reactions (Scheme 1.5). We can see that the barrier is governed by a similar $DA - D3A^*$ avoided crossing.\textsuperscript{17} Whereas the two carbons in the alkene of the radical addition are still bound via a $\sigma$ bond (we broke a $\pi$ bond), in this case we break the $\sigma$ bond (i.e., the only bond) between $Y$ and $Z$. Possible charge transfer configurations are shown in Scheme 1.6.

As was the case in radical addition reactions, the reaction exothermicity (through $G$) and the magnitudes of the ionization potentials and electron affinities of the reactants (through mixing of the charge transfer configurations into the ground state) govern the height of the barrier in radical abstraction and transfer reactions.\textsuperscript{17}

To conclude this section, it is important to note that the curve-crossing model is very useful and powerful in analysing computational results, but because it is not always clear beforehand what configurations will be important, its predictive value for unknown reaction types may be limited. Especially in the case of radical addition reactions, it has clearly demonstrated its value as will be shown in the following section, in which some of the results will be discussed on which the Fischer–Radom model [Eq. (1.5)]\textsuperscript{30} is based.

\[
\begin{align*}
X^* + Y - Z & \rightarrow X - Y + Z^* \\
X^* + Y \cdot \cdot \cdot Z & \rightarrow X^* \cdot \cdot \cdot Y + Z^*
\end{align*}
\]

Scheme 1.5

\[
\begin{align*}
X^* \cdot \cdot \cdot [Y \cdot Z]^+ & \rightarrow X^+ \cdot [Y \cdot \cdot \cdot Z]^-
\end{align*}
\]

$\Phi_{CT,1} = D^-A^+$

$\Phi_{CT,2} = D^+A^-$

Scheme 1.6
1.6 APPLICATIONS IN FREE-RADICAL POLYMERIZATION

In this section, the theoretical concepts outlined in this chapter so far will be applied to problems of relevance to free-radical polymerization. Several different aspects of radical addition and propagation will be discussed, followed by a discussion of some problems in chain transfer reactions.

1.6.1 Radical Addition and Propagation

1.6.1.1 General Aspects

As already eluded to at several occasions in this chapter, radical additions have been widely studied using ab initio molecular orbital theory. A large number of papers have appeared since the early 1980s, but without denying the importance of many of the early papers, we will focus our discussion on a series of papers by Wong et al.,38–43 Heuts et al.,31,35,47,60,67,68 Coote et al.,69–71 and Huang et al.72 The results in these papers were obtained with current state-of-the-art levels of theory, and appear to be of most relevance to polymer chemistry. For comparisons with other theoretical studies, I refer to the original papers of which the results are discussed here. First some general aspects on suitable levels of theory will be discussed,42,43,47 followed by a discussion of reaction barrier formation in (small) radical additions,38–41,73 which results in formulation of the model proposed by Fischer and Radom [see Eq. (1.5)].30 Then we will have a look at the factors that govern the frequency factors for radical addition reactions, and see how simple geometric and steric arguments can explain particular observations in free-radical polymerization.31,35,72 Finally, we will have a look at copolymerization reactions, where theoretical chemistry has played an important role in justifying and describing the penultimate unit effect.67,69–71 However, before we can start with all of this, one important point, which we have ignored so far, still needs to be addressed: the effect of the reaction medium.

In our theoretical descriptions, we have thus far considered only gas-phase reactions. All the described models and theories can incorporate the effect of solvents (all in a different way), but this will make the descriptions naturally more complicated. Fortunately, it is not likely that we need to incorporate medium effects for most of our mechanistic studies, as experimental gas- and liquid-phase data of radical reactions show similar trends for substituent effects with the absolute rate coefficients differing by about a factor of 10.30 Careful analysis by Fischer and Radom suggests that calculated barriers may be a few kJ/mol higher than those of liquid-phase reactions and that frequency factors may differ by a factor of roughly 2–5. Solvent polarity can significantly affect the barrier if the charge transfer states are relatively low in energy, as polar solvents will stabilize these states, which will lead to a lowering in reaction barrier.17 However, all these effects are relatively small compared to the effects we address using “simple” gas-phase reactions.30 Using more complicated (and not necessarily more accurate) theories will only cloud the picture, and hence we will only focus on gas-phase theoretical results.

We have seen in previous sections that we can use ab initio molecular orbital theory to calculate all the parameters required in transition state theory to predict
the rate coefficient for radical addition (or propagation) and that we can analyze the components determining the reaction barrier formation via the curve-crossing model. We have already discussed the fact that it is of utmost importance that all the properties required in our predictions and analyses are calculated with appropriate levels of theory. It was shown in a comprehensive assessment by Heuts et al.\textsuperscript{47} that the properties required for calculating molecular partition functions, specifically, molecular geometries, harmonic frequencies, and rotational barriers, are reliably obtained at relatively simple levels of theory, such as HF/6-31G*. Hence Arrhenius frequency factors [Eq. (1.13)] and temperature corrections to the barrier [Eq. (1.12)] and the reaction enthalpy [Eq. (1.8)] are reliably calculated at simple levels of theory. However, the situation is very different for the calculation of reaction enthalpies and reaction barriers, which need to be calculated using higher levels of theory.\textsuperscript{42,43,47} This is caused mainly by the effect of spin contamination (see above) on the calculated energy rendering UMP methods unsuitable for adequately describing radical addition reactions. Although UHF/6-31G* geometries generally yield satisfactory results in single-point energy calculations of radical reactions and the bulk of studies regarding radical reactivity is based on these geometries, it was found that better results are obtained using B3-LYP/6-31G* geometries.\textsuperscript{30,43} Reliable absolute reaction enthalpies are obtained using the CBS-RAD procedure, which agrees well with experimental data (showing a correlation coefficient $R^2$ of 0.93).\textsuperscript{30,43} Other procedures, including RMP2, PMP2, B3-LYP, and QCISD (except for the AM1 and UMP2 procedures) yield satisfactory results (although with greater deviations from experimental data) showing good correlation with the CBS-RAD results ($R^2 = 0.98–0.99$). For barriers, methods such as CBS-RAD and G3(MP2)-RAD are recommended,\textsuperscript{30,43} but these procedures are too expensive for many systems of interest and can currently be applied only to small systems. Comparison of CBS-RAD data with available experimental data yields good agreement, with a mean deviation of 1.7 kJ/mol.\textsuperscript{30} Reasonable alternatives for larger systems were found to be B3-LYP/6-31G* (which gives surprisingly good agreement with CBS-RAD), B3-LYP/6-311 + G(d,p), or B3-LYP/6-311 + G(3df,2p).\textsuperscript{30,43} Good correlations with trends observed using the CBS-RAD procedure are also observed for QCISD(T) and QCISD (both with $R^2 = 0.99$), RMP2 ($R^2 = 0.98$), and PMP2 ($R^2 = 0.96$). The interested reader is referred to the original papers for extended comparisons.\textsuperscript{30,42,43} In what follows, general trends will be discussed.

In Fig. 1.19 a schematic representation is given for the addition of substituted methyl radicals to substituted ethylenes. Four key geometric parameters are indicated: $r$(C---C) (the length of the forming CC bond), $\phi_1$ and $\phi_{\text{attack}}$ (the angles that the two reactant fragments make with the forming bond), and $\phi_{\text{pyr}}$ (the deviation from planarity of the hydrogens attached to the alkene carbon forming the bond.

First we compare these parameters for the additions of methyl ($X = H$), ethyl ($X = \text{CH}_3$) and propyl ($\text{CH}_2$CH$_3$) radicals to ethylene ($Y = H$), which are listed in Table 1.2. It can be seen that except for $r$(C---C), which decreases slightly in going from methyl\textsuperscript{42} to ethyl radical,\textsuperscript{47} all other parameters are roughly constant (further extension of the chain yields parameters very similar to those of the propyl radical
addition). This result is very positive in that it allows us to use small-radical models to describe the reaction site of large polymeric radicals (see text below).

Also listed in Table 1.2 are the corresponding bond lengths and angles in the product radicals. Again, it can be seen that increasing the chain length does not significantly affect these geometric parameters. Furthermore, it can be seen that all the angles are smaller than the corresponding parameters in the product radicals. The behavior of these parameters, especially of $\phi_{\text{pyr}}$ (which is roughly $0^\circ$ in the reactant and $56^\circ$ in the product), clearly demonstrates that the reaction coordinate does not solely consist of the forming CC bond length (see also Fig. 1.3).

A final note in this section should be made regarding the conformation of the transition structure. In Fig. 1.19, the substituent X is in an anti position as compared to the substituted ethylene. However, in some cases a gauche conformation may have a lower energy (e.g., in the case of the additions of ethyl and ethylbenzene radicals to ethylene), and the pathway through this transition state structure will hence have a lower barrier.47

![Figure 1.19](image)

**Figure 1.19** Definition of key geometric parameters for the addition of a range of substituted alkyl radicals to substituted ethylenes.

<table>
<thead>
<tr>
<th>(X)</th>
<th>(r(\text{C}\cdots\text{C})) (Å)</th>
<th>(\phi_{\text{attack}}) (deg)</th>
<th>(\phi_{\text{pyr}}) (deg)</th>
<th>(\phi_1) (deg)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.246</td>
<td>109.1</td>
<td>21.8</td>
<td>—</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>(1.537)$^c$</td>
<td>(113.1)$^c$</td>
<td>(55.9)$^c$</td>
<td>(110.9)$^c$</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3)</td>
<td>2.232</td>
<td>109.8$^c$</td>
<td>22.8</td>
<td>105.9</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>(1.539)$^c$</td>
<td>(113.4)$^c$</td>
<td>(56.0)$^c$</td>
<td>(112.6)$^c$</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_2\text{CH}_3)</td>
<td>2.234</td>
<td>109.7$^c$</td>
<td>22.7</td>
<td>106.4</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>(1.539)$^c$</td>
<td>(113.4)$^c$</td>
<td>(56.0)$^c$</td>
<td>(113.0)$^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Values within parentheses apply to product radicals. For definitions, see Fig. 1.19 (Y = H).

$^b$ Not reported.

$^c$ Not reported in given reference, but part of the overall output of reported results.60

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42 THEORY OF RADICAL REACTIONS
1.6.1.2 Barrier Formation

The effect of different substituents in methyl radicals and \( \text{CH}_2=\text{CHY} \) have also been studied, and in Tables 1.3 and 1.4, the results of key geometric parameters are listed for the transition states of the additions of \( \text{CH}_3^* \), \( \text{CH}_2\text{OH}^* \), \( \text{CH}_2\text{CN}^* \), and \( \text{C(CH}_3)_3^* \) to \( \text{CH}_2=\text{CHY} \) (\( Y = \text{F}, \text{H}, \text{NH}_2, \text{Cl}, \text{CHO}, \text{CN} \)).\(^{40,41}\)

From Table 1.3 it can be seen that the length of the forming CC bond lies roughly between 2.17 and 2.31 Å (UHF/6-31G*), and it is clear that this bond length is affected by both the radical and the alkene substituent.

In Table 1.4, the calculated angles of attack and pyramidalization (UHF/6-31G*) are listed, and although their values depend on the radical and the alkene, the differences are generally small and appear to be a bit more random. Values for \( \phi_{\text{attack}} \) range from 107.2° to 113.0°, and those for \( \phi_{\text{pyr}} \) have a slightly wider range from 18.6° to 28.8°.

### TABLE 1.3 Calculated Lengths (UHF/6-31G*) of the Forming CC Bond in Transition States for Addition of Four Different Substituted Methyl Radicals to a Range of Substituted Ethylenes

<table>
<thead>
<tr>
<th>Y</th>
<th>( \text{CH}_3^* )</th>
<th>( \text{CH}_2\text{OH}^* )</th>
<th>( \text{CH}_2\text{CN}^* )</th>
<th>( \text{C(CH}_3)_3^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>2.246</td>
<td>2.226</td>
<td>2.173</td>
<td>2.207</td>
</tr>
<tr>
<td>H</td>
<td>2.246</td>
<td>2.222</td>
<td>2.177</td>
<td>2.200</td>
</tr>
<tr>
<td>\text{NH}_2</td>
<td>2.240</td>
<td>2.220</td>
<td>2.178</td>
<td>2.207</td>
</tr>
<tr>
<td>Cl</td>
<td>2.264</td>
<td>2.245</td>
<td>2.181</td>
<td>2.215</td>
</tr>
<tr>
<td>CHO</td>
<td>2.312</td>
<td>2.291</td>
<td>2.230</td>
<td>2.265</td>
</tr>
<tr>
<td>CN</td>
<td>2.313</td>
<td>2.287</td>
<td>2.219</td>
<td>2.267</td>
</tr>
</tbody>
</table>

\( ^a \)See Fig. 1.19 for definitions. \( \text{CH}_3^* \), \( \text{CH}_2\text{OH}^* \), and \( \text{CH}_2\text{CN}^* \) data taken from Ref. 40; \( \text{C(CH}_3)_3^* \) data, from Ref. 41.

### TABLE 1.4 Calculated Angles of Attack and Pyramidalization (UHF/6-31G*) in Transition States for Addition of Four Different Substituted Methyl Radicals to a Range of Substituted Ethylenes

<table>
<thead>
<tr>
<th>Y</th>
<th>( \phi_{\text{attack}} ) (deg)</th>
<th>( \phi_{\text{pyr}} ) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3^* )</td>
<td>( \text{CH}_2\text{OH}^* )</td>
<td>( \text{CH}_2\text{CN}^* )</td>
</tr>
<tr>
<td>F</td>
<td>109.9</td>
<td>108.2</td>
</tr>
<tr>
<td>H</td>
<td>109.1</td>
<td>108.7</td>
</tr>
<tr>
<td>\text{NH}_2</td>
<td>111.0</td>
<td>109.8</td>
</tr>
<tr>
<td>Cl</td>
<td>108.9</td>
<td>107.8</td>
</tr>
<tr>
<td>CHO</td>
<td>107.6</td>
<td>107.4</td>
</tr>
<tr>
<td>CN</td>
<td>107.5</td>
<td>107.2</td>
</tr>
</tbody>
</table>

\( ^a \)See Fig. 1.19 for definitions. \( \text{CH}_3^* \), \( \text{CH}_2\text{OH}^* \), and \( \text{CH}_2\text{CN}^* \) data taken from Ref. 40; \( \text{C(CH}_3)_3^* \) data, from Ref. 41.
In Table 1.5, the calculated barriers and reaction enthalpies (QCISD/6-311G** + ZPVE) are listed, and it should be noted that these values deviate in an absolute sense from the better and recommended CBS-RAD procedure. However, the used procedure here has proven to have an excellent correlation with the better procedure and hence is expected to reproduce trends very well.

It can be seen from Table 1.5 that both the reaction barrier and the reaction enthalpy are greatly affected by the substituents in both the radical and the alkene. Furthermore, these effects appear to be very systematic. In general, the barriers for CH₂CN* addition are highest for a given alkene as compared to the addition of the other three radicals, irrespective of the alkene substituent. Similarly, the addition of C(CH₃)₃ always appears to have the lowest barrier. Finally, except for the addition of CH₂CN*, the barriers of these radical additions decrease with increasing reaction exothermicity, as is more clearly illustrated by Fig. 1.20.

The data for the CH₃, CH₂OH*, and CH₂CN* additions all show a linear correlation between the barrier height and reaction enthalpy with good coefficients of determination (R² > 0.95). It should be noted at this point that the line of the methyl addition lies highest; for a given reaction enthalpy, the barrier is highest for methyl radical addition. This means that the barriers of all the other radical additions experience additional stabilizing effects that lower the barrier at a given reaction enthalpy. These stabilizing effects are provided by low-lying charge transfer states, which are not significantly operative in the methyl radical additions.

The relative energies of the charge transfer states (D⁺A⁻ and D⁻A⁺) for the radical additions are listed in Table 1.6, and it can immediately be seen that the charge transfer states in methyl radical addition indeed lie very high (except for the D⁻A⁺ state of the addition to CH₂=CH₃) and are unlikely to play a significant role in the barrier formation. Hence it can be concluded that polar effects are relatively unimportant in the addition of a methyl radical to substituted ethylenes. For the CH₂OH* and C(CH₃)₃* additions, we observe that generally (again with the exception of addition to CH₂=CH₂) the D⁺A⁻ states are relatively low in energy and

### Table 1.5 Calculated Barriers and Enthalpies (QCISD/6-311G** + ZPVE) for Additions of Four Different Substituted Methyl Radicals to a Range of Substituted Ethylenes

<table>
<thead>
<tr>
<th>Y</th>
<th>CH₃⁺</th>
<th>CH₂OH*</th>
<th>CH₂CN*</th>
<th>C(CH₃)₃⁺</th>
<th>CH₃⁻</th>
<th>CH₂OH⁻</th>
<th>CH₂CN⁻</th>
<th>C(CH₃)₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>39.8</td>
<td>35.0</td>
<td>42.3</td>
<td>21.6</td>
<td>-94.2</td>
<td>-87.5</td>
<td>-63.2</td>
<td>-89.5</td>
</tr>
<tr>
<td>H</td>
<td>38.9</td>
<td>32.7</td>
<td>42.5</td>
<td>21.4</td>
<td>-93.5</td>
<td>-87.1</td>
<td>-63.3</td>
<td>-87.8</td>
</tr>
<tr>
<td>NH₂</td>
<td>36.3</td>
<td>32.5</td>
<td>30.7</td>
<td>17.9</td>
<td>-100.2</td>
<td>-91.4</td>
<td>-72.1</td>
<td>-95.7</td>
</tr>
<tr>
<td>Cl</td>
<td>32.5</td>
<td>24.6</td>
<td>35.9</td>
<td>13.6</td>
<td>-105.9</td>
<td>-97.8</td>
<td>-74.5</td>
<td>-99.1</td>
</tr>
<tr>
<td>CHO</td>
<td>28.7</td>
<td>18.3</td>
<td>33.9</td>
<td>6.5</td>
<td>-120.7</td>
<td>-118.6</td>
<td>-92.9</td>
<td>-120.5</td>
</tr>
<tr>
<td>CN</td>
<td>24.3</td>
<td>11.7</td>
<td>32.6</td>
<td>1.9</td>
<td>-129.3</td>
<td>-123.7</td>
<td>-93.4</td>
<td>-124.5</td>
</tr>
</tbody>
</table>

a CH₃⁺, CH₂OH*, and CH₂CN* data taken from Ref. 40; C(CH₃)₃⁺ data, from Ref. 41.
Figure 1.20  Plot of barrier height \( \Delta E^\dagger \) against reaction enthalpy \( \Delta H_r \) (QCISD/6-311G**) for the addition of \( \text{CH}_3\text{^*} \) (○), \( \text{CH}_2\text{OH}\text{^*} \) (■), \( \text{CH}_2\text{CN}\text{^*} \) (△), and \( \text{C(CH}_3\text{)_3}\text{^*} \) (×) to a range of substituted alkenes \( \text{CH}_2=\text{CH}Y \), with \( Y = \text{F, H, NH}_2, \text{Cl, CHO, and CN} \). The solid regression lines are given by
\[
\Delta E^\dagger = 77.4 + 0.41\Delta H_r \quad (\text{CH}_3\text{^* addition, } R^2 = 0.979); \\
\Delta E^\dagger = 82.6 + 0.56\Delta H_r \quad (\text{CH}_2\text{OH}\text{^* addition, } R^2 = 0.950); \\
\Delta E^\dagger = 65.9 + 0.50\Delta H_r \quad (\text{C(CH}_3\text{)_3}\text{^* addition, } R^2 = 0.972). \]
Note that there is no apparent linear correlation between barrier and reaction enthalpy for \( \text{CH}_2\text{CN}\text{^*} \) addition. [\( \text{CH}_3\text{^*}, \text{CH}_2\text{OH}\text{^*}, \text{and } \text{CH}_2\text{CN}\text{^* data taken from Ref. 40; } \text{C(CH}_3\text{)_3}\text{^* data taken from Ref. 41.} \]

TABLE 1.6  Calculated Energies of Charge Transfer States (eV), [G2(MP2)] for Additions of Four Different Substituted Methyl Radicals to a Range of Substituted Ethylenes

<table>
<thead>
<tr>
<th>Y</th>
<th>( \text{CH}_3\text{^*} )</th>
<th>( \text{CH}_2\text{OH}\text{^*} )</th>
<th>( \text{CH}_2\text{CN}\text{^*} )</th>
<th>( \text{C(CH}_3\text{)_3}\text{^*} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{YD}^+ \text{A^-} )</td>
<td>( \text{D^-A^+} )</td>
<td>( \text{D^-A^+} )</td>
<td>( \text{D^-A^+} )</td>
<td>( \text{D^-A^+} )</td>
</tr>
<tr>
<td>F</td>
<td>11.39</td>
<td>10.33</td>
<td>9.05</td>
<td>10.51</td>
</tr>
<tr>
<td>H</td>
<td>11.63</td>
<td>10.54</td>
<td>9.30</td>
<td>10.72</td>
</tr>
<tr>
<td>( \text{NH}_2 )</td>
<td>11.69</td>
<td>8.14</td>
<td>9.35</td>
<td>8.32</td>
</tr>
<tr>
<td>Cl</td>
<td>11.05</td>
<td>9.94</td>
<td>8.71</td>
<td>10.12</td>
</tr>
<tr>
<td>CHO</td>
<td>9.74</td>
<td>10.17</td>
<td>7.46</td>
<td>10.35</td>
</tr>
<tr>
<td>CN</td>
<td>10.00</td>
<td>10.94</td>
<td>7.66</td>
<td>11.12</td>
</tr>
</tbody>
</table>

\( \text{CH}_3\text{^*}, \text{CH}_2\text{OH}\text{^*}, \text{and } \text{CH}_2\text{CN}\text{^* data taken from Ref. 40; } \text{C(CH}_3\text{)_3}\text{^* data, from Ref. 41.} \)
lower than the $D^-A^+$ states.\textsuperscript{17,30,40,41,73} This indicates that the charge transfer states, in which charge has been transferred from the radical to the alkene, can interact with the ground states and hence lower the barriers for these additions; CH$_2$OH$^*$ and C(CH$_3$)$_3^*$ display nucleophilic behavior in the addition reactions to the studied range of substituted alkenes.\textsuperscript{17,30,40,41,73} Similarly, the CH$_2$CN$^*$ always displays electrophilic behavior for the studied addition reactions ($D^-A^+ < D^+A^-$). From the presented results, it has been concluded that energetically significant polar contributions to the transition state in radical addition reactions arise when the relative energy of one of the charge transfer configurations drops below $\sim 9\, \text{eV}$.\textsuperscript{40,41,73} (Fischer and Radom mention values of 7–8 eV in their review, which also discusses experimental data).\textsuperscript{30}

It is also interesting to investigate the structure of the transition state in the light of the curve-crossing model. We saw previously that if the initial energy gap $G$ changes (see also Fig. 1.17), we expect to see a change in the location of the transition structure. Since the reaction exothermicity is directly correlated to $G$, we expect to see a change in the location of the transition state with changing reaction enthalpy.\textsuperscript{17} In Fig. 1.21, the length of the forming CC bond in the transition state is plotted against the reaction enthalpy for all the reactions considered in this section.

![Plot of C–C bond length (UHF/6-31G*) in the transition structure against reaction enthalpy $\Delta H_r$ (QCISD/6-311G**) for the addition of CH$_3^*$ (○), CH$_2$OH$^*$ (■), CH$_2$CN$^*$ (Δ), and C(CH$_3$)$_3^*$ (×) to a range of substituted alkenes CH$_2$=CHY, with Y = F, H, NH$_2$, Cl, CHO, and CN. The solid regression line for t-butyl radical addition is given by $r = 2.03 - 1.92 \cdot 10^{-3} \Delta H_r$ ($R^2 = 0.975$); the solid regression line for the addition of the remaining three radicals is given by $r = 2.03 - 2.21 \cdot 10^{-3} \Delta H_r$ ($R^2 = 0.953$). [CH$_3^*$, CH$_2$OH$^*$ and CH$_2$CN$^*$ data taken from Ref. 40; C(CH$_3$)$_3^*$ data taken from Ref. 41.]
It is immediately clear that there is a linear correlation, even if we consider all the data points in a single set. The regression coefficient for the overall data set is reasonable ($R^2 = 0.869$), but better regressions are obtained when treating the C(CH$_3$)$_3^*$ data individually. We now observe two very good regression lines, with the tert-butyl line below that of the other studied radicals. This can be explained by the fact that the contribution from the charge transfer configurations is largest here, which leads to some additional stabilization of the transition structure (the electrostatic attraction pulls the two fragments closer together). Furthermore, it may seem surprising that the CH$_2$CN* data lie on the same line as those of the CH$_3^*$ and CH$_2$OH* radicals, whereas there was clearly no linear relationship between the barrier and the enthalpy for these additions (see Fig. 1.20).

As an explanation for this observation, it has been proposed that mixing of charge transfer configurations has an insignificant effect on the position of the barrier, but a large effect on its height; only in cases of very strong polar effects, such as seen in the C(CH$_3$)$_3^*$ reactions, deviations will start to occur. Arnaud et al. studied the addition of methyl radical to a wider range of substituted ethylenes (including capto-dative alkenes) at the B3-LYP/6-311G** level of theory and found a very similar relationship, $r = 1.981 - 0.0033 \Delta H_r (R^2 = 0.984)$, which further strengthens the general arguments presented by Radom and co-workers.

To summarize this part on barrier formation in radical addition reactions, we can clearly identify the following important factors which play a role in barrier formation:

- **Reaction Exothermicity.** The larger the exothermicity, the lower the barrier.
- **The Singlet–Triplet Energy Gap, $G$, of the Alkene.** The smaller $G$, the lower the barrier. The size of $G$ and the reaction exothermicity are closely related, as shown before; the smaller $G$, the larger the exothermicity. Together, they lead to Bell–Evans–Polanyi-type behavior [Eq. (1.1)], and are incorporated in the term ($50 + 0.22 \Delta H_r$) of the Fischer–Radom model [Eq. (1.4)]. Furthermore, the overall exothermicity effects determine the position of the transition state; the larger the reaction exothermicity, the larger the length of the forming C–C bond in the transition state.
- **Polar Effects.** These effects are operative when $[I(R) - EA(A)]$ or $[I(A) - EA(R)] < 9–9.5$ eV (or 7–8 eV when including experimental data), and will lower the barrier further than that given by the Bell–Evans–Polanyi relationship. They are incorporated via the terms $F_n$ and $F_c$ in the Fischer–Radom model [Eq. (1.4)].

### 1.6.1.3 Frequency Factors

In the previous section, the factors controlling barrier formation in radical addition reactions were discussed, without any discussion of the factors controlling the frequency factors for addition reactions. Since the barriers (and hence the activation energies) can vary widely, they are in general the most important factors determining the overall order of magnitude of the propagation rate coefficient $k_p$. 

APPLICATIONS IN FREE-RADICAL POLYMERIZATION 47
Variations in frequency factors (for long-chain propagation) are in general smaller, and from transition state theory arguments it can be concluded that they are confined to a region of about $10^2$–$10^7$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. (Note: For a given frequency factor, a range of activation energies from 10–35 kJ/mol represents a range of $k_p$ values over four orders of magnitude.) This has led most workers in the field of small-radical additions to focus on the activation energies and pay less attention to frequency factors; for example, Fischer and Radom lump all primary radical additions together as having a log $[A/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})] = 8.5$ and all tertiary radical additions with log $[A/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})] = 7.5$. Considering the very small variations in transition state structures, this is indeed justified, however, many smaller effects (of interest to the polymer chemist) are overlooked in lumping the frequency factors. In what follows we will discuss some of these aspects in detail.

We have seen in the section on transition state theory that the frequency factor $A$ is determined by the ratio of molecular partition functions of the transition state and the reactants, and for simplicity we will equate $A$ to the preexponential factor in Eq. (1.7) [which means that we also equate the activation energy to the critical energy; see Eqs. (1.7), (1.12), and (1.13)]

$$A \approx \frac{k_B T}{h} \frac{Q_i}{Q_{\text{radical}} Q_{\text{monomer}}}$$  \hspace{1cm} (1.42)

It was shown that the ratio of partition functions is governed by masses ($Q_{\text{trans}}$) and overall geometries ($Q_{\text{rot}}$) of the reactants and transition state, and by the internal vibrations and rotations ($Q_{\text{int}}$). The latter contribution to $A$ [Eq. (1.42)] was shown to be dependent largely on the transitional modes, and since this is the only "non-straightforward" contribution in Eq. (1.42), let us now look at the transitional modes for propagation in more detail. In Fig. 1.22, the six transitional modes for the addition of ethyl radical to ethylene, namely, a model for the propagation step in ethylene polymerization, and their respective UHF/6-31G* harmonic frequencies are shown.47

The first transitional mode ($v_1$) is the motion along the reaction coordinate and its imaginary frequency, which does not enter $Q_{\text{int}}$, reflects the magnitude of a C–C bond stretch in a normal molecule. The lowest real frequency transitional mode ($v_2$) is the rotation of the monomer molecule about the axis through the two carbons that are forming a bond, and arises from the loss of one of the external rotations of the free ethylene molecule. This motion has been identified as the lowest real transitional mode in all published studies on radical additions to date (although it is still a limited number, i.e., the propagation reactions of ethylene,31,35,47 acrolein,35 acrylonitrile,72 methacyrilonitrile,72 and the addition of ethylbenzene radical to ethylene).34 Hence it is conceivable that this mode is in general the lowest transitional mode. As such, we should consider this motion in some more detail, as it will also be important for discussions later in this chapter.

We have seen in the section on transition state theory that rotational motions have a very different potential energy profile on displacement as compared to a harmonic oscillator, and hence should be treated as internal rotations (see Fig. 1.6).3 Especially
the low-frequency transitional modes, corresponding to rotational motions, and with harmonic frequencies lower than \( \sim 200 \text{ cm}^{-1} \) (i.e., the thermal energy at room temperature) should not be treated as harmonic oscillators.\(^{31}\) This means that we should not use the vibrational partition functions, but rather the hindered rotor partition functions; this latter approach requires us to calculate the rotational potentials, and studies thus far indicate that the results obtained at the HF/6-31G\(^*\) level of theory (even within the transition state) are satisfactory,\(^ {31,35,47}\) but that semi-empirical methods lead to erroneous potentials.\(^ {35,72}\) The studies reported so far in the literature all indicate that the frequency factors calculated by treating the low-frequency torsional motions as hindered rotors are a factor of \( \sim 2–6 \) higher than those obtained by treating all motions as harmonic oscillators.\(^ {31,34,35,72}\) The studies on ethylene polymerization suggest that this difference becomes smaller with increasing chain length of the radical,\(^ {31}\) and those on the addition of the ethylbenzene radical to ethylene that the difference becomes smaller at lower temperatures.\(^ {34}\) The latter result is easily explained by the fact that at lower temperatures the thermal energy is too low to “escape out of the well” (see Fig. 1.6) and that the experienced potential energy surface is very close to that of a harmonic oscillator.

The fact that the lowest real transitional mode is a rotation about the forming C–C bond is very important, as it explains certain experimental observations. Increasing the hindrance to this rotation via the introduction of substituents on the

**Figure 1.22** Schematic representation of the six transitional modes in the transition state for the addition of an ethyl radical to ethylene, and their respective harmonic frequencies (UHF/6-31G\(^*\)).\(^ {47}\)
carbon will increase the barrier to rotation and hence will lead to a reduction in the partition function associated with this mode. However, introduction of the same substituents in the monomer will increase the moment of inertia of the rotation and hence increase the partition function. The overall effect on the partition function will be determined by the relative magnitudes of these two effects. However, in general it is expected that the effect of increasing the rotational barrier is greater than that of the increased moment of inertia, and hence a decrease in the partition function is expected, as illustrated for the propagation reactions in methacrylonitrile and acrylonitrile.72

The second lowest real transitional mode, i.e., a bending mode of the two fragments \(v_3 = 178 \text{ cm}^{-1}\) also seems to arise from the loss of external rotations of the reactants.47 Again, it seems that this mode is also very general, as both the methacrylonitrile/acrylonitrile propagation72 and the ethylbenzene addition to ethylene34 studies report similar motions with low frequencies. Introduction of large substituents at the \(\alpha\) position is likely to increase the steepness of the potential energy well and therefore reduce the contribution of this motion to the partition function (and hence the frequency factor).

The remaining three transitional modes are also likely to be general, but are more complicated in additions of substituted radicals with substituted ethylenes. However, the effect of larger substituents is likely to be smaller on these motions as the lower ones do not directly involve the \(\alpha\) substituents in the radical and are also relatively high in frequency [the contribution to \(A\) from higher frequency modes is relatively small; see Eqs. (1.21) and (1.28)].

In the light of the preceding observations and the theory outlined in the section on transition state theory, let us now summarize how different substituents in monomer and radical will individually affect the magnitude of the frequency factors:

- Larger substituents \(\Rightarrow\) monomer mass \(\uparrow\) \(\Rightarrow\) \(Q_{\text{trans, monomer}}\uparrow\) [Eq. (1.25)] \(\Rightarrow\) \(A\downarrow\) [Eq. (1.42)]
- Larger substituents \(\Rightarrow\) monomer size \(\uparrow\) \(\Rightarrow\) \(Q_{\text{rot, monomer}}\uparrow\) [Eq. (1.27)] \(\Rightarrow\) \(A\downarrow\) [Eq. (1.42)]
- Larger substituents \(\Rightarrow\) moment of inertia in internal rotations and vibrations \(\uparrow\) \(\Rightarrow\) \(Q_{\text{int}}\uparrow\) [Eq. (1.30)] \(\Rightarrow\) \(A\uparrow\) [Eq. (1.42)]
- Larger substituents \(\Rightarrow\) hindrance transitional modes \(\uparrow\) \(\Rightarrow\) \(Q_{\text{int}}\downarrow\) [Eq. (1.30)] \(\Rightarrow\) \(A\downarrow\) [Eq. (1.42)]
- The overall effect depends on the relative magnitudes of the abovementioned effects, but initial theoretical and experimental results suggest replacement of H by CH₃ in \(\alpha\) position \(\Rightarrow\) \(A\downarrow\) (see below)

1.6.1.4 Chain-Length Dependence of \(k_p\) So far, we have considered only small-radical additions to substituted ethylenes, mainly because calculations on large-radical systems are currently not feasible. A skeptical polymer chemist may say that these additions are not relevant to polymer chemistry as the chain lengths are much larger and to some extend this polymer chemist is correct. Indeed, the small
radical system may not reflect the total physical picture, but it is still a very adequate model for polymer propagation if we apply some “tricks” to introduce the polymer chain.

With respect to the reaction barrier, we are in the fortunate situation that the polymer chain is only to a small extend directly involved in the reaction, and that the largest electronic effects determining the reaction barrier are caused by the monomer and the substituents in the direct vicinity of the reaction site. This is not to say that the substituents further away from the radical site do not affect the barrier (as we will see later), but they are of minor importance as compared to the $\alpha$ substituent effects. Hence to a first approximation, trends in barriers observed for small-radical additions should be semi-quantitatively applicable to propagation barriers. 30

The effect of chain length on the frequency factor is of a mechanical nature—it influences the effects of mass and size. To incorporate these effects, we just “added” a high mass to the end of the radical, which should mimic the effect of the mass of the polymer chain on the moments of inertia for torsional and vibrational motions (the higher mass of the chain will increase both $Q_{\text{vib}}$ and $Q_{\text{int rot}}$). 31,35 It was found that this procedure yields adequate results when the radical is of a dimeric or larger nature, as effects of the penultimate unit in the radical on the hindrances of certain internal motions in the radical and the transition state, and in particular some of the transitional modes, cannot be taken into account when considering only a monomeric radical. 31,35 Models for polymeric radicals used by Gilbert and co-workers are schematically shown in Fig. 1.23.

This approach was tested for the propagation reaction in ethylene, where a range of alkyl and their corresponding (high-mass model) polymeric radical additions to

![Figure 1.23](image-url)  
**Figure 1.23** Schematic representation of the small-radical models used in transition state theory calculations of long-chain propagation reactions. The $\omega$ hydrogen atom is replaced by a high mass to mimic the mechanical effects of the polymeric chain.
ethylene was studied. A decrease by a factor of 3 in frequency factor is observed when increasing the alkyl radical from ethyl \((1.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) to heptyl \((5.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})\) radical, and the polymeric frequency factor converges (at a dimeric “polymer” radical) toward a value in the range of \((1.0–2.2) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), which is within the experimental uncertainty: \(0.9 \times 10^7 < A < 1.9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\). These results, based on mechanical arguments within the framework of transition state theory, thus support the idea that the rate coefficient for propagation is chain-length-dependent and that the propagation rate coefficient of the first step \((k_p^1)\) is significantly larger than that for the propagation of polymeric radicals \((k_p : k_p^1 \approx 10 \times k_p)\).  

1.6.1.5 Steric Effects on the Propagation Rate Coefficient

In Fig. 1.24, the two most important low-frequency modes (<200 cm\(^{-1}\)) in the transition state of the propagation reaction are shown. The first, \(\tau_1\), corresponds to a rotation of the monomer about the forming C–C bond, while \(\tau_2\) corresponds to a simultaneous bending of the two angles associated with the forming C–C bond. These modes were found to be important in all systems studied theoretically to date.

We have already seen that a different conformation of the transition state can lead to a different energy and hence a different barrier. From the discussion on frequency factors so far, we can now also conclude that different conformations could have different hindrances of the internal modes, and hence will lead to different frequency factors. It is therefore clear that syndiotactic and isotactic addition reactions may have significantly different activation energies and frequency factors. A clear example of the former is shown in the work by Huang et al., who studied the propagation reactions of methacrylonitrile and acrylonitrile. In the case of methacrylonitrile the activation energies were found to be about 32.5 and 43.0 kJ/mol for the syndiotactic and isotactic additions, respectively (B3-LYP/6-31G*, QCISD/6-31G*). For acrylonitrile values of 26.9 and 33.2 kJ/mol (B3-LYP/6-31G*), and 38.3 and 44.7 kJ/mol

![Figure 1.24](image_url)
(QCISD/6-31G*) for the syndiotactic and isotactic additions, respectively were found. The results for both monomers indicate that the syndiotactic addition is favored over the isotactic addition by about 10 kJ/mol for methacrylonitrile and about 6 kJ/mol for acrylonitrile (note that these differences can affect the rate coefficients by factors of about 40 and 10, respectively, assuming an unchanged frequency factor).

A study of the effect on the frequency factor by the tacticity of the transition structure has been reported by Heuts et al.,35 who found that the isotactic addition in acrolein polymerization had a frequency factor (\(A_{\text{isotactic}} \approx 4.6 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}, \text{HF/3-21G}\) about 35% higher than that of the syndiotactic addition (\(A_{\text{syndiotactic}} \approx 3.4 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}, \text{HF/3-21G}\)). It is conceivable that this effect will be smaller for the propagation reaction of 1,1-disubstituted monomers (with substituents of similar sizes), and larger for monosubstituted monomers with a large substituent (or even 1,1-disubstituted monomers with one small and one very large substituent). Combining this with the discussion above for methacrylonitrile72 (\(A_{\text{syndiotactic}} \approx 2.2 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}, \text{HF/6-31G*}\)) and acrylonitrile72 (\(A_{\text{syndiotactic}} \approx 6.8 \times 10^6 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}, \text{HF/6-31G*}\)) it is indeed conceivable that the \(k_p\) for syndiotactic addition in these systems is a factor of 10–40 higher than that for isotactic addition.

These theoretical studies are in line with the experimental observation that the propagating methyl methacrylate radical prefers syndiotactic over isotactic addition. Another example in the literature that could be explained with the theoretical model is the difference found between the \(k_p\) values of cis- and trans-4-tert-butylocyclohexyl methacrylate (BCHMA),80 as the \(k_p\) value for trans-BCHMA is higher than that for the cis isomer. In a study on the polymerization behavior of cis- and trans-2-cyclohexyl-1,3-dioxanyl methacrylate (CHDMA),81 however, only small differences in \(k_p\) values were found whereas larger differences in the termination rate were found.

Let us now explicitly look at the effect of an \(\alpha\) substituent in the monomer, starting our discussion with some of the experimental results shown in Table 1.7. First, it is clear that the introduction of an \(\alpha\)-methyl group in butyl acrylate82 (resulting in butyl methacrylate)83 reduces the frequency factor by a factor of \(\sim 5\), whereas an increase in activation energy is observed of \(\sim 5\) kJ/mol. A further increase of the size of the second \(\alpha\) substituent (resulting in dimethyl itaconate)84 results in an additional 20-fold decrease in frequency factor and a small increase in activation energy of about 2 kJ/mol. Moving on to the styrenic monomers, we see that the frequency factor of styrene85 is within the same order of magnitude as butyl acrylate (about 2 times higher) with a much higher activation energy; the latter is clearly caused by different electronic substituent effects. The introduction of an \(\alpha\)-methyl group, resulting in \(\alpha\)-methyl styrene,86 decreases the frequency factor by an order of magnitude and increases the activation energy by about 4 kJ/mol (it should be noted that the values reported for \(\alpha\)-methyl styrene could not be established with great certainty, but it is expected that the reported values are indeed good estimates).86 We can also compare the Arrhenius parameters of butyl acrylate further with those of vinyl acetate87 and we observe a very similar frequency factor and a slightly higher activation energy (3 kJ/mol), again conceivably due to a different electronic
substituent effect. Finally, we can compare the Arrhenius parameters of butyl methacrylate with those of methacrylonitrile.\textsuperscript{88} Again, we observe very similar frequency factors and a different activation energy due to different electronic substituent effects.

To summarize the experimental observations, we can say that the results suggest that (1) the introduction of an $\alpha$-methyl group results in a 5–10-fold decrease in

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$A$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$E_{\text{act}}$ (kJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl acrylate</td>
<td>$1.8 \times 10^7$</td>
<td>17.4</td>
<td>82</td>
</tr>
<tr>
<td>Butyl methacrylate</td>
<td>$3.8 \times 10^6$</td>
<td>22.9</td>
<td>83</td>
</tr>
<tr>
<td>Dimethyl Itaconate</td>
<td>$2.2 \times 10^5$</td>
<td>24.9</td>
<td>84</td>
</tr>
<tr>
<td>Styrene</td>
<td>$4.3 \times 10^7$</td>
<td>32.5</td>
<td>85</td>
</tr>
<tr>
<td>$\alpha$-Methyl Styrene</td>
<td>$1.5 \times 10^6$</td>
<td>36.7</td>
<td>86</td>
</tr>
<tr>
<td>Vinyl Acetate</td>
<td>$1.5 \times 10^7$</td>
<td>20.4</td>
<td>87</td>
</tr>
<tr>
<td>Methacrylonitrile</td>
<td>$2.7 \times 10^6$</td>
<td>29.7</td>
<td>88</td>
</tr>
</tbody>
</table>
the frequency factor and possibly in an increase of the activation energy by about 5 kJ/mol, (2) increasing the size of the second $\alpha$ substituent causes a further decrease in frequency factor, and (3) monomers with similar size substituents have similar frequency factors.

If we now compare these experimental observations with what is expected from theory, we can say that indeed we expect the observed trends for the frequency factors; the situation for the activation energies is not as obvious at this moment, but the satisfactory agreement between the activation energies of small-radical additions with corresponding polymerization reactions as reported by Fischer and Radom ($E_{\text{act}}$ for propagation is generally about 2 kJ/mol higher than that for corresponding small-radical addition) suggests that the Fischer–Radom model also has predictive value for polymerization reactions. 30

The only study to the author’s knowledge that explicitly discusses the effect of the introduction of an $\alpha$-methyl group on the Arrhenius parameters of propagation is the study by Huang et al.,72 and their results show a ~3-fold reduction of the frequency factor in going from acrylonitrile (for which no experimental Arrhenius parameters are available) to methacrylonitrile. As outlined before, the effect of the $\alpha$-methyl group is operative in several different contributions to the frequency factor, but the authors conclude that the main reduction is caused by the difference in $Q_{\text{rot}}$ of the monomers; in the studied system, the effect of greater hindrances decreasing $Q_{\text{int}}^+$ is almost completely canceled by the effect of the greater moments of inertia increasing $Q_{\text{int}}^\text{f}$. The authors also tried to explain the difference in activation energy of the two monomers, but this result is a bit ambiguous, because it is not clear from their study whether the activation energy for acrylonitrile is larger or smaller than that for methacrylonitrile. At the B3-LYP/6-31G* level of theory it is smaller by about 6 kJ/mol, which seems to be in accordance with what is observed experimentally for the (meth)acrylates and ($\alpha$-methyl)styrene (see Table 1.7). However, the QCISD/6-31G* result is exactly the opposite; it is higher by about 6 kJ/mol. Both procedures were shown to correlate well with higher levels of theory, so it is not a priori clear which result is more appropriate.42,43 However, in the most recent studies by Radom and co-workers, a clear preference for B3-LYP as a cost-effective alternative level of theory seems to appear as for the addition of methyl radical to a wide range of substituted ethylenes the B3-LYP/6-31G* procedure yields results in very good agreement with those obtained by the expensive and generally recommended CBS-RAD procedure.30,43 In the light of this, the B3-LYP result, namely, the activation energy for acrylonitrile, is about 6 kJ/mol lower, is probably more likely. An analysis by the authors of the factors that possibly cause the difference in activation energies for the acrylonitrile and methacrylonitrile systems leads to the conclusion that this difference is caused mainly by differences in steric effects, comprised of angle strain and nonbonded interactions, and loss of electron delocalization in the transition state.72

In summary, observed experimental trends in homopolymerization reactions are well explained within the theoretical framework outline above.

1.6.1.6 Effect of Deuteration A small effect that can also be explained with our current theoretical understanding of propagation is the rate-enhancing effect
observed with deuterated monomers (excluding effects on the termination reaction, which may also be important).\textsuperscript{31,35} Perdeuteration will have a significant effect on the frequency factor because of changes in the moments of inertia of the external rotation of monomer (Eq. (1.26)) and in the internal rotations and vibrations [Eq. (1.30)]. Since the hydrogen atoms are not involved in the reaction coordinate to any significant extent, there will be no primary isotope effect, and perdeuteration will conceivably affect only the frequency factor.\textsuperscript{31,35} This effect has been modeled for the propagation reactions of ethylene/deuterated ethylene ($A$ increases by $\sim 16\%$)\textsuperscript{31} and methyl methacrylate/deuterated methyl methacrylate ($A$ increases by $\sim 22\%$),\textsuperscript{35} both comparing favorably with experimental rate enhancements found in the styrene/deuterated styrene (28%)\textsuperscript{89} and methyl methacrylate/deuterated methyl methacrylate (28%)\textsuperscript{90} systems.

### 1.6.1.7 Homologous Series

The theory outlined above also rationalizes the Arrhenius parameters for propagation in a homologous series of monomers. Of the available experimental data, those of the methacrylates and substituted styrenes are probably the most reliable. In the methacrylate series, the values of $k_p$ seem to generally increase with increasing size of the ester group, but the data do not allow for an unambiguous conclusion whether this effect is mainly on the frequency factor or the activation energy.\textsuperscript{91} Either way, an effect on either parameter is likely to be relatively small as the effect on activation energy should decrease with increasing distance from the radical site (both from an electronic and steric point of view), and possible hindrances of the transitional modes and an increase in $Q_{\text{monomer}}$ are counteracted by the increased moments of inertia for these modes.\textsuperscript{72} Overall, this leads to a relatively narrow range of Arrhenius parameters for the methacrylates; taking all data into account, with substituents $R$ (see Scheme 1.7), including substituents such as methyl, dodecyl, isobornyl, benzyl, and cyclohexyl groups, the following ranges of Arrhenius parameters are obtained: $A = (2–6) \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $E_{\text{act}} = 20.5–23.5$ kJ/mol.\textsuperscript{91} A similar situation exists for the parasubstituted styrenes, in which a slightly larger electronic effect exists; for substituents $X$ including methoxy, methyl, fluorine, chlorine, and bromine groups, the Arrhenius parameters lie in the following range: $A = (3–9) \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $E_{\text{act}} = 31–35$ kJ/mol.\textsuperscript{91}

### 1.6.1.8 Penultimate Unit Effects in Copolymerization

One of the most important areas in free-radical polymerization in which the use of theoretical chemistry has been very beneficial is the copolymerization of monomers $M_i$ and $M_j$, where it has yielded direct information on the existence and nature of the

![Scheme 1.7](image-url)
penultimate unit effect; this information has not been unambiguously and directly accessible by experiment thus far. It has been known since about 1980 that the failure of the terminal model for free-radical copolymerization (Scheme 1.8) is due largely to neglect of the penultimate unit effect on the propagation rate coefficient. The penultimate model takes the penultimate unit explicitly into account when considering the individual propagation reaction (Scheme 1.9).

Within the terminal model, both the copolymer composition and average propagation rate coefficient expressions require knowledge of the homopropagation rate coefficients and the two monomer reactivity ratios \( r_i \) and \( r_j \) (see Scheme 1.8). The penultimate model requires the homopropagation rate coefficients \( k_{iii} \) and \( k_{jjj} \) and the four monomer reactivity ratios \( \rho_i \) and \( \rho_j \) for the description of the copolymer composition and additionally the two radical reactivity ratios \( s_i \) and \( s_j \) for the description of the average propagation rate coefficient (see also Chapter 6). Experimentally all these parameters are only accessible by fitting experimental data to model expressions and because so many uncertainties are involved, the physical meaning of the obtained parameters is often limited. This difficulty has not facilitated the task of exploring the existence and possible causes of the penultimate unit effect. As possible causes of a penultimate unit effect factors as radical stabilization, steric and polar effects have been suggested, but no direct experimental proof has been available for a long time, and this is where theoretical chemistry stepped in.

Let us first consider possible steric penultimate unit effects. It is clear from the theory outlined above regarding the frequency factors for propagation that the partition functions of the internal motions in the transition state are highly dependent on the steric hindrances and conformation around the reaction site (see also Fig. 1.24). It is clear that if we change the penultimate unit in the radical, we will automatically change the hindrances of the internal motions and the conformation.

\[
\begin{align*}
\text{~M}_i^* + \text{M}_k & \xrightarrow{k_{ik}} \text{~M}_i^* \text{M}_k^* & k = i \text{ or } j \\
\end{align*}
\]

\[r_i = \frac{k_{ii}}{k_{ij}} \quad r_j = \frac{k_{jj}}{k_{ji}}\]

\[s_i = \frac{k_{ji}}{k_{ii}} \quad s_j = \frac{k_{ij}}{k_{jj}}\]

**Scheme 1.8**

**Scheme 1.9**
around the reaction site, and since all these (probably small) effects enter the overall molecular partition function in a multiplicative way [see Eqs. (1.22) and (1.30)], changes in frequency factor by a factor of 2–3 are conceivable. Hence in general it is conceivable that the following inequality is valid.\[^67\]

\[
A_{iik} \neq A_{jik} \quad \text{with} \quad k = i \text{ or } j
\]  

(1.43)

It is clear that the closer \(M_i\) and \(M_j\) are in shape and size, the closer \(A_{iik}\) is to \(A_{jik}\), but that if they are very different in size and shape, that \(A_{iik}\) and \(A_{jik}\) will be very dissimilar. If we apply this to the penultimate reactivity ratios, we can make a few predictions. Suppose that \(M_i\) and \(M_j\) are similar in size and shape; then the effect of a different penultimate unit may cancel in the expressions of the frequency factors of the monomer reactivity ratios, as the radical in both numerator and denominator of the expression is affected to the same (small) extent: \[^67\]

\[
\frac{A_{iii}}{A_{iij}} \approx \frac{A_{jii}}{A_{jjj}} \approx \frac{A_{ii}}{A_{ij}}
\]  

(1.44)

When we compare this to the situation of the radical reactivity ratios, then the radicals in the numerator and denominator are not affected to the same extent: \[^67\]

\[
\frac{A_{jii}}{A_{iii}} \neq 1
\]  

(1.45)

Hence, if small steric penultimate unit effects are present, it is conceivable that these are most prominently present in the radical reactivity ratios rather than the monomer reactivity ratios. \[^67\] Let us now suppose that one of the monomers, say, \(M_i\) is much larger than \(M_j\). We will now be able to see a marked effect on both the radical and the monomer reactivity ratios. A penultimate unit \(M_j\) will now reduce the steric hindrance and strain as compared to a \(M_i\) penultimate unit, and the overall effect on the frequency factor is likely to be largest when the terminal unit and/or the monomer are \(M_i\). The overall effect on the monomer reactivity ratios (at least their frequency factors) is now given by \[^67\]

\[
A_{jii} \gg A_{iij} \quad \Rightarrow \quad \frac{A_{jii}}{A_{iij}} > \frac{A_{jii}}{A_{ij}} \quad (r''_i > r'_i)
\]  

(1.46)

\[
A_{ijj} < A_{ijj} \quad \Rightarrow \quad \frac{A_{ijj}}{A_{iij}} > \frac{A_{ijj}}{A_{jjj}} \quad (r''_j > r'_j)
\]  

(1.47)

We cannot directly compare this prediction with experimental data, but it is interesting to note that for the system styrene/acrylonitrile (where it is conceivable that strong polar effects also play a role) this behavior of the monomer reactivity ratios is indeed observed. \[^95\text{--}99\] If we now turn our attention to the radical reactivity ratios, it is clear that the effect of a changing penultimate unit is most prominent in the
most congested system, that is, the system with both terminal unit and monomer being $M_i$:\textsuperscript{67}

$$\frac{A_{ji}}{A_{ii}} > 1 \quad (\sim s_i) \quad \text{and} \quad \frac{A_{ij}}{A_{jj}} \leq 1 \quad (\sim s_j) \quad (1.48)$$

Because of the problems associated with the determination of radical reactivity ratios,\textsuperscript{92} this prediction is difficult to test. However, a experimental study on the copolymerization of styrene with the highly hindered dimethyl itaconate indeed suggests the relief of hindrances and steric strain on the propagation rate coefficient of dimethyl itaconate radical when styrene is the penultimate unit.\textsuperscript{100}

It is clear that penultimate unit effects are likely to contain an entropic contribution. Furthermore, as Coote et al. have clearly shown, the penultimate unit effect is also likely to contain a significant enthalpic contribution.\textsuperscript{69–71} These workers studied the $\gamma$-substituent effect in the addition of $\alpha, \gamma$-substituted propyl radicals to substituted ethylenes, which is the smallest possible model for the study of a penultimate unit effect.

First, the addition reaction of 3-X-propyl radicals to monosubstituted ethylenes (all in extended conformations and anti-addition) was studied:\textsuperscript{69}

$$X-\text{CH}_2\text{CH}_2\text{CH}^* + \text{CH}_2=\text{CHY} \rightarrow X\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}^* \quad (1.49)$$

In Table 1.8, the calculated reaction barriers are shown for several different substituents, and it is immediately clear from these data that the penultimate unit can affect the barrier and that the magnitude of this effect depends on both the $\gamma$ substituent and the alkene. For the alkenes ethylene and fluoroethylene we do not observe any significant penultimate unit effects on the barriers, whereas the other

\begin{table}[h]
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{X} & \textbf{RSE}\textsuperscript{a} (kJ/mol) & \multicolumn{4}{c|}{\textbf{Barrier}\textsuperscript{b} (kJ/mol)} \\
\hline
& & $Y = \text{H}$ & $Y = \text{F}$ & $Y = \text{NH}_2$ & $Y = \text{CHO}$ & $Y = \text{CN}$ \\
\hline
\text{H} & 0.00 & 30.3 & 30.8 & 25.7 & 17.8 & 14.6 \\
\text{NH}_2 & 1.00 & 29.9 & 30.6 & 25.0 & 18.6 & 15.1 \\
\text{F} & 0.25 & 30.0 & 30.6 & 23.1 & 20.0 & 16.8 \\
\text{CN} & -1.54 & 29.6 & 30.2 & 21.1 & 20.7 & 17.8 \\
\hline
\end{tabular}
\caption{Calculated Radical Stabilization Energies and Reaction Barriers at 0 K for Addition of 3-X-Propyl (XCH\textsubscript{2}CH\textsubscript{2}CH\textsuperscript{*}) Radicals to Substituted Ethylenes (CH\textsubscript{2}=CHY)}
\end{table}

\textsuperscript{a}Calculated as the energy change in Eq. (1.50): RMP2/6-311 + G(3df,2p)/B3-LYP/6-31G* + ZPVE (scaled B3-LYP/6-31G*).

\textsuperscript{b}Estimated at QCISD(T)/6-311G**//HF/6-31G* + ZPVE (scaled B3-LYP/6-31G*).

\textit{Source:} All data taken from Ref. 69.
three alkenes clearly show the presence of penultimate unit effects. In order to rationalize these observations, these workers investigated whether radical stabilization effects could possibly be a cause. Radical stabilization energies of the studied radicals are also listed in Table 1.8, and are calculated as the energy change of the reaction:69

\[
X-\text{CH}_2\text{CH}_2\text{CH}_2^* + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow X-\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2^* \quad (1.50)
\]

We can see from Table 1.8 that both the NH$_2$ and F $\gamma$ substituents have a stabilizing effect and that the CN $\gamma$ substituent has a destabilizing effect on the radical. However, none of these effects is particularly large, and hence are not expected to play a significant role in the penultimate unit effect on the reaction barrier.69

In order to investigate whether polar effects possibly play a role, the curve-crossing approach outlined before was chosen by Coote et al.,69 and adiabatic electron affinities and vertical ionization potentials were determined for all the radicals and monomers in this study (see Table 1.9).

From Table 1.9 it can be seen that both CH$_2$=CHCHO and CH$_2$=CHCN have a relatively high electron affinity, and polar effects might be expected for reactions with radicals with a relatively low ionization potential. Monomer CH$_2$=CHNH$_2$ has a relatively low ionization potential, and hence polar effects are expected in reactions with radicals with a relatively high electron affinity. In Table 1.10, the low-lying charge transfer states (i.e., $I - EA < 9 - 9.5$ eV) are shown, and it is immediately clear from the data that the additions to CH$_2$=CHNH$_2$, CH$_2$=CHCHO, and CH$_2$=CHCN all have polar contributions to the transition state energy. If we now return to barriers listed in Table 1.8, we can see that all the reactions showing significant penultimate unit effects in the barrier also have large polar contributions. Hence we may conclude that polar effects contribute to the penultimate unit effect and that any radical stabilization effects are negligible in these systems.69

In order to investigate the $\gamma$-substituent effect in electronically more complicated and interesting systems (so far, we only looked at $\gamma$-substituent effects of a

TABLE 1.9 Calculated Vertical Ionization Energies ($I$) and Adiabatic Electron Affinities ($EA$) for a Range of 3-X-Propyl (XCH$_2$CH$_2$CH$_2^*$) Radicals and Substituted Ethylenes (CH$_2$=CHY)$^a$

<table>
<thead>
<tr>
<th>X, Y</th>
<th>$EA$ (eV)</th>
<th>$I$ (eV)</th>
<th>$EA$ (eV)</th>
<th>$I$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.01</td>
<td>8.40</td>
<td>-1.86</td>
<td>10.58</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>0.26</td>
<td>8.14</td>
<td>-1.92</td>
<td>8.18</td>
</tr>
<tr>
<td>F</td>
<td>0.40</td>
<td>8.68</td>
<td>-1.62</td>
<td>10.37</td>
</tr>
<tr>
<td>CN</td>
<td>0.68</td>
<td>9.06</td>
<td>-0.23</td>
<td>10.98</td>
</tr>
<tr>
<td>CHO</td>
<td>—</td>
<td>—</td>
<td>0.03</td>
<td>10.21</td>
</tr>
</tbody>
</table>

$^a$Calculated at the G2(MP2) level of theory. Data taken from Ref. 69.
propagating propyl radical), Coote et al. introduced α substituents in the γ-substituted propyl radicals and studied their additions to ethylene (additional substitution in ethylene would have made the calculations unfeasible at the time of study).70

\[
\text{X–CH}_2\text{CH}_2\text{CH}_3^* + \text{CH}_2=\text{CH}_2 \rightarrow \text{X–CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^* \quad (1.51)
\]

For these reactions, all calculated in fully extended conformations and anti addition, reaction barriers were calculated and the effect of radical stabilization [now defined as the energy change of the reaction shown in Eq. (1.52)] and polar contributions to the transition state were investigated. The results of this study are summarized in Table 1.11.70

\[
\text{X–CH}_2\text{CH}_2\text{CH}_3^* + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{X–CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_3^* \quad (1.52)
\]

### Table 1.10 Nature and Energy Level (eV) of Relevant Charge Transfer States in Addition of 3-X-Propyl (XCH$_2$CH$_2$CH$_2$) Radicals to Substituted Ethylenes (CH$_2$=CHY)$^a$

<table>
<thead>
<tr>
<th>X</th>
<th>Y = H</th>
<th>Y = F</th>
<th>Y = NH$_2$</th>
<th>Y = CHO</th>
<th>Y = CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>—</td>
<td>—</td>
<td>D$^-$A$^+$ = 7.92</td>
<td>D$^+$A$^-$ = 8.11</td>
<td>D$^+$A$^-$ = 8.37</td>
</tr>
<tr>
<td>F</td>
<td>—</td>
<td>—</td>
<td>D$^-$A$^+$ = 7.78</td>
<td>D$^+$A$^-$ = 8.65</td>
<td>D$^+$A$^-$ = 8.91</td>
</tr>
<tr>
<td>CN</td>
<td>—</td>
<td>—</td>
<td>D$^-$A$^+$ = 7.50</td>
<td>D$^+$A$^-$ = 9.03</td>
<td>D$^+$A$^-$ = 9.29</td>
</tr>
</tbody>
</table>

Note: $^a$ Calculated from data in Table 1.9.

### Table 1.11 Calculated Reaction Barriers, Radical Stabilization Energies, and Relevant Charge Transfer States in Addition of 1-Z,3-X-propyl (XCH$_2$CH$_2$CHZ$^*$) Radicals to Ethylene

<table>
<thead>
<tr>
<th>X</th>
<th>Z = H</th>
<th>Z = F</th>
<th>Z = CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>30.3</td>
<td>26.3</td>
<td>37.0</td>
</tr>
<tr>
<td>F</td>
<td>30.0</td>
<td>25.6</td>
<td>37.0</td>
</tr>
<tr>
<td>CN</td>
<td>29.6</td>
<td>25.4</td>
<td>34.5</td>
</tr>
</tbody>
</table>

Note: $^a$ Barrier at 0 K in kJ/mol, estimated at QCISD(T)/6-311G**//HF/6-31G* + ZPVE (scaled B3-LYP/6-31G*).

$^b$ Radical stabilization energy (kJ/mol), calculated as the energy change in Eq. (1.52): RMP2/6-311+G(3df,2p)/B3-LYP/6-31G* + ZPVE (scaled B3-LYP/6-31G*).

$^c$ Relative energy level of relevant charge transfer state (eV).

$^d$ All charge transfer states are D$^-$/A$^+$ states.

Source: All data taken from Ref. 70.
As before, the addition reactions of \( \gamma \)-substituted propyl radicals to ethylene do not show any significant penultimate unit effect on the barrier, even though some (de)stabilization effects in the radicals are present. A similar picture is also found for the addition of \( \gamma \)-substituted 1-F-propyl radicals to ethylene, where even larger (de)stabilization effects are observed. The only relatively large penultimate unit effect (\(-2.5 \text{ kJ/mol}\)) that is observed is for the reaction between the 1,3-dicyanopropyl radical and ethylene, which also has a large radical (de)stabilization energy (\(-9.2 \text{ kJ/mol}\)). Hence, only \( \sim 27\% \) of the penultimate unit effect in radical stabilization seems to be carried over to the reaction barrier.\(^7^0\) However, this reaction also has a large contribution from polar effects as evidenced by the low-lying \( \text{D}^-\text{A}^+ \) state, and hence we cannot unambiguously assign the penultimate unit effect on the barrier to the radical stabilization effect. It is interesting to note that although polar effects should also be operative in the addition of 3F,1CN-propyl radical (with a radical stabilization energy of \(-4.5 \text{ kJ/mol}\), which is similar to that of 3CN,1F-propyl radical), no penultimate unit effects in the barrier are observed.

Finally, Coote et al. studied the effect of reactant and transition state conformation on the penultimate unit effect for several \( \gamma \)-substituted propyl radicals to mono-substituted ethylenes.\(^7^1\) They found that the penultimate unit effect on the barrier is highly dependent on the conformations of reactant and transition state. For the addition of a 3F-propyl radical to \( \text{CH}_2\text{=CHF} \) they find a range of penultimate unit effects from \(-3.6 \text{ to } +2.9 \text{ kJ/mol}\), for the addition of 3CN-propyl to \( \text{CH}_2\text{=CHCN} \) a range from \(-2.1 \text{ to } +5.8 \text{ kJ/mol}\) and for the addition of 3CN-propyl to \( \text{CH}_2\text{=CHNH}_2 \) a range from \(-8.8 \text{ to } -1.6 \text{ kJ/mol}\).\(^7^1\) The results are explained by the fact that interactions occur between the \( \gamma \) substituent in the radical, the unpaired electron, and the monomer.\(^7^1\) The interactions can be so strong that they can counteract the effects expected from charge transfer states based on the reactants. Furthermore, it is clear that these different conformations will all have different frequency factors, and that the overall rate coefficient will be a weighted average of all the rate coefficients of each individual pathway.\(^7^1\) At present it is unclear what the overall effect on the rate coefficient will be. However, it is beyond doubt that penultimate unit effects are caused by a wide range of causes, including steric effects in the frequency factor,\(^6^7\) polar effects in the barrier,\(^6^9\text{–}7^1\) intramolecular interactions in the transition state,\(^6^7,7^1\) and possibly radical stabilization effects.\(^7^0\) Furthermore, models based on just a single effect cannot provide an adequate representation of the physical chemistry in free-radical copolymerization.\(^6^9\text{–}7^1\)

1.6.2 Atom Abstraction and Chain Transfer

1.6.2.1 General Aspects

Most theoretical studies on radical abstraction reactions have focused on small radicals, such as hydroxyl radicals and small saturated species, often containing fluorine atoms. In general, the relevance of these studies to free-radical polymerization is limited, and for this reason the discussion of atom abstraction reactions will be much shorter than that of the radical additions, and we will focus on only two studies reported in the literature, i.e., chain transfer to monomer\(^6^0,6^8\) and backbiting in the free-radical polymerization of ethylene.\(^1^0^1\)
Furthermore, we will discuss the broader impact of these limited studies on our understanding of chain transfer in free-radical polymerization.

Let us start with some general aspects of the theoretical procedures involved in these studies. In principle we can calculate the rate coefficient for a hydrogen transfer reaction using conventional transition state theory, but we have to correct for a process called quantum-mechanical tunneling,\textsuperscript{8,102–104} which is important when the reaction involves the transfer of light atoms. Tunneling allows the hydrogen atom to some extent to be transferred through the barrier rather than over it, and hence increases the rate coefficient. Many studies have and are still dealing with an accurate description of this effect, but considering the complexity of this problem, which is far beyond the scope of this chapter, we will consider only the simple Wigner tunneling correction.\textsuperscript{104} In this case we will need to multiply the rate coefficient obtained by conventional transition state theory calculations \([k_{\text{TST}}; \text{see Eq. (1.7)}]\) by a temperature-dependent correction factor \(\kappa(T)\). The overall rate coefficient \(k\), is now given by\textsuperscript{104}

\[
k = \kappa(T) \cdot k_{\text{TST}} \tag{1.53}
\]

where the Wigner tunneling correction is given by

\[
\kappa(T) = 1 - \frac{1}{24} \left( \frac{ihv}{k_B T} \right)^2 \tag{1.54}
\]

In this expression \(v\) is the imaginary frequency of the normal mode along the reaction coordinate, which is normally left out of the expression of \(k_{\text{TST}}\). We will see that the overall correction is relatively small in the studies that are discussed in this chapter.

Assessment of levels of theory for the problems discussed in this section is limited, but we found that the following procedures, which roughly correspond to a modified G2(MP2) level of theory,\textsuperscript{105,106} were required for obtaining adequate results:60,68

- B3-LYP/6-31G* for geometry optimization, calculation of frequency factors, and calculation of ZPVE
- QCISD(T)/6-311G** for the calculation of vibrationless barriers together with a basis set correction from 6-311G** to 6-311 + G(3df,2p) at the PMP2 level of theory

### 1.6.2.2 Chain Transfer to Monomer in Ethylene Polymerization

Chain transfer to monomer is an important reaction in free-radical polymerization. For example, it intrinsically limits the maximum attainable molecular weight,\textsuperscript{107} is assumed to be the kinetic event responsible for exit in emulsion polymerization,\textsuperscript{108} and potentially limits the applicability of living radical polymerization techniques for producing narrow polydispersity polymers.\textsuperscript{109,110} In many cases the chain transfer to monomer
reaction is assumed to proceed via a hydrogen transfer or hydrogen abstraction reaction between the growing radical and the monomer molecule. It is not always clear which hydrogen atoms are abstracted and in which direction the hydrogen transfer takes place. For example, it is often assumed that abstraction of vinylic hydrogens, which have a very strong C–H bond, is unlikely to occur. One theoretical study published to date has explicitly investigated this problem for the free-radical polymerization of ethylene using the model system of an ethyl radical and ethylene. The two possible reactions are a hydrogen transfer reaction from radical to monomer [Eq. (1.55), which is thermoneutral (reactants and products are the same), and a hydrogen abstraction reaction from the monomer by the radical [Eq. (1.56)]. This latter reaction involves the breaking of a strong $sp^2$ C–H bond and the formation of a weaker $sp^3$ C–H bond; the reaction is endothermic ($\Delta H_r = +40.1$ kJ/mol calculated at a modified G2(MP2) level of theory).

$$\text{CH}_3\text{CH}_2^\bullet + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}_2^\bullet \quad (1.55)$$

$$\text{CH}_3\text{CH}_2^\bullet + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_3 + \text{CH}_2=\text{CH}^\bullet \quad (1.56)$$

From the thermochemistry we would probably expect that the thermoneutral hydrogen transfer reaction is favored over the endothermic hydrogen abstraction reaction. However, it was shown that the activation energy of the second reaction is about 50 kJ/mol lower and hence the hydrogen abstraction of the vinylic hydrogen in the monomer is the most likely pathway for chain transfer to monomer in ethylene polymerization. This result will be discussed in more detail below. First some general and important aspects of the transition structures for both reactions will be discussed.

The transition states of the hydrogen transfer and hydrogen abstraction reactions with some key geometric parameters calculated at the UHF/6-31G* level of theory are shown in Fig. 1.25. Although there are significant differences in the conformations, the overall sizes of the transition states and the distances between the two reactant moieties in the transition states (i.e., ~2.8 and ~2.7 Å in the transfer and abstraction transition states, respectively) are very similar. This similarity in overall geometry leads to similar overall external rotational contributions to the frequency factor. Furthermore, the overall sizes are similar to that of propagation, except that the chain transfer transition states are less tight (the two reactant moieties in the propagation transition state are separated by ~2.3 Å). It should also be noted that the hydrogen transfer reaction proceeds through a symmetrical transition state, whereas this is not the case for the hydrogen abstraction reaction. If we consider the partial C–H bonds in the abstraction transition state (Fig. 1.25b), it is clear that the forming C–H bond is shorter than the breaking C–H bond; that is, the transition state is more productlike. This is in accordance with a late transition state for an endothermic reaction.

The transitional modes in the two chain transfer transition states have also been determined. Of the transitional modes, those with the lowest real frequencies are shown in Fig. 1.26. As was the case in propagation, the lowest real frequency
Figure 1.25  Transition structures for the hydrogen transfer (a) and hydrogen abstraction (b) reactions between ethyl radical and ethylene with some key geometrical parameters (UHF/6-31G*).60

Figure 1.26  Schematic representation of the lowest real transitional modes and corresponding harmonic frequencies (HF/6-31G*) in the hydrogen-transfer (above) and hydrogen-abstraction (below) reaction between ethyl radical and ethylene. All modes correspond to external rotations in the reactants.60
transitional mode for both transition states is (roughly) a rotational mode in which the monomer molecule rotates about an axis connecting the two carbon atoms between which the hydrogen atom is being transferred (the partition functions for these modes in the two chain transfer transition states are very similar). Since the two reactant moieties have a greater separation in these transition states as compared to the propagation transition state, these rotational modes are virtually unhindered. This observation means that the partition functions for this rotation in the transfer transition states are larger than that in the propagation transition state.60

Considering the other two low-frequency modes in the chain transfer transition structures (both corresponding to external rotations in the reactants), we see again a great similarity between the two cases. Furthermore, these modes are quite similar to those previously seen in propagation (see Fig. 1.22).35,60

The similarities between the transition states for the two chain transfer reactions lead to very similar partition functions and frequency factors; the frequency factor for the hydrogen transfer reaction is $3.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and that for the hydrogen abstraction reaction is $7.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (both values calculated without tunneling corrections).60,68 These frequency factors are higher than that for propagation because of the smaller hindrances of the transitional modes.31,35,68

The critical energies for the hydrogen transfer reaction [Eq. (1.55)] is 128.1 kJ/mol, and that for the hydrogen abstraction reaction [Eq. (1.56)] is 80.0 kJ/mol [both values calculated at a modified G2(MP2) level of theory]. Without tunneling corrections, these critical energies lead to activation energies of 129.8 and 81.8 kJ/mol, respectively. The effect of tunneling estimated by the Wigner tunneling correction was found to be small. The final kinetic parameters of the two reactions are listed in Table 1.12.68

Using the reaction between a heavy mass-substituted butyl radical (see Fig. 1.23) and ethylene as a model for chain transfer to monomer in ethylene polymerization, a frequency factor of $1.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 333 K is obtained.35 Similar to what was discussed previously for propagation, we expect a chain length dependence for $k_{tr}$. If we compare the theoretical results with experimental results, a reasonable agreement is obtained. At 523 K, the calculated frequency factor is $3.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,60 which compares favourably with the value reported by Buback and

| Table 1.12 Calculated Kinetic Parameters for Hydrogen Transfer and Hydrogen Abstraction Reactions between Ethyl Radical and Ethylene |
|---------------------------------|-----------------|-----------------|
| $E_0^a$ (kJ/mol)                | 128.1           | 80              |
| $E_{act}^b$ (kJ/mol)            | 125.7           | 77.6            |
| $A^c$ (dm$^3$ mol$^{-1}$ s$^{-1}$) | $3.7 \times 10^8$ | $8.5 \times 10^8$ |
| $\Delta H_f^d$ (kJ/mol)         | 0               | 40.1            |

$^a$ Barrier at 0 K, calculated at a modified G2(MP2) level of theory.
$^b$ Activation energy at 298.15 K, with Wigner tunneling correction.
$^c$ Frequency factor at 298.15 K, with Wigner tunneling correction (HF/6-31G*).68
co-workers, i.e., \((0.4–5.2) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) (recalculated from \(C_M\) data using experimental \(k_p\) data).\(^{111}\) The activation energies also compare favorably at 523 K: experimental \(E_{\text{act}} = 74 \pm 8 \text{ kJ/mol},\)\(^{111}\) theoretical \(E_{\text{act}} = 82 \text{ kJ/mol}\) (using Wigner tunneling correction).\(^{60}\)

The theoretical results clearly show that the endothermic hydrogen abstraction from the monomer is kinetically favored over the thermoneutral hydrogen transfer from radical to monomer (see Table 1.12 and Fig. 1.27). Although at first glance this result is unexpected, it can be explained in a simple way using the curve-crossing model.\(^{58}\)

In Eqs. (1.57) and (1.58), the two reactions are represented in terms of the involved electronic rearrangements. Comparison of these two electronic rearrangements immediately shows why the hydrogen transfer reaction has a higher barrier. The initial energy gap \(G\) for the hydrogen transfer reaction contains two contributions, namely, the singlet–triplet excitation energies of the \(sp^3\) C–H bond of the radical and of the \(\pi\) bond in the monomer; in other words, two bonds need to be broken for this reaction. In the hydrogen abstraction reaction, only the \(sp^2\) C–H bond needs to be broken and \(G\) contains only the singlet–triplet energy gap of the

---

**Figure 1.27** Schematic representation of the energy profiles along the reaction coordinates for the hydrogen abstraction (full line) and hydrogen transfer (dashed line) reactions between ethyl radical and ethylene.

---
sp$^2$ C–H bond. Hence, the much larger value for $G$ in the case of the hydrogen-transfer reaction causes the much larger barrier.$^{68}$

\[
\begin{align*}
\dot{\text{CH}}_2\text{CH}_2\dot{\text{H}} & \xrightarrow{\text{transfer}} \text{CH}_3\text{CH}_2\dot{\text{H}}
\text{CH}_3\dot{\text{CH}}_2\dot{\text{CH}}=\text{CH}_2 & \xrightarrow{\text{abstraction}} \text{CH}_3\text{CH}_2\dot{\text{H}} \text{CH}=\text{CH}_2
\end{align*}
\]

(1.57) (1.58)

This study clearly indicates the role that theory can play in elucidating mechanisms which are difficult to access experimentally.

1.6.2.3 Chain Transfer Constants The discussion so far has focused on addition and hydrogen transfer reactions between a radical and a monomer. When we now consider the transition state theory expression for these two reactions, it is clear that the only differences between the two expressions are the partition function and the energy of the transition state; all reactant properties are the same. If we now consider the transition state properties, we can see from Fig. 1.19, 1.22, 1.25, and 1.26 that there are great similarities, including the overall geometries and the transitional modes (see Fig. 1.28).$^{35}$

The main difference between the two transition structures, however, is that the transition state for hydrogen transfer is less tight; the transitional modes are less hindered and hence lead to a greater $Q_{\text{int}}$, which in turn leads to a larger $A$ ($A$ for chain transfer to monomer in ethylene polymerization $\approx 10 \times A$ for ethylene propagation).

![Transition State of Propagation](image1.png)

![Transition State of Chain Transfer](image2.png)

**Figure 1.28** Schematic representation of the transition states of propagation and chain transfer to monomer in the free-radical polymerization of ethylene. The most important low-frequency modes in both transition states are also depicted. Note the similarity of the transitional modes in both cases.
This implies that the preexponential factor of the chain transfer constant ($C_M$), specifically, $A_{\text{chain transfer}}/A_{\text{propagation}}$, should typically have a value between 1 and 10.\(^{35}\) It would be interesting to test this prediction against experimental data, but unfortunately not many reliable experimental Arrhenius parameters for chain transfer to monomer are available to date. Unfortunately, the only available reliable data available to date suggest that $A_{\text{chain transfer}} < A_{\text{propagation}}$. The preexponential factors of $C_M$ have been reported as $\sim 0.02$, $\sim 0.2$, and $\sim 0.1$ for butyl acrylate,\(^{112}\) styrene,\(^{113}\) and methyl methacrylate,\(^{114}\) respectively. The main causes of these discrepancies are unclear; these results could indicate that the chain transfer to monomer reaction does not involve a reaction similar to those studied here (this argument is conceivable for styrene, where chain transfer to monomer is assumed to involve a Diels–Alder product of styrene).\(^{115}\) Naturally, it could also mean that the theoretical results obtained for ethylene polymerization are not as general as they seem. It is clear that more theoretical and experimental studies are required to investigate this problem.

Since it is unlikely that the activation energies for chain transfer to monomer will significantly change within a homologous series (similar to what we have seen in propagation), and the factors governing the frequency factors for chain transfer and propagation are similar, we can expect similar behaviour of the chain transfer and propagation rate coefficients in a homologous series. This implies that chain transfer constants in a homologous series should not vary to a great extent, and might, to a first approximation, be considered constant. Insufficient reliable experimental data are currently available to test this prediction.

It is also of interest to consider what we would expect to see for chain transfer constants to chain transfer agents. First, if we consider the chain transfer reaction to dodecanethiol, we may conceivably expect a transition structure similar to the ones we discussed in detail above. We may therefore expect that within a homologous series, the chain transfer constant to this chain transfer agent should not change significantly.\(^{35}\) An experimental result that indicates that this is indeed the case has been reported for the chain transfer reactions of methyl methacrylate, ethyl methacrylate, and $n$-butyl methacrylate, respectively, with $n$-dodecane thiol. The chain transfer constants at $60^\circ\text{C}$ for these three systems were found to be $0.68 \pm 0.02$, $0.71 \pm 0.02$, and $0.65 \pm 0.02$, respectively.\(^{116}\)

Finally, it is interesting to compare the chain transfer behavior with dodecanethiol and CBr$_4$ of methyl methacrylate\(^{117}\) and dimethyl itaconate\(^{118}\) (DMI; see Table 1.7). These two monomers have fairly similar activation energies for propagation\(^{84,119}\) (and considering the nature of the two monomers, we conceivably expect similar activation energies for chain transfer), but DMI has a much lower frequency factor because of the steric crowding.\(^{84}\) For the chain transfer reaction to CBr$_4$, we expect quite a crowded transition structure because of the large Br atom that is transferred, and although the transition state of hydrogen transfer is less tight, we still expect that the transitional modes will be affected by steric hindrances to an extent similar to that for the transitional modes in propagation. This implies that the additional hindrances of the large DMI as compared to methyl methacrylate are likely to cancel in the ratio $A_{\text{transfer}}/A_{\text{propagation}}$, resulting in similar chain transfer constants to CBr$_4$ for
methyl methacrylate and DMI. Experiment shows that they are indeed very similar; $C_S(\text{MMA}) \approx 0.2^{117}$ and $C_S(\text{DMI}) \approx 0.3^{118}$ at 60°C. A different situation exists for the chain transfer reaction with dodecanethiol, where we expect the transition state to be less tight, and hence the additional hindrances in the propagation reaction of DMI are now less felt in its chain transfer reaction. Hence the frequency factor of propagation is conceivably affected to a much larger extent than that for chain transfer, and the overall effect will be that the ratio $A_{\text{transfer}}/A_{\text{propagation}}$ for DMI increases as compared to that for MMA. Hence, we expect a larger $C_S$ for DMI, and that is indeed what we observe experimentally: $C_S(\text{MMA}) \approx 0.8 \pm 0.1^{117}$ and $C_S(\text{DMI}) \approx 2.8 \pm 0.5^{118}$ at 60°C.

### 1.6.2.4 Backbiting in Ethylene Polymerization

As a final example of the application of theoretical chemistry in free-radical polymerization, backbiting in ethylene polymerization will be discussed.\(^{101}\) This reaction, which is also very important in the free-radical polymerization of acrylates, leads to short-chain branching. A schematic representation of the overall mechanism is shown in Scheme 1.10.

The first step in this mechanism is an intramolecular hydrogen abstraction reaction from the fifth CH$_2$ unit in the polymer chain, leading to a midchain radical that undergoes further reactions leading to several different branch sizes.\(^{101}\) This first step was investigated using transition state theory and ab initio molecular orbital theory by Gilbert and co-workers.\(^{101}\) These workers used two different model systems to describe the reaction: a radical chain consisting of 6 and a radical chain consisting of 7 carbon atoms. It was found that the 6-carbon system is not sufficiently large to adequately describe the internal motions and hence the 7-carbon system was used to model the backbiting reaction using transition state theory (see Fig. 1.29). It should

![Scheme 1.10](image-url)
be noted that the ratio of partition functions in Eq. (1.7) contains the partition function of only a single reactant and that transitional modes do not occur in this system.

Evaluation of the partition functions for the polymeric backbiting reaction (using a high-mass-substituted 7-carbon system) yields a frequency factor $A = 10^{12.7} \text{s}^{-1}$ (calculated at HF/6-31G*). The size of the system limited the level of theory that was applied to calculate the critical energy to reaction. For the 6-carbon system, critical energies were calculated up to QCISD(T)/6-311G** and for the 7-carbon system up to QCISD(T)/6-31G*. The availability of barriers at several different levels of theory for both the 6-carbon and 7-carbon systems allows for a reasonable extrapolation to a QCISD(T)/6-311G** barrier for the 7-carbon system. However, there are some questions about the original method of extrapolation, and a better extrapolation would possibly be one of the two following approximations:

\[
\text{QCISD(T)/6-311G**}_{7\text{-carbon}} \approx \text{QCISD(T)/6-31G*}_{7\text{-carbon}} + \Delta_{\text{basis set}} \tag{1.59}
\]

\[
\text{QCISD(T)/6-311G**}_{7\text{-carbon}} \approx \text{QCISD(T)/6-311G**}_{6\text{-carbon}} + \Delta_{\text{system}} \tag{1.60}
\]

where the subscripts 7-carbon and 6-carbon refer to the two model systems, $\Delta_{\text{basis set}}$ is a basis set correction from 6-31G* to 6-311G** obtained at lower levels of theory, and $\Delta_{\text{system}}$ is the difference between the critical energies of the 7-carbon and 6-carbon systems at lower levels of theory. If we use the following data (values in kJ/mol)

\[
E_0 \approx 50 \text{ kJ/mol}
\]

Figure 1.29  Schematic representation of the potential energy profile along the reaction coordinate for the backbiting reaction in ethylene polymerization. Indicated barrier was estimated at the QCISD(T)/6-311G** level of theory.
from the original work, namely, \( \{ \text{QCISD(T)/6-31G*} \}_{7\text{-carbon}} \approx 64, \Delta_{\text{basis set}} \approx -10 \) and \( \{ \text{QCISD(T)/6-311G**} \}_{6\text{-carbon}} \approx 69, \Delta_{\text{system}} \approx -16 \), then the extrapolated QCISD(T)/6-311G** critical energy for the 7-carbon system is 50–53 kJ/mol, which is \( \sim 10 \text{ kJ/mol} \) lower than the reported values. Using an experimental value for the volume of activation, which accounts for the pressure dependence of the rate coefficient, the activation energy for the 7-carbon system is given by \( E_{\text{act}} \approx E_0 + 8,^{101} \) which, with the new estimate of \( E_0 \), would give a value \( \sim 60 \text{ kJ/mol} \).

The calculated Arrhenius parameters for the branching rate coefficients allows for the calculation of the branching ratio. Gilbert and co-workers compared their results with experimental data and observed a significant overestimation by the theoretical approach. It is conceivable that the activation energy was not calculated at a sufficiently high level of theory (and the current theoretical value is too high) and that the frequency factor is incorrect by a factor of 2–5. On the other hand, the experimental procedures to determine branching ratios are very difficult, so it is not inconceivable that there is a substantial experimental error. Either way, the very large discrepancy between theory and experiment clearly indicates that additional work on short-chain branching is required. The experimental difficulties render theory to be a powerful alternative as the required information can be accessed directly. However, in order to rely on theory to guide experimental work for this particular problem, theory needs to be pushed further to its limits until we are certain that we have reached convergence with level of theory or accurate experimental data need to become available against which lower (but sufficiently high) levels of theory can be calibrated.

### 1.7 CONCLUDING REMARKS

This chapter was meant to bridge the apparent gap between theoretical chemistry and polymer chemistry and to highlight some successful theoretical studies of problems in free-radical polymerization. Several applications were discussed with a major emphasis on the propagation reaction. When we consider the work on radical addition reactions, we see a very beneficial interplay between experiment and theory. Although theory sometimes over- or underestimates particular effects, the deviations are often systematic, and trends are adequately reproduced. Since the underlying physics of a chemical reaction are often inaccessible by experiment, theory can be used to study these underlying aspects. A good example is the study of small-radical additions; using experimental and theoretical data, Fischer and Radom were able to develop a relatively simple model for radical additions, which is fully based on fundamental theory.

Furthermore, we have seen how steric factors affect frequency factors for propagation and chain transfer, and how, on the basis of these considerations, experimental data show understandable patterns. Theory has also greatly enhanced our understanding of copolymerization kinetics, where the precise nature of the penultimate unit effect could be studied explicitly.
Some examples, of which the backbiting problem is representative, also show the
great potential of theory to be used to study problems that are difficult to investigate
by experiment, but for which the required computational power to push theory to its
limits is currently not available.

Overall we can see that theory is a great companion to experimental chemistry
and the increasing computational power will allow the study of more complex
systems. It is not likely that (in the near future) theory will replace experiment,
but it will be a great aid in interpreting and designing experiments that answer
some of our more fundamental questions. The further development of accurate com-
putational procedures (especially in density functional theory and hybrid semiempiri-
cal/ab initio methods) and the availability of large amounts of accurate
experimental data will allow us to study more complex problems, including prob-
lems of relevance to transition-metal-mediated radical polymerizations.

In conclusion, theoretical chemistry should be considered as a helpful tool in
understanding and designing experimental chemistry, and not as a separate branch
of chemistry suitable only for philosophers speaking in their own language of
complicated theoretical procedures and basis sets.

ACKNOWLEDGMENTS

I gratefully acknowledge Bob Gilbert and Leo Radom, who got me started in this
field and taught me most of its underlying principles. Many aspects covered in
this chapter are the results of my work with them and their work with other colla-
borators. Useful discussions and collaborations with George Bacsak, Christopher
Barner-Kowollik, Michelle Coote, Tom Davis, Takeshi Fukuda, Ton German, Mer-
edith Jordan, Ian Maxwell, Graeme Moad, Addy Pross, and Greg Russell have also
significantly contributed to this chapter.

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