

Table 5.5 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 $E_a \leq 0.15 \frac{\text{kcal}}{\text{mol}} \cdot T$
Radical reacts via a catalytic cycle
Atoms transferred one atom at a time
Must be cycle
Include all reactions satisfying $E_a \leq 0.07 \frac{\text{kcal}}{\text{mol}} \cdot T$
Should have a cycle satisfying $E_a \leq 0.05 \frac{\text{kcal}}{\text{mol}} \cdot T$
Termination Step—radicals recombine
<i>Exceptions:</i> no catalytic cycle where atoms are transferred one atom at a time

5.6 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. Then 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.

Table 5.6 Some examples of ion reactions

Reaction	Simplified Mechanism	Typical Application
Isomerization $\text{CH}_3\text{CH}_2\text{CH}=\text{H}_2$ $\xrightarrow{\text{H}^+} \text{CH}_3\text{CH}=\text{CHCH}_3$	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}^+ \rightarrow$ $[\text{CH}_3\text{CH}_2\text{CH}^+\text{H}-\text{CH}_2] \rightarrow$ $\text{CH}_3\text{CHC}=\text{CHCH}_3 + \text{H}^+$	Octane enhancement, monomer production
Cracking $\text{C}_{10}\text{H}_{20} \xrightarrow{\text{H}^+} 2\text{C}_5\text{H}_{10}$	$\text{C}_{10}\text{H}_{20} + \text{H}^+ \rightarrow [\text{C}_{10}\text{H}_{21}]^+ \rightarrow$ $\text{C}_5\text{H}_{10} + \text{C}_5\text{H}_{11}^+$ $\text{C}_5\text{H}_{11}^+ \rightarrow \text{C}_5\text{H}_{10} + \text{H}^+$	Crude-oil conversion, biological conversions
Alkylation $\text{CH}_3\text{OH} + \text{C}_6\text{H}_6 \xrightarrow{\text{H}^+}$ $\text{CH}_3\text{C}_6\text{H}_5 + \text{H}_2\text{O}$	$\text{CH}_3\text{OH} + \text{H}^+ \rightarrow \text{CH}_3^+ + \text{H}_2\text{O}$ $\text{CH}_3^+ + \text{C}_6\text{H}_6 \rightarrow \text{CH}_3\text{C}_6\text{H}_6^+$ $\text{CH}_3\text{C}_6\text{H}_6^+ \rightarrow \text{CH}_3\text{C}_6\text{H}_5 + \text{H}^+$	Pharmaceutical production, monomer production, fine chemicals
Esterification $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} \xrightarrow{\text{H}^+}$ $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$	$\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$ $\text{CH}_3\text{OH} + \text{H}^+ \rightarrow \text{CH}_3^+ + \text{H}_2\text{O}$ $\text{CH}_3^+ + \text{CH}_3\text{COO}^- \rightarrow$ $\text{CH}_3\text{COOCH}_3$	Soap production, fragrance production

Table 5.6 gives some examples of important ionic reactions, including isomerization, cracking, alkylation, and esterification. *Isomerization* is a process where one takes a molecule and rearranges it. *Cracking* is a process where you take a big molecule and break it into two smaller molecules. *Alkylation* is the opposite of cracking, where you take two molecules and combine them into one bigger molecule. *Esterification* is a special case of alkylation where you combine acids and alcohols to form soaps or detergents. These four reactions represent more than \$400 billion of yearly production, so they are certainly quite important.

Most ionic reactions occur in solution or on solid catalysts. However, ionic reactions are also seen in certain other systems such as plasma reactors and mass spectrometers. In this section, we will discuss the reactions of ions in the gas phase. Reactions in solution will be briefly mentioned in Section 5.9.

First, it is important to note that the reactions of ions are not fundamentally different from reactions of neutral species. The reactions often proceed via an initiation-propagation mechanism, where first the ions are formed, then the ions react through a catalytic cycle, and finally ions are neutralized. However, there are some important differences, as outlined in Table 5.7.

In practice, many ionic reactions are run in solution, and in solution reactions do not necessarily follow a catalytic cycle. For example, in an $\text{S}_{\text{N}}1$ reaction, you form an ion and it reacts, but there is no catalytic cycle reforming the initial ion. Instead you feed the ions into the solution.

Industrially, most ionic reactions do follow catalytic cycles, as do most ionic reactions in biology. Thus, although there are some exceptions, the majority of important ionic reactions follow catalytic cycles.

For example, the dehydration of ethanol



Table 5.7 Key differences between ionic reactions and radical reactions

Radical Reaction	Ionic Reaction
Most follow initiation-propagation reactions	Many follow initiation-propagation reactions, but several do not
Bonding like that in stable molecules; intermediates have structures similar to those in stable molecules	Species often have three-centered two-electron bonds
Atom transfer reactions predominate	Isomerization and cracking can go with modest barrier
Intrinsic barriers determined by Pauli repulsions between the reactants	Pauli repulsions small for bare ions; intrinsic barriers determined by interactions in the solvent cage (hard to predict)
Preferred mechanisms easy to predict	Preferred mechanisms hard to predict; determined by solvents and other protecting groups

goes by the following mechanism in the presence of HCl. First, the acid dissociates, yielding protons (i.e., H^+) and chloride ions:



Then the protons react with the ethanol to yield a charged complex:



Then the charged complex decomposes, yielding a water and an ethyl cation:



Then the ethyl cation decomposes, yielding ethylene and the proton:



Finally, the proton can recombine with chlorine:



There is one subtle point—it is hard to form ions in the gas phase. One often uses electrons to produce ions. So, for example, one could replace reaction (5.112) by



where e^- is an electron.

Reaction (5.112) is a classic initiation reaction. Reactions (5.113)–(5.115) are classic propagation reactions. Reaction (5.116) is a classic recombination reaction. Therefore, there are some similarities between reactions of ions and reactions of radicals. Still, one finds that the actual individual steps are quite different with ions than with radicals. Consequently, even though both radicals and ions follow initiation-propagation

reactions, the products of ion-molecule reactions are quite different than the products of radical-molecule reaction.

For example, in Section 5.4.4 we noted that there are two key reactions when a deuterium reacts with ethane, an exchange reaction:



and a dehydrogenation:

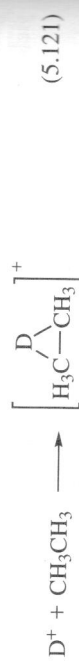


In principle, one might also see bond scission:



However, reaction (5.120) has never been observed experimentally.

If one instead runs the reaction with D^+ , the main reactions are



In reaction (5.121), one forms a complex with a three-centered two-electron bond, while in reaction (5.122), the species decomposes to yield deuterated methane and methyl radicals. Li et al. (1989) examined these reactions with a molecular beam and found that reaction (5.121) had an activation barrier of zero while reaction (5.122) had an activation barrier of less than 2 kcal/mol. Computations by Carnero (1994) suggest that both reactions are unactivated as is loss of H_2 from the complex. By comparison, Lee and Masel (1996) calculated that reaction (5.120) has an activation barrier of 45 kcal/mol.

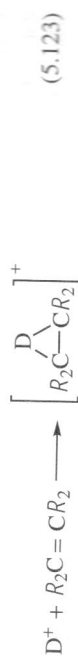
This example illustrates two key differences between the reactions of ions and those of neutral species: (1) species with unusual bonding configurations are stable and (2) the activation barriers for reactions of ions are quite different from the activation barriers of neutral species.

The fact that the activation barriers change greatly can be easily understood in light of ideas presented in Section 5.4.5. In Section 5.4.5, we found that the activation barrier for reaction (5.120) was associated with a repulsion between the electrons in the incoming deuterium and the electrons in the ethane, causing the balloonlike orbitals to flatten out. In fact, if one replaces the deuterium with a D^+ , there will be no electrons on the D^+ , so there will be no repulsions. As a result, the reaction is not activated. Consequently, positive ions are much more reactive than neutral radicals.

The absence of electrons also allows the unusual bonding in the intermediates to occur. As noted above, when a D^+ reacts with an ethane, the deuterium ends up in a three-centered two-electron bond. At first, this may seem to be a very strange bonding configuration. However, if you think about it a little bit, you will realize that there is no place else that the deuterium can go. A bare deuterium has a huge electron affinity, 13 eV (325 kcal/mol), so there is a huge driving force for the deuterium to

grab onto an electron. An ethane has all of its normal bonding orbitals filled. However, with a 13-eV driving force, the incoming hydrogen will form a bond somewhere. The incoming deuterium craves electrons, and the richest source of electrons in ethane is the C-C bond. One could imagine the deuterium instead bonding to a single methyl group. However, that is a much less electron-rich environment than the carbon-carbon bond. Therefore, the most likely place for the D^+ to react is along the carbon-carbon bond. Consequently, when a deuterium reacts with an ethane, one would expect the D^+ to form a three-centered two-electron bond as is observed.

One can extend these arguments to the reaction of olefins. For example, consider the reaction of a D^+ with a substituted ethylene. The carbon-carbon double bond on the ethylene is a very rich source of electrons, so that initially the D^+ will react to form a three-centered two-electron complex:



In other words



It is not obvious that the species in equation (5.124) is stable. Other possibilities include an ion with charge on one center:



or a species where the R groups have migrated:



Experimentally, when $R = H$, species (5.124) is the most stable; when $R = CH_3$, species (5.125) is the most stable; however, when $R = C_5H_6$ the species in (5.126) is the most stable. For the analysis here, it is not really important to know which of these species is the most stable. However, the key thing is that the ions can exist in several isomers, including an isomer where one species bridges between two carbon centers. Further, there are hardly any barriers to convert one isomer into another because there are no Pauli repulsions.

Now those two factors lead to interesting chemistry. There are two key types of reaction that usually happen only with ions: cracking and isomerization. **Cracking** is a reaction where one starts with a heavy hydrocarbon and breaks up the hydrocarbon into smaller fragments. The actual reaction involves a series of carbon-carbon bond scission processes like those in equations (5.120) and (5.122).

Notice that such reactions will occur with low barriers if the species are positively charged. In contrast, high barriers will be seen with neutral species. Therefore, if one

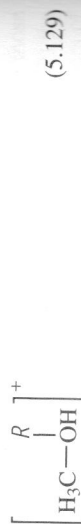
wanted to crack a hydrocarbon, one would run the reaction under conditions where a positive ion would form.

Similarly, **isomerization** is a process where one takes a ligand (i.e., an R group) and moves it around a molecule. With an ion, one can form a bridging intermediate like that in equation (5.126), so isomerization is easy. On the other hand, with a radical, the bridging species is unstable. Consequently, isomerization reactions have much lower barriers with ions than with radicals.

5.7.1 The Mechanisms of Reactions of Carbocations

Next, I want to talk about the detailed mechanism of the reactions of carbocations. A carbocation is a positively charged hydrocarbon ion. Examples include $C_3H_7^+$ and $C_3H_9^+$. Carbocation chemistry has been studied in great detail in solutions and in solid catalysts. The reactions have been less heavily studied in the gas phase. Generally, the reactions of carbocations are fairly complex. There are many intermediates and very many interconnecting reactions. Many of the species have unusual bonding. I generally find it difficult to predict the stability of the various species. Consequently, it is slightly harder to make detailed predictions of the reaction pathways of the ions than to predict reaction pathways of radicals. Still, as we will see, the analysis is easy provided you know what intermediates can form.

To start off, it is useful to review some of the literature. Martens and Jacobs (1990) and Vogel (1985) point out that there are two key types of carbocations that one can consider: carbonium ions and carbenium ions. **Carbonium ions** are formed by adding a H^+ or a R^+ to a paraffin. Examples of carbonium ions include



Years ago, people perceived carbonium ions as having five coordinated carbon atoms, three coordinated oxygen atoms, and fairly localized charges. However, people now know that there are bridging species and that the charge is distributed throughout the molecule.

Carbenium ions are formed by adding a H^+ or a R^+ to a double bond or the removal of a proton from a paraffin. Examples of carbenium ions include



Carbonium ions often have three coordinated carbon atoms. However, there are also bridging species and cyclic structures.

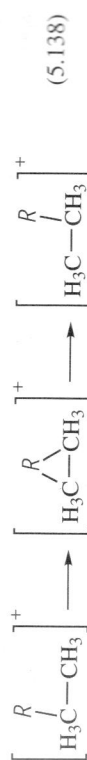
Generally, carbonium ions react via two pathways: cracking and isomerization. During cracking of a carbonium ion, a proton reacts with a paraffin to form a bridging species:



Then the bridging species decomposes to yield a smaller hydrocarbon fragment and a carbonium ion:



Isomerization of carbonium ions occurs when a linear carbonium ion rearranges to form a bridged species and then goes back to a linear species:



Carbonium ions can also crack and isomerize. In the gas phase, reaction (5.138) has an intrinsic barrier of less than 4 kcal/mol, which makes the reaction very rapid. Cracking occurs via β -scission, where the bond between the α carbon and the β carbon breaks to yield an olefin and a smaller carbenium ion:

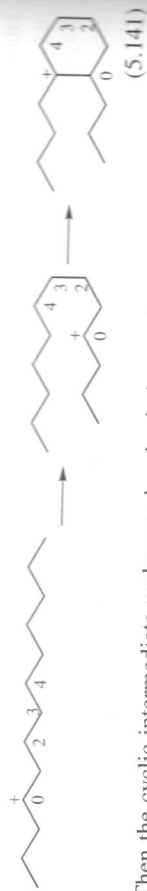


There are two pathways for isomerization: a standard 1,2 shift, where an R group migrates to an adjacent site; and a reaction where a cyclic intermediate forms. Reaction (5.140) is an example of a 1,2 shift:



Notice that the R group shifts to the right. These 1,2 shifts are the primary isomerization route with a small hydrocarbon. With a modest-sized hydrocarbon, one also sees

isomerization via cyclic intermediates. First the molecule reacts to form a cyclic intermediate as shown in equation (5.141):

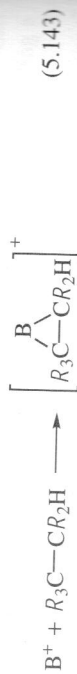


Then the cyclic intermediate undergoes bond scission as shown in reaction (5.142):



One can also stop reaction (5.142) at the first step to yield a cyclic product. In gas-phase reactions (5.140)–(5.142) are extremely rapid and often reach equilibrium in a very short time. In a solvent, the reactions are a little slower because you need to move solvent molecules out of the way. In the latter case, the intrinsic barriers to reaction are associated with motions of the solvent molecules, and not the intrinsic barriers to rearrangements of the reactants.

Carbenium ions can also participate in alkylation reactions, where a carbenium ion B^+ reacts with a paraffin or olefin to yield a carbonium or carbenium ion:



The carbonium or carbenium ion can then lose a proton to yield a higher-molecular-weight species:



There are many combinations here. One can form a cyclic product, and then isomerize the product to form a larger ring. One can then undergo bond scission to yield a myriad of products.

For example, Figure 5.7 shows some of the reactions of tridecylcation ($C_{13}H_{25}^+$). Only sixteen reactions are shown in the figure. However, Martens and Jacobs actually found 70 total reactions. In the top reaction in the figure, the molecule starts out with the charge centered on the carbon atom labeled zero in the figure. During the reaction, the molecule pivots around the 2 carbon, bringing the 0 carbon and the 3 carbon in close proximity. Then a bond forms between the 0 carbon and the 3 carbon, forming a four-centered ring. A proton migrates, moving the charge.

Then the ring opens again. The other reactions on the page are similar, except that different size rings form. This example illustrates the complexity of ion reactions. Table 5.8 shows the products of the reaction. Note that there are 12 main products and at least 70 reactions in the reaction network. Consequently, the mechanism is rather complex. One thing that people do know is that the stability of the ions varies with the degree of branching. For example, Table 5.9 shows the heat of formation of several $C_{10}H_{21}^+$

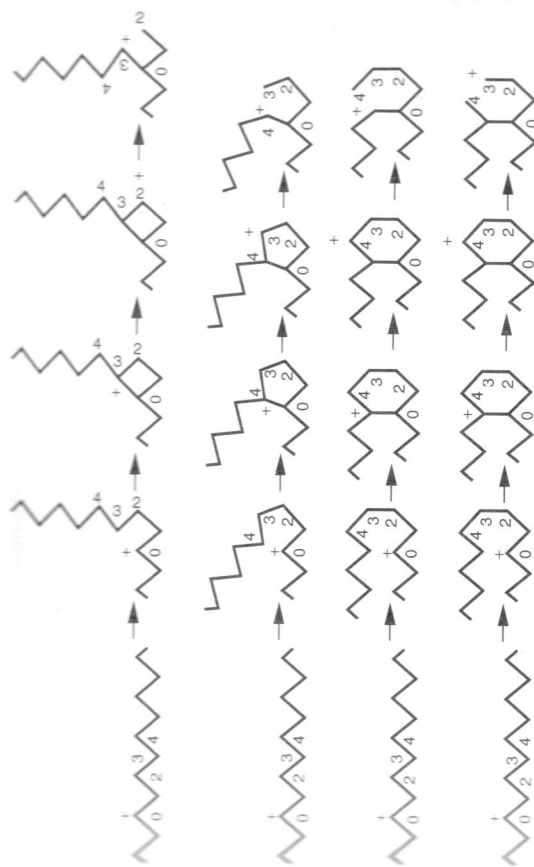


Figure 5.7 Some of the reactions of a tridecylcation. [Adapted from Martens and Jacobs (1990)].

Table 5.8 The products of tridecylcation ($C_{13}H_{25}^+$) isomerization in different environments

Species	Production in the Gas Phase	Production in Platinum/CAY Zeolite Catalyst		Production in Platinum/USY Zeolite Catalyst
		Platinum/CAY Zeolite	Platinum/USY Zeolite	
2-Methyldodecane	9.3	7.0	11	
3-Methyldodecane	17.7	15.1	17.9	
4-Methyldodecane	19.0	18.4	18.0	
5-Methyldodecane	19.1	22.8	19.6	
6-Methyldodecane	19.1	23.4	19.4	
3-Ethylundecane	2.7	1.9	2.7	
4-Ethylundecane	3.4	3.4	3.4	
5-Ethylundecane	3.9	3.6	3.9	
4-Propyldecane	2.2	2.0	2.2	
5-Propyldecane	1.0	0.7	1.0	
5-Propyldecane	1.8	1.4	1.8	
5-Propyldecane	0.7	0.3	0.7	

Source: Results of Martens and Jacobs [1990].

ions. Notice that the branched ions are more stable than the linear ions. Consequently, at equilibrium, one would expect to form highly branched species. You remember from organic chemistry that in small molecules, a primary ion is less stable than a secondary ion, which is less stable than a tertiary ion. That rule also works from a simple ion. With a more complex ion, it is easier to think about the ion stability in terms of Brauman and Blair's (1971) model, where you view the stabilization of the ion, as an interaction between the charged site and the polar stable alkyl groups. The more alkyl groups you get near the charged site, the more the charge will be stabilized. One can get alkyl groups next to the

Table 5.9 The relative stability of some $C_{10}H_{21}^+$ intermediates

Intermediate	Heat of Formation, kcal/mol	Intermediate	Heat of Formation, kcal/mol
1-Butyl cation	+138	2-Methyl-2-butyl cation	-12
2-Methyl-1-propyl cation	+130	2-Methyl-2-pentyl cation	-19
2-Butyl-cation	+67	3-Methyl-3-pentyl cation	-19
2-Methyl-2-propyl cation	0	2,3-Dimethyl-2-pentyl cation	-21

Source: After Martens and Jacobs (1990).

charged site by moving from a primary to a secondary to a carbocation. However, one can also stabilize charge by making the alkyl groups more polarizable, or by adding long chains that can coil up to bring the ends of the chains in close proximity to the charged center. In my experience, it is not so easy to predict the relative stability of carbocations because of chain coiling. However, Martens and Jacobs (1990) show that if one knows the stability of the ion, one can sometimes predict the products of the carbocation reaction from equilibrium. See Martens and Jacobs for details.

5.8 PREDICTION OF THE MECHANISM OF IONIC REACTIONS

Next, we will be discussing the prediction of the mechanism of gas-phase ionic reactions. Generally, it is pretty easy to guess the mechanism of an ionic reaction in the gas phase, provided the key intermediates are known. For example, let's start with the reaction



We would expect that the first step would be the formation of a carbenium ion:



Then the species could undergo a series of isomerization and cracking reactions as indicated in Figure 5.8. As with radicals, the first step in predicting a mechanism is to write down all of the reactions that could occur. One then does calculation using equation (5.41) to see which reactions can occur. Generally, with a carbenium ion, the intrinsic barriers are all small; usually 1–5 kcal/mol. This means that in the gas phase all of the reactions in Figure 5.8 will occur. As a result, the system will quickly reach equilibrium. The cracking reaction [reaction (5.137)] is slow because it is thermodynamically unfavorable. However, the situation in a solvent is different because there are significant barriers to rearrange the solvent molecules. Unfortunately, we cannot predict the barriers in a solvent, so mechanisms are difficult to guess.

As the butene pressure in the system goes up, one also gets alkylation reactions



and transfer reactions

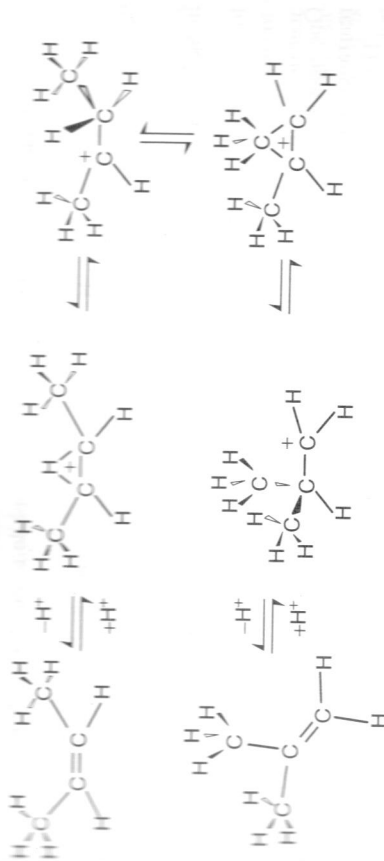


Figure 5.8 The mechanism of the reaction $CH_3CH=CH_2 + H^+ \rightarrow$ products at low pressure.

In reaction (5.147), the $C_8H_{17}^+$ is a transient species, not a true intermediate. The result is some very complex chemistry.

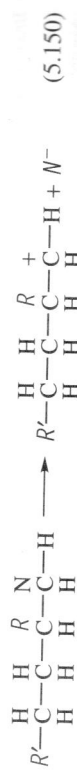
Now, with a carbenium ion, all of the reactions occur with low barriers. However, if you do the same reactions with a carbonium ion by replacing the butene in reaction (5.147) with butane, there are significant barriers. Unfortunately, at present, such reactions have not been studied in enough detail to permit useful predictions.

6.0 REACTIONS IN POLAR SOLUTION

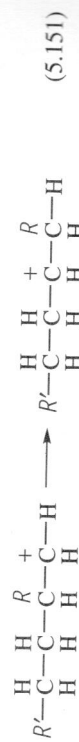
So far in this chapter we have been discussing the mechanisms of reactions in the gas phase. However, now we are going to change topics and start to consider reactions in solution. From a practical standpoint, reactions in solution are quite important. Virtually all organic and inorganic syntheses are run in solution. All biological reactions are run in solution. Most of the reactions you ran in freshman chemistry and organic chemistry occurred in solution. Most of the chemical reactions in the human body and in other living things occur in solution.

Unfortunately, there is insufficient room in this book to discuss solution chemistry of molecules in any detail. You should consult your organic or biochemistry books for discussions of these reaction systems.

Still, we will need a few concepts for the discussion later in this book. You probably remember S_N1 and S_N2 reactions from your organic chemistry class. During an S_N1 reaction, a molecule containing a nucleophile breaks apart in solution to yield a carbenium ion and a nucleophile:



where N^- is a nucleophile. The carbenium ion can then rearrange or crack to yield a new ion:



Then the species can react with a second nucleophile to yield a stable product:



In S_N2 reactions the nucleophile reacts with a stable molecule and exchanges:



One nucleophile replaces another without the appendant groups undergoing significant rearrangements.

The S_N2 reactions are very similar to the reactions of radicals in the gas phase. One observes the same basic chemistry—single atom transfers are fast; ligand transfers are slower. Everything is more complex because all of the species are charged.

The similarities are not as close with S_N1 reactions. S_N1 reactions look something like ion reactions in the gas phase. First, there is a step where an ion forms. Then the ion rearranges. One observes isomerization cyclizations and cracking. Then a stable species forms again. The reaction is not a complete cyclic process, so the kinetics are different. However, there are some qualitative similarities between an S_N1 reaction in solution and an ion reaction in the gas phase.

The one major difference between reactions in the gas phase and in solution is that ionic species are stabilized by the presence of the solution. For example, as noted above in the gas phase, carbonium ions are hard to form. Well, in water or other polar solvents, one can form carbonium ions are much more stable than in the gas phase. Consequently, one can form carbocations without using electrons to ionize the species.

The presence of the solvent also changes the intrinsic barriers to ionic reactions. Generally, intrinsic barriers are higher in solution than in the gas phase. Recall that in the gas phase, ion reactions like those in equation (5.121) are often virtually unactivated, because there are no Pauli repulsions between the reactants. When the reactants dissolve in solution, everything changes. It is unusual to get a bare ion in solution. Instead, the ion is generally surrounded by a solvent cage as shown in Figure 5.9. In order for a reaction to occur, one needs to first distort the ion cage so the reactants can get close enough to react. The distortion of the ion cage generally produces a repulsion similar to the Pauli repulsions seen in radical reactions.

Unfortunately, at present, it is very hard to predict how much the intrinsic barrier changes as a result of the solvent. For example, if one runs a reaction in water, the water

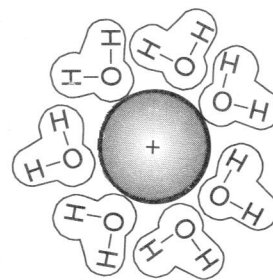


Figure 5.9 A schematic of the solvent cage around an ion in solution.

forms a hydrogen-bonded cage around each ion. The cage needs to be distorted when a reaction occurs, but the exact nature of the distortion is unclear. Consequently, it is difficult to make any predictions.

Fortunately, the changes in the intrinsic barriers do not really change the mechanism of a reaction. One sees all the same elementary reactions in solution that one sees in the gas phase. It is just that the relative rates of reactions change in the solution. The changes in rate will be discussed in Chapter 13.

Glah et al. (1997) show that one can often, but not always, predict mechanisms of reaction without considering the changes in the intrinsic barriers because of the solvent. It is not obvious, but if one species can be in two different reactions, then the intrinsic barriers to both reactions will change in the presence of the solvent. Often, the intrinsic barriers to all of the reactions of a species are changed by a similar amount. In such cases, one can still predict accurate mechanisms by ignoring the changes that occur in the intrinsic barriers in the presence of the solvent.

In practice, however, you want the solvent to affect the rate. After all, in organic synthesis, you want to only make a few products and not make others. People use the solvent to direct reactions. For example, if you wanted to get a specific reaction, you would use a solvent that surrounds the part of the molecule that you want to protect, so no chemistry could happen there. You can also use a counterion or an enzyme for a similar purpose. In practice, the solvent should be an active participant in reactions because that gives you opportunities to optimize selectivity.

One substantial difference between carbocation reactions in the gas phase and in solution is that in solution one can get direct reactions with the solvent. For example, water can take up protons. The reactions with the solvent limit the stability of the carbocations. That can have important implications for mechanisms. This will be discussed in Chapter 13.

In my experience, it is much harder to predict the reaction mechanisms in a solvent than in the gas phase. One needs much more background. Consequently, the discussion will be deferred to Chapter 13.

5.10 REACTIONS ON METAL SURFACES

NEXT we want to discuss the mechanisms of another important class of reactions: reactions on metal surfaces. Table 5.10 lists some important reactions that occur on the surfaces of metal. Metal surfaces are used extensively as catalysts to promote hydrogenation, dehydration, and oxidations. Reactions on metal surfaces are also important to corrosion and the production of integrated circuits.

Reactions on metal surfaces look similar to radical reactions except that the reactants are not radicals. Instead, the reactants are species that have a bond to the surface. The surface acts like a solvent to stabilize radicals in the same way that water acts as a solvent to stabilize ions.

For example, the reaction $O_2 + 2H_2 \longrightarrow 2H_2O$ can occur in the gas phase. According to Hinshelwood (1946), some of the key steps in the mechanism are

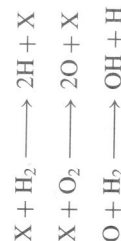
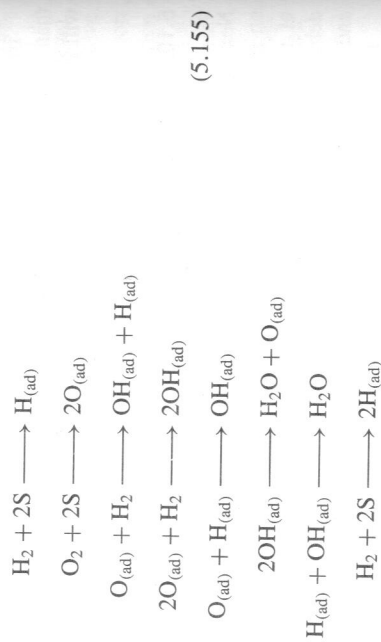


Table 5.10 Some examples of reactions on metal surfaces

Hydrogenation	Chemical production
$N_2 + 3H_2 \rightleftharpoons 2NH_3$	Crude-oil upgrade
$C_2H_4 + H_2 \rightleftharpoons C_2H_6$	Essential oil upgrade
Dehydrogenation	Octane enhancement
$C_2H_4 \xrightarrow{Pt} C_2H_2 + H_2$	Monomer production
Oxidation	Catalytic converters
$2CO + CO \xrightarrow{Pt} 2CO_2 + N_2$	Monomer production
$C_2H_4 + \frac{1}{2}O_2 \xrightarrow{Ag} C_2H_4O$	Chemicals production
$2NH_3 + 4O_2 \xrightarrow{Pt} N_2O_5 + 3H_2O$	
Chemical vapor deposition	Connections on integrated circuits
$Al(C_2H_5)_3 \xrightarrow{Al} Al + 3C_2H_4 + \frac{3}{2}H_2$	
$Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)}$	Corrosion



Anton and Cadogan (1991) examined the mechanism of hydrogen oxidation on a Pt(111) surface. They found that the main reactions were



where the notation (ad) is used to designate that the species are attached to the platinum surface. Notice there is a close similarity between the mechanism of hydrogen oxidation in the gas phase [reaction (5.154)] and the mechanism on the surface [reaction (5.155)]. The elementary steps and intermediates are almost the same. Consequently, one can often think about a reaction on a surface as being a gas-phase reaction except that the intermediates of the reaction are bound to the surface.

The fact that the reacting species are bound to the surface during the surface reaction has important implications. The surface acts like a solvent to stabilize the radicals. Unpaired electrons in the radicals pair up with the free electrons in the metal to produce

stable species. The result is that the intermediates of the reaction are stable species rather than radicals. Still, the species adsorbed on metal surfaces often follow reaction pathways that are quite similar to reaction pathways of radicals in the gas phase, although they do not always do so.

People often picture surface reactions via a catalytic cycle, where surface intermediates are created and then destroyed. For example, Figures 5.10a and 5.10b show the catalytic cycles for the production of water via the mechanism in equation (5.155). Water is produced in two reactions in equation (5.155): (1) the disproportionation of OH and (2) the direct reaction between $H_{(ad)}$ and $OH_{(ad)}$. The first reaction dominates when the oxygen concentration is low. The second pathway dominates when the oxygen concentration is high.

In the first pathway, the surface starts out covered by oxygen. Hydrogen adsorbs on the oxygen to yield OH groups. Two OHs then couple to yield H_2O and a bare site. Oxygen then adsorbs on the bare site to get back to the initial conditions.

In the second pathway, the surface starts out empty. Hydrogen and oxygen adsorb. The adsorbed species then reacts to yield water and regenerate the clean surface.

All steady-state catalytic reactions can be viewed as occurring via a catalytic cycle where surface species are formed and destroyed. The cycles are similar to those discussed previously for gas-phase reactions. However, there is an important difference between reactions in the gas phase and on a surface. In the gas phase, radicals are rather unstable species. As a result, one has to go to rather high temperatures before one gets a high enough concentration of radicals to get a reasonable rate. In contrast, when a radical binds to a surface, the dangling bond in the radical forms a bond to the surface, producing a species that is stable. As a result, one can get a reasonable concentration of adsorbed radicals at low temperatures. For example, at 300 K, less than one hydrogen molecule in 10^{15} dissociates in the gas phase, while on a platinum surface, more than 99.9% of the hydrogen dissociates. The result is that hydrogen on platinum is much more reactive than gas phase H_2 .

The hydrogen on platinum is not as reactive as a hydrogen radical in the gas phase, however. The hydrogen atoms on the surface are bound to the platinum and are no longer radicals. As a result, the hydrogen atoms on the surface are less reactive than free hydrogen radicals in the gas phase. However, the effect of the reduced reactivity is smaller than the effects of the enhanced concentration of hydrogen atoms. As a result, at moderate temperatures, the hydrogen/oxygen reaction occurs much faster over a platinum catalyst

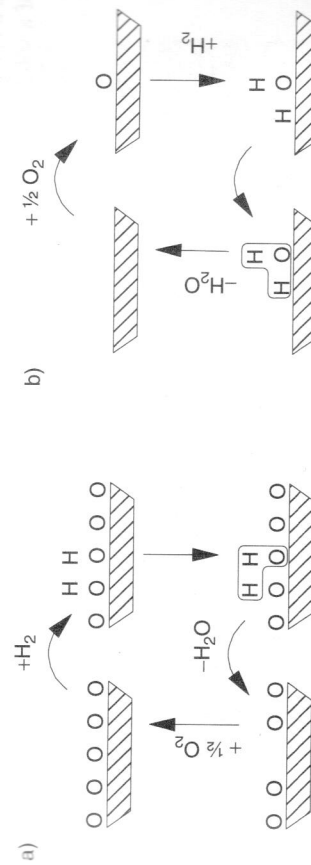


Figure 5.10 Catalytic cycles for the production of water (a) via disproportionation of OH groups and (b) via the reaction $OH_{(ad)} + H_{(ad)} \rightarrow H_2O$.

than in the gas phase. At room temperature, a hydrogen oxygen mixture remains stable for years. However, if one puts a platinum wire in the mixture, the mixture will explode. In general, metal surfaces stabilize reactive intermediates. That greatly speeds up the initiation steps in the mechanism. The speedup of the initiation reaction is why catalytic reactions have so much higher rates than do gas-phase reactions.

Masel (1996) also notes that surfaces can stabilize di- and triradicals. That allows new chemistry to occur on a surface that would not occur in the gas phase. Details are given in Chapter 12.

There is one key difference in the nature of the initiation reaction between the mechanism of the reaction in the gas phase and the mechanism of a reaction on the surface. In the gas phase, the initiation step always involves the scission of a bond. On a surface, the key initiation is the **adsorption** of one or more of the reactants onto the surface. During adsorption, a molecule attaches itself to a surface that changes the properties at the molecule so that the reactions change as well. We call the species bond to surfaces **adsorbed** molecules or **adsorbates**. Masel (1996) has presented a detailed discussion of adsorption.

There is some important notation. We will use a subscript (ad) to designate an adsorbed species. That way we can distinguish between adsorbed species, and species in the gas phase.

5.11 GENERAL CONCEPTS ABOUT ADSORPTION AND REACTION ON SURFACES

Before we talk about specific mechanisms of surface reactions, we need to discuss some general concepts for surface reactions. There is a lot of information here, and students often find it overwhelming. My best advice is to stick with it. The material will get easier after you have read it a couple of times.

The first general concept is that surface reactions occur in what is called an *adsorbed phase*. The adsorbed phase is a layer of gas that is bound to the surface. Figure 5.11 shows what the adsorbed phase is like when ethylene adsorbs on platinum. The surface consists of an ordered layer of platinum atoms indicated as circles in the figure. Platinum, is a metal, and metals have many *lots* of free electrons. When ethylene adsorbs on platinum, some of the ethylene adsorbs intact. Other ethylene molecules react to form a variety of hydrocarbon fragments. Some of the hydrocarbon fragments form strong bonds to the platinum atoms, while some of the other fragments are free to move around. The result is a complex mixture that has properties somewhere between those of a liquid and those of a solid.

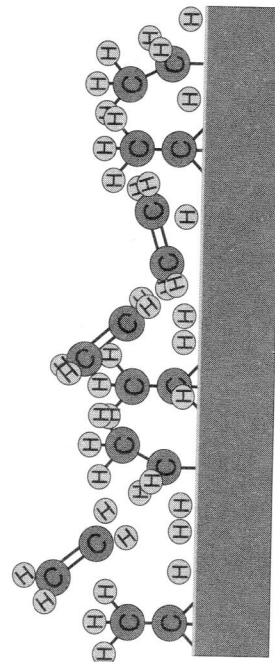


Figure 5.11 An illustration of the adsorbed phase when ethylene adsorbs on platinum.

People spend their entire lifetimes studying adsorption. There is a tremendous amount of information about the topic. For now, the key thing to remember is that a surface reaction usually occurs in a thin layer of molecules attached to the surface. The layer can be disordered like a liquid or ordered like a solid. Still, the key feature is that there is a thin layer of adsorbed molecules and reaction occurs in that layer.

The next key point is that there are two types of adsorption: **molecular adsorption** and **dissociative adsorption**. In molecular adsorption, the molecule adsorbs intact, while in dissociative adsorption, a bond breaks in the adsorbed molecule. One finds that bonds break easily during a surface reaction, so it is not unusual for a molecule to dissociate on adsorption.

For example, when O_2 adsorbs onto platinum at 300 K, the oxygen dissociates, yielding two oxygen atoms. H_2 dissociates into two hydrogen atoms. C_2H_4 dissociates to yield a $CH_3C\equiv$ group and an adsorbed hydrogen. At 100 K, H_2 still dissociates. However, O_2 and C_2H_4 adsorb molecularly.

The fact that bonds can break during adsorption is quite important, because it means that one can produce atoms or other very reactive species in the adsorbed layer. Consequently, surface reactions are often quite rapid.

The high reaction rates on metal surfaces make metal surfaces very active catalysts. Metals are good at producing radicals, so they tend to catalyze radical reactions. Ionic reactions are rarely catalyzed by metals, although there are a few exceptions.

In order to know whether a surface will catalyze a given reaction, it is important to know whether a given molecule dissociates on a given surface. Figure 5.12 gives a chart that one can use to see if a given molecule dissociates. Note that metals in the middle part of the periodic table are the most active for dissociation.

Another key concept for surface reactions is that the reactions occur on distinct **surface sites**. Surface sites are defined as the place on the surface where reactions can occur.

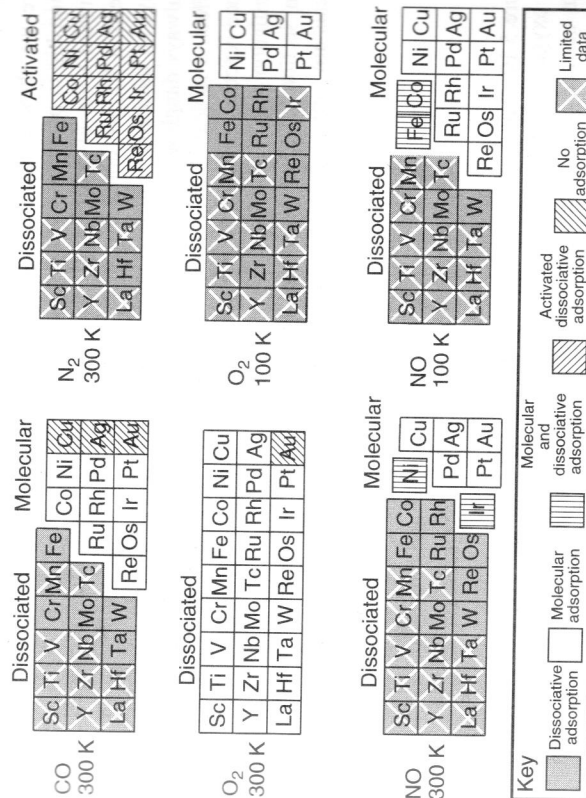


Figure 5.12 The metals that dissociate CO , NO , N_2 , O_2 , and CO at various temperatures.

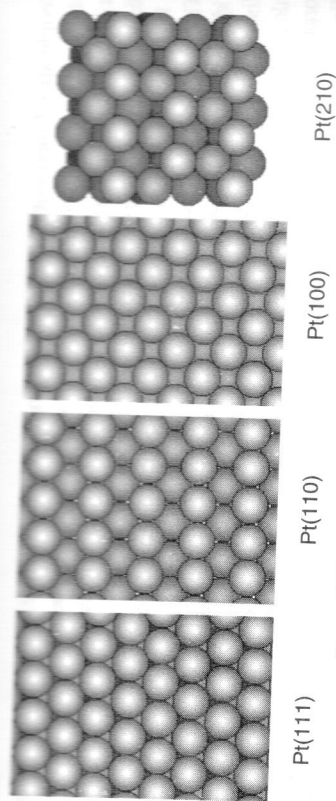


Figure 5.13 Pictures of some common surface structures.

Sometimes, the surface site consists of a specific arrangement of metal atoms. Other times, only a single bare metal atom is sufficient. Experimentally, one often finds that the rates of surface reactions are greatly enhanced if a specific arrangement of atoms is available on the surface of the catalyst. However, that is never an absolute requirement. Often, there is an ordered arrangement of sites in the surface of a catalyst. Figure 5.13 shows a picture of some surface structures. The surface atoms are indicated as spheres in the photo. Notice that one has an ordered arrangement of surface atoms. If each surface atom is a reactive site, then one will also have an ordered arrangement of surface sites.

5.12 PREDICTION OF THE MECHANISMS OF SURFACE REACTIONS

Next, we want to discuss how one can predict the mechanisms of reactions on metal surfaces. The material will build on the analysis in Sections 5.4.1–5.4.3, 5.4.5, and 5.4.6, where we showed that one can combine a series of empirical rules and the Polanyi relationship to predict the mechanism of reactions.

First, I want to note that all reactions on metal surfaces are propagation reactions. In Section 5.2, we noted that when we run a reaction in the gas phase, the first step is always an initiation step. Reactions on metal surfaces are a little different, in that there are always dangling bonds and free electrons in a metal surface, so that the surface is, in effect, a radical. Consequently, one does not have to form radicals at the start of the surface reaction. Instead, the bare surface is a radical. Consequently, one does not need an initiation step.

In Section 5.4.1, we noted that all propagation reactions go in catalytic cycles where radicals are formed and destroyed. In the same way

All surface reactions occur in cycles where bare surface sites are formed and destroyed.

$$(5.156)$$

Figure 5.10 shows a typical catalytic cycle. The surface starts out empty. Hydrogen and oxygen adsorb. The adsorbed species then react to yield water and regenerate the clean surface. Notice that we start with a bare surface site at the beginning of the reaction, and end with a bare surface site at the end of the reaction in agreement with requirement (5.156).

According to rule (5.68), when radicals react in the gas phase, the mechanism generally consists of a series of elementary reactions where a single atom is transferred from one species to the next as described in Section 5.4.6.

Reactions on metal surfaces are very similar to radical reactions in the gas phase. Generally, molecules first adsorb. Then, they transfer one atom at a time to yield products. For example, Figure 5.14 shows the mechanism of methanol decomposition



on a platinum surface called Pt(110). The methanol adsorbs molecularly. Then the methanol loses one hydrogen at a time to yield products. This mechanism differs from the mechanism of methanol decomposition in the gas phase because there is no initiation reaction. Still, the methanol follows the general rule that atoms are transferred one atom at a time into products.

Before we proceed, we need to define some notation. We will designate a surface site by the symbol S. With this notation, the second reaction in Figure 5.14, where an adsorbed methanol reacts with the surface site to yield an adsorbed methoxy (CH_3O) plus an adsorbed hydrogen atom, can be written



where the subscript (ad) is used to indicate that we have an adsorbed species.

Next, we need to note that, just as in the gas phase, one does not always simply transfer one atom at a time during a surface reaction. For example, Figure 5.15 shows the mechanism of ethanol decomposition on platinum. The ethanol first sequentially dehydrogenates to yield an acetyl (CHCO) intermediate. Then the C–C bond breaks to yield CO and an adsorbed methyl group.

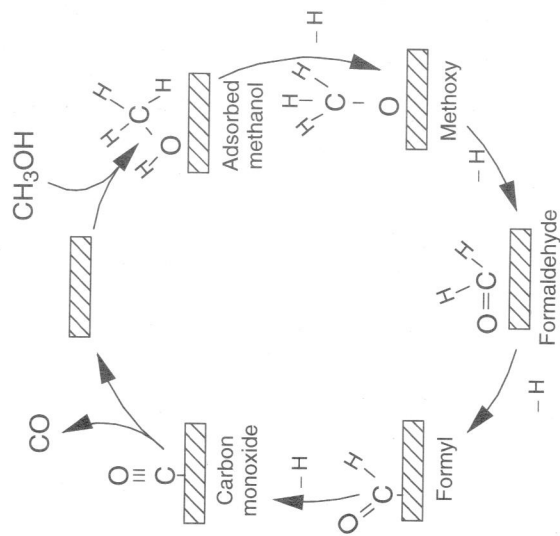


Figure 5.14 The mechanism of methanol decomposition on Pt(110).

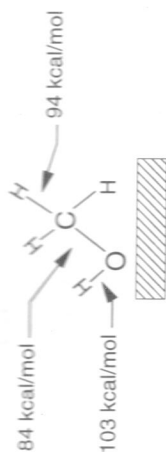


Figure 5.16 Bond energies in methanol.

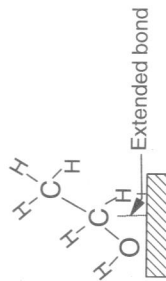


Figure 5.17 The transition state for C-H scission in adsorbed ethanol.

this a proximity effect because only bonds close to the surface can break. Generally, the proximity effect adds about 10–20 kcal/mol to intrinsic barriers, so it is quite important.

5.12.2 A Specific Example: Ethanol Decomposition of Platinum

As an example of the analysis, in this section, we will try to predict the mechanism of ethanol decomposition on platinum. We will assume that the intrinsic barrier for the scission of a O-H or C-H bond is about 15 kcal/mol. The intrinsic barrier for the scission of a C-C or C-O bond is about 45 kcal/mol as described in Section 5.4.6.

In principle, ethanol could decompose by a host of different reaction pathways. The ethanol can sequentially dehydrogenate. The C-O bond could break before any other reaction occurs. Now, let's ask which reaction is most favored if the intrinsic barrier for the scission of a C-C or O-C bond is 45 kcal/mol while the intrinsic barrier to the scission of a C-H or O-H bond is 15 kcal/mol.

Figure 5.18 shows the bond energies in ethanol. Notice that the C-C bond is the weakest bond in the molecule. Therefore, if all of the intrinsic barriers to bond scission were equal, one would expect the C-C bond in ethanol to be easier to break than the C-H, O-H and C-O bonds. However, if one considers the difference in intrinsic barrier, one would come to a very different conclusion. Notice that the intrinsic barrier for the scission of a C-C or O-C bond is 30 kcal/mol higher than the intrinsic barrier of the scission of a C-H or O-H bond. Consequently, the C-O bond would be harder to break

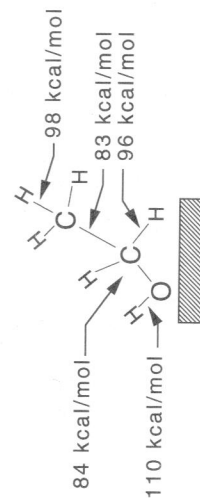


Figure 5.18 Bond energy in ethanol.

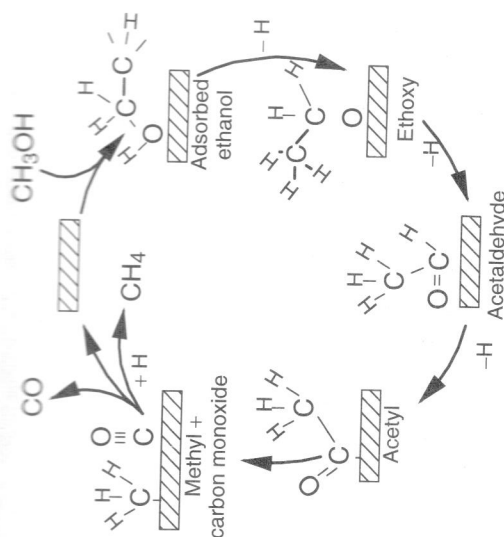


Figure 5.15 The mechanism of ethanol decomposition on Pt(111).

Notice the acetyl group could still lose hydrogens, so the fact that the C-C bond breaks is an exception to the rule that molecules gain or lose one atom at a time during reactions on solid surfaces.

5.12.1 Intrinsic Barriers to Surface Reactions

Next we will discuss how one can predict mechanisms of reactions on solid surfaces. In Section 5.4.6, we noted that one can use the Polanyi relationship to predict the mechanism of the reactions in the gas phase. Lee and Masel (1996) showed that one can use the same ideas to predict the mechanism of reactions of simple hydrocarbons, oxygenates, and amines on metal surfaces. The idea is that when you run a reaction on a surface, the reactants and products of the reaction are stabilized. However, in many cases, the intrinsic barriers to the reaction do not change. In that case, one can use equation (5.41) to predict the barriers to surface reactions. One then follows the procedures in Section 5.4.6 to predict the mechanism of the reaction.

There are two major changes when we have reactions on metal surfaces. There is a proximity effect that bonds only in close proximity to the surface can break, and there is a role of d electrons, which can weaken bonds and thereby make them easier to break.

The proximity effect is discussed in Section 10.11 of Masel (1996). The basic idea is that bonds can break only when the bonds are in close proximity to the surface. For example, Figure 5.16 shows the bond energies and geometry of methanol adsorbed on platinum. Notice that the CH bond is weaker than the OH bond. Therefore, on the basis of thermodynamics, one would expect the C-H bond to be easier to break than the O-H bond. However, experimentally, the OH bond is easier to break than the CH bond. Lee and Masel [1996] analyzed this case and found that the issue is what Masel [1996] called a proximity effect. Figure 5.17 shows a diagram of the transition state for C-H scission bond. During reaction, the carbon and hydrogen both need to form a bond to the platinum. There is no problem forming a platinum-hydrogen bond, but it is hard to form a platinum-carbon bond because the hydrogen gets in the way. Masel [1996] calls

than either the O-H or C-H bond. Therefore, both the C-H and O-H bond should break at lower temperatures than the C-C bond.

Now consider whether the O-H or C-H bond should be easier to break. Notice that the C-H bond is weaker than the O-H bond. Therefore, on the basis of bond energies alone, the C-H bond should break more easily than the O-H bond. However, if one looks at the reaction in detail, one finds that there is a proximity effect that substantially raises the intrinsic barrier for C-H bond scission. During reaction, carbon-surface and hydrogen-surface bonds form. Figure 5.17 shows a possible transition state for the reaction. Notice that it is hard to form a carbon-surface bond because the carbon-hydrogen bonds get in the way. One does not know how much energy this costs without doing detailed calculations. However, Masel and Lee [1996] did quantum-mechanical calculations that suggest that these repulsions raise the intrinsic barriers by 24 kcal/mol.

One can do the same analysis on the O-H bond scission step. In the case of O-H bond scission, there are some extra intrinsic barriers due to the repulsions of the empty dangling bonds on the ethanol. However, those effects would be expected to be much smaller than the extra 24 kcal/mol repulsion if the C-H bond breaks. Therefore, on the basis of an analysis of the intrinsic barriers, one would expect O-H bond scission to have a lower activation barrier than C-H, C-C, or C-O bond scission, even though the O-H bond is the strongest bond in ethanol. Therefore, we conclude that, per an analysis of the intrinsic barriers, the first step in ethanol decomposition should be O-H bond scission to yield an ethoxy intermediate, as shown in Figure 5.15. That is what has been observed experimentally on all of the transition face metals that have been examined previously except Pt(110)(1 × 2) and Pt(331), where the notation Pt(110) (2 × 1) and (311) refers to platinum catalysts with surface arrangements called (110) (2 × 1) or (311) as shown in Figure 5.19.

One can continue the analysis to predict a mechanism of ethoxy decomposition on metals. Again, we note that the C-C bond in ethoxy is 10 kcal/mol weaker than the C-H bond. Therefore, if one considered bond energies only, one would expect the C-C bond in ethoxy to break before the C-H bond. However, the intrinsic barriers go in the opposite directions. The intrinsic barriers for C-H bond scission are much lower than the intrinsic barriers for C-C bond scission. If one plugs numbers into equation (5.41), one finds that

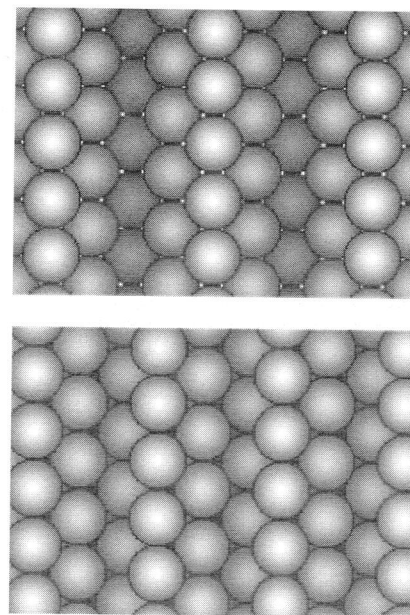


Figure 5.19 The arrangement of the platinum atoms in Pt(311) and Pt(110) (1 × 2).

the overall activation barrier for ethoxy dehydration should be 10–20 kcal/mol lower than the activation barrier for C-C bond scission in ethoxy. Consequently, the ethoxy should sequentially dehydrogenate to produce an acetaldehyde and an acetyl intermediate as indicated in Figure 5.15.

The analysis changes after the acetyl intermediate forms. In Chapter 5, we will provide some methods to estimate heats of reactions. If one uses the methods from Chapter 6, one finds that on platinum, the reaction



is favored by about 44 kcal/mol over the reaction



Reaction (5.160) has a 20–40 kcal/mol lower intrinsic barrier than does reaction (5.159), but that lower intrinsic barrier is overcome by the 44-kcal/mol difference in ΔH_r . Therefore, according to equation (5.41), reaction (5.159) should have a lower activation barrier than reaction (5.160). Consequently, one would expect the acetyl intermediate to decompose via reaction (5.159) rather than reaction (5.160). Experimentally, one finds that ethoxy decomposition follows the mechanism in Figure 5.15 in all of the cases examined so far except in the case of ethoxy decomposition on Rh(111).

The point of this exercise is that one can make useful predictions with very few numbers: rough estimates of the heats of adsorption and intrinsic barriers. In other work, Lee and Masel (1997) have suggested that one can successfully predict the mechanism of ethylene, methanol, ethanol, acetaldehyde, methyl iodide, methylamine, and ethyl iodide decomposition on most of the loose-packed faces of transition metals examined to date using the same simple analysis!

Now, I would like to say that this procedure will always work, but unfortunately, I cannot. For example, Cong et al. (1998) found that on a stepped surface, such as that of Pt(110) (1 × 2) shown in Figure 5.19, ethanol decomposes by one of two pathways: the pathway shown in Figure 5.15 or, a pathway where the C-C bond breaks at low temperature. This second pathway is not expected from the materials in this section. Brown and Barteau [1996] also found an exception during ethanol decomposition on Rh(100). These exceptions are currently being actively investigated but, are not well understood at present.

In my experience, one can guess at a mechanism of a surface reaction and be right 95% of the time. However, there are occasional exceptions and the exceptions are not understood.

5.13 GENERIC TYPES OF SURFACE REACTIONS

There is one other detail of importance to the prediction of mechanism of surface reactants. Some of the species that participate in the reaction might not be strongly attached to the surface. People in the literature often discuss the participation of gas-phase species, and weakly bound complexes on surface reactions.

There are three generic types of surface reaction: **Langmuir-Hinshelwood** mechanisms, **Rideal-Eley** mechanisms, and **precursor** mechanisms. Figure 5.20 shows a schematic of these three mechanisms for a hypothetical reaction $A + B \rightarrow AB$. In the

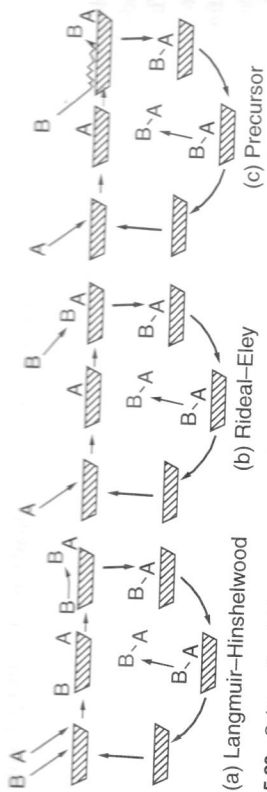


Figure 5.20 Schematic of (a) Langmuir-Hinshelwood, (b) Rideal-Eley, and (c) precursor mechanisms for the reaction $A + B \Rightarrow AB$ and $AB \Rightarrow A + B$.

Langmuir-Hinshelwood mechanism, A and B first adsorb onto the surface of the catalyst. Next, the adsorbed A and B react to form an adsorbed A-B complex. Finally, the A-B complex then desorbs. In what's now called the *Rideal-Eley* mechanism,¹ the reactant A chemisorbs. The A then reacts with an incoming B molecule to form an A-B complex. The A-B complex then desorbs. In the precursor mechanism, A adsorbs. Next, B collides with the surface, and enters a mobile precursor state. The precursor rebounds along the surface until it encounters an adsorbed A molecule. The precursor then reacts with the A to form an A-B complex which desorbs.

Each of these reactions in Figure 5.20 can also occur in reverse as shown in Figure 5.21. For example, one can run the Langmuir-Hinshelwood reaction in reverse by adsorbing an A-B molecule, heating to allow the A-B to decompose into adsorbed A and B, and then desorbing the A and B. Alternatively, if the adsorbed A-B molecule

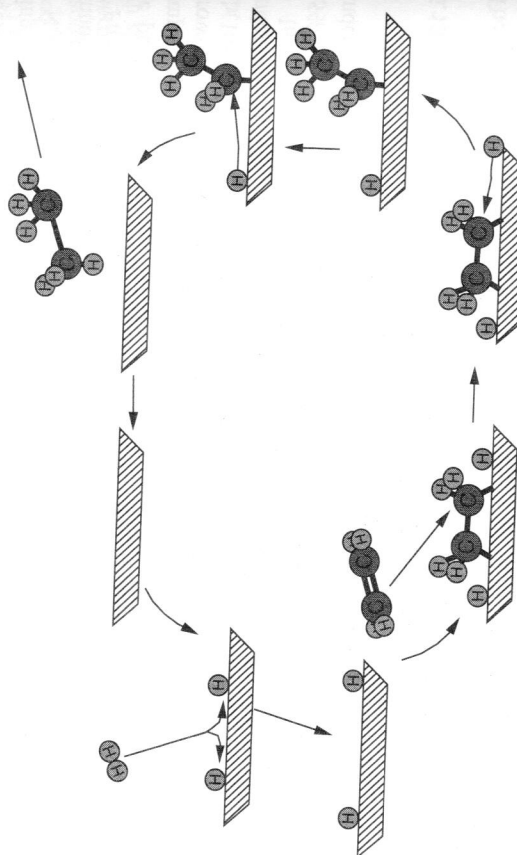


Figure 5.21 A Langmuir-Hinshelwood mechanism for the reaction $C_2H_4 + H_2 \Rightarrow C_2H_6$.

¹ In their original papers, Rideal and Eley [1940, 1941] did not distinguish between what is now called a *Rideal-Eley* mechanism and a precursor mechanism. However, more recent workers now make a distinction. See Weinberg [1992] for details.

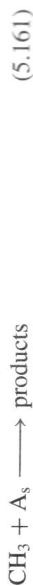
decomposes to yield an adsorbed A molecule and a gas-phase species B, one would have the reverse of the Rideal-Eley mechanism. If a precursor forms on the way to the products, then one would have the precursor mechanism.

In the literature, the precursor mechanism is sometimes referred to as the **trapping-mediated** mechanism. Similarly, the Rideal-Eley mechanism is sometimes referred to as the **Eley-Rideal** mechanism.

All of the surface reactions that have been studied so far can be viewed as following a Langmuir-Hinshelwood mechanism, a Rideal-Eley mechanism, a precursor mechanism, or some combination of these three mechanisms.

For example, Figure 5.21 shows the mechanism of ethylene hydrogenation seen at very low pressure on a platinum catalyst. First, the hydrogen adsorbs and dissociates. Then, the ethylene adsorbs. Then, one adds one hydrogen at a time to the adsorbed ethylene to yield products. Notice that in the mechanism in Figure 5.21, the reactants adsorb and then react. Therefore, the mechanism in Figure 5.21 is a classic Langmuir-Hinshelwood mechanism. Langmuir-Hinshelwood mechanisms are quite common in the literature. Most catalytic reactions go via Langmuir-Hinshelwood mechanisms.

Reactions used to deposit films on surfaces, on the other hand, are thought to often go (proceed) via Rideal-Eley mechanism. For example, one grows CVD (chemical vapor deposition) diamonds by heating methane to produce CH_3 groups in the gas phase. The CH_3 groups then react with a cool surface to produce a diamond film. Harris (1990, 1993) examined the mechanism theoretically and proposed the mechanism shown in Figure 5.22. First, the methyl groups adsorb on the surface, forming a hydrocarbon layer. The CH_3 groups from the gas phase react with the hydrocarbon layer to form a hydrogen-terminated diamond surface. Finally, other CH_3 groups react with the layer to remove excess hydrogen (hydrogen also desorbs). Notice that each of these reactions follow the general reaction scheme



where a gas-phase species, $CH_{3,g}$, reacts with a surface intermediate, A_s , to form products. Hence, classically, this is a Rideal-Eley mechanism.

In my experience, the key difference between catalytic reactions and film growth reactions is that in catalysis, one usually runs the reaction at low temperatures. When the temperatures are low, the reactants do not dissociate until the reactants adsorb onto the surface. In that case, reactions happen only after all of the species adsorb. Only Langmuir-Hinshelwood reactions are seen. On the other hand, film growth reactions often

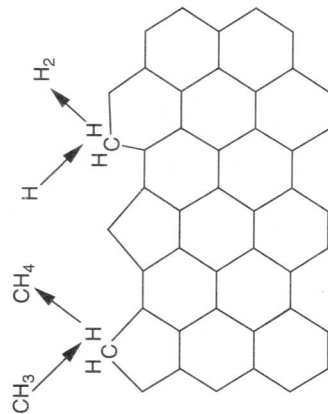


Figure 5.22 A Rideal-Eley mechanism for diamond deposition.

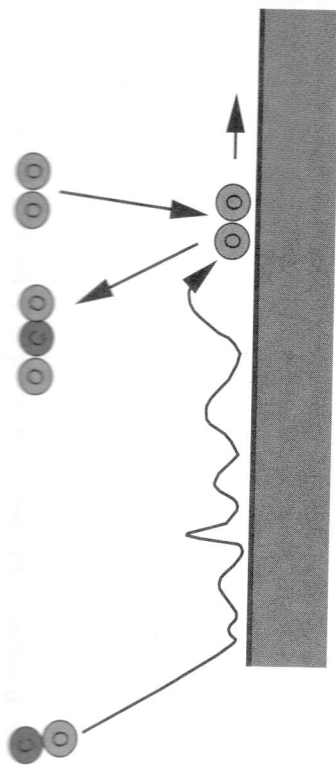


Figure 5.23 A precursor mechanism for the reaction $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_{\text{ad}}$.

run at much higher temperatures. Radicals can form in the gas phase. When a radical hits a surface, the radical can react before it adsorbs. One can observe Rideal–Eley mechanisms of radicals.

I do not have a good example of a precursor mechanism. People cannot actually observe precursors because the precursors remain on the surface for perhaps only 10^{-6} seconds. Consequently, one can never tell for sure whether a reaction goes via a precursor. There is some experimental evidence that the reaction



can go via the precursor mechanism shown in Figure 5.23. First the oxygen adsorbs and dissociates. Then a CO collides with the surface and wanders around until the CO finds an adsorbed oxygen atom. Then the two species react to form a CO_2 molecule, which desorbs.

If one glances at Figure 5.23, it is not immediately obvious that this is a precursor mechanism and not a Langmuir–Hinshelwood mechanism. After all, the CO and O_2 both enter the surface phase and then react. However, people say that this is a precursor mechanism because the CO reacts with the oxygen before the CO has had time to form a strong bond with the surface. Of course, at this point, no one has directly observed the precursor, so no one knows for sure whether the CO forms a bond to the surface before it reacts. In my view, the best available evidence is that the CO bonds before the CO reacts. However, there are others who disagree.

In my experience, most reactions that were originally thought to proceed via a precursor mechanism are now thought to go by other mechanisms. Still, people discuss precursor mechanisms at length in the literature. Therefore, I thought that it would be important to mention them.

5.14 REACTIONS ON ACID SURFACES

So far we have been talking about reactions on metal surfaces. Next, we want to move on and briefly mention reactions on solid acids. Students usually think about acids as being liquids, but there is a whole class of solid acids. For example, one can put protons into an ion exchange resin to create a solid acid. In the analysis and detergent industries, one uses special silica aluminates, specifically mixtures of SiO_2 and alumina

(Al_2O_3) called *zeolites*. The zeolites are highly porous structures whose surfaces have been specially treated to create Lewis or Brønsted acid sites. It is possible to make a zeolite with a $\text{p}K_a$ of -10 . Recall that by comparison, 1 N H_2SO_4 has a $\text{p}K_a$ of 1 and water has a $\text{p}K_a$ of 7.

Reactions on solid acids are a cross between reactions on metal surfaces and reactions in acid solution. As in a metal, the reactions occur at distinct sites on the acid's surface and as in a metal, the reaction usually follows a Langmuir–Hinshelwood rate law. Also as in a metal, the reactions go via a catalytic cycle where protons are consumed and regenerated. Still, on a solid acid, most of the key intermediates are ions. The reaction pathways look more like reactions in solution than reactions on metal surfaces.

In particular, reactions on solid acids usually follow the mechanisms outlined in Sections 5.4 and 5.4.1. Olefins, paraffins, and alcohols react with protons in the acid to yield carbenium or carbonium ions. The carbenium and carbonium ions react as described in Sections 5.4 and 5.4.1. One observes the same cracking, isomerization, and alkylation reactions in a solid acid that one observes in the gas phase or in a superacid solution. The only difference is that there are mass transfer limitations that limit the products produced when the reacting molecules are big.

Solid acids are widely used as catalysts. They are also used as ion traps, for example, in detergents and other cleaners.

The analysis of mechanisms of reactions in solid acids is very similar to the analysis of reactions of ions in the gas phase. Martens and Jacobs (1990) suggest that all of the ideas in Sections 5.4 and 5.4.1 apply to solid acids, and indeed the results in Table 5.8 show that reactions in solid acids behave very similarly to ionic reactions in the gas phase. Generally, one can predict the qualitative behavior of solid acid catalysts using the material in Sections 5.4 and 5.4.1 (see Martens and Jacobs (1990) for details).

6.15 SUMMARY

In summary, then, in this chapter we reviewed the mechanisms of simple reactions in the gas phase and in various environments. We found that there are basically two types of reaction pathways: radical pathways and ionic pathways. The radical pathways usually consist of an initiation step where radicals are formed, a series of propagation steps where products are produced in a catalytic cycle, and a series of termination steps where radicals recombine. We found that one can often predict the reaction pathway using the Polanyi relationship, some knowledge of intrinsic barriers, and a few empirical rules. In particular, the intrinsic barriers for atom transfer reactions are usually 30 kcal/mol lower than the intrinsic barriers for transfer of molecular ligands. As a result, atomic transfer reactions usually dominate in the gas phase.

Ionic reactions are more complicated in that there are no empirical rules for prediction of reaction mechanisms. Generally, ionic pathways consist of a series of additions, isomerizations, and bond scissions. In the gas phase all of the processes have low intrinsic barriers, which means that the reactions quickly reach equilibrium. However, if one runs the reaction in a solvent, the rearrangements of the solvent cage determines the intrinsic barrier. The forces due to the rearrangements of the solvent cage are still not well understood, which makes prediction of reaction pathways more difficult.

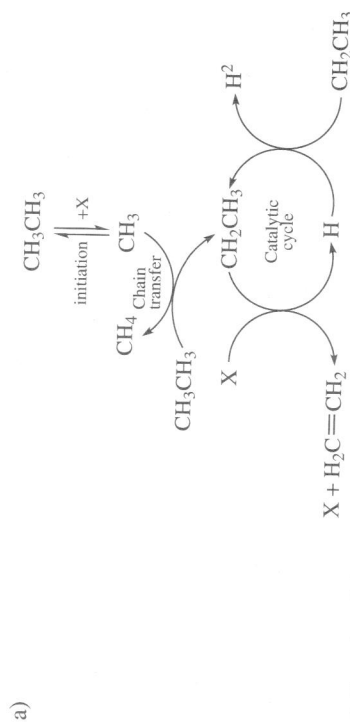
5.16 SOLVED EXAMPLES

Example 5.A The reaction $\text{CH}_3\text{CH}_3 \Rightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2$ obeys the following mechanism:



(+ other reactions)

- Make a diagram of the reaction similar to that in Figure 5.3
- Identify the initiation step, the transfer step, the propagation steps, the termination steps. Also indicate whether the propagation steps are associations, β -hydrogen transfer, etc.
- Does the mechanism obey the rules in the Section 5.4.7
- Estimate the activation barrier for each step.
- Calculate the temperature where equation 5.35 is satisfied.

Solution

- Step 1 — initiation
Step 2 — chain transfer
Step 3 — propagation (β -hydrogen elimination)
Step 4 — propagation (hydrogen transfer)
Step 5 — termination
- Does follow rules

There is an initiation step (step 1)

There is a catalytic cycle (step 3 and 4)

There is a termination step (step 5)

We will verify the activation barriers below

- Estimate the activation barriers

First consider: $\text{CH}_3\text{CH}_3 + \text{X} \rightarrow 2\text{CH}_3\cdot + \text{H}$

- Step 1: estimate ΔH_r

From NIST Web book (<http://webbook.nist.gov>)

$$\Delta H_f(\text{CH}_3\text{CH}_3) = -20.0$$

Therefore

$$\Delta H_r(\text{CH}_3\cdot) = +34.8 \text{ kcal/mol}$$

$$\Delta H_r = 2(34.8) - (-20.0) = 89.6 \text{ kcal/mol}$$

- Step 2: estimate E_A using Table 5.4. This is a simple bond scission reaction. From Table 5.4

$$E_A = 1 + \Delta H_r = 90.6 \text{ kcal/mol}$$



- Step 1: estimate ΔH_r

From the NIST web book

$$\Delta H_f(\text{CH}_3\text{CH}_3) = -20.0 \text{ kcal/mol}$$

$$\Delta H_f(\text{CH}_3\cdot) = +34.8 \text{ kcal/mol}$$

$$\Delta H_f(\text{CH}_4) = -17.9 \text{ kcal/mol}$$

$$\Delta H_f(\cdot\text{CH}_2\text{CH}_3) = +28.4 \text{ kcal/mol}$$

Therefore

$$\Delta H_r = 17.9 + 28.4 - 34.8 - (-20.0) = -4.3 \text{ kcal/mol}$$

- Step 2: estimate E_A using Table 5.4. This is an atom transfer reaction. From Table 5.4

$$E_A = 10 \text{ kcal/mol} + 0.3(-4.3) = 8.7 \text{ kcal/mol}$$



- Step 1: estimate ΔH_r

From the NIST web book

$$\Delta H_f(\text{CH}_2\text{CH}_3) = +28.4 \text{ kcal/mol}$$

$$\Delta H_f(\text{CH}_2\text{CH}_2) = +12.5 \text{ kcal/mol}$$

$$\Delta H_f(\text{H}) = +52.1 \text{ kcal/mol}$$

$$\Delta H = 52.1 + 12.5 - 28.4 = +36.2 \text{ kcal/mol}$$

- Step 2: estimate E_A using Table 5.4. This is an endothermic β -scission reaction. From Table 5.4

$$E_A = 15 + 0.7(36.2) = 40.3 \text{ kcal/mol}$$

Example 5.B Consider the following alternate mechanism for ethylene production from ethane



- a) Does this mechanism follow all of the rules at 810 K?
 b) Is this mechanism more or less likely than the mechanism in Example 5.A?

Solution

a) This does follow the rules!

- 1) There is an initiation step (step 1)
- 2) There is a catalytic cycle (steps 2,3,6)
- 3) There is a termination step (step 5)

(Check all steps obey constraint in equation 5.36 Steps 1,2,3,5 do (see Example 5.A)
 (Check step 6 $\text{H}\cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_4 + \cdot\text{CH}_3$)

Step 1: estimate ΔH_r

From the Nist webbook

$$\Delta H_f(\text{H}\cdot) = +52.1 \text{ kcal/mol}$$

$$\Delta H_f(\text{CH}_3\text{CH}_3) = -20.0 \text{ kcal/mol}$$

$$\Delta H_f(\text{CH}_4) = -17.9 \text{ kcal/mol}$$

$$\Delta H_f(\cdot\text{CH}_3) = +34.8$$

$$\Delta H_r = 34.8 + (-17.9) - 52.1 - (-20.0) = -15.2 \text{ kcal/mol}$$

Step 2: estimate E_A using Table 5.4. This is a ligand transfer reaction to hydrogen. From Table 5.4

$$E_A = 45.0 + 0.5 + (-15.2) = 37.4 \text{ kcal/mol}$$

This reaction is in the catalytic cycle

$$E_A \leq \left(0.05 \frac{\text{kcal}}{\text{mol}}\right) T = (0.05)(810 \text{ K}) = 40.5 \frac{\text{kcal}}{\text{mol}}$$

- Therefore all constraints are satisfied
 b) Which mechanism is better?



Step 1: estimate ΔH_r

From the NIST web book

$$\Delta H_f(\text{H}) = +52.1 \text{ kcal/mol}$$

$$\Delta H_f(\text{CH}_3\text{CH}_3) = -20.0 \text{ kcal/mol}$$

$$\Delta H_f(\text{CH}_2\text{CH}_3) = +28.4 \text{ kcal/mol}$$

$$\Delta H_2 = 0 \text{ kcal/mol}$$

Therefore

$$\Delta H_r = 0 + 28.4 - 52.1 - (-20.0) = -3.7 \text{ kcal/mol}$$

Step 2: estimate H_r using Table 5.4. This is a hydrogen transfer reaction. From Table 5.4

$$E_A = 10 + 0.3(-3.7) = 5.9 \text{ kcal/mol}$$



Step 1: estimate ΔH_r

$$\Delta H_r = -89.6 \text{ kcal/mol (reverse reaction 1)}$$

Step 2: estimate H_r using Table 5.4. This is a recombination reaction. From Table 5.4

$$E_A = 1 \text{ kcal/mol}$$

e) Calculate temperature such that

$$E_A \leq 0.15 \frac{\text{kcal}}{\text{mol}^\circ \text{K}} \text{ for initiation}$$

$$E_A \leq 0.07 \frac{\text{kcal}}{\text{mol}^\circ \text{K}} \text{ for all propagation}$$

$$E_A \leq 0.05 \frac{\text{kcal}}{\text{mol}^\circ \text{K}} \text{ for catalytic cycle}$$

For initiation, $E_A = 90.6 \text{ kcal/mol}$

$$T \geq 90.6/0.15 = 604 \text{ K}$$

For propagation.

$$T \geq 40.3/0.05 = 806 \text{ K}$$

Therefore any temperature above 806 K will satisfy all constraints.