Welcome students to this module of the paper CHC 101.

The paper title is Inorganic and Organic Chemistry-Section B. I am Miss Flavia Travasso, working as Assistant Professor in the Department of Chemistry at St. Xavier's College, Mapusa-Goa.

The module which I'll be covering today is cleavage of bonds, homolysis and heterolysis.

In this module we will be covering the cleavage of bonds, homolysis and heterolysis.

Through this module, the students will be able to understand the cleavage of bonds, differentiate between homolysis and heterolysis, describe the pathway for the formation of free radicals and ions, and cite examples for homolysis and heterolysis.

Coming to the cleavage of bonds.

Organic compounds are covalent in nature, that is, they contain covalent bonds. A covalent bond represents a shared pair of electrons between two atoms.These shared pair of electrons can be represented as two dots or as a dash. Chemical reactions involve the breaking of existing bonds and formation of new bonds. Bond breaking is also called as cleavage or fission.

Cleavage of a bond involves breaking down of a molecular orbital to give atomic orbitals. Molecular orbitals are at a lower energy, that is they are most stable than atomic orbitals. Therefore, energy has to be supplied to break a bond. Let us consider a covalent bond between two atoms A & B.

Here the cleavage of the A-B bond can happen depending on the relative electronegativities of the Atom A & B involved. Let us take two cases, one wherein the atoms involved have equal electronegativities. Here, what happens is when the A-B bond breaks, each atom of the bond retains one electron. In the second case, we have the cleavage of the A-B bond where the atoms involved have different electronegativities that is, the electronegativities are unequal. When the cleavage of the bond happens, whichever atom has the higher electronegativity that atom takes both the electrons. So, in this case we can see over here, if we have atom A having higher electronegativity, atom A takes away both the electrons and thus gets a negative charge. If we have a case where Atom B has a higher electronegativity atom, B takes the electrons and that gets a negative charge. Assuming that sufficient energy is available, a covalent bond can undergo cleavage in two ways. The first is homolysis or homolytic cleavage. In Greek homo means the same. In Chemistry terms, lysis means cleavage. The second type of cleavage is heterolysis or heterolytic cleavage. In Greek hetero means different.

Let us see homolysis or homolytic cleavage first. In homolysis the atoms involved have equal electronegativities. Homolysis involves the breaking of the covalent bond in such a way that each of the two atoms joined by the bond retains one electron each. The products of Homolysis are free radicals, so such reactions take place by the free radical mechanism.

Let us consider the cleavage of a bond between two atoms A & B. Here the two atoms involved have equal electronegativities, so upon breaking of the bond between A & B, the two atoms involved get one electron each.

The movement of electrons in homolytic cleavage is shown by half barbed arrows. These arrows are shown in the slide here. Half barbed arrows are also called as fish hook arrows, or single head arrows. These arrows are used to denote the movement of a single electron. We can see here that the breaking of the A-B bond happens using the half barbed arrows, wherein one electron goes to Atom A and the other electron goes to Atom B. The products of homolytic cleavage of a covalent bond are two free radicals which are electrically neutral. Free Radicals have one unpaired electron as they have neither lost or gained an electron, but got the electron back which they had contributed for bond formation. Thus, the A-B bond can be broken homolytically and this cleavage is denoted by half barbed arrows.

And the products of this cleavage are two free radicals.

Homolysis is the most common mode of fission in the vapor phase. Homolytic reactions are usually initiated by heat, light or organic peroxides.

Let us now see some examples of homolysis. In the first example we have the breaking of the C-Cl bond, homolytically in presence of light. The cleavage happens in such away that each of the Cl atom gets one electron.

In the second example, we have the breaking of the C-Br. bond in presence of light. Upon cleavage of the C-Br bond, we get two bromide free radicals.

The third example involves the cleavage of the oxygen- oxygen bond in hydrogen peroxide to give two hydroxyl free radicals.

The 4th example is the cleavage of the oxygen-oxygen bond in dibenzoyl peroxide.

The oxygen-oxygen bond in dibenzoyl peroxide is a weak bond, so it breaks homolytically in presence of heat to give two free radicals. In the 5th example, we have the cleavage of the C-N bond in azoisobutyronitrile that is AIBN. In this particular example, we can see that the two C-N bonds are broken simultaneously so that the products are two free radicals and the formation of nitrogen molecule.

Now coming to heterolysis or the heterolytic cleavage. Heterolysis involves atoms of different electronegativities. It involves an unequal breaking of the covalent bond, wherein the more electronegative atom retains both the electrons of the broken bond. In heterolysis, ions are formed, so we have positively charged or negatively charged ions formed. Such reactions are most common in organic chemistry.

Let us consider the cleavage of the A-B bond between two atoms A & B. In the first case we have the cleavage wherein the Atom A has a higher electronegativity than Atom B, so in this case what happens is Atom A takes away both the electrons and thus gets a negative charge, whereas Atom B gets a positive charge. Similarly, if we see the second example, B Atom has a higher electronegativity compared to Atom A, so B takes away both the electrons upon the breaking of the A-B bond and therefore it gets a negative charge.

In heterolysis, the movement of electrons is denoted by a double barbed arrow. The double barbed arrow denotes the movement of two electrons. So we can see a case wherein Atom A has more electronegativity than Atom B. In this case the movement of the electrons of the bond is towards Atom A. If you see this case where the atom B has more electronegativity compared to Atom A, then the movement of the electrons is towards atom B. Atom that take both electrons gets a negative charge while the other atom gets a positive charge as it loses the one electron which it had contributed. The results of heterolytic bond cleavage is the formation of ions. Thus we can see that the A-B bond can break heterolytically and this cleavage is shown by a double barbed arrow and the products are the formation of ions.

Heterolytic bond cleavage leads to formation of ionic species which are very reactive and carry charges on the carbon.

Species getting a positive charge on the carbon atom are called carbocations, whereas species carrying a negative charge on the carbon atom are called carbanions. Let us now see some examples for heterolysis. In the first example, we can see the breaking of the C-Br bond.

Here the cleavage of the bond happens heterolytically wherein Br atom being more electronegative, takes away both the electrons. Therefore we get a methyl carbocation. In the second example, we can see the breaking of the C-Br bond in ethyl bromide. The cleavage of the C-Br bond gives the ethyl carbocation.

In the third example, we can see the breaking of the C-Br bond in isopropyl bromide. This results in the formation of a secondary carbocation. In the fourth example, we see the cleavage of the C-Br bond in tertiary butylbromide. Here, the cleavage of the C-Br bond results in the formation of a tertiary butyl carbocation. This type of cleavage of the bond heterolytically is an important step in the SN1 mechanisms.

These are the references which were used for this module.

Thank you.