

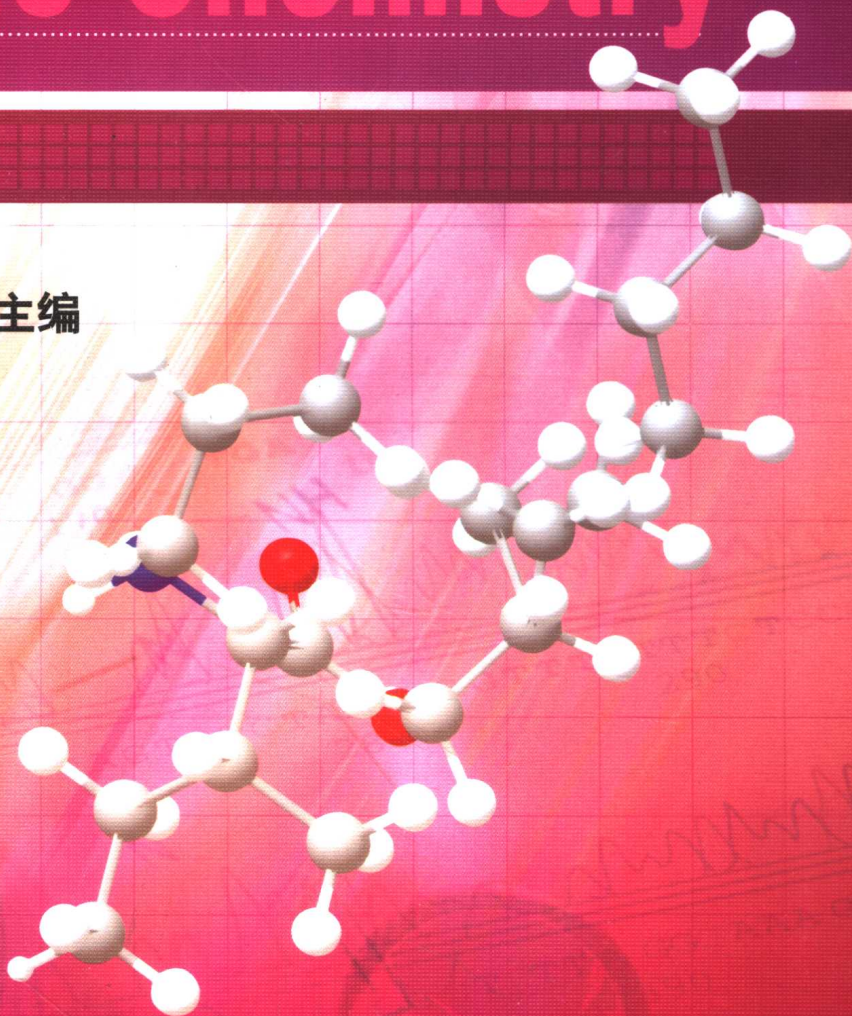
高等学 校 教 材

有机化学

Organic Chemistry

(英文版)

朱红军 王兴涌 主编



化学工业出版社

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· 北京 ·

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前 言

有机化学双语教学已经成为目前有机化学教学改革的一个重要举措，国内许多学校均作了有关的尝试，但是一般都是选用国外原版教材，与国内教材不匹配，使得教师在讲授和学生在学习时都非常不便，因而效果受到极大的影响。本教材就是针对这一情况而编写的《有机化学》双语版教材。

本教材参考了国外一些原版教材，按照我们的教学实践和国内的实际情况进行编写，也吸收了国外名教材的优点与有机化学的新成果，同时还在部分章节之后介绍了一些著名的有机化学家的事迹，以激励学生们继承他们献身科学的敬业精神。全书在最后编排了索引，和国际教材接轨，方便本教材的使用。

全书共 22 章，朱红军编写了第 1、7、20、21、22 章，王兴涌编写了第 10、16 章，郭成编写了第 18、19 章，汪海波编写了第 13、17 章，关建宁编写了第 3、4 章，陈静编写了第 11、12 章，马鸿飞编写了第 8 章，万嵘编写了第 2、5 章，肖涛编写了第 9 章，韩国志编写了第 6 章，宋广亮编写了第 14 章，徐浩编写了第 15 章，李玉峰和徐斌也参加了部分章节的编写。朱红军教授和王锦堂教授审核了全书。

本书是有关双语教材的首次尝试，希望能对提高国内有机化学双语教学水平和改善双语教学效果有所帮助。本教材可作为各专业有机化学课程的教材，也可作为有关工矿企业和科研院所的科研人员的参考书。

由于编者水平和时间仓促等方面的原因，本书还存在着一些不足之处。希望各位读者不吝指正。

编 者

2007 年 4 月

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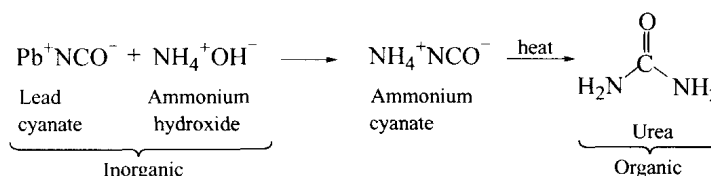
Chapter 1

Introduction

1.1 The development of organic chemistry

What is organic chemistry? The term organic chemistry was first used freely by the Swedish chemist Berzelius in 1806, although it may have been used somewhat early by others. At first no methods were known for preparing organic compounds outside of living organisms, and the erroneous conclusion was reached that a mysterious vital force was necessary to form such compounds. This vitalistic theory was later overthrown by German chemist Wöhler.

In 1828 when Friedrich Wöhler attempted to synthesize ammonium cyanate, NH_4CNO , and instead obtained urea.



Wöhler's discovery was important because it gave impetus to a long series of experiments in which chemists probed the nature of the chemical substances that exist in living organisms and in petroleum and coal, which are formed from the remains of plants and animals that lived long ago.

Chemistry today is unified. The same principles that explain the simplest inorganic compounds also explain the most complex organic ones. The only distinguishing characteristic of organic chemicals is that all contain the element carbon. So organic chemistry is the chemistry of compounds of carbon. Nevertheless, the division between organic and inorganic chemistry, which began for historical reasons, maintains its practical convenience...and to further the progress of students.

Although carbon is the principal element in organic compounds, most also contain hydrogen, and many contain nitrogen, oxygen, phosphorus, sulfur, chlorine, or other elements. But why is carbon special? The answer to this question comes from the unique ability of carbon atoms to bond together, forming long chains and rings. Carbon, alone of all elements, is able to form an immense diversity of compounds, from the simple to the staggeringly complex—from methane, with 1 carbon atom, to DNA, which can have tens of billions.

1.2 The structural theory of organic chemistry

Organic chemistry is a study of relationship between the structures of molecules and their

reactions. So the structural theories of organic chemistry are the fundamental theories of organic chemistry.

The structural theory of organic chemistry is the same as we learning in inorganic chemistry. So we give some brief attention to the structural theory.

1.2.1 Atomic orbitals

An understanding of the atom starts with the model of massive, positively charged nucleus surrounded by a moving cloud of electrons, whose negative charge balances the positive nuclear charge. Electrons could be considered as a type of wave and that the motion electrons in the atom could be represented by mathematical wave equations, i.e., each electron is found within a specific region of space, called an orbital (Figure 1-1).

An atomic orbital can be thought of as the picture that would be obtained if we could perform time-lapse photography of an electron within an atom—a sort of cloud of electrons about the nucleus. The picture shows that each electron is localized within the atom, in regions whose shape and dimension are determined by quantum numbers.

We therefore "label" an atomic electron by four "quantum numbers":

$n = 1, 2, 3, \dots$, denoting energy;

$l = 0, 1, \dots, n-1$, denoting angular momentum;

$m = -l, \dots, l$, denoting orientation (the "magnetic quantum number");

$s = -1/2, 1/2$, denoting spin (m_s is also used in place of s).

The set of four numbers (n, l, m, s) identifies the "quantum state" of the electron. Chemists use letters in place of numbers for l (s, p, d, f, etc.), and so an $n=3, l=1$ electron would be denoted "3p".

The following images (Figure 1-1) should give you a feel for what sorts of "orbits" these numbers correspond to. The images are cross sectional cuts of three dimensional orbits, so to get a complete picture you have to think of them as rotated around the vertical axis.

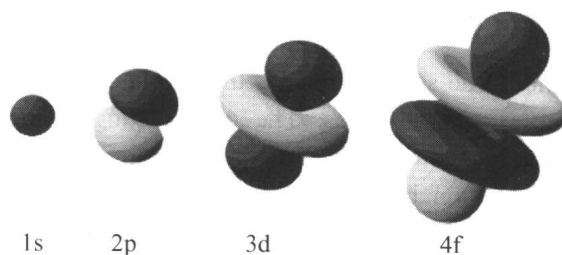


Figure 1-1 Some orbital of electrons.

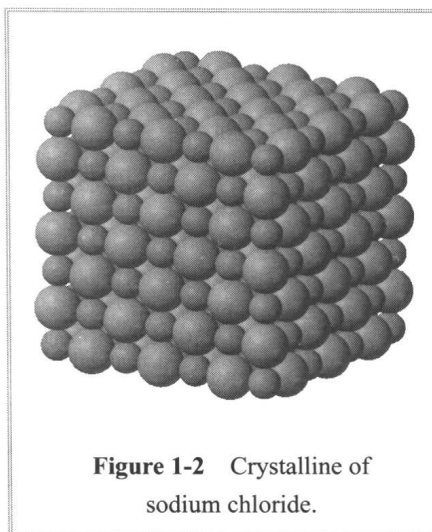
1.2.2 Ionic bonding

Compounds are divided broadly into two classes, ionic and covalent.

Ionic compounds are composed of ions, which are units of matter that may be single atoms or groups of atoms, bearing positive or negative charges. Ionic compounds are usually crystalline solids with high melting points. Many of these compounds dissolve in water to form solutions that conduct electricity. Sodium chloride NaCl , is a typical example of an ionic compound. Sodium acetate, $\text{Na}^+\text{CH}_3\text{CO}_2^-$, is also an ionic compound, and the negative charged ion (CH_3CO_2^-) contains

covalent bonds.

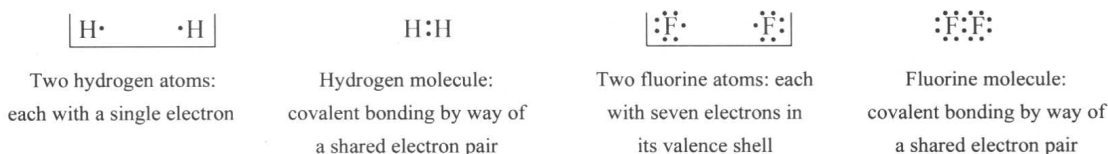
The forces that act between charged particles are called electrostatic forces. Ionic bonding consists of electrostatic attractions between ions of opposite charge. For example, crystalline sodium chloride (Figure 1-2), each sodium ion is surrounded by 6 chloride ions, and chloride ion is surrounded by 6 sodium ions. The ions are held in place by strong electrostatic forces between ions of opposite charge. So sodium chloride has a high melting point, 801°C , and very high boiling point, 1413°C . These physical properties are an indication of the strength of the electrostatic forces holding the ions together. Large amounts of energy must be applied to the sodium chloride crystal to overcome the electrostatic forces that hold the ions in place in the crystal lattice and allow them to move past each other in liquid sodium chloride. Even more energy is necessary to further separate the ions in going from the liquid to vapor state.



1.2.3 Covalent bonding

In covalent compounds, the structural units are molecules having no net charge. Covalent compounds may be gases, liquids, or solids.

For the simple diatomic molecule H_2 , it is clear that if two H approach one another closely, the unpaired electron from each can be shared most effectively when it is in the region between the two nuclei, as if the two individual atomic 1s orbitals overlapped. A similar picture results for the molecule F_2 from the overlap of the 2p orbitals of each fluorine atom. Structural formulas of this type in which electrons are represented as Lewis structures.



The situation becomes more complicated when we consider overlapping the atomic orbitals of carbon so that it can achieve a filled valence shell. To solve the difficulties that arise, chemists introduced the concepts of molecular orbitals and hybridization.

1.2.4 Hybridization

(1) sp^3 hybrid and bond in methane

Let's look at the structure of CH_4 that would result if bonding were the result of overlapping the atomic orbitals of carbon and hydrogen. The electron configuration of carbon is $1s^2 2s^2 2p_x^1 2p_y^1$, has only two half-filled orbitals. So how can it have bonds to four hydrogens? In 1930s Linus Pauling offered an ingenious solution to the puzzle. That is the hybrid orbital theory. He began with a simple idea: "promoting" one of the 2s electrons to the empty $2p_z$ orbital gives four half-filled orbitals. The second party of Pauling's idea was novel: mix together (hybridize) the four valence orbitals of carbon ($2s$, $2p_x$, $2p_y$ and $2p_z$) to give four half-filled orbitals of equal energy. The four new orbitals are called sp^3 hybrid orbitals (Figure 1-3).

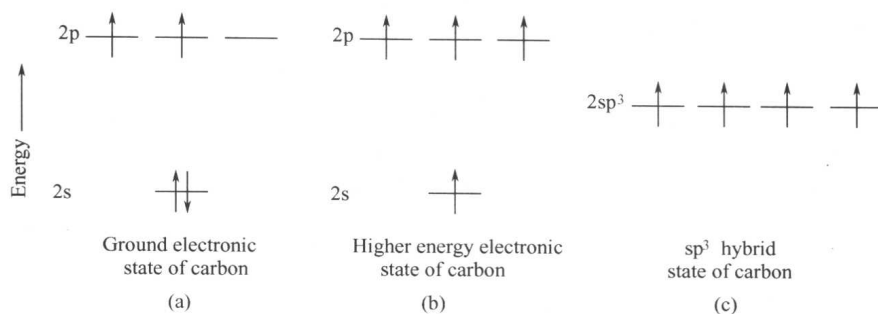


Figure 1-3 (a) Electron configuration of carbon in its most stable state. (b) An electron is “promoted” from the 2s orbital to the vacant 2p orbital. (c) The 2s orbital and the three 2p orbitals are combined to give a set of four equal-energy sp^3 -hybridized orbitals, each of which contains one electron.

Each sp^3 hybrid orbital has two lobes of unequal size. More of the electron density on one side of the nucleus is greater than the other (Figure 1-4 and Figure 1-5).

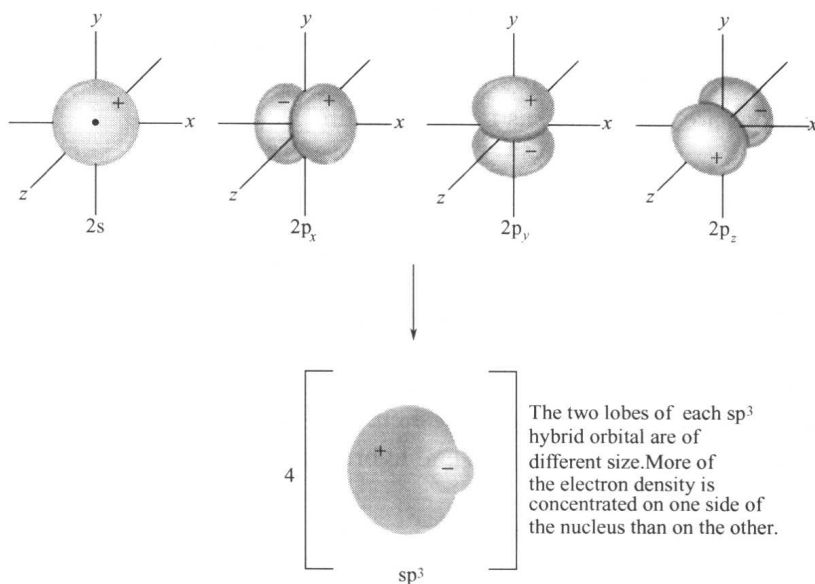


Figure 1-4 Representation of orbital mixing in sp^3 hybridization. Mixing of one s orbital with three p orbitals generates four sp^3 hybrid orbitals. Each sp^3 hybrid orbital has 25% s character and 75% p character. The four sp^3 hybrid orbitals have their major lobes directed toward the corners of a tetrahedron, which has the carbon atom at its center.

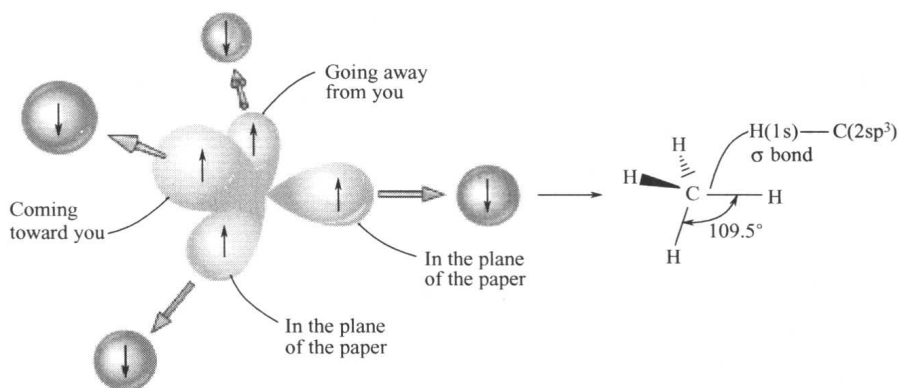


Figure 1-5 The sp^3 hybrid orbitals are arranged in a tetrahedral fashion around carbon. Each orbital contains one electron and can form a bond with a hydrogen atom to give a tetrahedral methane molecule.

(2) sp^2 hybrid and bond in ethylene (Figure 1-6, Figure 1-7 and Figure 1-8)

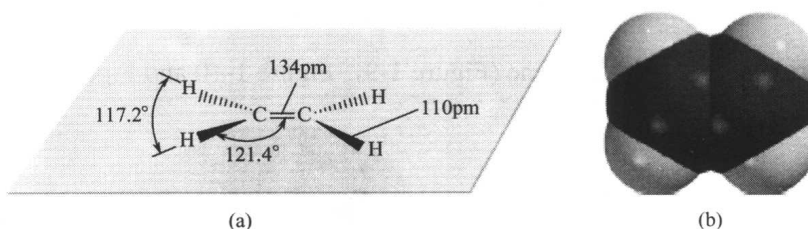


Figure 1-6 (a) All the atoms of ethylene lie in the same plane. All the bond angles are close to 120° , and the carbon-carbon bond distance is significantly shorter than that of ethane. (b) A space-filling model of ethylene.

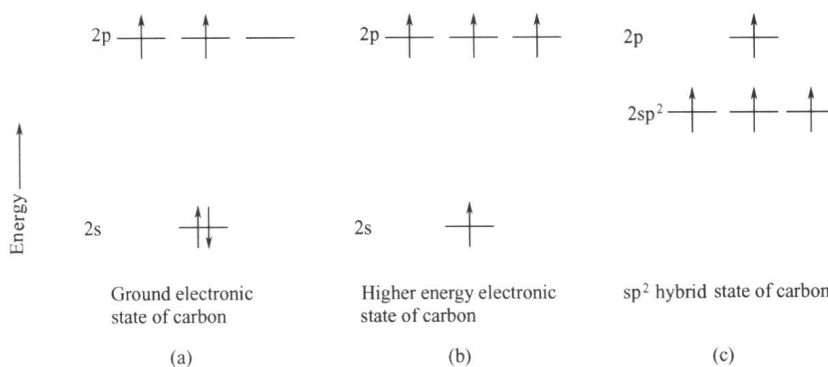


Figure 1-7 (a) Electron configuration of carbon in its most stable state. (b) An electron is "promoted" from the 2s orbital to the vacant 2p orbital. (c) The 2s orbital and two of the three 2p orbitals are combined to give a set of three equal-energy sp^2 -hybridized orbitals. One of the 2p orbitals remains unchanged.

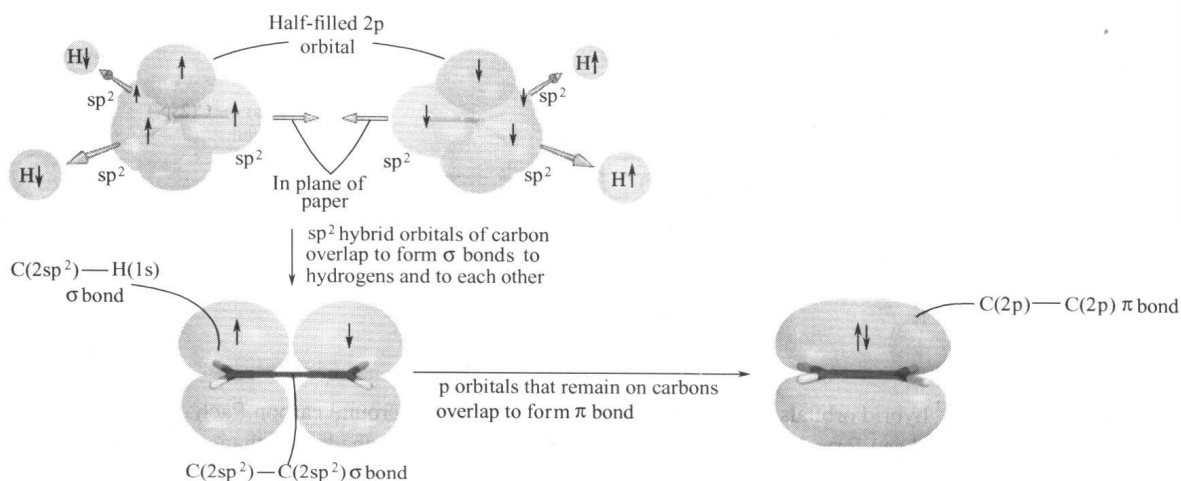


Figure 1-8 The carbon carbon double bond in ethylene has a σ component and a π component. The σ component arises from overlap of sp^2 -hybridized orbitals along the internuclear axis. The π component results from a side-by-side overlap of 2p orbitals.

(3) sp hybrid and bond in acetylene (Figure 1-9, Figure 1-10 and Figure 1-11)

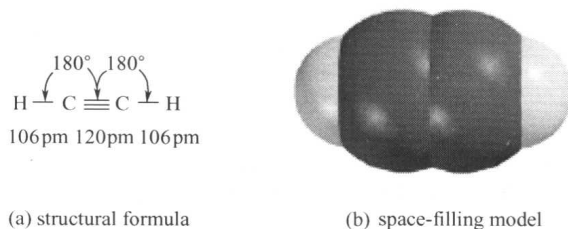


Figure 1-9 Acetylene is a linear molecule

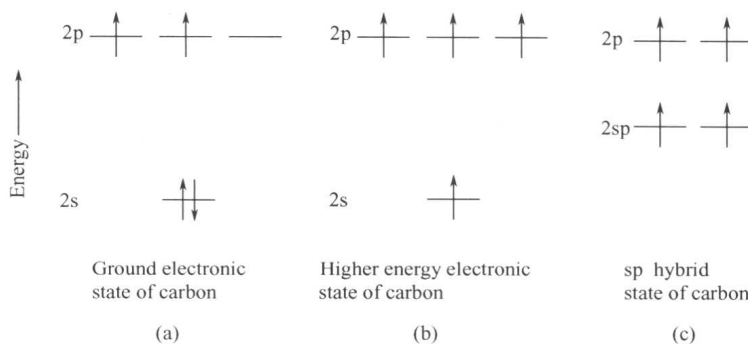
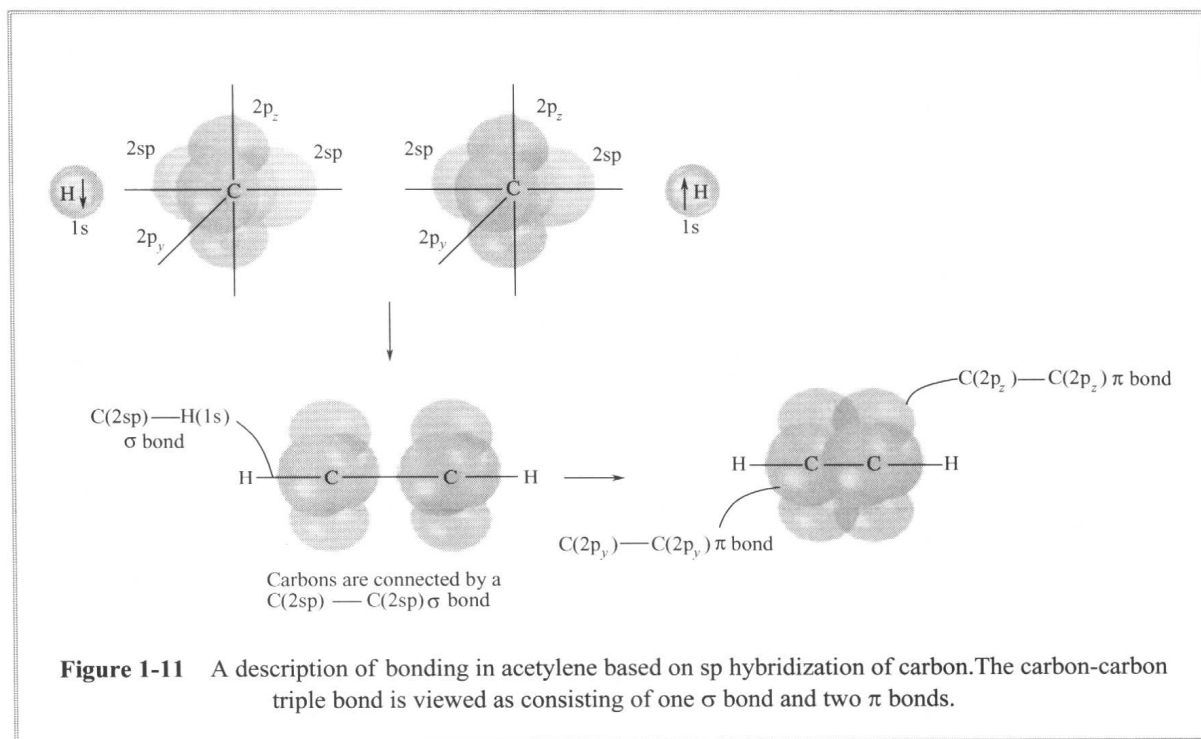


Figure 1-10 (a) Electron configuration of carbon in its most stable state. (b) An electron is "promoted" from the 2s orbital to the vacant 2p orbital. (c) The 2s orbital and one of the three 2p orbitals are combined to give a set of two equal-energy sp -hybridized orbitals. Two of the 2p orbitals remain unchanged.



1.2.5 Polar covalent bond, electronegativity and dipole moment

The H-H bond in H_2 , Cl-Cl bond in Cl_2 and C-C bond in ethane are covalent, in which the two electrons are shared equally by the two atoms, so we called these bonds nonpolar covalent bond. But the bond C-Cl in chloromethane CH_3Cl share the electrons unsymmetrically, the bond is a polar covalent.

Bond polarity is due to differences in electronegativity (EN), the intrinsic ability of an atom to attract the shared electrons in a covalent bond. The tendency of an atom to draw the electrons in a covalent bond toward itself is referred to as its electronegativity. An electronegative element attracts electrons; an electropositive one donates them. The most commonly cited electronegativity scale was devised by Linus Pauling and its presented in Table 1-1.

