





## Reaction Mechanisms in Organic Chemistry



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*For my Wife Jale.*



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## Preface

For more than 40 years, I have taught courses on reaction mechanisms in organic chemistry at undergraduate and graduate level throughout my academic career. During my classes, I realized that many students do not like organic chemistry and most believe that it is a lesson to be memorized. I have searched for a way to change this idea. Organic chemistry is a systemic field like mathematics and hence memorizing is not necessary. Students need to know the reaction mechanisms in organic chemistry and understand their many common points. For example, there are many condensation reactions and students usually try to memorize them. However, they all have the same mechanisms and students must learn this. Starting from that point, I decided to write a book about these reaction mechanisms and emphasize the points common to them.

In my lectures, I always tell the students that chemical reactions occur because of a reaction between an acid and a base (a Lewis acid and a Lewis base). Therefore, they should learn the acid/base concepts very well in order to understand chemistry. For this, they need to determine in which part of a molecule the electron density is increased or decreased. They can achieve this by fully understanding the factors that influence electron density. In other words, they should have a firm grasp of the mesomeric effect and the inductive effect. A student who comprehends these concepts can predict what product will be formed as a result of a chemical reaction and will not rely on memorization. Therefore, I included these concepts in the first part of this book. I explained the mesomeric effect and inductive effect through detailed examples.

Another disadvantage faced by students is that most of them cannot perceive organic compounds in a three-dimensional structure. For this, the concept of hybridization needs to be explained clearly and understood fully. Then, the students can imagine the three-dimensional structure and understand how isomers are formed in some reactions. Therefore, I explained hybridization in detail in the introduction part.

A further aspect of organic chemistry that confuses students is oxidation/reduction. For this, they should know oxidation numbers well and not mix them up with formal charges. This subject is examined in detail in the book, along with examples.

After this introduction, the students begin to grasp the reactions quickly. I included substitution, elimination, and addition reactions as the essential ones. A student who has taken a one-semester organic chemistry course can easily comprehend these issues. Then, I examined the reactions derived from the carbonyl group. I emphasized that essential reactions are significant in this subject, which is very broad. With a good grasp of the carbonyl group's polarization and the acidity of the alpha proton, students can understand the carbonyl group and realize how simple condensation reactions are.

In the part on aromaticity, I first explained classical reactions after the concepts of aromaticity. Here too, I tried to find common points mechanistically. After these chapters, I moved on to more advanced topics that both undergraduate and graduate students can follow.

The chemistry of intermediates is extremely important mechanistically. A student who has learned the chemistry of the intermediate well can fully understand organic chemistry. For this reason, I focused extensively on carbocations, carbanions, radicals, and carbenes, which are involved as intermediates during the reactions. A student who can deal with these issues will have a full understanding of all the rearrangements.

The book's final chapters are devoted to the Woodward–Hoffmann rules and modern C–C couplings. These are subjects written for both undergraduate and graduate students.

In summary, in this book, I tried to discourage students from relying on memorization by drawing attention to reaction mechanisms' common points. I hope that this book will be useful to both undergraduate and graduate students at any time.

There may be one name on the front cover, but every book is the result of the hard work of many people. I gratefully acknowledge the following professors for their helpful critiques of this book at many stages during its development. They devoted a tremendous amount of time to review this book and made valuable suggestions.

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Although every effort has been made to eliminate all possible errors, it is likely that some typographical mistakes remain in the text. I would welcome comments from the readers, particularly those that point out mistakes so that they can be corrected, as well as suggestions for additions or other changes that will make the book more valuable to the reader.

This book of extensive scope could not have been produced without the excellent support I have had from many people at John Wiley-VCH. I would particularly like to thank the Editorial Director, Dr. Gudrun Walter, and the Executive Commissioning Editor, Dr. Elke Maase. They have been of great assistance at every stage of production. I am deeply grateful to my managing editor, Katherine Wong, who was always ready to do whatever was needed to make this book the best that it could be.

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I would also like to thank my daughter Gülşah, my son-in-law Onur, and son Berkay for their continued support and encouragement during the writing process.

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January 2021

*Metin Balci*  
*Ankara, Turkey*

## About the Author



*With his wife Jale*

Metin Balcı was born in Erzurum, Turkey, in 1948. He received his “Diplom Chemiker” degree in 1972, followed by a PhD degree in 1976 from the University of Cologne, where he worked with Professor Emanuel Vogel. He did postdoctoral work with Professors Harald Günther (Siegen, Germany), Waldemar Adam (Puerto Rico), and W. M. Jones (Florida).

In 1980, he joined the Department of Chemistry at Atatürk University and he became a full professor there in 1987. He spent one year (1986) at the University of Cologne and one year (1996–1997) at Auburn University (USA) as a guest professor. In 1997, he moved to Middle East Technical University in Ankara because of its reputation.

Metin Balcı has received several prizes, including the 1983 “Junior Research Prize” and the “Scientific Award” in 1989 from the Scientific and Technical Research Council of Turkey. Furthermore, he was awarded the “Science Prize” by the Science and Technology Foundation in 1990 and the

“Chemistry Prize” by the Chemistry Foundation and the “Science Prize” by the Ministry of Culture in 1991. He has received the Best Teacher of the Year Award (2000, 2003, and 2004) and the Distinguished Teaching Award at Middle East Technical University. His name was given to the NMR labs in the Department of Chemistry, Atatürk University, in 2010. He is an elected member of the Turkish Academy of Sciences.

His main research interest involves the synthesis of cyclitols, endoperoxides, cyclic strained compounds, bromine chemistry, and heterocyclic compounds. He has published 280 scientific papers and he retired in 2015. He has also published books entitled *Basic  $^1H$  and  $^{13}C$  NMR Spectroscopy* (426 pages, Elsevier, January 2005 and Turkish version in 2000 by METU Press). *The Reaction Mechanism in Organic Chemistry* (in Turkish, 2008) and an autobiography, *Science Rising from the East*, in 2019 (in Turkish) were published by the Turkish Academy of Sciences.

Metin Balcı has always maintained a strong interest in the great outdoors. He enjoys observing nature, hiking, skiing, and reading, as well as world travel.



## Abbreviations

9-BBN	9-borabicyclo[3.3.1]nonane
ABCN	1,1-azobis(cyclohexanecarbonitril)
acac	acetylacetonate
AIBN	azobisisobutyronitrile
BH(Sia) <sub>2</sub>	disiamylborane
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	binaphthol
Boc	<i>t</i> -butyloxycarbonyl
COD	cyclooctadiene
COT	cyclooctatetraene
CSA	camphorsulfonic acid
DBA	bis(dibenzylideneacetone)
DBU	1,8-diazabicyclo-[5.4.0]undec-7-ene
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DIBAL	diisobutyl aluminum hydride
DIOP	<i>O</i> -isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DIPT	diisopropyl tartrate
DMDO	dimethyldioxirane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DPPF	[1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II)
DPPP	bis(diphenylphosphino)propane
EPR	electron spin resonance spectroscopy
ESCA	electron spectroscopy for chemical analysis
HBpin	pinacolborane
HIA	hydride ion affinity
HMPA	hexamethylphosphoramide
HOMO	highest occupied molecular orbital
HSAB	hard and soft acids and bases
ISC	intersystem crossing
KHMDS	potassium bistrimethylsilylamide
LDA	lithium diisopropylamide
LHMDS	lithium bis(trimethylsilyl)amide
LTMP	lithium tetramethylpiperidine
LUMO	lowest unoccupied molecular orbital
<i>m</i> -CPBA	<i>meta</i> -chloroperbenzoic acid
MMPP	magnesium monoperoxyphthalate
MNDO	modified neglect of differential overlap
NBS	<i>N</i> -bromosuccinimide
<i>n</i> -BuLi	<i>n</i> -butyllithium
NICS	nucleus-independent chemical shift

NMO	<i>N</i> -methylmorpholine- <i>N</i> -oxide
NMP	<i>N</i> -methylpyrrolidone
PEPSI	pyridine enhanced precatalyst, preparation, stabilization, and inhibition
PIFA	phenyl-iodine(III) bis(trifluoroacetate)
PLE	pig liver esterase
PTAD	4-phenyl-1,2,4-triazoline-3,5-dione
RAMP	( <i>R</i> )-1-amino-2-methoxymethylpyrrolidine
SAMP	( <i>S</i> )-1-amino-2-methoxymethylpyrrolidine
SOMO	singly occupied molecular orbital
TASF	tris(diethylamino)-sulfonium difluorotrimethylsilicate
TBAF	tetrabutylammonium fluoride
TBDMS	<i>t</i> -butyldimethylsilyl
TEBA	triethylbenzylammonium salt
TFA	trifluoroacetic acid
TFPAA	trifluoroperacetic acid
THF	tetrahydrofuran
THP	tetrahydropyran
TIBSA	2,4,6-triisopropylbenzene sulfonyl azide
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMSOK	potassium trimethylsilylolate
PBDPSCI	<i>t</i> -butyl(chloro)diphenylsilane
TPP	tetraphenylporphine
XPS	X-ray photoelectron spectroscopy

## 1

## Basic Concepts

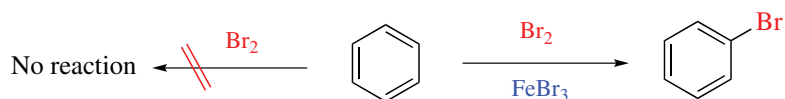
## 1.1 Introduction to Reaction Mechanisms

Chemical reactions are the processes by which chemicals interact to form new chemicals with different compositions. A new compound formed as a result of a chemical reaction does not bear the properties of the starting compounds; it has its own unique properties. In order for a chemical reaction to begin, some conditions (temperature, pressure, catalyst, etc.) must exist. For some compounds, it is sufficient to bring them together to start a chemical reaction. For example, water and sodium (provided they do not come in contact with air) are normally stable. However, a very violent reaction happens when these two come together. Sodium metal reacts rapidly with water to form a colorless solution of sodium hydroxide (NaOH) and releases hydrogen gas.



There is a common point regarding all chemical reactions, namely, transfer of electrons from one reactant to another (electron exchange). Therefore, one of the starting compounds should be capable of denoting electrons, while the other should accept electrons. In order for electron exchange to take place, some reactions require catalysts. A catalyst is a substance that can be added to a reaction to increase the reaction rate without being consumed in the process. The function of catalysts is to facilitate electron transfer by activating bond electrons and to lower activation energies ( $E_a$ ). As a result of electron transfer, some bonds are broken, some bonds rearrange, and new bonds are formed.

Benzene is an unreactive compound in the presence of halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ , or  $\text{I}_2$ ) because they are not electrophilic enough to attack the benzene ring and disrupt its aromaticity. However, the halogens must be activated by Lewis acid catalysts such as  $\text{FeBr}_3$  or  $\text{AlBr}_3$ .  $\text{FeBr}_3$  accepts electron pairs from bromine and makes it much more electrophilic. For a detailed mechanism, see Section 6.6.



Let us roughly analyze the processes that occur during the reaction of sodium with water. We see that the hydrogen atom, which is bonded to oxygen, breaks off from oxygen and forms hydrogen gas by binding to another hydrogen atom; on the other hand, the neutral sodium atom is oxidized by donating an electron and forming an ionic bond with the hydroxyl anion. This reaction appears to be very simple. However, complex processes are involved. We need to understand how products are formed as a result of a reaction. When a reactant turns into a product, we should look at which intermediates are involved during this reaction.

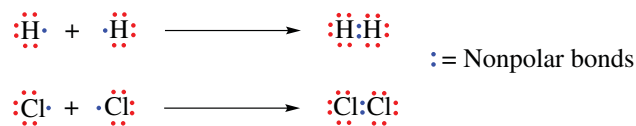
If we have a good understanding of what is going on at the intermediate stages, then we can guess what kind of products are formed as a result of the reaction. The step-by-step sequence of the intermediate stages of a reaction until the product is formed is called the *reaction mechanism*.

We have to understand what is happening at the intermediate levels. Otherwise, if we try to learn about a chemical reaction by writing reactants on one side of the equation and products on the other side, we will not be able to master organic chemistry. If the reaction mechanism is learned well, then one can see that organic chemistry is as enjoyable and systematic

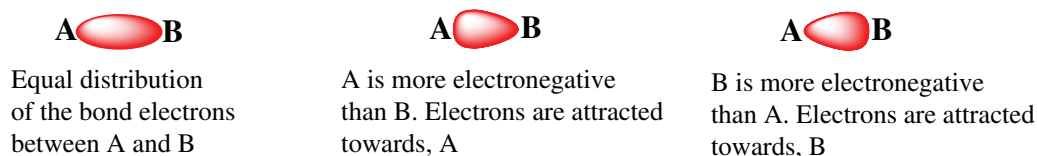
as mathematics. This is because, once the reaction mechanism is known, it is possible to predict what reaction will occur between two reactants and what products will be formed. Otherwise, if the reactions are learned without examining the mechanism (a type of learning based on memorizing), it becomes clear that organic chemistry cannot be understood. Then, organic chemistry becomes extremely boring.

Let us go back to the beginning. We emphasized that all chemical reactions occur as a result of electron exchange. To decide whether a compound is an electron donor or not, it is necessary to examine its electronic structure. In other words, it is necessary to examine the bonds between atoms and how the bonds are polarized.

The elements share electrons so that each atom attains a noble gas configuration. For example, two chlorine atoms can each attain a filled second shell by sharing their unpaired valence electrons. A bond formed by sharing electrons is called a *covalent bond*. Similarly, the hydrogen molecule,  $H_2$ , can also form a covalent bond by sharing electrons. The atoms that share the bonding electrons in the  $H-H$  and  $Cl-Cl$  covalent bonds are identical. Such bonds are called nonpolar covalent bonds. In some compounds, the bonding electrons are shared equally between the atoms.



In contrast, the bonding electrons between two different atoms are more attracted to one atom than to another because of different electronegativities (the ability of an atom in a molecule to attract electrons toward itself). The symmetrical distribution of the electrons between the two atoms is disrupted. This condition is called *bond polarization*.

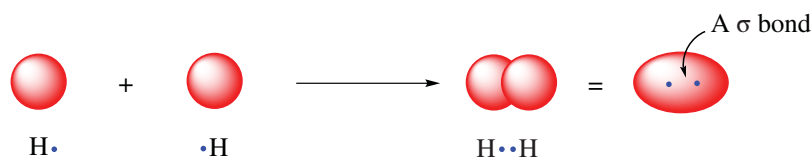


If electrons are attracted more strongly by A, the electron density increases around atom A and decreases around B. Therefore, this polarization makes A and B atoms more reactive. In such a case, groups with high electron density prefer to bind to atom B, while those with low electron density prefer to bind to atom A. In order to understand the reaction mechanism, electron polarization between bonds must be known very well. In this chapter, we first discuss about bonds, and in the next section, we focus on bond polarization. Here, I would like to draw the attention of the reader to two concepts. The first is the *inductive effect* and the second is the *mesomeric effect*. For a student who knows and understands these two concepts well, it will be easier and more enjoyable to travel along the paths of organic chemistry that seem to be winding.

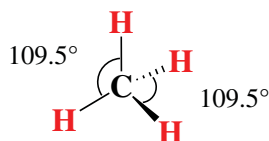
One of the other important points in organic chemistry, after learning bonding theory, is to think of molecules in a three-dimensional environment and estimate their true structures. This is an extremely simple thing. However, in order to understand it, it is necessary to work with simple organic models.

## 1.2 Covalent Bonding and Hybridization

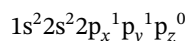
In organic chemistry, unlike in inorganic chemistry, we deal with covalent bonds. Bonds are formed by overlapping of orbitals and the placement of electrons in these orbitals. Let us first look at how a hydrogen molecule is formed. The covalent bond between two hydrogen atoms is formed when the 1s orbital of one hydrogen atom overlaps with the 1s orbital of a second hydrogen atom as shown below. Overlapping orbitals can be pure orbitals as well as hybrid orbitals.



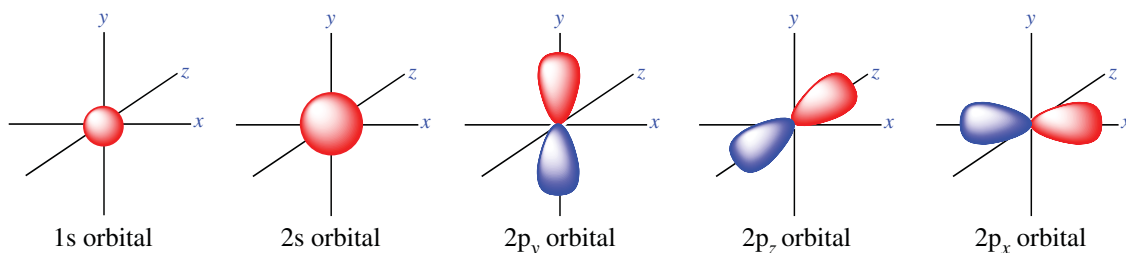
We will begin the discussion with the simplest molecule in organic chemistry, methane ( $\text{CH}_4$ ), with only one carbon atom. It is well known that the carbon atom is located in the center of the methane molecule, and it has four covalent C—H bonds. All the four bonds have the same length, and all bond angles are also the same ( $109.5^\circ$ ). This structure, which forms a smooth tetrahedron, is called a *tetrahedral* structure.



In the perspective formula, the hydrogen atoms shown with solid lines and the carbon atom are located in the paper plane. The bond represented as a dashed wedge projects behind the plane of the paper. The bond represented as solid wedge projects out of the paper (toward the viewer). To understand this structure of the methane molecule, it is necessary to first examine the electronic configuration of the carbon atom. The electronic configuration of the carbon atom is as follows:

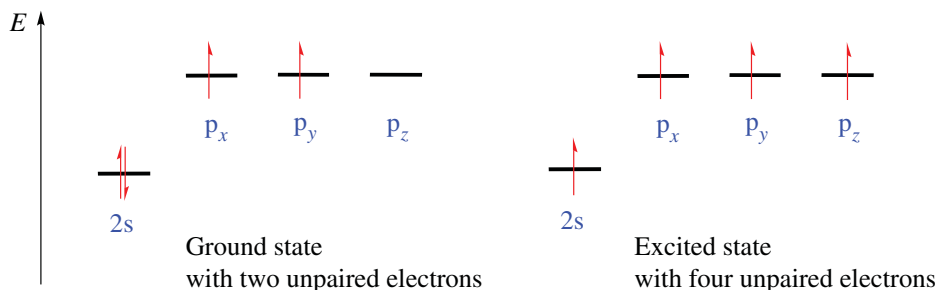


The atomic orbitals of the carbon atom are shown in Figure 1.1. The 2s orbital is drawn larger than the 1s orbital. Because the 2s orbital is in a location more remote from the core, it covers a larger area than the 1s orbital. The energy levels of these orbitals are different. The energy level of the 2s orbital is lower than that of the p orbitals. The energy levels of the 2p orbitals are equal to each other; in other words, they are degenerated.



**Figure 1.1** Atomic orbitals of the carbon atom.

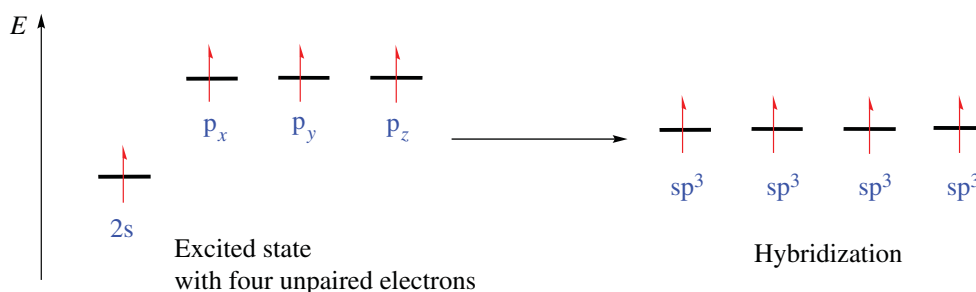
The carbon atom has only two unpaired electrons in its electronic configuration. This indicates that this atom can form only two covalent bonds, but with two covalent bonds, it would not complete its octet configuration. However, we know that the carbon atom forms four covalent bonds. Now, we need an explanation why carbon forms four covalent bonds. Without unpaired electrons, this configuration does not allow four bonds to be made. With a small amount of energy, one electron from the 2s orbital can be promoted into the empty  $2p_z$  orbital (Figure 1.2). This energy is readily compensated for by bond formation.



**Figure 1.2** Electronic configuration of the carbon atom in the ground state and the excited state.

Now, this configuration of carbon can form four covalent bonds. If carbon uses an s and three p orbitals to form these four bonds, the bond formed with p orbitals will be different from the bond formed with an s orbital. On the other hand,

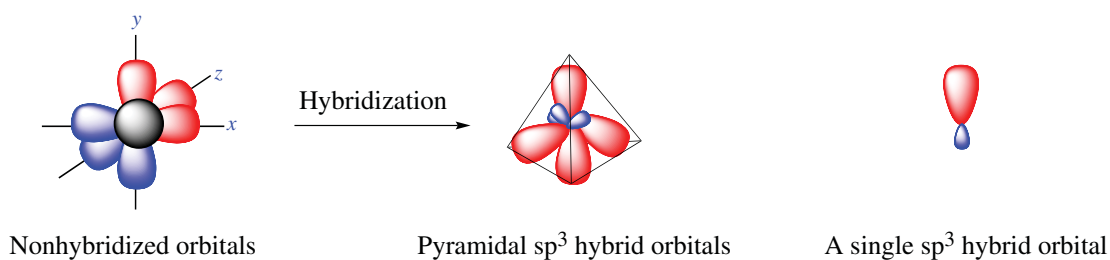
we know from spectroscopic studies that methane has a tetrahedral structure and the four C—H bonds in methane are identical. We have to answer the question *How can the carbon atom form four identical bonds by using three p orbitals and one s orbital?* Carbon uses the hybrid orbitals. To be able to generate this geometry, the 2s orbital on carbon is mixed with all the three 2p orbitals to make four equivalent  $sp^3$  orbitals with tetrahedral symmetry (Figure 1.3).



**Figure 1.3** Electronic configuration of the carbon atom in the ground state and the hybridized state.

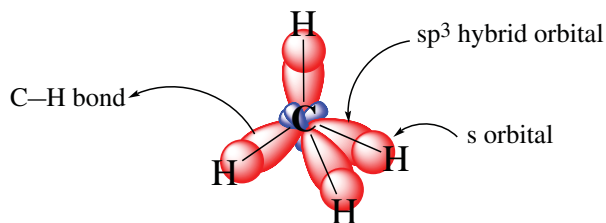
### 1.2.1 $sp^3$ -Hybridization of Carbon

Now, we know why the bonds in methane are equal. One s orbital and three p orbitals of the carbon atom combine to form four new orbitals. The concept of combining was proposed by Linus Pauling in 1931. Because the number of combining orbitals is 4, the number of newly formed orbitals is also 4. The phenomenon of orbitals creating new orbitals by combining with each other is called *hybridization*. These new orbitals (hybrid orbitals) are formed by the combination of one s and three p orbitals, and so they are called  $sp^3$  hybrid orbitals. The superscript 3 above the letter “p” indicates that three p orbitals were mixed with one s orbital to form hybrid orbitals. These orbitals are expressed as “s-p-three”; “s-p-cubed” is wrong. The hybridization involved is called  $sp^3$  hybridization. The energies of these hybrid orbitals are equal. The hybrid orbitals formed create a pyramidal structure (tetrahedral) and the angles between the hybrid orbitals are  $109.5^\circ$  (Figure 1.4). The new  $sp^3$  hybrid orbitals consist of two lobes such as the p orbitals. However, the lobes of an  $sp^3$  orbital are not the same size. The larger lobe is used in covalent bond formation. Each  $sp^3$  orbital has a 75% p character and 25% s character. This ratio is very important. As we explain some reactions later in the book, we will return to the s and p ratios of the hybrid orbitals.

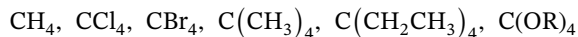


**Figure 1.4** Shape of the  $sp^3$  hybrid orbitals.

After explaining hybridization, we can go back to the methane molecule. The bonds between the carbon and hydrogen atoms in the methane molecule are not formed by the combination of pure s or p orbitals. The four  $sp^3$  hybrid orbitals of carbon can combine with four hydrogen s orbitals forming in methane ( $CH_4$ ). Because the  $sp^3$  hybrid orbitals are equal, the bonds formed by the carbon atom are also equal, and the methane molecule has a pyramidal structure.

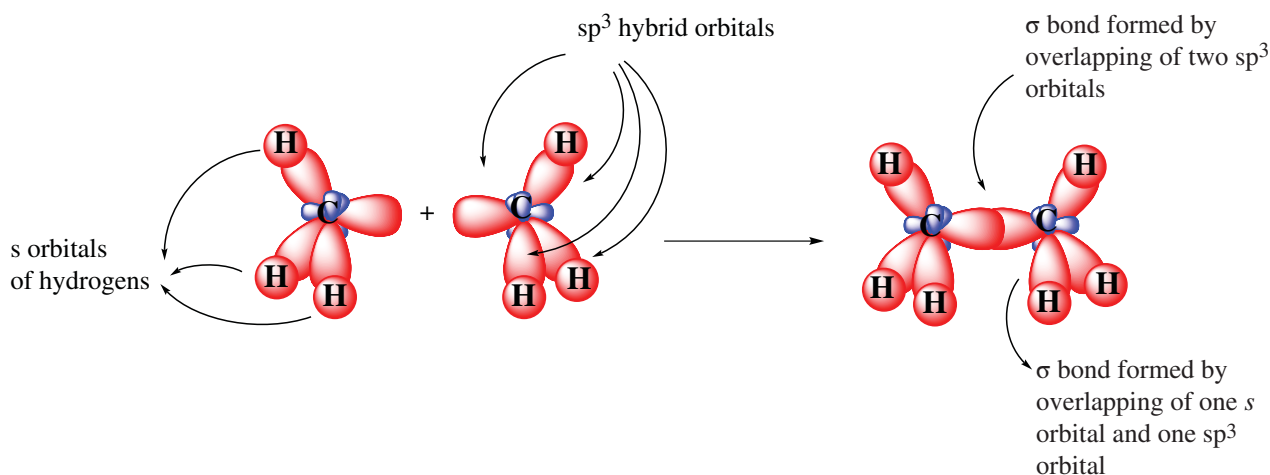


If two orbitals overlap along the bond axis (i.e. end-to-end overlap of atomic or molecular orbitals), the bond formed is called a  $\sigma$  bond. In saturated carbon compounds, the bonds that connect atoms are  $\sigma$  bonds, and the hybridization of the carbon atom is always  $sp^3$ . For example, the hybridization of the carbon atom in carbon tetrachloride ( $CCl_4$ ) is  $sp^3$ . The structure is a pyramidal structure just like in methane, and all carbon–chlorine bonds are equal. In all compounds given below, the angle between the bonds is  $109.5^\circ$  as the substituents are equivalent.



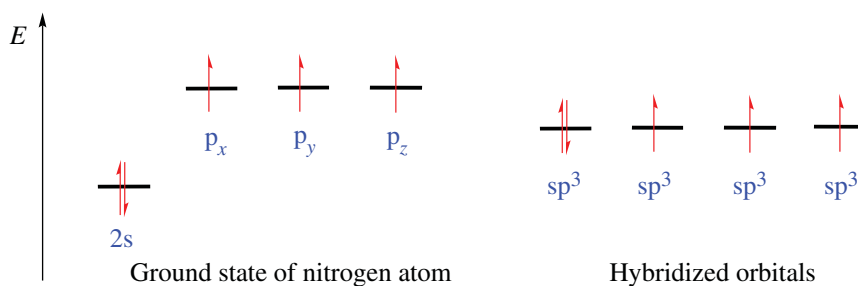
However, if different substituents are attached to the carbon atom, the hybridization of the carbon atom in saturated systems (tetravalent carbon) does not change, but there are some deviations from the ideal tetrahedral structure. The bond angles of some atoms and bond lengths vary according to the connected groups.

After examining the methane molecule, let us apply hybridization to the ethane molecule. In this case, we need to examine each carbon atom separately. Both carbon atoms in ethane are  $sp^3$  hybridized and they are tetrahedral. These hybrid orbitals then combine and form  $\sigma$ -bonds. The ethane molecule has seven  $\sigma$ -bonds. Six of them are  $\sigma$  bonds that bind hydrogen atoms, and they are formed by overlapping of  $sp^3$  hybrid orbitals of carbon atoms with  $s$  orbitals of hydrogen atoms. This reveals that  $\sigma$  bonds can also be formed by the combination of different orbitals. The C–C bond is formed by overlapping of one  $sp^3$  orbital of one carbon with an  $sp^3$  orbital of the other carbon (Figure 1.5).



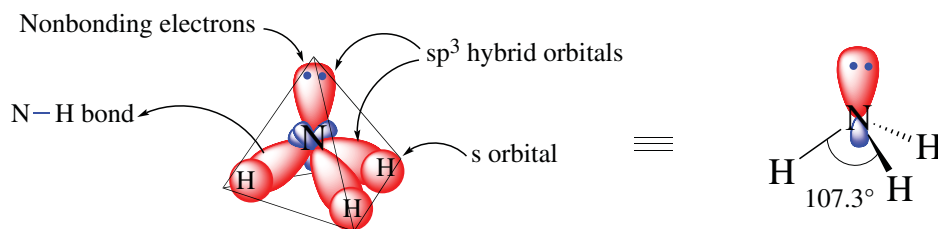
**Figure 1.5** Overlap of two  $sp^3$  orbitals to form the carbon–carbon bond in ethane.

What sort of orbitals describe the bonding in compounds such as ammonia and water having bonding and nonbonding pairs of electrons? Let us examine hybridization in ammonia ( $NH_3$ ). The outer shell of the nitrogen atom consists of one  $s$  orbital and three  $p$  orbitals, as in the carbon atom. Nitrogen has five valence electrons. According to the basic electronic configuration of the nitrogen atom, the nitrogen has three unpaired electrons, which explains why nitrogen is trivalent, as three covalent bonds are needed for octet formation. Three  $p$  orbitals can be used for overlapping with the  $s$  orbitals of hydrogen atoms, leaving the nonbonding electrons in the  $2s$  orbital. However, this arrangement does not minimize the repulsion between the electrons. The best solution is again  $sp^3$ -hybridization. During the formation of ammonia, one  $2s$  orbital and three  $2p$  orbitals of nitrogen combine to form four hybrid orbitals having equivalent energy, which is then considered an  $sp^3$  type of hybridization just like the carbon atom (Figure 1.6).



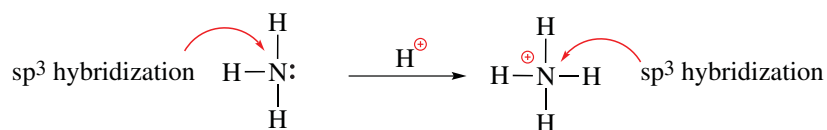
**Figure 1.6** The electronic configuration of nitrogen atom in the ground state and the hybridized state.

Three of the  $sp^3$  orbitals are used to bond the hydrogen atoms. The lone electron pair settles in the remaining fourth  $sp^3$  hybrid orbital. This orbital is called a *nonbonding orbital* and the electrons in this orbital are called *nonbonding electrons*. Because the  $sp^3$  hybrid orbitals form a pyramidal structure, the hydrogen atoms attached to the nitrogen atom also form a pyramidal structure. The H—N—H bond angles are  $107.3^\circ$  in ammonia and it has an almost tetrahedral structure. Now, we can understand why ammonia does not have a planar structure (Figure 1.7).



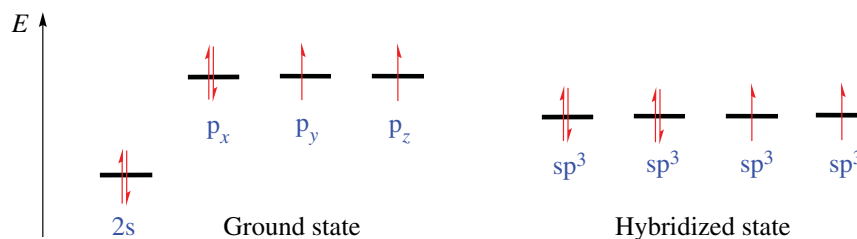
**Figure 1.7** Hybridization and bonding in ammonia ( $\text{NH}_3$ ).

The bonds made by nitrogen with hydrogen atoms are equivalent. While three of the four  $sp^3$  hybrid orbitals of the nitrogen atom are used for N—H bonds, the remaining fourth  $sp^3$  orbital contains the lone pair of electrons. Because the four hybrid orbitals in the ammonia molecule are not used equally as they are used in methane, a small deviation from the pyramidal structure occurs. One would expect this angle ( $107.3^\circ$ ) to be larger than in methane ( $109.5^\circ$ ) because of the repulsion between hydrogen atoms. As these nonbonding electrons are not shared, they are relatively close to the nitrogen atom. Therefore, they exert increased repulsion on the N—H bond electrons, thereby leading to bond-angle compression. Such a push brings the hydrogen atoms closer together.



When ammonia is treated with an acid (HCl), ammonia will be protonated and an ammonium salt will be formed. Hybridization of the nitrogen atom does not change. It remains as  $sp^3$ . Because four hydrogen atoms are attached to the nitrogen atom, they form a smooth tetrahedron and the angle between the hydrogen atoms changes from  $107.3^\circ$  to  $109.5^\circ$ . When determining hybridization, we need to think of nonbonding electrons like a substituent.

We are faced with a similar situation in the  $\text{H}_2\text{O}$  molecule. It may be thought that this molecule is linear in the first stage. However, we know from the experimental measurements that the bond angle in water is  $104.5^\circ$ . Let us examine the basic electronic configuration of oxygen first. Two of the six electrons in the outer shell are located in the  $2s$  orbital. The other four electrons are in the three  $2p$  orbitals. Two electrons populate the  $2p_x$  orbital. Therefore, oxygen has two unpaired electrons in two  $2p_y$  and  $2p_z$  orbitals, which reveals why oxygen forms two covalent bonds with other atoms (Figure 1.8).



**Figure 1.8** The ground-state electronic configuration of the atomic oxygen atom and the hybridized oxygen atom.

Using the atomic orbitals ( $p$  orbitals) directly for bonding is not a good model for describing bonding in water, as the angle between the bonds would be expected to be  $90^\circ$ . As mentioned, we know that is not the case. Again, the best solution is  $sp^3$  hybridization. During the formation of water, one  $2s$  orbital and three  $2p$  orbitals of oxygen combine to form four hybrid orbitals, which is then considered an  $sp^3$  type of hybridization as for the carbon atom. Two  $sp^3$  orbitals are used for

overlapping with the s orbitals of hydrogen atoms, leaving the two pairs of nonbonding electrons in the remaining 2  $sp^3$  hybrid orbitals (Figure 1.8). Because the  $sp^3$  hybrid orbitals form a pyramidal structure, the hydrogen atoms attached to the oxygen atom with the nonbonding electrons also form a pyramidal structure. The H—O—H bond angle is  $104.5^\circ$  in water and it has an almost tetrahedral structure. Now, we can understand why water does not have a linear structure (Figure 1.9). The  $H_2O$  molecule is not linear but angular. The repulsions between lone pairs and bonding pairs is expected to be greater, causing the H—O—H bond angle to be smaller than the ideal  $109.5^\circ$ .

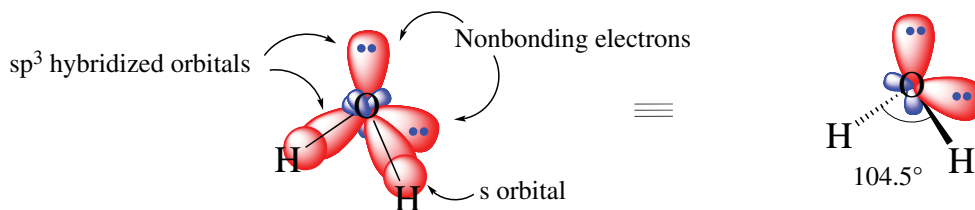


Figure 1.9 Hybridization and bonding in the  $H_2O$  molecule.

### 1.2.2 $sp^2$ -Hybridization of Carbon

Before examining  $sp^2$ -hybridization, let us briefly consider the overlap of the orbitals and how double bonds are formed. Orbitals can overlap in two ways:

1. Head-to-head overlap
2. Side-to-side overlap

So far, we have seen the head-to-head overlap of different orbitals. Head-to-head overlap of atomic orbitals or hybridized orbitals generates  $\sigma$  bonds where the electron density is centered along the internuclear axis. As one can see from Figure 1.10, pure orbitals as well as hybridized orbitals can interfere and form  $\sigma$  bonds. The electrons in these orbitals are called  $\sigma$  electrons.

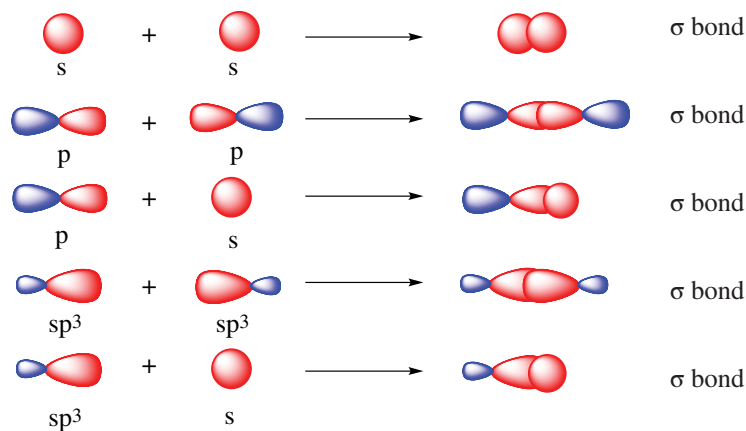
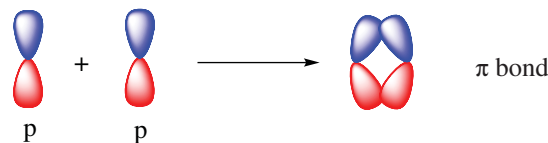


Figure 1.10 Formation of  $\sigma$  bonds by head-to-head overlap of different orbitals.

We have discussed the formation of a  $\sigma$  bond between different elements. The question is: *Is it possible to make a double bond between the carbon atoms and how can we do it?* The two carbon atoms are most easily connected along the axis via  $\sigma$  bonds. Because a  $\sigma$  bond fills the space between the two carbon atoms with electrons, it is not possible to connect these atoms with a second  $\sigma$  bond by head-to-head overlap. Therefore, the two carbon–carbon bonds in a double bond cannot be identical and so the second or third bonds must be different from the  $\sigma$  bond. The second bond of the double bond in ethylene can be constructed from side-to-side overlap of pure p orbitals of each carbon atom. Some elements use their d orbitals to form a bond.

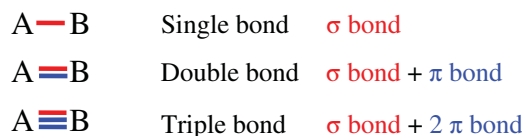
Since there is no d orbital in the carbon atom, we will not examine the overlap with d orbitals here. However, these overlaps are important in inorganic elements having d orbitals such as sulfur and phosphorus. As can be seen in Figure 1.11,

p orbitals can overlap side-to-side to form a new bond above and below the axis that connects atoms. This bond is called a  $\pi$  bond.  $\pi$  Bonds are formed by the overlap of pure p orbitals (unhybridized orbitals). The electrons that make up  $\pi$  bonds are called  $\pi$  electrons.

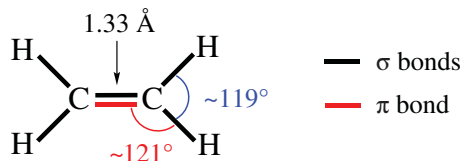


**Figure 1.11** The formation of the second C–C bond by side-to-side overlap of pure p orbitals.

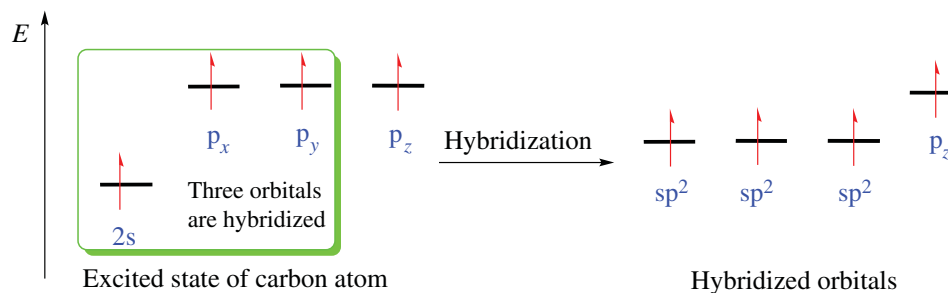
Now, let us try to form a double bond between the two carbon atoms. In organic chemistry, two elements can be connected by single, double, or triple bonds. For these bonds, two, four, and six electrons are needed, respectively. Regardless of the number of bonds, one of these bonds is definitely a  $\sigma$  bond. Because  $\sigma$  bonds are axially connecting the atoms, there cannot be more than one bond on this line. The second and third bonds are formed only through pure p orbitals, and these bonds are  $\pi$  bonds. Thus, we can make the following generalization:



If there is a single bond between the two atoms, this bond is always a  $\sigma$  bond. When there are two bonds, one is a  $\sigma$  bond and the other is a  $\pi$  bond. In triple bonds, the first bond is a  $\sigma$  bond and the other two are  $\pi$  bonds. This rule always holds. Before we create a double bond between two carbon atoms, let us first examine the ethylene molecule, the smallest member of carbon compounds containing a double bond. The angle between the hydrogen atoms is approximately  $119^\circ$  and the angle between the H–C=C atoms is  $121^\circ$ .



Each carbon is bonded to three atoms. As one of the pure p orbitals will be used for the  $\pi$  bond, the remaining orbitals, an s orbital and two of the p orbitals, will hybridize (Figure 1.12).



**Figure 1.12**  $sp^2$ -Hybridization.

Let us examine the orbitals in the second shell of the carbon atom again. They are an s orbital and three p orbitals oriented in the x, y, and z directions. Now, we remove any of these p orbitals, which will be used for making the double bond, and examine the position of the remaining orbitals. The remaining orbitals (1 s and 2 p orbitals) are located in a plane (Figure 1.13). The s orbital is also in this plane because of its spherical structure. In the ethylene molecule, carbon atoms make three  $\sigma$  bonds apart from the  $\pi$  bond. If carbon uses an s and two p orbitals to form the bonds with carbon and hydrogen atoms, the bond formed with p orbitals will be different from the bond formed with the s orbital. We would expect