

PREDICTION OF THE MECHANISMS OF REACTIONS

PRÉCIS

In Chapter 4, we showed that if one knows the mechanism of a reaction and the rate constants for all of the elementary steps in the mechanism, one can calculate a rate equation for the reaction.

The objective of this chapter is to give some insights into the mechanisms of reaction. We will start with gas-phase reactions and present some empirical rules to predict reaction mechanisms. We will then move on to reactions in liquids and on solid surfaces, and discuss how mechanisms can be predicted in those cases. We will find that we can often get accurate predictions with relatively simple methods.

5.1 INTRODUCTION

The study of the mechanisms of simple reactions had its start in the latter part of the nineteenth century. At the time, people were still unsure why the kinetics of simple reactions were so different from what one would expect from the stoichiometry of a reaction. In 1898, people first realized that reactions followed complex mechanisms. In the 1920s and 1930s, there were several attempts to predict mechanisms. However, the work was largely unsuccessful. That is as far as the theory went up until 1950.

In fact, up until 1985, no one seriously discussed the idea that one might be able to predict the mechanisms of simple reactions. However, as computers became faster, people started to talk about the idea that one might be able to predict mechanisms, and not just measure mechanisms. Unfortunately, much of the information has been discussed only at meetings and has not made it into the general literature. Still, I believe that the ideas that are coming out now are important enough, and simple enough, that students and others ought to know about them. In this chapter, we will discuss how one can predict reactions mechanisms.

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5.1 INTRODUCTION

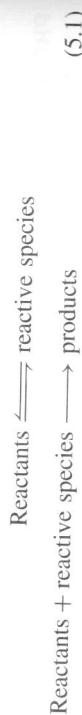
The study of the mechanisms of simple reactions had its start in the latter part of the nineteenth century. At the time, people were still unsure why the kinetics of simple reactions were so different from what one would expect from the stoichiometry of a reaction. In 1898, people first realized that reactions followed complex mechanisms. In the 1920s and 1930s, there were several attempts to predict mechanisms. However, the work was largely unsuccessful. That is as far as the theory went up until 1950.

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First, we will discuss why reaction follow complex mechanisms and then we will work out some rules for prediction of the mechanisms of gas-phase reactions, surface reactions, and reactions in solution. If you can predict mechanisms, you know all of chemistry, so clearly we cannot cover everything. However, we wanted to provide some principles that readers could use to understand mechanisms.

5.2 WHY DO REACTIONS FOLLOW COMPLEX MECHANISMS?

The first question we want to ask is why reactions follow complex mechanisms; why don't the reactants instead combine in one step to produce products? The answer is pretty simple. In most reactions in industrial practice, the reactants are stable molecules. A stable molecule is by definition stable, that is, relatively unreactive. As a result, a direct reaction between the reactants is usually slow. There are exceptions, of course. If you react sodium with chlorine, you get a direct reaction between the reactants. However, most organic or inorganic reactions start with stable, unreactive species. If you start with a stable unreactive species, you need to do something to the species before that species becomes reactive. Generally, most reactions follow the general mechanism

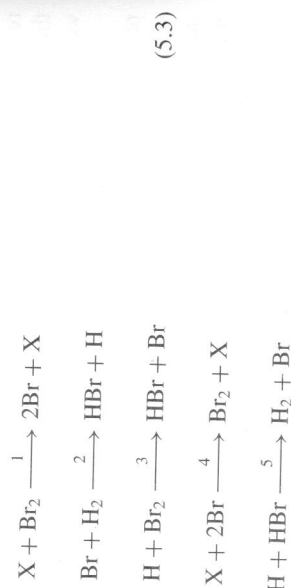


As seen in reaction (5.1), you first produce a reactive species, and then the reactive species reacts with more reactants to form products. You can form the reactive species by breaking a bond in the species or by exciting the species with, for example, a laser. The excited species can be a vibrationally excited molecule or something like a radical or an ion. In the gas phase, the excited species is most often a radical. However, if you start with an unreactive molecule, you almost always need to create a reactive molecule before significant reaction can occur.

For example, let's consider the case that was discussed in Chapter 4: the reaction between hydrogen and bromine to yield HBr:



In Chapter 4, we noted that the mechanism of the reaction is



where X is a collision partner (i.e., any other species that can collide with Br₂ as described in Sections 4.3 and 8.1.1). Notice that we formed a reactive species, namely, a radical in step 1. The radical then reacts to form products. The formation of a reactive species is a common feature of most chemical reaction mechanisms.

6.9 PREDICTION OF MECHANISMS OF REACTIONS OF GAS-PHASE SPECIES

In the remainder of this chapter, we will discuss how one can predict the mechanism of a variety of different reactions. We will first do gas-phase reactions, then move on to reactions in liquids and on surfaces.

Let's start with gas-phase reactions. Most gas-phase reactions follow what are called *initiation-propagation mechanisms*. Initiation-propagation mechanisms were mentioned in Chapter 4. Consider the idealized reaction



where a molecule of A reacts with a molecule of B to produce two products, P₁ and P₂. This reaction is said to follow an initiation-propagation mechanism when the reaction goes as follows:

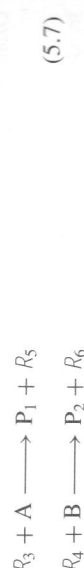
First, there is an **initiation step** where a collision partner X collides with one of the reactant molecules, and breaks a bond in the reactant to produce two radicals, which I will call R₁ and R₂:



Then there may be a **transfer step** where one of the radicals reacts to form a more reactive species. R₃ and R₄, and two side products C and D:



Then the radicals react with the reactants or the products in a series of **propagation steps** to yield a series of new radicals, R₅ and R₆:



Additional propagation steps occur where R₅ and R₆ react to regenerate R₃ and R₄:



Finally, the radicals can recombine in what is called a **termination step**:



There are many different combinations. Still, the key feature of an initiation-propagation mechanism is that first there is an initiation step where radicals are formed. Then, there are a series of steps where radicals react to form products. Finally, there are a series of termination steps where radicals are destroyed.

Most gas-phase reactions go via initiation-propagation mechanisms. For example, Rice (1932) examined the decomposition of a wide variety of organic compounds, including aliphatic and olefinic hydrocarbons, aldehydes, ketones, esters, amines, and carboxylic acids, and found that in all cases, the reaction went by an initiation-propagation mechanism. Therefore, if one wanted to guess at a mechanism of a gas-phase reaction, one would guess an initiation-propagation mechanism.

Let's look back at mechanism (5.3) and show that it follows an initiation-propagation mechanism. Reaction 1 in mechanism (5.3) is an initiation step. Reactions 2 and 3 are propagation steps. Reaction 4 is a termination step. Reaction 5 is the reverse of reaction 2. Clearly, mechanism (5.3) is an initiation-propagation mechanism.

Another important initiation-propagation reaction is the reaction that happens in the cylinders of your car. During the power cycle of your car, a mixture of air and gasoline is put into the cylinders of the car. Nothing happens until the spark plugs fire, producing radicals. Then the propagation reactions occur, producing power. Termination reactions include reactions with tetraethyl lead (TEL) or methyl *tert*-butyl ether (MTBE), and reactions that occur on the walls of the cylinders.

Table 5.1 Examples of initiation-propagation mechanisms

Reaction	Example Mechanism
Combustion, e.g., $\text{CH}_4 + \text{O}_2 \Rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{other products}$	$\text{O}_2 \rightleftharpoons 2\text{O}$ $\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$ $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$ $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3 + \text{O} + \text{O}$ $\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2 + \text{H}_2\text{O} + \text{other products}$ $\text{OH} \rightarrow \text{walls}$ $\text{CH}_3 \rightarrow \text{walls}$
Free-radical polymerization, e.g., ethylene \Rightarrow polyethylene with a free-radical catalyst, R_2	$\text{R}_2 \rightarrow 2\text{R}\cdot$ $\text{R}\cdot + \text{C}_2\text{H}_4 \rightarrow \text{R}(\text{C}_2\text{H}_4)\cdot$ $\text{R}(\text{C}_2\text{H}_4)\cdot + \text{C}_2\text{H}_4 \rightarrow \text{R}(\text{C}_2\text{H}_4)_2\cdot$ $\text{R}(\text{C}_2\text{H}_4)_n\cdot + \text{C}_2\text{H}_4 \rightarrow \text{R}(\text{C}_2\text{H}_4)_{n+1}\cdot$ $\text{R}(\text{C}_2\text{H}_4)_m\cdot + \text{R}(\text{C}_2\text{H}_4)_n\cdot \rightarrow \text{R}(\text{C}_2\text{H}_4)_{m+n}\text{R}$
Ozone depletion	$\text{O}_2 + h\nu \rightarrow 2\text{O}$ $\text{O} + \text{O}_2 + \text{X} \rightarrow \text{O}_3$ $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}$ $\text{Cl} + \text{O}_3 \rightarrow \text{O}_2 + \text{ClO}$ $\text{ClO} + \text{O} \rightarrow \text{O}_2 + \text{Cl}$
Hydrocarbon pyrolysis	$\text{X} + \text{CH}_3\text{COH} \rightarrow \text{CH}_3 + \text{COH} + \text{X}$ $\text{CH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CO} + \text{CH}_4$ $\text{CH}_3\text{CO} + \text{CH}_3\text{OH} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$ $\text{COH} + \text{X} \rightarrow \text{CO} + \text{H} + \text{X}$ $\text{H} + \text{CH}_3\text{COH} \rightarrow \text{CH}_4 + \text{COH}$ $\text{H} + \text{CH}_3\text{COH} \rightarrow \text{CH}_3 + \text{CO} + \text{H}_2$ $2\text{CH}_3 + \text{X} \rightarrow \text{C}_2\text{H}_6 + \text{X}$ $\text{H} + \text{CH}_3 + \text{X} \rightarrow \text{CH}_4 + \text{X}$ $\text{H} + \text{CH}_3\text{CO} + \text{X} \rightarrow \text{CH}_3\text{COH} + \text{X}$

Table 5.1 gives several other examples of initiation-propagation reactions. Readers should convince themselves that each of these reactions is an initiation-propagation mechanism.

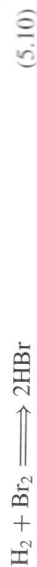
Most gas-phase reactions of neutral species go via initiation-propagation reactions.

In the literature, initiation-propagation reactions of gas-phase species are also called *radical reactions*, since the reactive species are radicals. They are also called *Rice-Herzfeld mechanisms* since Rice and Herzfeld were early proponents of the mechanisms.

6.4 PREDICTION OF THE MECHANISM OF INITIATION-PROPAGATION MECHANISMS

Next, we will discuss the prediction of the mechanism of simple gas-phase reactions. Our objective will be to develop some quantitative tools that one can use to predict the mechanisms of reactions.

To start, let's again consider the following reaction:



Our general scheme to predict the mechanism of these reactions will be to

- Guess or predict all of the species that are likely to form during the reaction.
- Write down all of the possible reactions of those species.
- Use various rules to pare down the list to manageable number of steps.

Generally the rules are that

- There must be at least one initiation reaction.
- The propagation reactions must occur in a cycle where radicals react to form new radicals and then the new radicals react to form the original radicals again.
- All of the steps in the catalytic cycle must have low activation barriers.
- There should be at least one termination reaction where two radicals react to form stable species.

Next, let us apply this scheme to predict a mechanism for reaction (5.10). For the sake of discussion, we will assume that HBr is the only product of the reaction, and that hydrogen and bromine atoms (i.e., radicals) are the only intermediates in the system. Under such circumstances, there are two possible initiation reactions:



The hydrogen atoms can react with each of the stable species in the system:





The bromine atoms can react with each of the stable species in the system:



The radicals can react with each other:



I also want to mention that years ago, people thought about the possibility of the reaction occurring via a four-centered complex:



They also considered reactions without collision partners, such as



Notice that reactions (5.11)–(5.24) are all of the possible reactions between H_2 , Br_2 , HBr , H , and Br . Therefore, the mechanism must involve *only* these elementary reactions.

Next, let's try to eliminate reactions. In Chapter 4, we noted that



Consequently, reactions (5.23) and (5.24) cannot occur.

In contrast, reactions (5.11)–(5.22) are perfectly good elementary reactions. There are two or more reactants and two or more products in each step, which means that in principle all of these reactions could occur. A more precise analysis shows that they *all* do occur at some rate. Therefore, in a sense, reactions (5.11)–(5.22) represent the complete mechanism at the reaction between H_2 and Br_2 .

The question is: Why did we say that reaction (5.2) follows mechanism (5.3) and not include reactions (5.11), (5.15), (5.17), (5.18), and (5.20)–(5.22)? This brings up a subtle point. When we say that reaction (5.2) follows mechanism (5.3), we are not saying that reactions (5.12)–(5.14), (5.16), and (5.19) are the only reactions that occur. Rather, we are saying that reactions (5.11), (5.15), (5.17), (5.18), and (5.20)–(5.22) occur so slowly that they have a negligible effect on the overall rate. More precisely, we can state that

The mechanism represents the principal route from reactants to products, but other reactions can, and do occur.

Now, the next question we want to address is: Could one have guessed the mechanism of reaction (5.2) without doing any experiments? The answer is "Yes". There are a series of empirical rules that one can use to tell you about the mechanisms of chemical reactions. One can often use those empirical rules to guess the preferred mechanism of a chemical reaction.

6.4.1 Empirical Rules to Predict Mechanisms of Gas-Phase Radical Reactions: Reactions to Include

There are two kinds of empirical rules: empirical rules to *exclude* reactions, and empirical rules to *include* reactions.

Let's start with the empirical rules to include reactions. Note that when one has an initiation–propagation reaction, there are certain requirements that one needs to satisfy to make the reaction happen. The first empirical rule is that

There must be at least one initiation reaction. (5.26)

I include this rule because students often forget that there must be an initiation step in any initiation–propagation reaction. Typically, the initiation step has a small rate. Consequently, students sometimes assume that the initiation step will not be important to the reaction. However, in practice, no reaction happens until the initiation step occurs. Earlier in this chapter, we noted that the reactions in the engine of your car follow an initiation–propagation reaction in which the initiation process is activated by the spark plugs. If you never fire the spark plugs and start the reaction, no reaction ever occurs. The same is true for any initiation–propagation reaction. Typically, the initiation steps have a much lower rate than do any other steps in the reaction mechanism. However, if one ignores the initiation step, one will never derive a correct rate equation.

You need to include at least one initiation step in every mechanism independent of whether the rate of the initiation reaction is small.

The next key requirement is

The propagation reactions must occur in a cycle where radicals react with the reactants to form new radicals and then the new radicals react to form the original radicals again. (5.27)

Requirement (5.27) is more complicated to understand, so let's go back to mechanism (5.3) and see what we mean. Notice that there are two propagation reactions in mechanism (5.3), which we have relabeled reactions (5.13) and (5.16). In reaction (5.16), a bromine atom reacts with H_2 to yield HBr plus a hydrogen atom. In reaction (5.13), a hydrogen atom reacts with a Br_2 to yield a second HBr and regenerate the original bromine atom. Consequently, one can view reactions (5.13) and (5.16) as a cyclic process where hydrogen atoms are created via reaction (5.16) and lost via reaction (5.13). Bromine atoms are created in reaction (5.13) and then lost via reaction (5.16).

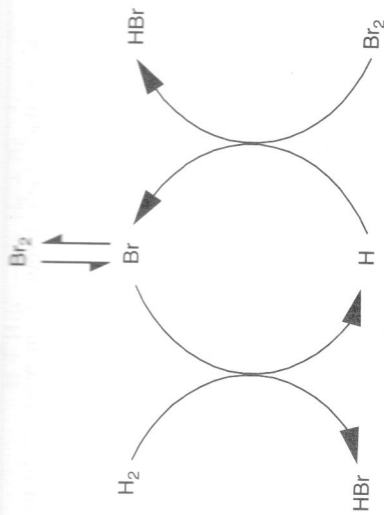


Figure 5.1 A cycle for HBr formation via reaction (5.3).

Figure 5.1 shows a pictorial representation of this mechanism. Figure 5.1 is a different representation of the mechanism than you are used to. In the figure, we label the key radicals and show how those radicals are formed and destroyed. Reactants and products are indicated by the ends of the arrows. Two arrows come together when a given pair of species react. The products of the reaction are indicated by arrows leading away from the encounter. For example, the curved arrows on the left of the figure indicate that H_2 is reacting with a bromine atom to yield a HBr and a hydrogen atom. This should be convinced that Figure 5.1 is a valid representation of the propagation steps for mechanism (5.3) before proceeding with this chapter.

Notice the cycle in Figure 5.1. Hydrogen atoms are formed and destroyed in a cyclic process. The cyclic nature of the propagation reaction is a key feature of initiation-propagation reactions. Radicals are very reactive species. Consequently, if one had a significant concentration of radicals in the system, one could produce a considerable amount of product by going around the cycle many times. Later in this book, we will refer to the cycle as a **catalytic cycle**. Catalytic cycles are key features of most reactions.

All kinds of cycles have been observed experimentally. One can have a simple cycle with only two radicals as shown in Figure 5.1 or a more complex cycle with eight intermediate species as shown in Figure 5.2. Still the key feature is that the cycle needs to loop back on itself (i.e., form the original intermediates) in order to produce a significant amount of product. For example, if one produced a chain of radicals and never got back to the original radicals, the reaction would go around the cycle once and stop. Relatively little product would be produced. In contrast, if the cycle loops back on itself, you can go around and around the cycle and produce lots of product. Consequently, cycles that loop back on themselves have a much higher net rate than do cycles that do not loop back on themselves. In actual practice, usually only cycles that loop back on themselves show appreciable steady-state rates. Noncyclic reactions are seen in laser photolysis, however. A related requirement is that

$$\text{All of the steps in the catalytic cycle must have low barriers.} \quad (5.28)$$

Again, in order to get much product, each of the steps in the catalytic cycle must have low barriers or else the cycle will be too slow. As a general rule of thumb, if you are

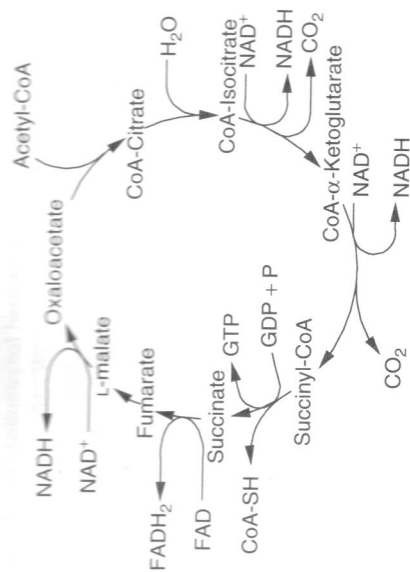


Figure 5.2 The tricarboxylic acid cycle. This cycle is the principal way that cells produce NADH. The NADH is subsequently used to convert ADP to ATP (adenosine diphosphate to adenosine triphosphate).

running the reaction at a temperature T , then the E_A , the activation barrier for each of the steps should satisfy

$$E_A < [0.07 \text{ (kcal-mol)/K}]T \quad (5.29)$$

to get a reasonable amount of product. Equation (5.29) tells you that if the propagation steps have high barriers, you need to run the reaction at high temperature to get a reasonable amount of product.

The last key requirement for an initiation-propagation mechanism is that:

$$\text{There should be at least one termination reaction where two radicals combine to yield stable species.} \quad (5.30)$$

Requirement (5.30) is different from requirements (5.26) and (5.27) because it says that there *should* be a termination reaction, not that there *must* be a termination reaction. There are some reactions where the termination reactions have extremely tiny rates. Still, if there were no termination reactions, radicals would build up in the system and could never be destroyed. Consequently, the system would have to get to steady state. Instead, the reactive mixture would explode. One can show that one can never get a steady-state reaction unless there is at least one termination reaction. Therefore, if one observes a steady-state reaction, there must be at least one termination reaction. One often sees several termination reactions.

Explosive reactions are exceptions. One can design a high explosive so that the substance explodes in the absence of a significant termination reaction. In actual practice, such systems are dangerous. However, they can be designed.

Industrially, however, one often adds something to a reacting mixture to enhance the termination reactions and thereby prevent unnecessary explosions. For example, in your car, people add octane enhancers [e.g., methyl t-butyl ether (MTBE) and tetraethyl-lead (TEL)] to better control the combustion process. The MTBE and TEL participate in termination reactions, so the fuel burns more smoothly. If you do not add MTBE, you get little explosions (knock), which tears your engine apart. In practice, one needs termination

Table 5.2 Key requirements for the mechanism for reaction $H_2 + Br_2 \rightarrow 2HBr$

Reaction	Requirement	Result
(5.26)	There must be an initiation reaction	Must include reaction (5.11) or (5.12)
(5.27)	Must have an catalytic cycle	Must include reaction (5.1) and (5.16)
(5.30)	There should be a termination reaction	Should include either (5.19), (5.20) or (5.21)

reactions to prevent explosions. That is why people add MTBE to gasoline. In practice, most reactions have termination steps, which is why we can state (5.28) as a requirement, even if it is not an absolute requirement.

Before we proceed, it is useful for the student to look back to Table 5.1 and verify that each of the conditions in Table 5.2 is obeyed for the reactions in Table 5.1.

Let's apply these rules to the HBr reaction. Requirement (5.26) (see Table 5.2) says that there must be an initiation reaction. If we apply requirement (5.26) to the HBr case, then we conclude that either reaction (5.11) or reaction (5.12) must occur during the reaction. Requirement (5.27) says that we must have a catalytic cycle to have an appreciable rate. If we apply requirement (5.27) to the HBr case, then we conclude that reactions (5.13) and (5.16) must be included in the mechanism. Requirement (5.30) says that there should be a termination step. If we apply requirement (5.30) to the HBr case, we conclude that either reaction (5.19), (5.20), or (5.21) should be included in the mechanism. Therefore, we know that the mechanism of HBr production must include reactions (5.13) and (5.16), and either reaction (5.11) or reaction (5.12), and either reaction (5.19) or reaction (5.20) or reaction (5.21). We do not know anything about reactions (5.14), (5.15), (5.17), (5.18), or (5.22).

5.4.2 Empirical Rules to Predict Mechanisms of Gas-Phase Radical Reactions: Reactions to Exclude

Next, we will provide some rules to exclude reactions from a mechanism. Generally, these rules are based on the fact that if the rate of a reaction is small enough, the reaction will have a negligible effect on the overall rate.

These rules are harder to apply because you must include at least one initiation reaction even though the initiation reaction has a low rate, and you must include at least one termination reaction even though the termination reaction has a low rate. Still, if there is more than one possible initiation reaction or termination reaction, one can use the rules in this section to choose the one that will be the most important.

The overall plan will be to estimate rate constants for reactions, and if a reaction has a small enough rate, exclude it. Generally, the methods in this chapter will let us determine rate constants to within only a few orders of magnitude. That is not good enough for detailed kinetics. However, it is good enough to eliminate reactions from mechanisms.

Our general approach will be to use various methods to estimate the activation barriers for reactions. We will eliminate all reactions that do not satisfy equation 5.29.

For the purpose of discussion we will assume that all of the reactions follow Arrhenius' law:

$$k_u = k_u^0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (5.31)$$

where k_u is the rate constant for the reaction, k_u^0 is the preexponential, E_a is the activation energy; k_B is Boltzmann's constant, and T is the absolute temperature.

Next, consider the initiation steps. The initiation steps, reactions (5.11) and (5.12), are called *unimolecular reactions*. We have a single reactant colliding with a collision partner to yield products. In Chapter 8, we will find that unimolecular reactions usually have a preexponential of about $10^{15 \pm 2} \text{ s}^{-1}$ /(molecule-second) independent of the details. Reactions (5.11) and (5.12) are both unimolecular reactions, and their preexponentials are very similar. Consequently, one could not distinguish between these two reactions on the basis of the preexponentials. The two reactions do, however, have quite different activation energies. To see that, we have to introduce our next empirical rule.

The activation energy for an initiation reaction, E_a^i can be approximated via

$$E_a^i = \Delta H_{A-A} + 1 \text{ kcal/mol} \quad (5.32)$$

where ΔH_{A-A} is the enthalpy change during the initiation reaction.

Let's use equation (5.32) to estimate the activation barriers for reactions (5.11) and (5.12). According to data in the Chemical Rubber Company Handbook (CRC) hydrogen has a bond energy of 103 kcal/mol while bromine has a bond energy of 45 kcal/mol. Therefore, according to equation (5.32), reaction (5.11) will have an activation barrier of about 104 kcal/mol while reaction (5.12) will have an activation energy of about 46 kcal/mol. If we plug back into equation (5.31), we find that at 800 K, reaction (5.11) will be a factor of 10^{15} slower than reaction (5.12). Reaction (5.11) is much slower than reaction (5.12). Therefore, little error will be created if we ignore reaction (5.11).

One can generalize the ideas in the previous paragraph to show

The most important initiation reaction will be the reaction that breaks the weakest bond in the reactants.

$$(5.33)$$

Physically, the weakest bond in the molecule is the easiest to break. Consequently, the weakest bond breaks first. There are some special cases where there are two bonds in the reactants that have almost the same energy. In those cases, both bonds break with reasonable rates. Still, such cases are exceptions. There is usually only one initiation step. During that step the weakest bond in the molecule breaks.

The implication of the discussion in the last paragraph is that while we have to include reaction (5.12) in the mechanism of HBr formation, we can ignore reaction (5.11).

Now, let's consider reactions (5.15) and (5.18), which are called **exchange reactions**. In an exchange reaction, one atom in a molecule is replaced by another identical atom in the same molecule. Exchange reactions often occur at a reasonably high rate. However, exchange reactions do not consume any reactants or radicals or produce any products. Consequently, they do not affect the overall rate of reaction. Therefore

Exchange reactions can be ignored when one is deriving a rate equation.

$$(5.34)$$

As a result, there is no reason to include reactions (5.15) and (5.18) in the mechanism of HBr formation. Physically, the reactions do occur at reasonably high rates. However, the reactions do not contribute to the formation of HBr. Therefore, they are not part of the mechanism of HBr formation.

Next, let's consider reactions (5.14) and (5.17), which are called **inhibition reactions**. In inhibition reactions, the products of the reaction react with a radical to produce a

reactant molecule. In the case of reactions (5.14) and (5.17), HBr reacts with a radical to produce either H₂ or Br₂. If one starts with the product and ends up with the reactants, one will definitely slow down the reaction, which is why reactions of this type are called "inhibition" reactions.

Now the question is whether we need to include reactions (5.14) and (5.17) in the mechanism. The answer is "Yes", provided that the reactions satisfy equation (5.29). According to data in the CRC, reaction (5.14) is 16 kcal/mol exothermic. The heat of reaction (5.14) on the basis of reaction (5.13). Consequently, there is no reason to exclude there is no reason to exclude reaction (5.14) on the basis of energetics, and we will see in the next paragraph that (5.17), however, is 40 kcal/mol endothermic. Consequently, if everything else is equal, one would expect reaction (5.17) to be much less important than reaction (5.14).

We can quantify the effect by using another empirical rule, called the **Polanyi relationship**, to estimate the difference in the rates of the two reactions. The Polanyi relationship was proposed by Polanyi and Evans to try to correlate activation barriers to reactions. According to the Polanyi relationship, E_a, the activation barrier for a given reaction, is related to ΔH_r, the heat of reaction, by

$$E_a = E_a^0 + \gamma_P \Delta H_r \quad (5.35)$$

where E_a⁰ is the intrinsic activation barrier and γ_P is the transfer coefficient. We will discuss the Polanyi relationship in detail in Chapters 10 and 11. Generally, E_a⁰ and γ_P vary with the reaction types and the shape of the bonds which form. One needs to consider these effects in detail, if one wants to predict an accurate value of the activation barrier. Fortunately, in Section 5.4.5, we will find it possible to get a rough approximation to the activation barrier if we assume that E_a⁰ is 12–16 kcal/mol for atom transfer reactions while γ_P is 0.2–0.5 for exothermic reactions and 0.5–0.8 for endothermic reactions. If we substitute into equation (5.35) with γ_P = 0.7, we find that reaction (5.17) should have an activation barrier of about 34 kcal/mol. By comparison, the same calculation shows that reaction (5.14) will have an activation barrier of only 6 kcal/mol. Both reactions have similar preexponentials. Clearly, at 400 K, reaction (5.14) will be much more important than reaction (5.17).

Still, in the homework set, we will ask the reader to show that if one loads HBr into the reactor and runs reaction (5.2) in reverse, one will need to include reaction (5.17). Actually, the HBr formation reaction is not very reversible. One needs to heat the system to almost 4000 K to get a reasonable conversion. Still, reaction (5.17) is important for the reverse reaction at 4000 K, even though it is not so important for the forward reaction at 400 K.

One can quantify this idea more carefully, using the material from Section 2.6. Generally, in order for an elementary reaction to have a significant rate, the activation energy for the reaction needs to be less than a critical value, E_a^{crit}, where

$$E_a < E_a^{\text{crit}} = \begin{cases} 0.07 \frac{\text{kcal}}{\text{mol} \cdot \text{K}} T & \text{for propagation reactions} \\ 0.15 \frac{\text{kcal}}{\text{mol} \cdot \text{K}} T & \text{for initiation reactions} \\ 0.05 \frac{\text{kcal}}{\text{mol} \cdot \text{K}} T & \text{for reactions in the catalytic cycle} \end{cases} \quad (5.36)$$

There are different values of the critical temperature for initiation and propagation reactions because initiation reactions have much smaller rates than do propagation reactions. Equation (5.36) allows you to tell whether a given reaction will be important at a given temperature.

According to equation (5.36), at 400 K we should include all reactions where E_a < (0.07 kcal/mol-K)(400 K) = 28 kcal/mol. On the previous page we found that Reaction (5.14) has an activation barrier of 6 kcal/mol while reaction (5.17) has a barrier of 34 kcal/mol. Reaction (5.14) satisfies equation (5.36) so it should be included at 400 K. Reaction (5.17) does not satisfy equation (5.36) at 400 K, so it should not be included at 400 K. Reaction (5.17) should be included at temperatures above 500 K, however.

At this point, we have eliminated reactions (5.11), (5.15), (5.17), and (5.18) from the mechanism of HBr formation and shown that we must include reactions (5.12)–(5.14) and (5.16).

Next, let's consider reactions (5.19)–(5.21), which are all termination reactions. According to rule, we know that we must have at least one termination reaction. The question is which one, and whether we need to have only one termination reaction or to include all three termination reactions. The question of which one is easy. There is another empirical rule:

One should include all termination reactions where the species produced in the initiation reaction combine to yield stable products. If there are transfer steps (defined later), one should include the species produced in the transfer steps, too.

$$(5.37)$$

In reaction (5.12), we produce bromine atoms, so we must include reaction (5.19) in the mechanism. It is not obvious whether to include reaction (5.20) and (5.21). Another empirical rule is that

Radical recombination reactions will usually have an activation energy of less than 2 kcal/mol

$$(5.38)$$

Thus, the rate constant for reactions (5.20) and (5.21) should be significant. One can, in fact, find conditions where reactions (5.20) and (5.21) are quite significant. Consequently, if I were guessing the mechanism of reaction (5.2), I would include reactions (5.20) and (5.21). However, when Bodenstein and Lund did experiments on HBr in 1906, they picked conditions where the hydrogen atom concentration was much less than the bromine atom concentration. In those special circumstances, the rate of reaction (5.19) is much larger than the rate of reactions (5.20) and (5.21). Consequently, it was acceptable to ignore reaction (5.20) and (5.21).

I want to note, however, that if you are predicting a mechanism, you are not going to know a priori that people are going to only want to take data under conditions where the hydrogen atom concentration is much less than the bromine atom concentration. Consequently, if one is asked to predict a mechanism, one should include reactions (5.20) and (5.21) even though under some conditions reactions (5.20) and (5.21) will not be important.

At this point, we have considered all of the reactions above except reaction (5.22). Reaction (5.22) is different from all of the rest in that it is a four-centered reaction.

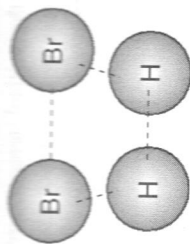


Figure 5.3 A stick diagram of a proposed transition state for reaction (5.22).

Many years ago, people used to talk about four-centered reactions. They would assume a transition state such as in Figure 5.3 and calculate properties. However 1965, Woodward Hoffman pointed out that a symmetric four-centered transition state is impossible with neutral molecules. We provide a detailed derivation of the rule in Chapter 10. However, the thing to remember for now is that in a symmetric four-centered transition state, one ends up trying to put four electrons into a single molecular orbital. That is quantum-mechanically forbidden. One can get sort of a four-centered transition state by first breaking two of the bonds. However, that is an energetically unfavorable process. Consequently

Four-centered transition states can be ignored when the reactants are neutral nonpolar molecules.

(5.39)

In summary, according to the rules in the last two sections, the mechanism of HBr formation must include reaction (5.12)–(5.14), (5.16), and (5.19) and probably should include reaction (5.20) and (5.21). If we look back to Bodenstein's mechanism of the reaction in equation (5.3), we see that we got the answer almost right. We predicted that all of the reactions which Bodenstein said occurs do occur. The only issue was that we included reactions (5.20) and (5.21), while in Bodenstein's original work [1906] these two reactions were ignored. Now it is hard to say that Bodenstein was wrong, since reaction (5.20) and (5.21) were not important under the specific conditions he considered. Still, I would include those two reactions in the mechanism since they are important under many conditions.

5.4.3 Additional Rules for More Complex Reactions

Next, we want to extend the ideas in the last two sections to more complex reactions. To keep this effort in perspective, note that we have spent several pages analyzing reaction (5.2), the formation of HBr, and believe it or not, reaction (5.2) was a particularly easy case. There were only two reactants. They were both diatomics, and all of the radicals were atoms. Anything else is going to be more difficult. Still, one can make useful predictions.

There are two general difficulties with extending these ideas to more complex reactions: (1) there are additional intermediates to consider and (2) there are many more reactions to consider. Let's talk about the issues of the number of intermediates first.

One of the problems with calculating the mechanism for a more complex reaction is that there are many more intermediates to consider. For instance, I have found that my chemical intuition is usually not able to predict all of the intermediates that could form. For example, let's consider the mechanism of HI formation:



HI formation is very similar to HBr formation, and so one might expect the mechanism of reaction (5.40) to be very similar to the mechanism of HBr formation [mechanism (5.3)]. In fact, however, an H_2I intermediate forms during reaction (5.40) while no similar intermediate is seen during HBr formation.

I cannot tell you a simple way to predict that the H_2I intermediate will be important during HI formation, even though the H_2Br intermediate is not important to HBr formation. One can calculate the stability of the intermediates using the quantum-mechanical methods discussed in Chapter 11. However, that is complicated. For now, my best advice is that if you are unsure whether an intermediate is stable, include it in the mechanism. The worst that will happen is that you will have some extra reactions to consider. However, if you are wrong, you will miss some key chemistry.

5.4.4 Intrinsic Barriers for Propagation Reactions

Once you know which intermediates are stable, you can start to predict mechanisms. The procedure is the same as in Section 5.4:

- Start with a guess of all of the intermediates in the system. Use quantum mechanics (Chapter 11) to verify that you are not missing any intermediates.
- Write down those intermediates.
- Use various rules to pare down the list of reactions.

The hard part is the last step. The general scheme is to use an empirical rule to estimate the activation barriers for each of the reactions in a mechanism. Earlier in this chapter, we presented three empirical rules to determine barriers to reactions: equation (5.32) for initiation reactions; equation (5.38) for termination reactions; and, a more general relationship, equation (5.35) for propagation reactions. According to equation (5.35), E_a , the activation barrier for a given reaction, is related to ΔH_r^\ddagger , the heat of reaction, by

$$E_a = E_a^0 + \gamma_P \Delta H_r \quad (5.41)$$

where E_a^0 is the intrinsic activation barrier and γ_P is the transfer coefficient. Equation (5.41) is the most important relationship in this chapter because it allows you to estimate an activation barrier for a given reaction from the heat of reaction. In this section, we will examine equation (5.41) in more detail to see how it can be used to produce mechanisms of reaction.

There are two terms in equation (5.41): an intrinsic barrier, and the transfer coefficient times the heat of reaction. The second term on the right side of equation (5.41), $\gamma_P \Delta H_r$, is easy to understand. This term is associated with the energy you gain or lose in converting the reactants into products. If you have an exothermic reaction, you gain energy as the reaction proceeds. The heat of reaction is negative, which means that, according to equation (5.41), the reaction is a little easier. In contrast, if you have an endothermic reaction, you lose energy as the reaction proceeds. The heat of reaction is positive, which means that, according to equation (5.41), the reaction is a little harder. There is a coefficient, γ_P , in propagation reactions. γ_P is usually between 0.3 and 0.7. Therefore, one does not get the full effect of the heat of reaction in equation (5.41). Still, there is the qualitative feature that exothermic reactions tend to be favored over endothermic reactions.

The intrinsic barrier in equation (5.41) is harder to understand. Physically, the intrinsic barrier provides a measure of the energy it takes to make the reaction happen if the heat of reaction were zero.

In order to get a physical picture of why intrinsic barriers arise, consider an example, the reaction



Reaction (5.42) is a simple reaction where a hydrogen atom approaches an ethane molecule and induces the carbon-carbon bond in the ethane to break.

If one looks at reaction (5.42) in detail, it is not at all obvious that the reaction would be activated. After all, one can imagine the reaction proceeding as in Figure 5.4. One starts off with a hydrogen and an ethane with a 88-kcal/mol carbon-carbon bond. During the reaction, the hydrogen comes up to the ethane and forms a partial carbon-hydrogen bond. Simultaneously, the carbon-carbon bond breaks. If one imagines that one has a partial carbon-hydrogen and a partial carbon-carbon bond, then one might imagine writing the bond energy of the system, E_{bond} , at any time during the reaction it:

$$E_{\text{bond}}(t) = E_{\text{H-C}}(t) + E_{\text{C-CH}_3}(t) \quad (5.43)$$

where $E_{\text{M-C}}(t)$ is the energy of the H-C bond at time t and $E_{\text{C-CH}_3}(t)$ is the energy of the carbon-methyl bond at time t .

If you have half of a carbon-carbon bond and half of a carbon-hydrogen bond, the E_{bond} comes out to be

$$E_{\text{bond}} = (0.5)(102 \text{ kcal/mol}) + 0.5(88 \text{ kcal}) = 95 \text{ kcal/mol} \quad (5.44)$$

According to this simple model, it seems that you have more total bond energy in the transition state than you do in the reactants, and this conclusion is verified by detailed quantum-mechanical calculations. Therefore, it is not obvious that reaction (5.42) is activated.

In fact, however, reaction (5.42) has an activation barrier of 44 kcal/mol. Lee and Masel [1996, 1997] examined the barriers to reaction (5.42) in some detail, and found that the main contribution to the barrier comes from the orbital distortions that occur during the reaction. During reaction (5.42), the 1s orbital in the hydrogen interacts with what is called the $3A_{1g}$ orbital on the ethane to induce the ethane's carbon-carbon bond to break. Diagrams of both orbitals are shown in Figures 5.5 and 5.6. In the figure, lightly colored lobes are used to designate positive orbitals, while darkly colored lobes are used to designate negative orbitals. When the hydrogen atom is far away from the ethane, the 1s orbital in hydrogen looks spherical, while the $3A_{1g}$ orbital has a central balloon-shaped orbital plus two kidney-shaped non-bonding lobes.

The $3A_{1g}$ orbital is constructed from a p orbital on each carbon plus some s orbitals on the hydrogens as indicated in Figure 5.5. The diagram on the left of Figure 5.5 shows

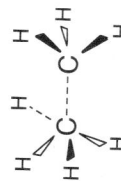


Figure 5.4 A stick diagram of the bonds during reaction (5.42).

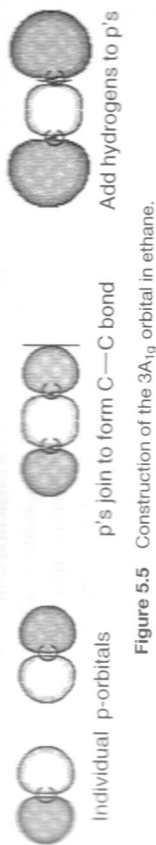


Figure 5.5 Construction of the $3A_{1g}$ orbital in ethane.

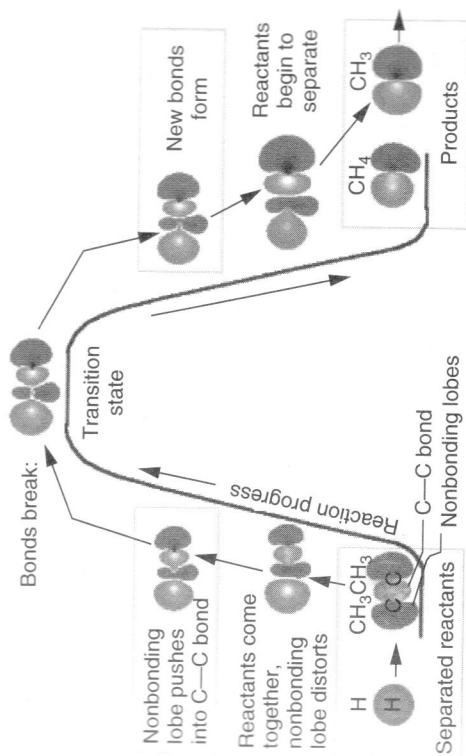


Figure 5.6 Orbital diagram during reaction (5.46) from Blowers and Masel (1999a,b).

what the p orbitals are like. The p orbitals have two lobes in a figure-eight configuration. One lobe of the p orbital has a positive sign. The other p orbital has a negative sign. I have shaded the positive orbital white in the figure while the negative orbital is shaded gray.

When the two carbon atoms come together to form a carbon-carbon bond, the two positive orbitals join to form a bond. The negative lobes stick out away from the carbon-carbon bond. The result is that the p orbital forms a carbon-carbon bond, plus two extra negative lobes. If one were forming C_2 , the orbitals would like the center diagram in Figure 5.5, with a C-C bond and two small negative lobes. However, in ethane, the hydrogens contribute electrons to the negative parts of the p orbital, causing the lobes to enlarge. The result is that the outer lobes of the $3A_{1g}$ orbital are larger than the bonding lobes. The outer lobe is kidney shaped, because we are showing a cross section where one of the hydrogens is in the plane while the other two hydrogens are out of the plane.

Now consider what happens when the hydrogen approaches the ethane. Figure 5.6 shows how the 1s and $3A_{1g}$ orbitals change when the hydrogen approaches the ethane. The 1s orbital on the hydrogen flattens out, while the kidney-shaped orbital on the ethane is pushed aside. I like to think about the orbitals as being two balloons. You know that when you push two balloons together, the balloons push apart. In the same way, the orbitals on the hydrogen atom and on the ethane push apart. This is really an electron-electron repulsion, moderated by bond distortion. Physicists call this a **Pauli repulsion**. It costs energy to overcome that repulsion. As a result, reaction (5.42) is activated.

The intrinsic barrier in equation (5.41) gives a measure of how much one needs to distort the orbitals to get reaction to happen. Generally, the intrinsic barrier is small (1–2 kcal/mol) for initiation reactions because one does not have to distort orbitals to

get the reaction to start. Similarly, in termination reactions, the lone pairs on the radicals form a bond during reaction. In those cases, the intrinsic barriers are also small. γ_p is approximately 1.0 for both initiation and termination reactions. In contrast, during a propagation reaction, one bond breaks and another forms. Figure 5.6 shows that one has to push the bonding orbitals out of the way before new bonds can form. It costs energy to push the orbitals out of the way. Consequently, propagation reactions generally have intrinsic barriers between 8 and 70 kcal/mol.

Next, we want to discuss how intrinsic barriers change as one changes the reaction. First, we want to note that there is a fundamental difference between transferring an individual hydrogen atom and transferring a molecular ligand. Let's go back to the ethane hydrogenolysis case mentioned earlier. If we ignore exchange, then there are two possible reactions which can occur when ethane reacts with a hydrogen atom. The carbon-carbon bond can break to yield methane:



or the incoming hydrogen can pick off a hydrogen atom from the ethane:



Lee and Masel [1996] found that reaction (5.45) has an intrinsic barrier of 45 kcal/mol while reaction (5.46) has an intrinsic barrier of 12 kcal/mol. Experimentally, only reaction (5.46) is seen.

It is important to consider why reaction (5.46) has a much lower intrinsic barrier than does reaction (5.45). When reaction (5.46) occurs, the hydrogen atom comes up along with the CH bond axis in the ethane. One has to distort the orbitals in the break in the C-H bond. However, the remaining orbitals in the ethane are largely unperturbed.

In contrast, when reaction (5.45) occurs, the hydrogen approaches the ethane along its C-C axis. The incoming hydrogen needs to push the C-H bonds in the ethane out of the way before any reaction can occur. That costs extra energy, so reaction (5.45) has a much higher intrinsic barrier than does reaction (5.46).

Lee and Masel [1996] showed that this extra barrier is associated with the energy to distort orbitals and not just the energy to move the C-H bonds. For example, the reaction



has almost the same intrinsic barrier as reaction (5.45) even though the hydrogen does not have to displace any atoms during reaction (5.47). The hydrogen does need to displace the lone-pair orbitals on the OH, however. This example shows that the intrinsic barriers are associated with orbital displacements and not just motions of individual bonds.

A key point is that it does not matter what molecular ligand one is transferring, one always sees intrinsic barriers of a similar magnitude. So for example, if we look at a series of radical transfer reactions such as



where R and R_1 are two hydrocarbon ligands one usually finds that the intrinsic barrier is between 40 and 60 kcal/mol independent of R and R_1 . In contrast, hydrogen transfer reactions of the form



Table 5.3 The intrinsic barriers for the exchange reaction

X	Intrinsic Barrier, kcal/mol
F	11
Cl	12.8
Br	10.8
I	9.7

Source: Results of Glukhoussev, Pross and Radom [1995].

have intrinsic barriers between 8 and 15 kcal/mol, independent of R and R_1 . If one looks in detail, one finds that the intrinsic barriers do depend slightly on R and R_1 . Typical variations in activation barriers are ± 5 kcal/mol. A 5-kcal/mol change in the barrier is sufficient to change the rate by a factor of 10^3 at 300 K. However, such a change is unimportant to the prediction of the reaction mechanism. Therefore, we will ignore those variations for the discussion in this chapter. These variations will be discussed in Chapter 11.

The other thing that one finds is that if one goes to stiffer orbitals, the intrinsic barriers rise. For example, Table 5.3 give the intrinsic barriers for a number of isotopic exchange reactions as reported by Glukhoussev et al. (1995). Notice that as one goes to stiffer atoms, the intrinsic barriers rise and then fall. Consequently, it is harder to transfer a stiff atom than a spongier one. The differences are only a couple of kilocalories, though.

Table 5.4 gives a selection of other intrinsic barriers and transfer coefficients for different types of reaction. The reader should refer to this table when predicting mechanisms of reactions.

Examples 5.A and 5.B show several examples to indicate how Table 5.4 is used to determine whether a certain mechanism is feasible. One should study those examples before proceeding with this chapter.

5.4.5 Extra Reactions with Larger Molecules

So far, we have been discussing reactions of simple diatomic molecules. Next, we want to discuss reactions of organic molecules containing several atoms.

Hyser (1970), Fossey, et al. (1995), Perkins (1994), and Alfassi (1999) offer good reviews of the reactions of organic molecules in the gas phase. Generally, most organic molecules follow mechanisms such as those we have already discussed, but, there are some extra reactions that can occur:

- Chain transfers
- Addition reactions
- Isomerizations
- Disproportionations
- Fragmentations
- β Scissions

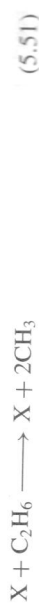
We will review each of these types of reaction next.

A *chain transfer reaction* is one where the initial step produces a simple radical, and then that radical reacts to form a new species before the catalytic cycle begins. Chain transfer is most important in a case where you produce one radical but another radical is more reactive.

For example, consider the reaction



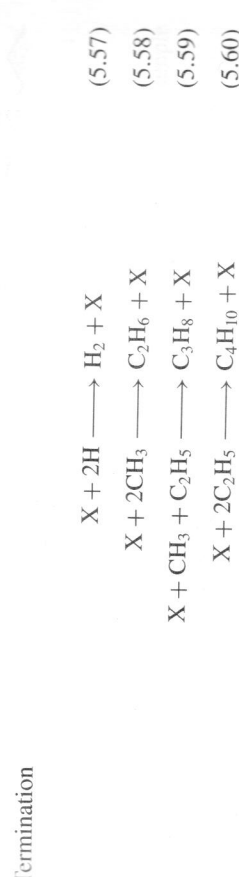
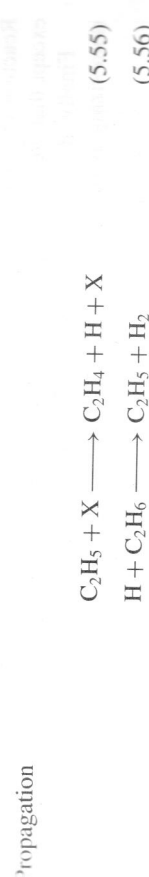
In Section 5.4.2, we noted that the weakest bond in the reactants usually breaks during the initiation step. Well, in ethane (H_3C-CH_3) the carbon-carbon bond is 11 kcal/mol weaker than any of the C-H bonds. Consequently, the carbon-carbon bond breaks during the initiation step.



In principle, the methyl radicals could react through a catalytic cycle to produce product. However, in the Examples 5.A and 5.B show that it is more likely that the methyl group reacts with ethane, to form an ethyl radical:



The ethyl radical is much more easily converted into the ethylene product. The reaction mechanism becomes



Reaction (5.52) is called a **chain transfer process**, since you convert one radical into another.

Table 5.4 Intrinsic barriers and transfer (coefficients for different types of reaction of neutral species).

Reaction	Example	Actual E_a^0 , kcal/mol	E_a^0 to Assume When Predicting Mechanisms, kcal/mol	Actual γ_p	γ_p to Assume when Predicting Mechanisms
Simple bond scission	$AB + X \rightarrow A + B + X$	0-1	1	1.0	1.0
Recombination	$A + B + X \rightarrow AB + X$ (X = a collision partner)	0-3	1	0.0	0.0
Atom transfer reaction $0 > \Delta H_r > -40$	$Rx + R_1 \rightarrow R + x - R_1$ (x = an atom)	8-16	12	0.2-0.6	0.3
Atom transfer reaction $0 \leq \Delta H_r \leq 40$	$R - x + R \rightarrow R + x - R_1$ (x = an atom)	8-16	12	0.4-0.8	0.7
Atom transfer reaction $\Delta H_r < -40$	$R - x + R \rightarrow R + x - R_1$ (x = an atom)	0-2	0	0	0
Atom transfer reaction $\Delta H_r > 40$	$R - x + R \rightarrow R + x - R_1$ (x = an atom)	0-5	2	0.9-1.0	1.0
Ligand transfer reaction to hydrogen	$H + R - R_1 \rightarrow HR + R_1$	40-50	45	0.4-0.6	0.5
Other ligand transfer reactions	$x + R - R_1 \rightarrow xR + R_1$ (x = an atom)	≥ 50	50	0.3-0.7	0.5
Endothermic β -hydrogen elimination	$RCH_2CH_2\cdot + X \rightarrow RCH=CH_2 + H\cdot + H$	12-25	15	0.5-1	0.7

5.4.6 Application to the Prediction of the Mechanisms of Reactions

Now, let's apply the findings in the last two sections to predict mechanisms of reactions. Lee and Masel (1997), and Broadbelt et al. (1994) have separately shown that one can use equation (5.41) to predict mechanisms of reactions. The idea is to follow the method described in Section 5.2. First, we postulate a series of possible intermediates, then look at all of the possible reactions of the intermediates, and use equation (5.41) to see which reactions are favored.

As noted previously

The most important initiation reaction will be the reaction that breaks the weakest bond in the reactants. (5.67)

One can derive equation (5.67) from equation (5.41) by noting that the intrinsic barrier for an initiation reaction is usually 1–2 kcal/mol and γ_P is about 1.0. ΔH_i for the scission of a weak bond is smaller than ΔH_i for scission of a strong bond. Consequently, according to equation (5.41), a weak bond will always be easier to break than a strong bond during the initiation step.

In contrast, during a propagation reaction, a weak bond may or may not be the easiest to break. For example, reactions (5.45) and (5.46) are both propagation reactions. Reaction (5.45) is 15 kcal/mol exothermic, while reaction (5.46) is only 8 kcal/mol exothermic. Consequently, on the basis of thermodynamics alone, one would expect reaction (5.45) to be favored over reaction (5.46). Note, however, that the intrinsic barrier to reaction (5.46) is 30 kcal/mol less than the intrinsic barrier reaction (5.45). That difference in intrinsic barriers is more than enough to overcome the difference in ΔH_i for the two reactions. Consequently, according to equation (5.41), one would expect reaction (5.46) to be favored over reaction (5.45).

Experimentally, reaction (5.46) has an activation barrier of 10 kcal/mol, while reaction (5.45) has never been observed. Lee and Masel calculate an activation barrier of 40 kcal/mol for reaction (5.45).

One can generalize this result to say that

During propagation reactions, if everything else is equal, it is usually easier to transfer atoms than to transfer molecular ligands. (5.68)

There are exceptions to equation (5.68) in cases where the differences in ΔH_i are large. However, equation (5.68) works about 98% of the time.

5.4.7 Example: Acetaldehyde Decomposition

Next, let's use the methods we have discussed so far to predict a mechanism for a simple gas reaction: the decomposition of acetaldehyde:



First, we note that this reaction is likely to go by an initiation–propagation mechanism. One cannot be 100% sure of that, but 99.9% of gas-phase reactions go by initiation–propagation reactions.

Another common reaction is called a β scission. Reactions (5.61) and (5.62) are examples of β -scission reactions.



In both cases, one breaks the σ bond at the β position from the radical, and forms a double bond with the β carbon. All β -scission reactions break σ bonds at the β position. β -Scission reactions are very common in the decomposition or combustion reactions of modest-sized molecules.

β Scissions are one example of a larger class of reaction called **fragmentation reactions**. Fragmentation reactions are reactions where a radical breaks apart to form a stable species and a new radical. For example



is a fragmentation reaction. Again, one forms a double bond that drives the reaction. The fragmentation reactions can also occur in reverse:



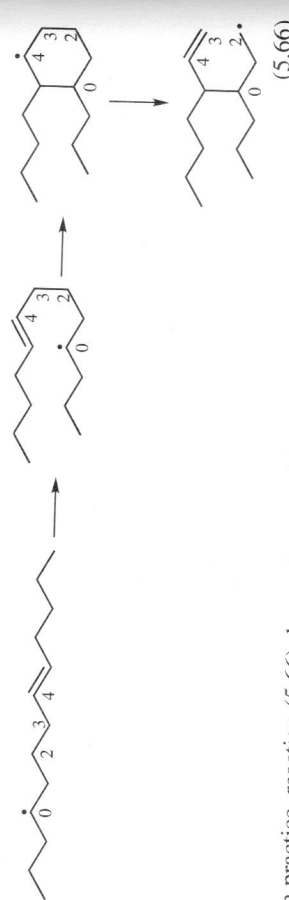
In this case, the radical adds across the double bond. Reaction (5.64) and the reactions where you add species to radicals are called **addition reactions**.

There is also the possibility of a **disproportionation reaction**. In a disproportionation reaction, two radicals react to form a stable species. For example, reaction (5.65) is a disproportionation reaction:



Reaction (5.65) is similar to the termination reactions discussed earlier in this chapter, except that we get two species as products instead of one.

Finally, if you have radicals with double bonds, there is the possibility of the radicals isomerizing as shown in equation (5.66):



In practice, reaction (5.66) does not occur with small molecules because the ring strain is too high. However, it can occur when there is a chain of five or more carbons. Therefore, it is called **five-centered isomerization**. This behavior gives a lot more reactions to consider when predicting a mechanism.

Next, let's try to predict the mechanism. According to rule (5.33), the first step in the mechanism will be a step where the weakest bond in the acetaldehyde breaks. According to the data in the CRC, the carbon-carbon bond is the weakest bond in acetaldehyde. Therefore, one would expect the initial step in acetaldehyde decomposition to be scission of the carbon-carbon bond



to yield a methyl group and a formyl group. Next, the methyl and formyls need to react via a catalytic cycle to produce the CO and CH₄ products, and to regenerate each of the radicals. For example, we might postulate that the methyl radical reacts with the acetaldehyde to produce methane. There are two possible reactions:



However, the H-C bond in the methyl group has a bond energy of 9 kcal/mol while the C-H bond in the formyl group has a bond energy of 96 kcal/mol. Reactions (5.71) and (5.72) have similar intrinsic barriers because both are atom transfer reactions. Therefore, one would expect reaction (5.71) to be slightly faster than reaction (5.72).

One can quantify these ideas as follows. First note that according to the CRC, the C-H bond in CH₄ has a bond strength of 104 kcal/mol.

Consequently, reaction (5.71) has a heat of reaction of $96 - 104 = -8$ kcal/mol, while reaction (5.72) has a heat of reaction of $99 - 104 = -5$ kcal/mol. One can calculate the activation barriers for both reactions from equation (5.35).

$$E_a[5.71] = 12 \text{ kcal/mol} + 0.3^*(-8 \text{ kcal/mol}) = 9.6 \text{ kcal/mol.}$$

$$E_a[5.72] = 12 \text{ kcal/mol} + 0.3^*(-5 \text{ kcal/mol}) = 10.5 \text{ kcal/mol.}$$

Therefore reaction (5.71) should be slightly faster than reaction (5.72), although both would likely occur at room temperature.

One might also consider the reaction



We analyze reaction (5.73) in problem 5.C. It has a high barrier so it is unlikely to occur.

In order to complete the cycle, we need the CH₃CO fragment to decompose to yield CO and regenerate the methyl group:



Similarly, the formyl (HCO) radical can react via a chain transfer process:



A second chain transfer process is



Analysis is given in Example 5.C.

One could also consider a closed cycle:



Reaction (5.78) has a high intrinsic barrier, but it is 19 kcal exothermic. Consequently, we need to do a calculation to see when to include it [we include it if equation (5.36) is satisfied].

The calculation is given in Example 5.C.

One also needs termination reactions. The following reactions are possible:



One then has to go back and use equation (5.41) to see which of these reactions are feasible. Reaction (5.80) is thermodynamically favored by 3.5 kcal/mol over reaction (5.79). Reaction (5.79) is a standard termination reaction, so it has an intrinsic barrier of 1-2 kcal/mol. Reaction (5.80), on the other hand, is a hydrogen atom transfer reaction. Hydrogen transfer reactions have intrinsic barriers of 10-14 kcal/mol. If one substitutes into equation (5.46) one finds that reaction (5.80) is unactivated. Therefore reactions (5.79) and (5.80) should both occur. Note however, that reaction (5.79) is required according to (5.37) while (5.80) is optional. Consequently, one would expect reaction (5.79) to predominate over reaction (5.80). A similar argument applies to reaction (5.83). At this point, we have considered reactions (5.70)-(5.83). There are no other alternatives or any other reactions. Consequently, reactions (5.70), (5.71), (5.76)-(5.79), (5.81), and (5.82) constitute the mechanism of acetaldehyde decomposition.

Benson analyzes this case in more detail and notes that at 700 K and 1 atm:

$$[\text{CH}_3] = 10^{-11.3} \text{ mol/liter}$$

$$[\text{CH}_3\text{CO}] = 10^{-13.6} \text{ mol/liter}$$

$$[\text{CHO}] = 10^{-14.6} \text{ mol/liter}$$

$$[\text{H}] = 10^{-17} \text{ mol/liter}$$

Therefore, Benson concluded under these conditions, reaction (5.81) is much faster than reaction (5.79), (5.80), (5.82), or (5.83). Reaction (5.79) is still required, however.

Benson's analysis can be generalized to any reaction. If one radical has a much higher concentration than the rest, then only that radical will matter to the termination reactions. In the literature, it has been proposed that one way to identify the most important termination reaction is to look at the catalytic cycle. If one reaction is much slower than all the rest, then the intermediates involved in that reaction will have the highest concentrations. Consequently, the most important termination reactions will be the reactions involving the intermediates participating in the slowest step in the catalytic cycle.

Unfortunately, that criterion is not easy to use. For example, in the acetaldehyde case, reaction (5.71) is exothermic while reaction (5.74) is endothermic. Reaction (5.71) is an

atom transfer reaction, so according to Table 5.4, reaction (5.71) should have a barrier of $12 + 0.3 \times (-14.8) = 7.6$ kcal/mol. In contrast, reaction (5.74) should have a barrier of $1 + 1.0 \times 11.3 = 12.3$ kcal/mol. Consequently, if everything else were equal, reaction (5.71) would be quicker than reaction (5.74).

In fact, however, reaction (5.74) has an unusually large preexponential, 10^{17} Å³/molecule-second). As a result, reaction (5.71) is slower than reaction (5.74) at high temperature. Under such conditions, CH₃ is the key intermediate so only reaction (5.81) matters. Still, I am not sure how you would know that the preexponentials were so different. (We discuss the preexponentials in Chapter 9.) Therefore, my advice is that if you have a case where the barriers are close, include all the termination reactions. That way you will be sure that you are right.

One can extend this analysis to many different reactions. More than 95% of the mechanisms of gas-phase reactions can be predicted by these procedures. I find it pretty easy to guess a mechanism of a gas phase reaction, if I know what kinds of intermediates are stable. In my experience, the hard part is deciding what intermediates and what initial group of reactions to consider. For example, is a species such as CH₂COH stable enough to form? If one can find a way to determine which species are stable, and what types of reactions to consider, one can predict the mechanism of the reaction using equation (5.46), assuming that the reaction occurs via an initiation-propagation mechanism.

5.5 GAS-PHASE REACTIONS THAT DO NOT FOLLOW INITIATION-PROPAGATION MECHANISMS

Next, we will discuss the gas-phase reactions that do not follow initiation-propagation mechanism. As noted previously, in 1932, Rice showed that all of the mechanisms of gas-phase reactions of hydrocarbons that had been studied before 1930 follow initiation-propagation mechanisms. However, since 1930, people have discovered a few gas-phase reactions that do not follow initiation-propagation mechanisms. In the next few sections, we will discuss gas-phase reactions that do not follow initiation-propagation mechanisms.

There are three groups of exceptions:

- Reactions where there is no feasible initiation-propagation mechanism from reactants to products
- Reactions where one of the steps in the catalytic cycle has a high barrier so that no reaction is feasible
- Reactions where concerted processes are possible

In the next several sections, we will discuss these exceptions.

5.5.1 Reactions with No Feasible Initiation-Propagation Mechanism

First, let's consider reactions where no initiation-propagation reactions is feasible. A key feature of the initiation-propagation reactions is that there is a catalytic cycle where radicals are formed and destroyed. If there is no catalytic cycle, one cannot have an initiation-propagation mechanism.

For example, Polanyi (1932) examined the reaction of sodium with chlorine in the gas phase:



Reaction (5.84) is special in that there is no initiation-propagation mechanism leading from reactants. For example, one can imagine a first step such as:



However, then what happens? If the chlorine atom reacted with the sodium atom, one would get stable NaCl and no radicals. There would be no catalytic cycle. As a result, this reaction cannot follow an initiation propagation mechanism. In fact, no one has found a catalytic cycle for reaction (5.84).

Polanyi (1932) showed that if you react Cl₂ with sodium dimers, the reaction does go via a catalytic cycle:



However, reaction (5.88) will not occur unless there are sodium dimers in the system. Polanyi showed that if there are no sodium dimers, the reaction goes by



In reaction (5.91), the chlorine atoms react with sodium atoms that are on the walls of the vessel.

This brings up an important point: if there is no catalytic cycle leading from reactants to products, then there will be no way for an initiation-propagation mechanism to occur. In such a case, the products must be formed by some other route: either a direct, concerted reaction between the reactants, as in step (5.90); or a wall reaction, as in reaction (5.91).

5.5.2 Association Reactions

One key class of reactions where no direct conversion is feasible are called association reactions. In an association reaction, two stable species come together to form products. For example, the reaction



is a simple association reaction, because two stable species come together to form products. It is easy to show that with an association reaction, there is no simple initiation-propagation mechanism leading from reactants to products. Consequently, the reaction must follow some other mechanism.

Usually, an association reaction will occur via a direct concerted process. For example, reaction (5.92) goes via



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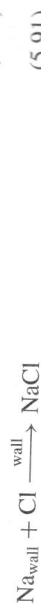


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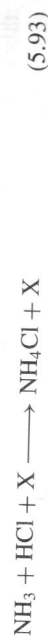
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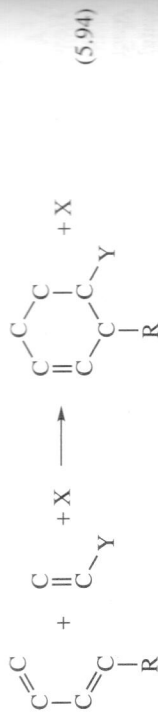
First, let's consider reactions where no initiation-propagation reactions is feasible. A key feature of the initiation-propagation reactions is that there is a catalytic cycle where radicals are formed and destroyed. If there is no catalytic cycle, one cannot have an initiation-propagation mechanism.

For example, Polanyi (1932) examined the reaction of sodium with chlorine in the gas phase:



No radicals are needed. In general, simple association reactions occur via concerted reactions. Initiation-propagation reactions seldom apply.

Another kind of association reaction is a Diels-Alder reaction:



Again, there is no initiation-propagation reaction leading from reactants to products, and so the reaction must occur via some other pathway such as a concerted addition. That is what occurs.

Generally, association reactions occur via concerted processes. Initiation-propagation reactions do not apply.

5.5.3 Reactions with High Barriers to Propagation Steps

In all of the reactions in Sections 5.4.1 and 5.4.2, one does not observe an initiation-propagation reaction because there is no feasible initiation-propagation mechanism leading from reactants to products. There are other groups of reactions, where there is a feasible initiation-propagation mechanism. However, one of the steps in the catalytic cycle has a high barrier. As a result, the catalytic cycle is slow; and most of the product molecules are produced by some other route. A key example is the *methane coupling reaction*:



Reaction (5.95) was first studied in 1919, but in 2000 people were still trying to determine a conclusive mechanism. In 1932, Kassel considered whether the reaction could occur via a simple initiation-propagation mechanism with an initiation step



with simple propagation cycle



and three termination steps:



However, Kassel found that this mechanism did not fit his data. There have been many arguments on this point. Hinshelwood showed that methane coupling could occur via this sequence of reactions. However, in practice, one does not produce much product via this route.

The cycle is so slow because there is a large barrier to reaction (5.98). Reaction (5.98) is the reverse of reaction (5.42), which was illustrated in Figure 5.4. Figure 5.4 shows that if you start with methane and methyls (i.e., the products in Figure 5.4), you need to distort the orbitals in the methane before the reaction can happen. Consequently, reaction (5.98) would be expected to have a large barrier. Lee and Masel [1996] calculate an activation barrier of 54 kcal/mol. The analysis in Example 5C gives 52.5 kcal/mol. Therefore, the catalytic cycle violates requirement (5.28). The reaction is never going to be fast enough to produce much product at a reasonable temperature.

What happens in practice is that the overall reaction is just really slow. You cannot get the catalytic cycle to occur at a reasonable rate. No other set of gas-phase reactions is feasible. Consequently, the reaction is slow unless you heat to 800 K.

5.5.4 Unimolecular Isomerization Reactions

The complications discussed in this section are particularly important to what I will call *unimolecular isomerization reactions*. A unimolecular isomerization reaction is a reaction where a single molecule rearranges to form a new product. Examples include



Many isomerization reactions proceed via initiation-propagation reactions. However, in reaction (5.102) there is no feasible initiation-propagation reaction leading from reactants to products. There is a possible mechanism for reaction (5.103), with an initiation step



a propagation step



and a termination step:



However, reaction (5.105) includes C-N bond scission, so it has a large intrinsic barrier. The reaction violates requirement (5.28). Consequently, the catalytic cycle for reaction (5.105) is not feasible.

Most isomerization reactions follow what is called the **Lindemann mechanism**. In the Lindemann mechanism, the reactants first collide with a collision partner to yield an excited species, and then the excited species reacts to form products. One can write the mechanism in a simple form as



Qualitatively, the mechanism in (5.107) can explain much of the data on unimolecular isomerization reactions. Experimentally, collision partners are needed to get unimolecular reactions to happen. Further, it has been shown that excited species are involved in the reaction process.

Table 6.6 Summary of the initiation-propagation mechanisms of radicals

Initiation step—weakest bond in reactants break to yield radicals; Must run at a temperature T satisfying $E_a \leq 0.15 \frac{\text{kcal}}{\text{mol}\cdot\text{K}} T$
Radical reacts via a catalytic cycle
Atoms transferred one atom at a time
Must be cycle
Include all reactions satisfying $E_a \leq 0.07 \frac{\text{kcal}}{\text{mol}\cdot\text{K}} T$
Should have a cycle satisfying $E_a \leq 0.05 \frac{\text{kcal}}{\text{mol}\cdot\text{K}} T$
Termination Step—radicals recombine
Exceptions: no catalytic cycle where atoms are transferred one atom at a time

6.6 SUMMARY OF INITIATION-PROPAGATION MECHANISMS

Table 5.5 summarizes the key requirements for initiation-propagation mechanisms. First, there is an initiation step where the weakest bonds in the reactants break to yield radicals, and the radicals react via a catalytic cycle where atoms are transferred one at a time, and the cycle leads back to the original radicals. Then there are termination steps. There are a few reactions that do not follow these general rules. Still, one can use the rules in Table 5.5 to predict mechanisms of a wide variety of gas-phase reactions, and be right 99% of the time.

I find it pretty easy to guess a mechanism of a gas-phase reaction, if I know what kinds of intermediates are stable. In my experience, the hard part is deciding what intermediates and what initial group of reactions to consider. For example, is a species such as CH_2COH stable enough to form? If one can find a way to determine which species are stable, and what types of reactions to consider, one can predict the mechanism of the reaction using the methods in this chapter.

Still, I have to admit that students find the prediction of mechanisms rather difficult. I think that the issue is partly information overload. In order to predict a mechanism, you need to know what the relative strengths of bonds are like, and what types of radicals can form. There is the trial-and-error procedure, where one guesses at a mechanism and then plugs into equation (5.46) to see if the mechanism is feasible. The only thing that I have to say about this is to stick with it. First, examine the solved examples, and convince yourself that the rules work for these reactions. Next, go back to all of the reactions mentioned so far in this chapter. First consider all of the reactions in Table 2.1. Label each step. Is it an initiation step or a propagation step? Is the step an association reaction, a β -hydride elimination...? Estimate the barrier for each step to see if the reaction follows equation 5.36. Then consider possible side reactions, and ask which side reactions are feasible. Finally try to predict the main reaction pathway. In my experience, most students learn to predict mechanisms, if they work at it.

5.7 REACTIONS OF IONS

At this point, I want to change topics and start to look at other classes of reactions. So far, the discussion in this chapter has focused on the reactions of neutral species. However, next, we will discuss the reactions of ions.

Still, mechanism (5.107) is too simple. If you look at reaction (5.102) in detail, you find that several excited states of cyclopropane contribute to the reaction. When the cyclopropane collides with a collision partner, the cyclopropane goes into one of the excited states. Then that excited state reacts to form a second excited state. Eventually, the excited state decomposes into products. It is not unusual for 20 excited states to be important to a unimolecular isomerization reaction. The result is a complex reaction network, even though the reaction appears simple.

5.5.5 Concerted Eliminations

A larger molecule also shows extra complications in the reaction path; there may be some extra pathways in addition to the standard initiation-propagation steps. For example, during butane pyrolysis, the initiation step is the scission of a carbon-carbon bond:



However, a competing process is a concerted hydrogen elimination.



Concerted reactions, where you break two or more bonds simultaneously, have high intrinsic barriers. For example, reaction (5.109) has an intrinsic barrier of about 60 kcal/mol. By comparison, reaction (5.108) has an intrinsic barrier of less than 2 kcal/mol. At first, one might think that it is obvious that reaction (5.108) will predominate. However, note that reaction (5.108) is 80.6 kcal/mol exothermic while reaction (5.109) is only 22.4 kcal/mol endothermic. Therefore, one does have to consider whether the difference in the heats of reactions is sufficient to overcome the difference in intrinsic barriers. If you plug into equation (5.41), you find that the answer is "No". Besides, reaction (5.109) does not produce any radicals, so you will not get a catalytic cycle. Still, in the literature, people discuss the concerted elimination processes in great detail, and say that there are cases where the concerted eliminations dominate.

In my experience in the gas phase, it is usually okay to ignore the concerted eliminations if one is considering only small molecules with no fluorines or chlorines. Under such circumstances, one can predict mechanisms easily. Large molecules are harder to consider because there are so many reactions and concerted eliminations occur. The result is a very complex reaction pathway. You need a computer to keep track of it.

The one place where there is some reasonable evidence for concerted eliminations is the reactions of chlorinated or fluorinated molecules. For example, Swihart and Carr (1998) examined decomposition of dichlorosilane and suggested that the primary initiation step is



At first sight, this reaction would not be expected to occur, because of the large barriers. However, the hydrogen in HCl is ionic. Later in this chapter, we will find that the reactions of ionic species have much lower intrinsic barriers than do the reactions of neutral species. The ionic transition state allows reaction (5.110) to occur.

Generally, one observes concerted eliminations only with chlorine and fluorine, and even then the concerted elimination process occurs only in the initiation step of the mechanisms.