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Lecture No. 1,2

22/2/2018

Introduction:

Structure and Properties

Organic chemistry is the chemistry of the compounds of carbon. The misleading name "organic" is a relic of the days when chemical compounds were divided into two classes, inorganic and organic, depending upon where they had come from. Inorganic compounds were those obtained from minerals; organic compounds were those obtained from vegetable or animal sources, that is from material produced by living organisms.

The structural theory

The structural theory is the basis upon which millions of facts about hundreds of thousands of individual compounds have been brought together and arranged in a systematic way. The structural theory is the framework of ideas about how atoms are put together to make molecules .It has to do with the order in which atoms are attached to each other, and with the electrons that hold them together . It has to do with the shapes and sizes of the molecules that these atoms form, and with the way that electrons are distributed over them.

The chemical bond before 1926

In 1916 two kinds of chemical bond were described : the ionic bond by Walther Kossel (in Germany) and the covalent bond G.N. Lewis (of the university of California) .Both Kossel & Lewis based their ideas on the following :

A positively charged nucleus is surrounding by electronic arranged in concentric shells or energy levels . There is maximum number of electrons

Organic Chemistry

that can be accommodated in each shell : two in the first shell, eight in the second shell, eight or eighteen in the third shell, and so on . The greatest stability is reached when the outer shell is full, as in the noble gases . Both ionic and covalent bonds arise from the tendency of atoms to attain this stable configuration of electrons .

The ionic bond results from transfer of electrons, as, for example, in the formation of lithium fluoride .

The covalent bond results from sharing of electrons, as, for example, in the formation of hydrogen molecule .

Quantum mechanics

In 1926 there emerged the theory known as quantum mechanics, developed, in the form most useful to chemists, by Erwin Schrodinger (of the university of Zurich). He worked out mathematical expressions to the motion of an electron in terms of its energy. These mathematical expressions are called *wave equations*, since they are based upon the concept that electrons show properties not only particles but also of waves.

Atomic Orbitals

A wave equation can not tell us exactly where an electron is at any particular moment, or how fast it is moving ; it does not permit us to plot a precise orbit about the nucleus . Instead, it tell us the probability of finding the electron at any particular place . The region in space where an electron

is likely to be found is called an orbital.

Electronic configuration ; Pauli exclusion principle

There are a number of " rules " that determine the way in which the electrons of an atom may be distributed, that is, that determine the electronic configuration of an atom . The most fundamental of these rules is the *Pauli exclusion principle* : only two electrons can occupy any atomic orbital, and to do so these two must have *opposite spine*. These electrons of *opposite spine* are said to be paired . Electrons of like spine tend to get as far from each other as possible .These tendency is the most important of all the factors that determine the shapes and properties of molecules .

Molecular orbitals

In molecules, as in isolated atoms, electrons occupy orbitals, and in accordance with much the same "rules" . These molecular orbitals are considered to be centered about many nuclei, perhaps covering the entire molecules ; the distribution of nuclei and electrons is simply the one that results in the most stable molecule .

To make the enormously complicated mathematics more workable, two simplifying assumptions are commonly made : (a) that each pair of electrons is essentially localized near just two nuclei, and (b) that the shapes of these localized molecular orbitals and their disposition of atomic orbitals in the component atoms.

The idea of localized molecular orbitals-or what are might call bond orbitals- is evidently not a bad one, since mathematically this method of approximation is successful with most (although not all) molecules .

The covalent bond

Now let us consider the formation of a molecule. For convenience we shall picture this as happening by the coming together of the individual atoms, although most molecules are not actually made this way. We make physical models of molecules out of wooden or plastic balls that represent the various atoms; the location of holes or snap fasteners tells us how to put them together.

Hybrid orbitals: sp

Let us next consider beryllium chloride, BeCl2 .Beryllium has no unpaired electrons. How are we to account for its combining with two chlorine atoms? Bond formation is an energy-releasing (stabilizing) process, and the tendency is to form bonds and as many as possible even if this results in bond orbitals that bear little resemblance to the atomic orbitals we have talked about. If our method of mental molecule-building is to be applied here, it must be modified. We must invent an imaginary kind of beryllium atom, one that is about to become bonded to two chlorine atoms.

Hybrid orbitals: sp²

Next , let us look at boron trifluoride, BF_3 .Boron has only one unpaired electron, which occupied a 2p orbital .

Hybrid orbitals: sp³

Now, let us turn to one of the simplest of organic molecules, methane, CH4 .Carbon has an unpaired electron in each of the two p orbitals, and on this basis might be expected to form a compound CH2 . (It docs, but CH2 is a highly reactive molecule whose properties center about the need to provide carbon with two more bonds.) Again, we see the tendency to form as many bonds as possible : in this case, to combine with four hydrogen atoms.

Unshared pairs of electrons

Two familiar compounds, ammonia (NH3) and water (H2O), show how unshared pairs of electrons can affect molecular structure. In ammonia, nitrogen resembles the carbon of methane. Nitrogen is sp3hybridized, but has only three unpaired electrons; they occupy three of the sp³ orbitals. Overlap of each of these orbitals with the s orbital of a hydrogen atom results in ammonia . The fourth sp³ orbital of nitrogen contains a pair of electrons.

Intramolecular forces

We must remember that the particular method of mentally building molecules that we are learning to use is artificial: it is a purely intellectual process involving imaginary overlap of imaginary orbitals. There are other, equally artificial ways that use different mental or physical models. Our method is the one. that so far has seemed to work out best for the organic chemist. Our kit of mental atomic models will contain just three "kinds" of carbon: tetrahedral sp³ -hybridized), trigonal (sp²hybridized), and digonal (sp-hybridized). By use of this kit, we shall find, one can do an amazingly good job of building hundreds of thousands of organic molecules. But, however we arrive at it, we see the actual structure of a molecule to be the net result of a combination of repulsive and attractive forces,, which are related to charge and electron spin.

(a) Repulsive forces. Electrons tend to stay as far apart as possible because they have the same charge and also, if they are unpaired, because they have the same spin (Pauli exclusion principle). The like-charged atomic nuclei, too, repel each other.(b) Attractive forces. Electrons are attracted by atomic nuclei as are the nuclei by the electrons because of their opposite charge, and hence tend to occupy the region between two nuclei. Opposite spin permits (although, in itself, probably does not actually encourage) two electrons to occupy the same region. In methane, for example, the four hydrogen nuclei are as widely separated as they can be. The distribution of the eight bonding electrons is such that each one occupies the desirable region near two nuclei the bond orbital and yet, except for its partner, is as far as possible from the other electrons. We can picture each electron accepting perhaps reluctantly because of their similar charges one orbitalmate of opposite spin, but staying as far as possible from all other electrons and even, as it wanders within the loose confines of its orbital, doing its best to avoid the vicinity of its restless partner.

Bond dissociation energy. Homolysis and heterolysis

We have seen that energy is liberated when atoms combine to form a molecule. For a molecule to break into atoms, an equivalent amount of energy must be consumed. The amount of energy consumed or liberated when a bond is broken or formed is known as the bond dissociation energy, D. It is characteristic of the particular bond.

Polarity of bonds

Besides the properties already described, certain covalent bonds have another property: polarity. Two atoms joined by a covalent bond share electrons; their nuclei are held by the same electron cloud.

Polarity of molecules

A molecule is polar if the center of negative charge does not coincide with the center of positive charge. Such a molecule constitutes a dipole: two equal and opposite charges separated in space.

<u>Structure and physical properties</u>

We have just discussed one physical property of compounds: dipole moment .Other physical properties like melting point, boiling point, or solubility in a particular solvent are also of concern to us. The physical properties of a new compound give valuable clues about its structure. Conversely, the structure of a compound often tells us what physical properties to expect of it.

Melting point

In a crystalline solid the particles acting as structural units ions or molecules - are arranged in some very regular, symmetrical way; there is a geometric pattern repeated over and over within a crystal. Melting is the change from the highly ordered arrangement of particles in the crystalline lattice to the more random arrangement that characterizes a liquid.

Intel-molecular forces

What kind of forces hold neutral molecules to each other ? Like interionic forces, these forces seem to be electrostatic in nature, involving attraction of positive charge for negative charge. There are two kinds of intermolecular forces: dipole-dipole interactions and van der Waals forces.

Boiling point

Although the particles in a liquid are arranged less regularly and are freer to move about than in a crystal, each particle is attracted by a number of other particles. Boiling involves the breaking away from the liquid of individual molecules or pairs of oppositely charged ions. This occurs when a temperature is reached at which the thermal energy of the particles is great enough to overcome the cohesive forces that hold them in the liquid. In the liquid state the unit of an ionic compound is again the ion. Each ion is still held strongly by a number of oppositely charged ions. Again there is nothing we could properly call a molecule .

A great deal of energy is required for a pair of oppositely charged ions to break away from the liquid; boiling occurs only at a very high temperature.

Solubility

When a solid or liquid dissolves, the structural units ions or molecules become separated from each other, and the spaces in between become occupied by solvent molecules.

In dissolution, as in melting and boiling, energy must be supplied to overcome the interionic or intermolecular forces.

Where does the necessary energy come from?

The energy required to break the bonds between solute particles is supplied by the formation of bonds between the solute particles and the solvent molecules: the old attractive forces are replaced by new ones .

Acids and bases

Turning from physical to chemical properties, let us review briefly one familiar topic that is fundamental to the understanding of organic chemistry: acidity and basicity.

The terms acid and base have been defined in a number of ways, each definition corresponding to a particular way of looking at the properties of acidity and basicity.

We shall find it useful to look at acids and bases from two of these viewpoints; the one we select will depend upon the problem at hand. According to the Lowry-Brønsted definition, an acid is a substance that gives up a proton, and a base is a substance that accepts a proton. According to the (Lewis) definition, a base is a substance that can furnish an electron pair to form a covalent bond, and an acid is a substance that can take up an electron pair to form a covalent bond.

Thus an acid is an electron-pair acceptor and a base is an electron-pair donor.

Isomerism

Before we start our systematic study of the different kinds of organic compounds, let us look at one further concept which illustrates especially well the fundamental importance of molecular structure: the concept of isomerism.

Different compounds that have the same molecular formula are called isomers.

They contain the same numbers of the same kinds of atoms, but the atoms are attached to one another in different ways.

Isomers are different compounds because they have different molecular structures.

This difference in molecular structure gives rise to a difference in properties; it is the difference in properties which tells us that we are dealing with different compounds.

In some cases the difference in structure and hence the difference in properties is so marked that the isomers are assigned to different chemical families, as, for example, ethyl alcohol and methyl ether. In other cases the difference in structure is So subtle that it can be described only in terms of three-dimensional models.

Other kinds of isomerism fall between these two extremes .