1
How Petroleum is converted into Useful Materials: Carbocations and Free Radicals are the Keys

1.1
The Conflicting Uses for Petroleum: The Chemical Industry and the Internal Combustion Engine

Petroleum is largely a complex mixture of saturated hydrocarbon molecules, the origins of which are prehistoric plants and animals. As we'll see, small numbers of molecules found in petroleum derive directly from the prehistoric precursors of biochemically active molecules found in all living species today. Chemists use these biomarkers or molecular fossils to study the history of petroleum and to decide where to drill for petroleum. But our story here is of wider interest. It is the story of petroleum as the source of trillions of kilograms of materials used all around us, the petrochemicals that provide textiles, plastics, adhesives, pharmaceuticals, rubbers and coatings to mention but a few. And to a far greater extent, it is the source of much of the energy that yields electrical power, warms our houses and propels our vehicles. Yet petroleum, as pumped from the earth, is ill-suited for these grand tasks. At the close of the nineteenth century it was useful only for illumination. To obtain the proper molecules to make everything from plastics to pharmaceuticals requires breaking petroleum into small molecules and introducing functional groups so that numerous chemical reactions can take place.

As important as petroleum is as a source of chemicals to produce products of the chemical industry, a much larger use in our modern society is the source of fuel for the internal combustion engine. In the USA, hundreds of millions of tonnes of petroleum are required annually (a tonne is 1000 kg, a metric ton). This is the same order of magnitude as the food we produce. For fuel, the molecules must be broken down to a molecular weight range consistent with the required volatility, and the structures must be rearranged so that combustion takes place with the control necessary for modern engines. The objective of the energy industry is to transform petroleum into both aromatic and aliphatic highly branched molecules with desirable combustion characteristics in automobile engines. The very different objective of the chemical industry, as indicated above, is to transform petroleum molecules into functional intermediates capable of participating in numerous chemical reactions.

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1.2
How do we achieve these Two Objectives? By Using two different Kinds of Cracking: One depends on Free Radicals and the Other on Carbocations

The story of how petroleum is changed into the molecules necessary for the chemical industry on the one hand and into gasoline on the other is the story of laying the foundation of chemical technology in the twentieth century. And this remarkable story rests on two of the most common intermediates in organic chemical reactions, the carbocation and the free radical. Without these highly reactive trivalent states of carbon, the use of petroleum to support our lives would be impossible. To understand the role of carbocations and free radicals we must first explore two processes to which petroleum fractions are subjected: steam cracking and catalytic cracking.

Cracking is a well-chosen word since the large molecules of petroleum are converted to smaller molecules, just as a large object may be "cracked" into pieces. Why does steam cracking require free radicals, and catalytic cracking carbocations? And why do these intermediates change the petroleum molecules in such different ways?

In *steam cracking*, the saturated hydrocarbons in petroleum are cracked to smaller molecules with double bonds. The conversion from larger molecules to smaller ones arises from the "cracking," that is, breaking of carbon–carbon bonds. The formation of the double bonds also arises from "cracking", that is, breaking carbon–hydrogen bonds to form H_2. In the smaller molecules present in petroleum and in natural gas such as ethane, propane and butane, carbon–hydrogen bonds are cracked and the corresponding olefins are formed. For the larger molecules, cracking of both carbon–carbon and carbon–hydrogen bonds is important.

Why is the formation of double bonds in petroleum-derived molecules so valuable for the chemical industry? The answer is the same for any functional group in organic chemistry – specific chemical reactivity. Virtually all chemical reactivity in organic chemistry is based on transformation of functional groups, and the double bond is the simplest of all the functional groups. The value of the double bond therefore arises for two reasons: (i) from its ease of formation by cracking of petroleum; and (ii) from its specific reactivity. If a double bond is present, then chemists can design chemical reactions to yield specific products. For example, the double bond in propylene allows formation of isopropylbenzene or polypropylene, while the double bond in ethylene allows formation of ethylene oxide or vinyl chloride. Saturated hydrocarbons, in contrast, generally are less reactive than olefins, and when a reaction is possible it does not occur in a specific manner. Chemical reactions of saturated hydrocarbons most often yield mixtures.

In *catalytic cracking*, large molecules are also broken into smaller ones. But the intermediate carbocations favor rearrangement of the often linear or cyclo-aliphatic carbon skeletons to highly branched, but still saturated hydrocarbons. Such molecules behave very well in the modern internal combustion engine. Every gas station tells us this when it touts high-"octane" number gasoline.

1.3
What is in Petroleum?

In Fig. 1.1, we see examples of the types of molecules found in petroleum. There is an enormous structural range, from small molecule gases to high molecular weight substances so nonvolatile that they cannot be vaporized at the highest accessible temperatures, even under high vacuum. In fact, petroleum contains so many different types of molecules of such varied structure that the tools of analytical chemistry are overwhelmed by the task of identifying all of them. The way that chemists deal with complex mixtures is by *fractionation*. The first task, then, is to fractionate petroleum by using, on a very large scale, a technique familiar to every chemist, fractional distillation. Some of the huge towers one observes when driving past a petroleum refinery are the distillation columns. What a difference from the small glass column used in the laboratory! But the

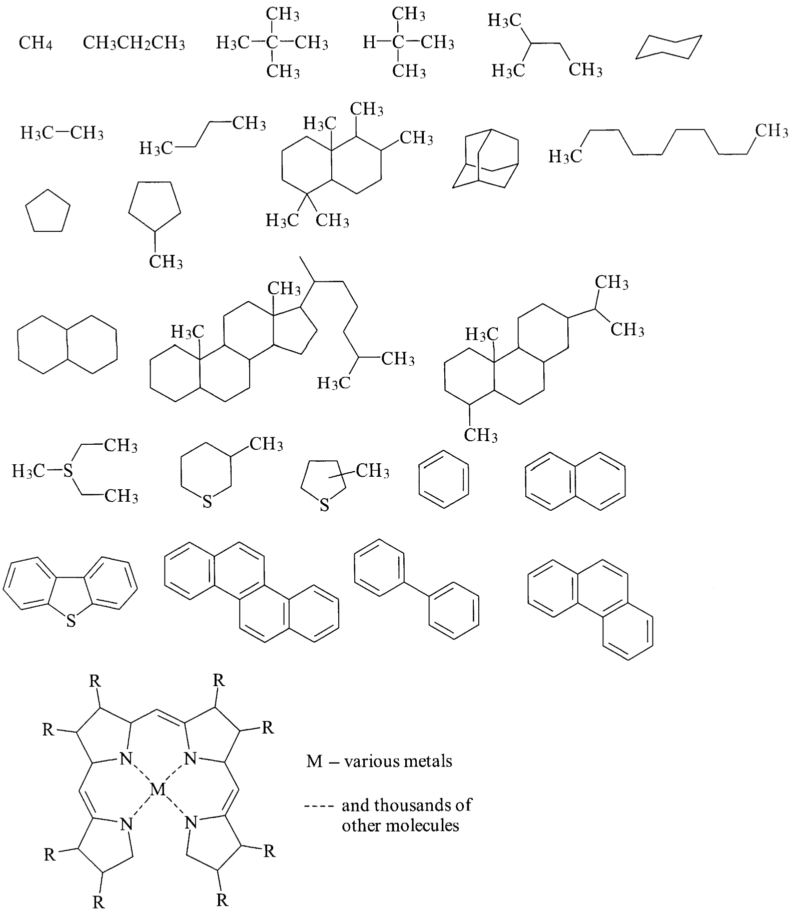


Fig. 1.1 Examples of the range of molecules found in petroleum.

Crude Oil Distillation

	Fraction	**Boiling Point Range**	**Comments**
1	Gases mostly CH_4	< 20°C	Similar to natural gas
2	Naphtha (light)	70—140°C	Largely C_5 to C_9 hydrocarbons
3	Naphtha (heavy)	140—200°C	Largely C_7—C_9 hydrocarbons
4	Atmospheric gas oil		
	Kerosene	175—275°C	Mostly C_9—C_{16} hydrocarbons
	Diesel Fuel	200—370°C	Mostly C_{15}—C_{22} hydrocarbons
5	Heavy Fractions	> 370°C	Molecules too involatile to distill under high vacuum
	Lubricating Oil Residual or heavy fuel Oil Asphalt or "resid"		

Fig. 1.2 Types of molecules found in various petroleum fractions.

principles applied are identical if one is fractionating 1 gram or thousands of tonnes. Fig. 1.2 relates the temperature range for distillation of the various fractions to the types of molecules present in the fraction. Certain of these fractions obtained by fractional distillation of the petroleum are then chosen for the different cracking processes.

1.4
The Historical Development of Steam Cracking

In addition to the two types of cracking already described, there is a third type, *thermal cracking*, which is less important today although it was the first type of cracking invented. The concept of thermal cracking is attributed to Professor Benjamin Silliman of Yale, who in 1855 suggested that during the distillation of petroleum (then known as rock oil, a term later replaced by petroleum, a contraction of the Latin *petra* (rock) and *oleum* (oil)) it decomposes and that some of these decomposition products might have economic value.

Economic value in the mid-nineteenth century meant fuel for lamps – a product that today we call kerosene and which is now used to fuel airplanes. Patents issued between 1860 and 1912 show that there was considerable interest in achieving higher kerosene yields from petroleum. But it was not until 1912 that William Burton and his associates at Standard Oil of Indiana were granted a patent that defined a practical process called thermal cracking. A plant, built one year later, produced equal amounts of gasoline (which by that time was a much sought-after product), kerosene and residual or unreacted petroleum.

Coking was a serious problem, and coke – a porous, hard, involatile residue consisting mostly of carbon – was removed after every 48-hour cycle by laborious means. The need to avoid labor costs led to the Dubbs process. This was a development of a father and son who shared an intense interest in petroleum. Dubbs originally named his son simply Carbon Dubbs. Later, Carbon assumed the middle name of Petroleum. Carbon then named his own daughters Methyl and Ethyl. In engineering school, Carbon learned about partial pressures, and accordingly suggested to his father that if water were included in the thermal cracking reaction then the partial pressures of the hydrocarbons would be reduced. Because coke formation arises from the combinations of the petroleum-derived molecules and their reactive free radical fragments, reducing the partial pressure reduced coke formation by limiting the number of collisions between these fragments. In this manner, steam cracking replaced thermal cracking for the transformation of petroleum into useful chemicals.

Most important from the chemist's point of view, both thermal cracking and steam cracking produced olefins. Although not as many olefins – and certainly not in the quantities produced today from petroleum – this early production of olefins nevertheless started the ball rolling toward the connection of the chemical industry to petroleum. As we shall see when we describe the mechanism of steam cracking, free radical chain reactions were responsible for producing the olefins. The modern steam cracker is today the heart and soul of the chemical industry because it produces three of the industry's basic building blocks: ethylene; propylene; and butadiene. Also produced by steam cracking are lesser amounts of isobutene, 1-butene, 2-butene, and C_5 olefin isomers, which are all important intermediates for the chemical industry. And, under certain conditions and using fractions of petroleum containing C_7–C_{12} hydrocarbons, steam cracking also produces benzene and toluene. Worldwide, this is a major source of these aromatics. Literally, there is here a cornucopia of molecules to form the foundation of the chemical industry and therefore of our modern world.

During the 1920s, Union Carbide and Standard Oil of New Jersey were the first companies to start experiments with steam cracking and the subsequent conversion to functional products of the ethylene and propylene produced. It was in fact in 1920 that Standard Oil reacted propylene with water in the presence of an acid catalyst to provide the first petrochemical, isopropanol, a classic Markovnikov addition of water to an alkene. Its major use was not for rubbing alcohol but for oxidation to acetone, a solvent whose first use was developed in World War I as a component for the preparation of the explosive, Cordite. In Chapter 9 (see Section 9.2), we shall discover how another route to acetone for its use in Cordite played a role in world history, and in Chapter 4 (Section 4.13) how Cordite is related to dynamite, the explosive that generated the wealth behind the Nobel Prizes.

Chemists long realized that knowledge of the specific reactivity of a functional group would allow prediction of the chemical behavior of a wide range of molecules containing that functional group. And steam cracking made widely available building blocks with the most basic functional group, the alkenes. Suddenly, all kinds of new possibilities were visualized because of the availability of large amounts of these olefins. Therefore it became necessary to understand the reactivity patterns of the double bond and the mechanisms of the possible reactions. This information was gained by research motivated by the needs of the chemical industry.

1.5
What was Available before Thermal and Steam Cracking?

What kinds of molecules with what functional groups were available to the chemical industry before alkenes? The initial major building blocks were aromatics – benzene, toluene, and naphthalene – and the exceptionally dangerous explosive, acetylene. The aromatics came from coke oven distillate or coal tar and were important early in the Industrial Revolution. Coke, noted above as a hard, nonvolatile residue of petroleum cracking, was first made from coal by distilling off the volatile components. Actually, a patent for the conversion of coal to coke was first issued in England in 1590, but it was not until 1768 that a certain John Wilkinson built a practical oven for converting coal to a purer form of carbon. As development progressed it became obvious that the distillate from the operation contained a wealth of chemicals. The benzene, naphthalene, and anthracene present in the coal tar provided the basis for synthetic dyes, which had properties that rivaled and even exceeded those of natural dyes. In the manner described above, the chemical industry found the beginnings that led to the huge enterprise it is today. It was, however, not until very much later that steam cracking made ethylene and propylene available so that benzene's two most important derivatives – ethylbenzene for styrene and isopropylbenzene for phenol and acetone – could be made cheaply. These processes will be discussed in Chapter 3.

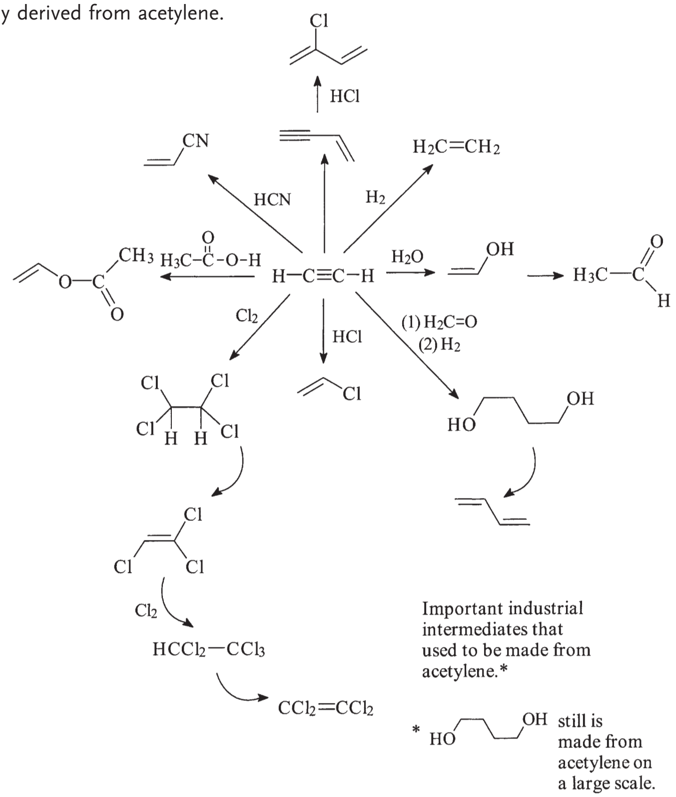
1.6
Acetylene was Widely Available before Steam Cracking and it was Exceptionally Useful but Many wanted to replace this Dangerous Industrial Intermediate. Happily, Double Bonds replaced Triple Bonds

Acetylene, which will be discussed extensively in Chapter 10, was important in the early days of the chemical industry. Its triple bond is capable of undergoing a wide range of reactions, and in addition there is a special reactivity of the hydrogen bound to the triply bonded carbon atom. Acetylene and alkynes in general are still used today in synthetic work to make complex molecules, and a whole chapter in most organic chemistry textbooks is devoted to acetylene. But acetylene is no longer a valuable part of the bulk chemical industry in spite of the fact that large-scale organic molecules were made from it before the advent of the alkenes from petroleum cracking.

Some of the most important chemicals supporting our modern technology – vinyl chloride, vinyl acetate, acetaldehyde, 1,4-butanediol, and from it 1,3-butadiene – could be prepared from acetylene (Fig. 1.3) although all these processes are now obsolete except for 1,4-butanediol preparation. Even here however, alternate processes are in use and will eventually take over. For the chemical industry, the double bond has displaced the triple bond.

What is the problem with acetylene? Why should the industry rush to replace acetylene with the alkenes produced by steam cracking of petroleum fractions? The answer, as will be discussed in detail in Chapter 10 (Sections 10.2 and 10.3), is found in its explosive characteristics and its cost.

Fig. 1.3 Chemicals historically derived from acetylene.



Important industrial intermediates that used to be made from acetylene.*

* still is made from acetylene on a large scale.

By 1920, the reaction of calcium carbide with water was the accepted way to make acetylene (Chapter 10, Section 10.4), which was used for lighting and welding torches. These applications still apply and take advantage of acetylene's high heat of combustion leading therefore to the extremely high temperatures reached when acetylene burns. In other words, the same character that makes acetylene so dangerous also, under controlled conditions, makes it so useful. At that time, The Union Carbide and Carbon Chemicals Company – a name derived from the source of acetylene – and a company name later shortened to Union Carbide, was founded to make olefins and aliphatic chemicals derived from acetylene.

George Oliver Curme, Jr., who was working at the Mellon Institute in Pittsburgh, had started working in 1913 on more economical routes to acetylene and demonstrated that acetylene could be produced via thermal cracking of hydrocarbons. Union Carbide became one of his sponsors. But ironically, while Curme attracted the attention of a company interested in acetylene production he discovered that olefins could also be produced by heating petroleum and realized that ethylene in terms of safety and cost had advantages over acetylene. Instead of focusing on acetylene, Curme started to work on developing a chemistry to replace acetylene-based processes with ethylene-based processes. Those ornery professors!

1.7
Petroleum yields Ethylene and lays the Groundwork for a New Kind of Chemical Industry

Thus, in the early part of the twentieth century it became apparent that useful industrial intermediates could be derived from alkenes and that alkenes – and especially ethylene and propylene – could be derived from petroleum. This provided Union Carbide with the impetus to start developing the petrochemical business, a commercial enterprise that would start with petroleum and through the intermediacy of olefins synthesize high value-added industrial intermediates. Standard Oil also recognized the opportunities as noted in the synthesis of isopropanol from propylene. Isopropanol was the world's first petrochemical (see Section 1.4). Suddenly, petroleum became useful not only for the combustion properties of its molecular constituents, which could be used to light lamps or power internal combustion engines, but also as a source of chemicals derived from alkenes. Witness the birth of the petrochemical industry!

The advent of polyethylene (Chapter 2, Section 2.2) immediately before World War II and the synthesis of styrene (Chapter 3, Section 3.3) as a component of synthetic rubber during World War II would not have been possible without a cheap source of ethylene. And steam cracking was a source far superior to the old method of dehydration of fermentation-based ethanol or the even more expensive hydrogenation of acetylene (Fig. 1.3).

By 1970, the steam cracker had firmly established itself as a way to produce ethylene and other alkenes, and acetylene was dropped from the list of the 50 most important chemicals in the United States. The conversion of Burton's, Dubbs' and Curme's developments into a modern cracker – the cost of which is close to one billion dollars – involved engineering work on the part of numerous companies. In 2002, the German company BASF and the Belgian company Fina, completed a cracker in the United States that produces 1.7 billion kilograms of product – 0.9 billion kilograms of ethylene and the remainder as C_3–C_4 alkenes. A world scale cracker, prior to this, produced 0.7 billion kilograms of ethylene. Even larger crackers than that of BASF are in the planning stages in 2002. In this business, bigger is better, that is, more economical.

1.8
But What about that Thirsty Internal Combustion Engine? The Development of Catalytic Cracking

Catalytic cracking of petroleum is designed to favor rearranging the molecular structure to maximize branching, rather than cracking the molecules into smaller fragments leading to double bonds, as is the situation in steam cracking. Although fragmentation does certainly occur, the petroleum fraction (see Fig. 1.2) most desirable for catalytic cracking is in the range of volatility compatible with end use as gasoline. The idea here is to maintain the volatility of these molecular components of petroleum while rearranging their structure from linear to branched hydrocarbons.

What's wrong with the volatile small molecules produced in modern steam crackers for use in internal combustion engines? Why is gasoline not produced this way? It could be, but our automobiles would not work very well. The reason is that in steam crackers the only source of energy for breaking down the petroleum molecules is heat; and the only chemical intermediates driving the chemical processes are free radicals. As we shall discuss in detail later, these conditions can break down the petroleum molecules but cannot cause rearrangements of the structure. If the original molecule in petroleum is linear, so the fragment produced by the bond breaking will be linear. There will be, with rare exceptions, no rearrangements of the carbon skeleton in the fragmentation reactions.

Gasoline contains both aromatic and aliphatic molecules and if the aliphatic molecules are linear hydrocarbons, saturated or not, one produces poor gasoline. Only hydrocarbons with branched structures and with the volatility compatible with the internal combustion engine, molecules in the range of C_8 hydrocarbons, allow for control of the rate of combustion necessary to drive these engines at their highest performance.

If the rate of combustion in the cylinders of the internal combustion engine is not compatible with the smooth movement of the pistons, the engine "knocks." Engines running on linear hydrocarbons such as *n*-heptane (assigned octane number zero) have high knocking characteristics, while branched hydrocarbons such as 2,2,4-trimethylpentane (assigned octane number 100) cause engines to run smoothly. The octane number of a fuel is the percentage of 2,2,4-trimethylpentane that must be mixed with *n*-heptane to give the same knocking behavior as the new fuel. Gasoline with an octane number of 86 therefore corresponds to an 86 : 14 mixture of the branched to the linear hydrocarbon.

How can we convert the linear hydrocarbons found in petroleum to branched hydrocarbons that will work well in the internal combustion engine? We need a chemical intermediate that can tear the molecules of petroleum apart and at the same time rearrange the carbon skeletons to branched structures (Fig. 1.4). As we shall see, the necessary intermediate is a carbocation and for its formation something more than heat is necessary. To produce a positive charge at the carbon atom, a carbocation, we need an acid catalyst – hence the name catalytic cracking.

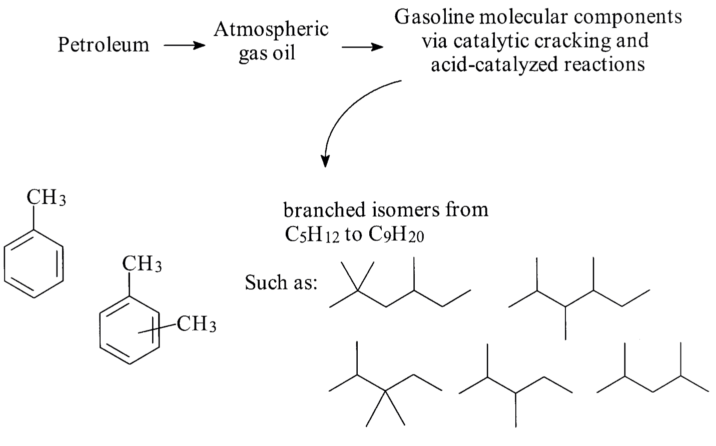


Fig. 1.4 The route to high-octane gasoline.

1.9
Discovery of the Proper Catalyst for Catalytic Cracking: From Natural Synthetic Zeolites

As internal combustion engines increased in power, the inadequacy of thermal and then steam cracking to produce appropriate gasoline became apparent. There is a legend in the petroleum industry that the first successful catalytic cracking process was invented during the 1920s by A.J. Houdry, who was searching for a better gasoline for his race car. Chemists had tried before to use acid catalysts for cracking, but these were based on aluminum trichloride, which proved inadequate. Houdry's catalyst was a natural clay or zeolite, a complex structure based on silica and alumina. We shall encounter zeolites again in Chapter 3 (Sections 3.6 and 3.7) on electrophilic aromatic substitution where the acidic characteristics necessary for that reaction are described.

The basic building units in the zeolites are tetrahedral arrangements of silicon and aluminum. Four oxygen atoms surrounding each metal atom bridge the metals into a complex network. But the remarkable characteristic of zeolites is that this network structure is formed with a regularity giving rise to a microporosity in which channels are formed of dimensions similar in size to that of small hydrocarbon and aromatic molecules, several Angstroms to tens of Angstroms across. These critical dimensions are subject to control by the synthetic methods now used to prepare the zeolites.

What is the nature of these channels? Because silicon is neutral in its tetravalent state, there is no charge associated with silicon bonded to four oxygen atoms. However, aluminum is neutral in its trivalent state and because every aluminum atom in the zeolite is bonded to four oxygen atoms, each aluminum atom carries a negative charge requiring, therefore, a counterion to balance this charge. Fig. 1.5 shows the general structure of part of the zeolite showing the bonding between the tetrahedral aluminum and silicon oxides and the formation of the cavity. The charge character of zeolites is seen clearly in the general formula for these substances with sodium as the positive counterion: $Na_x[(AlO_2)_x(SiO_2)_y][H_2O]_y$.

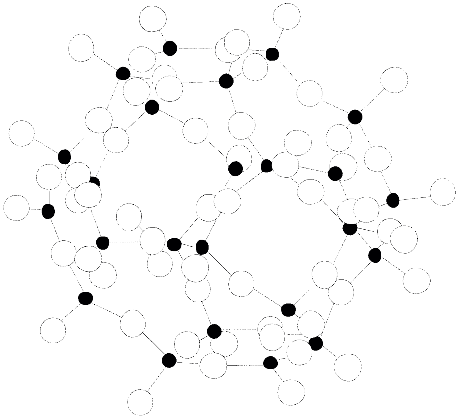


Fig. 1.5 Zeolite structure. The arrangement of AlO_4 and SiO_4 tetrahedra which gives the cubo-octahedral cavity in some zeolites and feldspathoids. • represents Si or Al. (Reproduced from *Advanced Inorganic Chemistry*, 3rd edition. F.A. Cotton and G. Wilkinson, Interscience/Wiley, 1972, p. 324.)

The channels therefore are highly polar! The counterion is usually a sodium ion, but methods are available to exchange the Na^+ for NH_4^+. If strong heating follows this exchange, ammonia is released leaving behind a proton as the positive counterion for the negative charge at each aluminum atom in the zeolite network. Not only are the channels now highly polar but they are also sources of Brønstead acidity, a potent chemical mix. As in an ancient Egyptian pyramid, the molecular guest of proper size and shape is led through these channels, as through a gauntlet, to inner chambers with all the walls lined with numerous charged aluminum atoms attended by their proton counterions. This shape and size selectivity of the zeolite is one of the most fascinating aspects of industrial zeolite catalysis. The chemistry catalyzed by this environment is therefore restricted to molecules of certain sizes, in contrast to exposure to a polar and acidic environment in open reaction vessels in which any molecule with the proper functionality may be subject to catalysis.

When Houdry first used these materials, they were found in nature as clays and very little was known about them. The natural zeolites had both the proper acidity on appropriate treatment and also pores of the proper size to admit suitable molecules found in petroleum. There followed the rearrangement into the branched structures necessary for a good gasoline. The zeolites used by Houdry made catalytic cracking practicable. They were a great improvement over earlier attempts by chemists at Gulf Oil Company to use acid catalysts based on aluminum trichloride, which was a rational choice considering its use in the Friedel–Craft reaction.

But Houdry's catalyst required frequent regeneration. It was not a complete success because coke – that old nemesis of thermal cracking – had to be burned off, and the intense heat required threatened the integrity of the catalyst. Nevertheless, two companies, Socony Vacuum Oil Co. (now ExxonMobil Oil Co.) and Sun Oil Co. both built Houdry plants in 1936. These plants were tiny by today's standards, but they proved that the process worked. And in fact they were just in time to provide gasoline for the battle of Britain, that famous war in the air that doomed the air superiority that Nazi Germany counted on for their ultimate success in World War II. The Luftwaffe had the right to expect success in the air war. After all, they had superior aircraft with more powerful engines and excellent pilots. But the British had gasoline produced by the Houdry catalytic cracking process – gasoline with the branched structure associated with high octane numbers. This gave the British airplanes the greater power and maneuverability that contributed greatly to dashing the myth of Nazi superiority.

Subsequently, The Standard Oil Development Co., working closely with noted thermodynamicist, W.K. Lewis of M.I.T., conceived the idea that a powdered zeolite catalyst might be useful. And from this evolved the process known as fluidized catalytic cracking (FCC). The powdered catalyst is "fluidized" in a vessel by gas jets and thus provides not only a huge area for access of the molecules to be subject to catalysis by the zeolites but also a convenient way to remove the heat of reaction. In addition, the zeolite catalyst can be transferred easily for it actually takes on the characteristics of a fluid, which has been described as having the characteristics of quicksand. Many improvements in the zeolite catalysts have been made in the ensuing years, mainly by using synthetic zeolites in place of the acid-leached montmorillonite clays originally used by Houdry. An important modification is a combination of these synthetic clays with a zeolite designated ZSM-5.

ZSM is an acronym for Zeolite Socony Mobil, the first name for the company that became Mobil, and subsequently ExxonMobil.

1.10
Let's compare the Mechanisms of Steam and Catalytic Cracking: Free Radicals versus Carbocations

Free radicals, the important intermediate in steam cracking and carbocations, the important intermediate for catalytic cracking, are both trivalent reactive species in which one electron is missing in the former and two in the latter. Thus, they share electron deficiency. For one example of a structural characteristic shared by carbocations and free radicals, organic chemists discovered long ago that increased stability arises from higher substitution in both of these intermediates. Both tertiary carbocations and tertiary free radicals are more stable than secondary ones, which are still more stable, respectively, than carbocations and free radicals based on primary carbon. The least stable are methyl free radicals or methyl cations. The quantitative data are found in Fig. 1.6, which presents the bond dissociation energies for formation of both free radicals and carbocations for various levels of substitution. The data clearly show that the bonds that must be broken to produce either carbocations or free radicals are weaker for a higher level of substitution and moreover that substitution makes a far larger difference to carbocations than to free radicals. We'll see the great importance of this latter fact in the discussion to follow.

1.11
How are Free Radicals formed in Steam Crackers and What do they do?

The chemical reactivities of carbocations and free radicals are very different as are the conditions for their formation. In the absence of either highly dipolar interactions on the

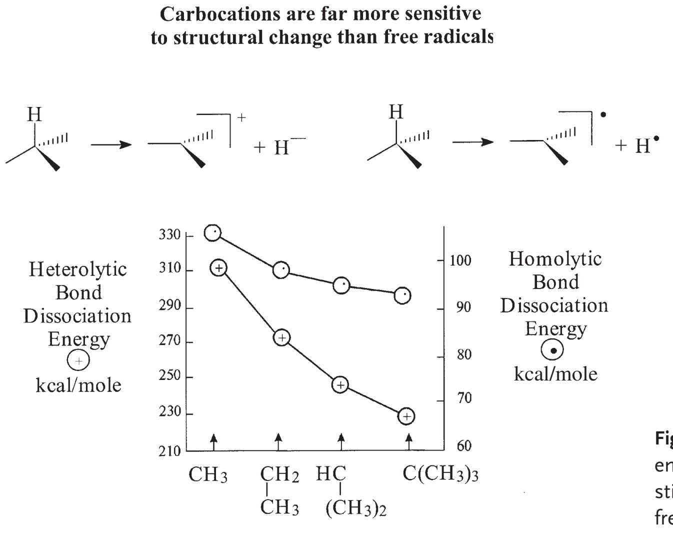


Fig. 1.6 Comparative plots of enthalpy versus degree of substitution for carbocations and free radicals.

one hand, or in polar solvents or acidic catalysts on the other hand, chemical bonds subjected to high energy tend to break homolytically. The fragments produced are free radicals. Each atom making up the covalent bond takes one of the shared electrons, and two free radicals are formed.

Chemical bonds are very strong, in the range of nearly 100 kcal per mole. Even at the high temperatures of the steam cracker, 650–900 °C, this means that enough homolytic breaking of carbon–carbon and carbon–hydrogen bonds in the petroleum molecules could not take place to account for the observed rapid breakdown of the petroleum. The petroleum molecules are exposed under the steam cracking conditions for only 30 to 100 milliseconds!

However, small concentrations of free radicals are produced. For example, reaction of oxygen with a hydrocarbon at these temperatures would lead to the abstraction of a hydrogen atom leading to both a carbon-based radical and a hydrogen peroxide radical. Homolytic breaking of carbon–carbon or carbon–hydrogen bonds does occur to a small extent, and this is another source of free radicals. The free radicals produced by these initiation steps, as seen below, can act far beyond their low concentrations to exert their effect on the petroleum. They are the initiation steps of a free radical chain process (Fig. 1.7). The propagation steps that follow these initiation steps do the major job leading to the conversion of petroleum to the low molecular weight olefins obtained.

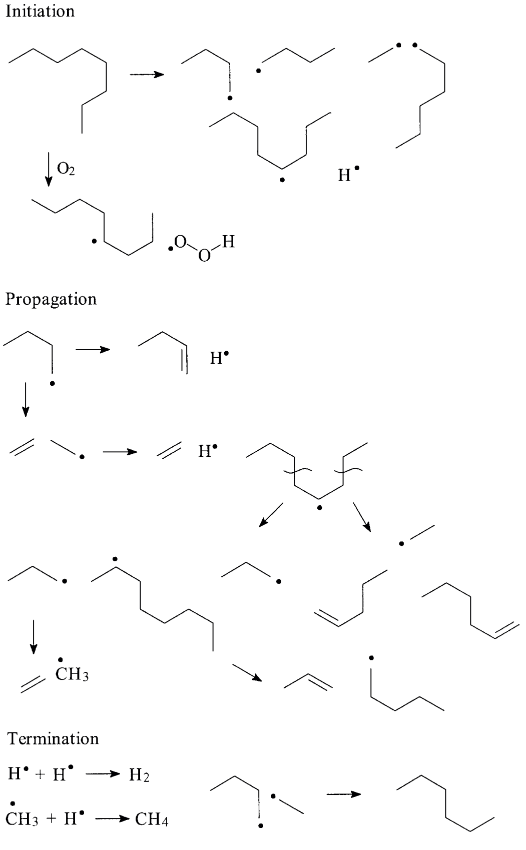


Fig. 1.7 Examples of reactions occurring in a steam cracker. Initiation, propagation and termination reactions of the chain process taking place for *n*-octane.

All the propagation steps in Fig. 1.7 are β-scissions, and each step propagates the free radical chain reaction since new free radicals are produced. Each new radical produced may then undergo another β-scission to produce another olefin and still another free radical, which may undergo another β-scission. At any step, a free radical produced may abstract a hydrogen atom from a new hydrocarbon molecule, thus further propagating the chain reaction by incorporating more molecular bystanders to enter into the chain process. Although from time to time two free radicals happen to come together and form a sigma bond and therefore reduce the overall concentration of free radicals in what is called a termination step (see Fig. 1.7), new initiation steps form new radicals to counter this loss. Remarkably, all of this happens in milliseconds as the petroleum fraction enveloped in steam passes down the hot tube to be transformed from a product pumped from the earth to low molecular-weight molecules of great value to the chemical industry.

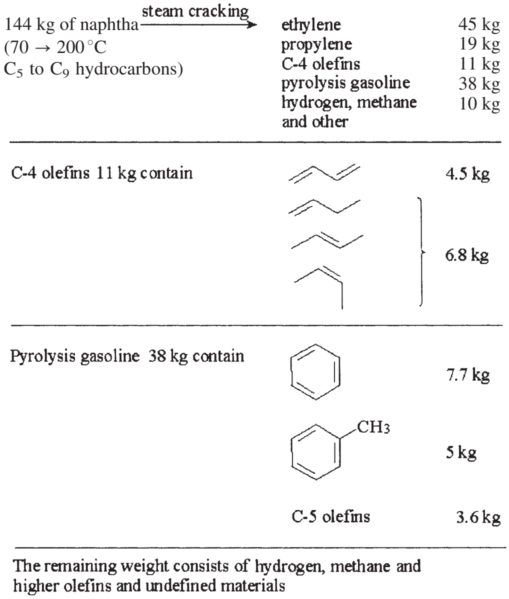
It is clear that the initial free radicals produced by the chemical reactions shown in Fig. 1.7 are capable of wreaking havoc, so-to-speak, among many molecules, cracking them to smaller molecules. In this way, a single initiation event can produce large numbers of olefin molecules, as many as thousands to one. The free radical chain reaction plays an important role in much of industrial chemistry. This is seen in two of many examples in Chapter 2 on the discussion of the free radical polymerization of ethylene (Section 2.2) and in Chapter 3 on the production of cumene hydroperoxide (Fig. 3.11). In every instance the essential steps are the same – initiation, propagation, and termination. What has just been described is no different from the mechanism of the classic example of the free radical chain reaction that produces methyl chloride from methane.

β-Scission, shown in the propagation steps in Fig. 1.7, is an interesting reaction in which the radical at the secondary site breaks a bond once removed from it in order to form a double bond. Here, we find a classic route taken by these high-energy intermediates. The β-scission certainly removes the uncoupled high-energy radical intermediate from the site it occupies, converting the radical to a π-bond. But it does this at the cost of breaking a sigma bond and forming another free radical. And the new free radical is now not secondary but primary, a higher energy state according to the data in the graph in Fig. 1.6.

But in free radicals the energy difference between primary and secondary radicals is not very large (see Fig. 1.6), therefore easing the β-scission path. The overall enthalpic increase – the process is endothermic – is compensated for by the increase in entropy that results from the breaking of the larger molecules into smaller ones. Most important is the high temperature, which following the rule of LeChatelier increases the equilibrium constant favoring the endothermic direction, the cracking path. Because heat is absorbed in going from petroleum to the cracking products, supplying heat favors this direction.

Full naphtha, the combined petroleum fractions labeled light and heavy naphtha in Fig. 1.2, containing predominantly hydrocarbons with five to nine carbon atoms (see Fig. 1.1) is one of the feedstocks (although not the only feedstock) used for steam cracking. The steam cracking of full naphtha produces large amounts of ethylene, propylene, butadiene, isomeric butenes, benzene, toluene and xylenes. In the words of the chemical industry, the value of the products of the cracking represent how much value is added to the petroleum (Fig. 1.8).

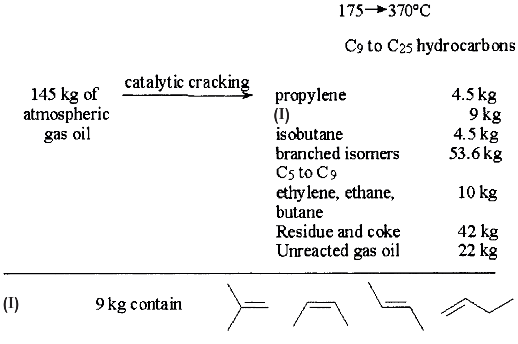
Fig. 1.8 Products created by the steam cracking of a petroleum fraction.



1.12
Now let's look at Catalytic Cracking and the Essential Role of Carbocations and their Ability to rearrange the Structure of Organic Molecules

When the natural clays were first introduced in the 1930s to improve the quality of gasoline (see Section 1.9), there was no understanding of the mechanism. It did not, however, take long for carbocations to be identified as the responsible reactive species. Two main lines of evidence supported this supposition. First, it was discovered that acidity – specifically Brønstead acidity – was critical to the function of the zeolite catalysts. Second, it was observed that isomerizations take place leading to the production of branched hydrocarbons. Many years of research on carbocations have shown their capacity to undergo skeletal rearrangements that interconvert constitutional isomeric forms.

Much is understood about what is happening in catalytic cracking: (a) the transformations undergone by petroleum molecules in a catalytic cracker arise from the intervention of carbocations; (b) the carbocations are formed from the petroleum molecules or their thermally cracked products by reacting with the acidic sites in the zeolite catalysts; and (c) the rearrangements producing constitutional isomers that are associated with the carbocations are not observed with free radicals. And here resides the difference between catalytic cracking and steam cracking (Figures 1.8 and 1.9). Steam cracking, rather than initiating rearrangements of the carbon skeletons of the petroleum molecules, yields ethylene as the most abundant product. This is the inevitable result of a series of β-scission reactions scissoring the unrearranged linear hydrocarbon chains in the atmospheric gas oil (Figures 1.7 and 1.8).



propylene	4.5 kg
(I)	9 kg
isobutane	4.5 kg
branched isomers C_5 to C_9	53.6 kg
ethylene, ethane, butane	10 kg
Residue and coke	42 kg
Unreacted gas oil	22 kg

Fig. 1.9 Examples of the molecular components obtained via catalytic cracking of atmospheric gas oil.

The branched molecules produced via catalytic cracking, which are useful for gasoline, are of far lower average molecular weight than the petroleum molecules in the gas oil fraction, which are in the range of mostly linear hydrocarbons of 9 to 25 carbons (Fig. 1.9). Therefore, not only rearrangement is occurring but also cracking – that is, breaking the molecules in the petroleum into smaller molecules but generally larger than the molecules produced in steam cracking. The difference is the difference between the reactivity of carbocations and free radicals.

1.13
What's going on inside those Zeolite Pores?

The nature of the zeolite catalysts and their gauntlet of acidic pores of narrow molecular size were described in Section 1.9. The chemistry in the catalytic cracking process takes place hidden in these analytically inaccessible and therefore somewhat mysterious pores. Although this hinders full understanding of the details of the chemical events that convert the molecules in petroleum to the branched hydrocarbons produced in the catalytic cracking process, petroleum chemists have a good idea of the overall mechanism.

The first problem is to understand how a saturated hydrocarbon is converted to a carbocation even in the presence of strong Brønstead acidity. There is evidence that a proton can react with a saturated alkane to form a carbocation via loss of hydrogen (Fig. 1.10). In essence, this amounts to the proton abstracting H^-, that is, a hydride ion, from the alkane. The tricoordinate positively charged carbon produced by this reaction, which we have been calling a carbocation, is also known as a carbenium ion and one will find the former in use in the industrial literature.

Another possibility for the formation of carbocations is that some thermal cracking occurs in the zeolitic pores of the catalytic cracker producing free radicals as in steam cracking and these free radicals undergo β-scission to form alkenes (Fig. 1.7). The double bond would be protonated very rapidly in the presence of the strong Brønstead acidity in the zeolite pore to form a carbocation. This proposal not only yields a mechanism for forming the carbocation but also offers an explanation for the cracking of the large molecules in the petroleum to the smaller molecules that occur in steam cracking. In the at-

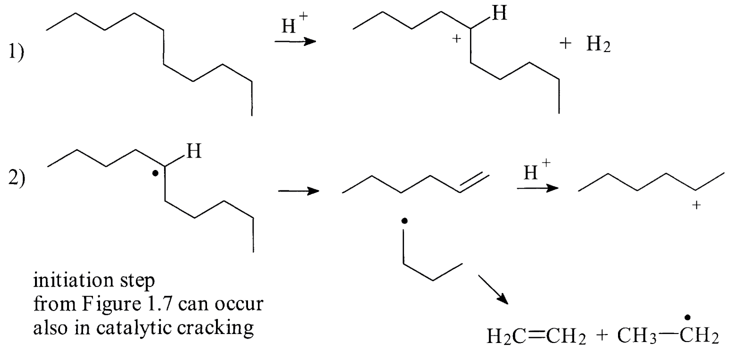


Fig. 1.10 Mechanisms for forming carbocations in catalytic cracking.

mosphere of steam cracking the absence of acidity translates to stability for the olefins produced, which are then products of the steam cracking process. However, in the environment of the zeolite pores in catalytic cracking the olefins produced would be protonated by the strong Brønstead acidity. These possibilities for initiation of the carbenium ions are shown in Fig. 1.10.

The carbocations once formed – as judged from their behavior in model systems under conditions where they can be studied in detail because they are not hidden in the pores of the zeolite – are known to undergo the kinds of rearrangements that produce exactly the branched molecules isolated from the catalytic cracker (see Fig. 1.9). Fig. 1.11 shows how the rearrangement of the 2-heptyl cation produced in the model reaction demonstrated in Fig. 1.10 can yield 2,3-dimethylpentane, one of the components of gasoline (see Fig. 1.4).

The key steps in this isomerization are 1,2-shifts of both an alkyl group and hydrogen. Some of the rearrangement steps shown in Fig. 1.11 are energetically uphill, processes that are aided by the high temperature of the catalytic cracking, which takes place in the region of 500 °C. Thus, secondary carbocations form primary carbocations or tertiary carbocations form secondary carbocations as momentary intermediates on the way to forming more stable carbocations (Fig. 1.11). All the rearrangement steps are reversible and favor the more substituted carbocation (Fig. 1.11). However, the unstable less-substituted carbocation, although not favored, can rapidly rearrange to the more stable carbocations (shown in Fig. 1.11), driving the structures increasingly toward the branched isomers. In other words, although there are some intermediate steps that raise the energy of the rearranging carbocation, the overall energetic direction is toward the most substituted carbocation (Fig. 1.11). The 1,2 shifts go on repetitively in the zeolite pores for every carbocation formed, thus eventually transforming linear to branched structures.

No one knows exactly how the isomerized carbocations are transformed to the neutral molecules released from the pores but it is likely that the alkenes produced, as shown in Fig. 1.9, arise from proton loss and hybride transfer reactions (Fig. 1.12). In this manner, the saturated alkanes are thought to arise from what are called chain transfer reactions, a term which is also used in polymerization as discussed in Chapter 2 (Section 2.3). In this process the isomerized carbocation abstracts a hydride ion (H^-) from a neutral molecule in the pore, as shown in Fig. 1.12, producing a new carbocation, which itself can then go on to

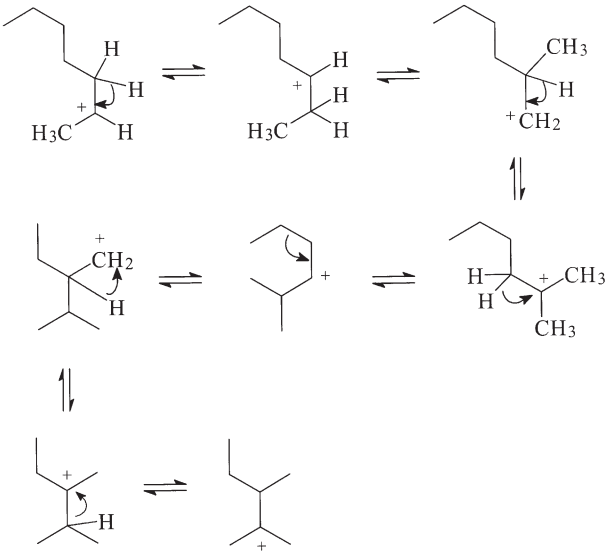


Fig. 1.11 Mechanistic detail of isomerization of the heptyl cation.

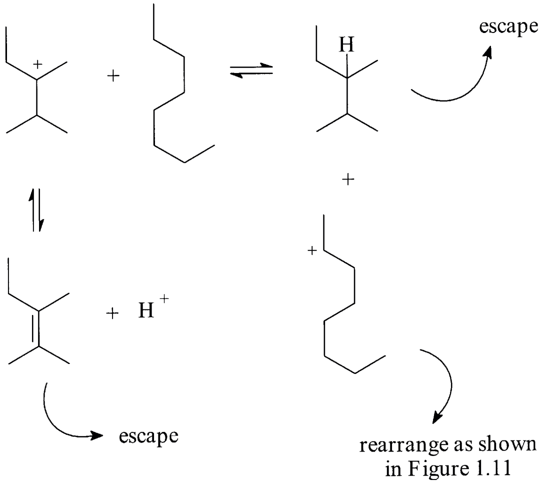


Fig. 1.12 Hydride transfer and proton loss can account for formation of the neutral products of catalytic cracking.

rearrange. These steps allow the release of the neutral molecules from the pore of the zeolite.

These highly energetic carbocations in the pores of the zeolite undergo other kinds of complex reactions with other molecules produced in these pores as well as with molecules directly from the petroleum. The ultimate result of much of this chemistry, which is still not clarified in its detailed steps, is the formation of residue and coke. It is not at all clear how this happens. A comprehensive picture of all the chemistry occurring in a catalytic cracker is still to be achieved, and this knowledge may well lead to a far more efficient use of petroleum. But whatever this picture shows, carbocations will certainly be the important intermediates.

1.14
Why do Steam Cracking and Catalytic Cracking produce such Different Results. Or, in Other Words, Why do Carbocations and Free Radicals behave so Differently?

What is the source of this difference between carbocations and free radicals? Although the tendency of the dependence of stability on structure is identical for carbocations and free radicals, the energy difference for structural change in carbocations is far larger than for free radicals (see Fig. 1.6). Carbocations are therefore driven to rearrange because the structural change on rearrangement gives rise to a large increase in stability. In this way, the positive charge can find a site, for example tertiary over secondary, that lowers appreciably the energy of the molecule (see Fig. 1.6). In a free radical a similar rearrangement, if it were possible (see below), would lower the energy of the molecule much less.

But most important, the β-scission path in a free radical is much more likely than this reactive path for a carbocation because the energy cost is far higher in such a scission in a carbocation (Fig. 1.6). β-Scission would produce a primary carbocation. β-Scission producing primary free radicals is far more likely (Fig. 1.7) and is the reaction responsible for cracking petroleum fractions to smaller molecules. This is the reason that steam cracking acts to break down the larger petroleum molecules to smaller molecules far more effectively than catalytic cracking (Figures 1.8 and 1.9). Here, we see how an important difference between free radicals and carbocations leads to molecules for the chemical industry, on the one hand, and fuel for the internal combustion engine, on the other hand.

In the steam cracker there is virtually no formation of branched hydrocarbons. Why not? The answer is not in the ease of β-scission, which is after all still enthalpically uphill even if the hill is not so steep (see Fig. 1.6), but rather in the fact that 1,2-shifts necessary for the rearrangements to the branched structures are restricted by the single electron occupation of the molecular orbitals in the free radicals. We cannot go into a discussion of molecular orbital theory and the source of the blocked 1,2 rearrangements of free radicals, except to try to stimulate the reader to search further by reading textbook discussions of what are called the Woodward–Hoffmann Rules and the general subject of orbital control of chemical reactions.

If nature worked otherwise, the free radical path could very well produce excellent gasoline and there would be no need for catalytic cracking. But in fact it is carbon in the positive state that is driven to rearrange its structure to satisfy the need for higher substitution; and it is allowed to carry out this rearrangement by the empty orbital associated with this positive charge. In this way catalytic cracking is the route to many of the molecules that eventually find their way into the high-octane gasoline necessary for modern engines.

1.15
Summary

The industrial drive to use petroleum to produce chemicals of greater use to society and therefore of added economic value led to the ultimate development of steam cracking and catalytic cracking. It is difficult to conceive of the development of modern technology without the transformations of the hydrocarbons in petroleum to the alkenes necessary for the chemical industry and the branched hydrocarbons necessary for the internal combustion engine. In this chapter, some key turning points in the development of petroleum chemistry are highlighted as are the essential roles played by free radicals and carbocations. The mechanistic difference between steam and catalytic cracking is essential to form the different products of these cracking processes.

The difference between free radicals and carbocations can be traced to a favored β-scission path taken by radicals while carbocation intermediates favor isomerization of the carbon skeleton. And this difference resides in the difference in the fundamental nature of these species. Producing radicals from the molecules in petroleum requires only supplying enough energy in the form of heat to overcome the homolytic bond energies and to initiate free radical chain reactions. In contrast, producing carbocations from these molecules requires a source of acidity, which was discovered when petroleum was subjected to high temperature in the presence of modified natural clays. That discovery stimulated the study of the chemistry of zeolites, which now can be synthesized industrially and are essential in the production of modern gasoline.

Some of the subjects treated in this chapter are listed below. These are key words and terms that act as reminders of the chapter's contents and should become a valuable part of your chemical vocabulary.

- Free radical chain mechanism
- Carbocation rearrangements
- Brønstead acidity
- Petroleum
- Alkenes
- Acetylene
- Branched hydrocarbons
- Isomerization reactions of carbocations
- Zeolites
- β-Scission of free radicals
- Steam cracking and catalytic cracking and their historical development
- Thermal cracking
- Gasoline

Study Guide Problems for Chapter 1

1. Predict the bonding and geometry in a free radical and in a carbocation using hybridization of atomic orbitals.
2. What evidence do you see in Fig. 1.1 for the biological source of petroleum? In what way might questions of chirality play a role in answering the question posed above and what kind of experiment would help to confirm your conclusion?
3. What are the various kinds of chemical reactions specific to carbon–carbon double bonds? Give as many examples as you can for each reaction type using propylene as the double bond-containing molecule, paying attention to the possible formation of isomers.
4. The first industrial process based on an olefin was hydration of propylene to yield isopropanol. How could you produce *n*-propanol from propylene? Give all reagents and show the mechanism of the reactions.
5. Propose detailed mechanistic steps for the formation of each of the industrial intermediates in Fig. 1.3.
6. Use the Kirk-Othmer *Encyclopedia of Chemical Technology* to discover what ultimate commercial use derives from each of the industrial intermediates in Fig. 1.3.
7. The reaction of calcium carbide, CaC_2, with water is highly exothermic. Offer an explanation for this high exotherm considering the pK_a of water.
8. How could acetaldehyde be synthesized from ethylene? Could propanal be synthesized from propylene in a parallel manner?
9. Propose a synthesis of styrene using benzene and ethylene as the carbon sources.
10. Why does formation of polyethylene from ethylene by any method produce large amounts of heat, a major problem for engineering polyethylene plants? Could a method be designed to produce polyethylene from ethylene that would be less exothermic?
11. How do the data in Fig. 1.6 relate to the difference between S_N1 and S_N2 reactions?
12. Chlorine reacts with methane under irradiation to yield methyl chloride among other products. Outline the mechanistic steps for this free radical chain reaction designating which are initiation, propagation, and termination.
13. When chlorine is heated with isobutane, a single monochlorinated hydrocarbon is overwhelmingly formed in spite of the fact that there are ten hydrogen atoms for which chlorine could be substituted. Use bond dissociation data from Fig. 1.6 as well as a table of bond dissociation energies in any textbook to determine the enthalpy difference for each step in the free radical chain processes that produce the product that predominates and, as well, any competitive products.
14. Propose steps that would produce 1,3-butadiene, and toluene and benzene (Fig. 1.7) in the steam cracking of full naphtha.
15. Catalytic cracking of atmospheric gas oil produces a wide variety of branched hydrocarbons varying in the range from about 5 to 9 carbons. Mechanistic proposals suggest that free radicals analogous to those formed in steam cracking give rise to olefin intermediates, which are then converted to carbocations and which then undergo rearrangements under the acid conditions of catalytic cracking. Write out detailed chemical reactions that follow these mechanistic ideas to form branched hydrocarbons with 6 carbons from linear hydrocarbons with 12 carbons.

16. Fig. 1.4 shows several 6-, 7- and 8-carbon branched hydrocarbons. Propose all steps that could take place in a zeolite pore from the respective linear hydrocarbon that could give rise to these components of gasoline.
17. Discuss how orbital symmetry ideas such as the basis of the Woodward–Hoffmann rules and the ideas of aromatic and anti-aromatic transition states relate to the fact that 1,2 rearrangements are observed in carbocations but not in carbanions. How might your discussion apply to the difference between steam and catalytic cracking of petroleum fractions?
18. Offer explanations for each of the terms in Section 1.15.