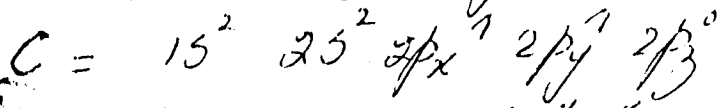


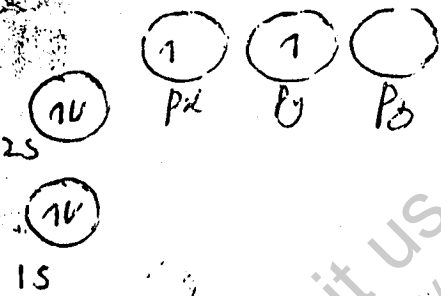
WHAT IS HYBRIDIZATION? WHAT TYPE OF HYBRIDIZATION IS PRESENT IN PROPANE, ETHENE & ETHYNE.

HYBRIDIZATION is a phenomenon in which different atomic orbitals of different energies merge to produce new orbitals which are identical to each other in all respects (size, shape, energy, no. of nodal planes, angles) but different from any one of combining orbitals. These are called HYBRID ORBITALS. The number of hybrid orbitals is always equal to number of atomic orbitals which have merged together.

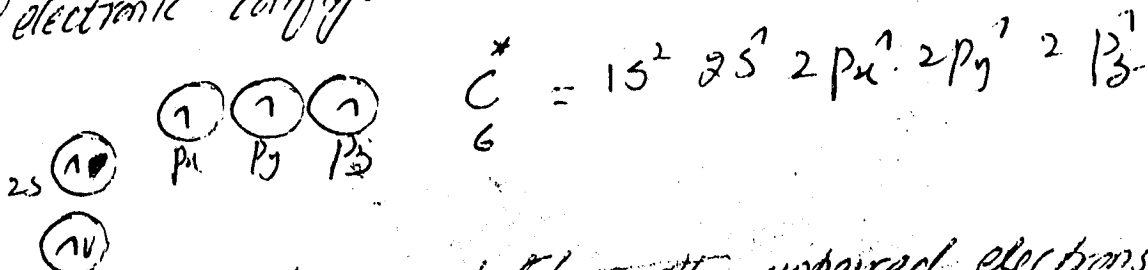
HYBRIDIZATION IN CARBON:- Carbon has atomic number "6". It has following electronic configuration.



It can be written as follows.



According to this configuration carbon should be divalent but carbon is tetravalent in most of its compounds. In order to explain seeming anomaly it is assumed that in excited state one electron from $2s^{n\uparrow}$ is promoted to empty $2p_z$ giving following electronic configuration

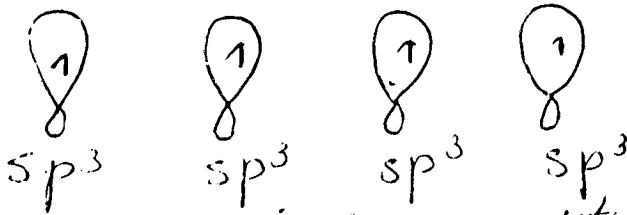
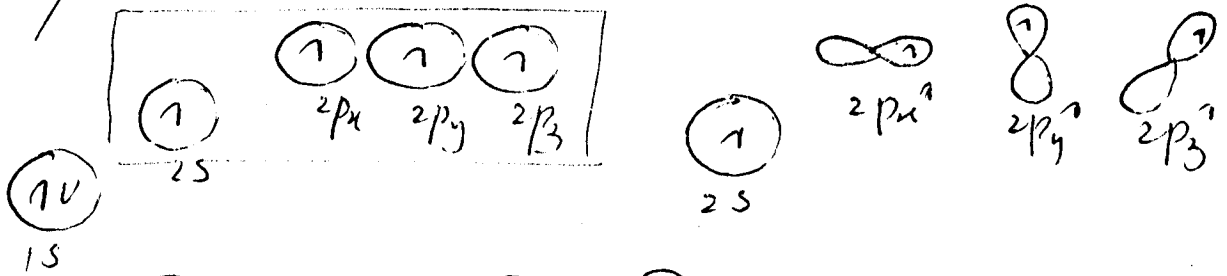


These four atomic orbitals with unpaired electrons may combine in three possible ways.

sp³ HYBRIDIZATION: (METHANE)

In this type of Hybridization 2s and three 2p orbitals are mixed to get four hybrid orbitals. These are called sp³ hybrid orbitals.

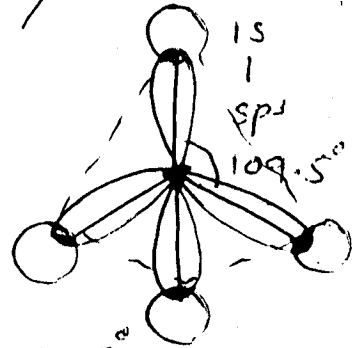
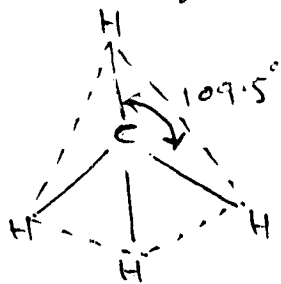
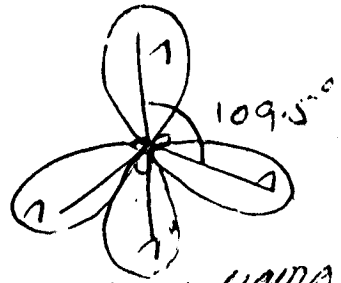
The "sp³" indicates that "s" and "p" have combined in 1:3 Ratio. Further each sp³ hybrid has "s" and "p" character in 1:3 ratio.



The four hybrid orbitals are situated at an angle of 109.5° from each other producing tetrahedral arrangement.

The four sp³ hybrid orbitals are not co-planar.

In methane these four sp³ hybrid orbitals overlap linearly with "1s" orbitals of four hydrogen atoms. Thus four sigma bonds of methane are formed due to sp³-1s overlap.

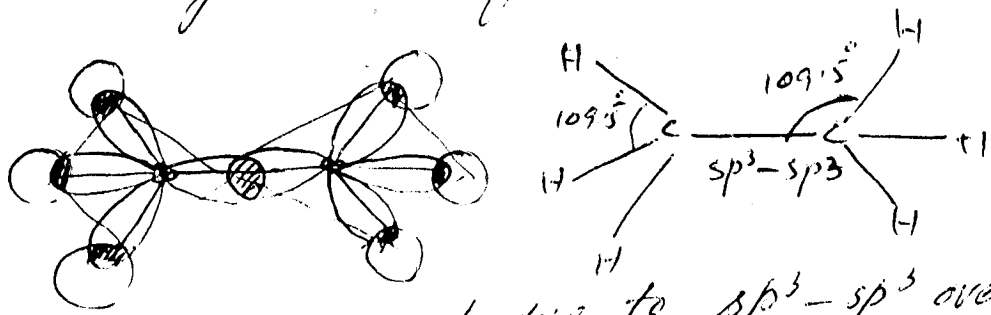


Thus each HCH bond angle is 109.5°.

Thus methane has tetrahedral structure.

ETHANE: - In ethane each carbon is sp³ hybridized. Four sp³ hybrid orbitals are produced on each carbon atom. These hybrid orbitals

are used in sigma bond formation.



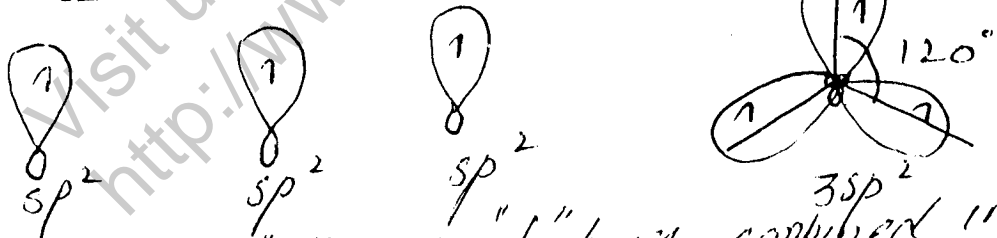
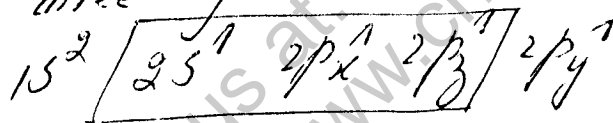
C-C sigma bond is formed due to sp^3-sp^3 overlap.

6 (C-H) sigma bonds are formed due to sp^3-1s overlap.

Thus ethane is also a nonplanar molecule.

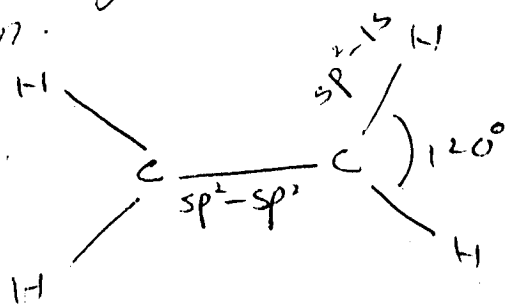
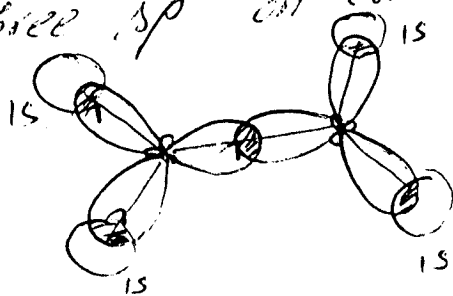
SP² - HYBRIDIZATION: - (HYBRIDIZATION IN ETHENE)

In sp^2 hybridization $2s^1$ and two of the three $2p$ orbitals combine to produce three hybrid orbitals. These three hybrid orbitals are situated at an angle of 120° from each other. Thus these are co-planar. The p orbital which has not been utilized in hybridization is called sp unhybridized p -orbital. It remains present perpendicular to three hybrid orbitals.



sp^2 indicates that "s" and "p" have combined in 1:2 ratio.

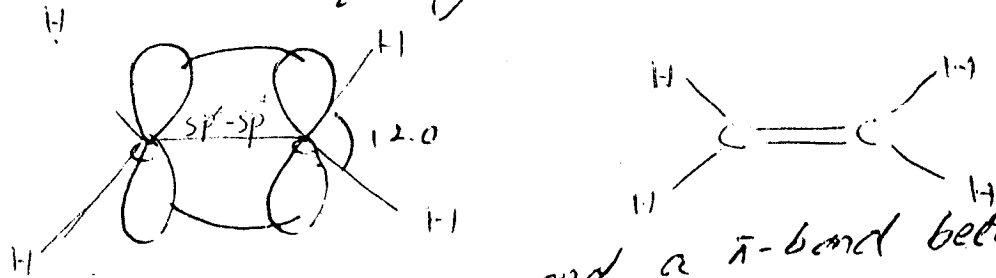
In ethene, each carbon is sp^2 hybridized producing three sp^2 on each carbon.



The C-C sigma bond is formed due to sp^2-sp^2 linear overlap. The four C-H sigma bonds are formed

due to sp^2 - $1s$ overlap, thus all hybrid orbitals are utilized in sigma bond formation.

One unhybridized p -orbital is present on each carbon atom. The two p -orbitals of two carbon atoms are so close to each other that they can have parallel overlap forming a π -bond.



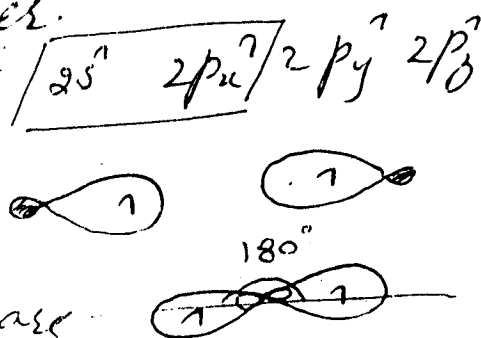
Thus there is a sigma and a π -bond between two carbon atoms.

Thus there are two different bonding m.o. between carbon atoms, one of them is σ B.M.O and other is π B.M.O. The π -bond is much weaker than a sigma bond. The electrons of π -bond are much more exposed to environment than σ -electrons. Thus compounds having π -bond are more reactive than compounds having σ -bonds only.

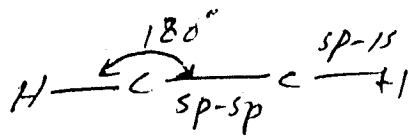
Whenever carbon is directly attached with three other atoms and bond angle is 120° there is sp^2 hybridization.

sp -HYBRIDIZATION: In this type of hybridization one s and one of three p orbitals combine to produce two hybrid orbitals. Each hybrid orbital is called sp hybrid. The two hybrid orbitals are situated at an angle of 180° from each other.

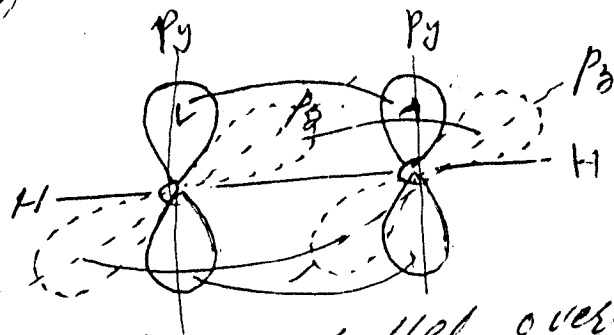
Two unhybridized p -orbitals are still present on each carbon. These p -orbitals are utilized in π -bond formation.



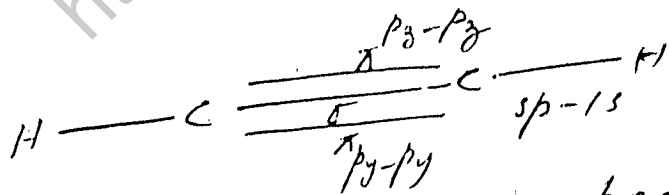
In acetylene (ethyne) each carbon is "sp" hybridized. C-C sigma bond is formed due to sp-sp linear overlap and C-H sigma bond is formed due to sp-1s overlap.



Two unhybridized p-orbitals are still present on each carbon atom. These p-orbitals are used in formation of two pi-bonds between two carbons.



"p_y" and "p_y" have parallel overlap to form one pi-bond and "p_z" and "p_z" have parallel overlap to form another pi-bond between two carbons. Thus there is a triple bond between two carbons. There is a sigma bond and two pi-bonds between two carbons.



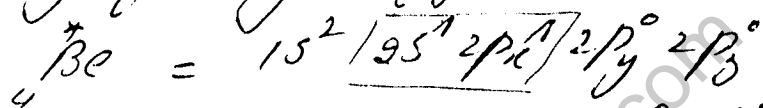
So far hybridization in carbon has been discussed but concept of hybridization is not restricted to carbon. Hybridization also occurs in other atoms like "Be", "B", "N", "O", etc. Further besides, sp³ sp², sp hybridization there are some other sorts of hybridizations like dsp², dsp³, d₂sp³ etc.

HYBRIDIZATION IN BERYLIUM.

Beryllium has atomic number "2" with electronic configuration ${}_{4}\text{Be} = 1s^2 2s^2 2p_x^0 2p_y^0 2p_z^0$

According to V.B.T. valency of an element depends upon number of unpaired electrons. The above electronic configuration of "Be" shows that "Be" should be INERT OR ZEROVALENT.

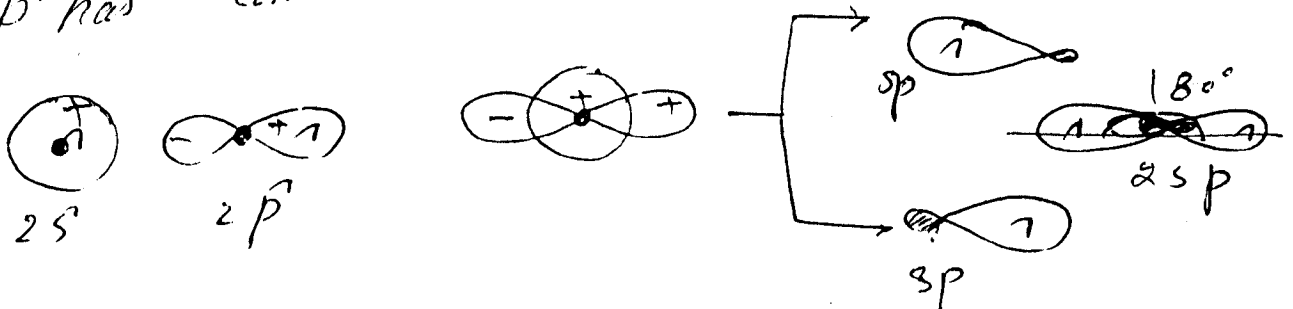
But "Be" is divalent in its compounds like BeCl_2 , BeH_2 etc. Its divalency can be explained considering that in excited state an electron from $2s$ is promoted to an empty "p" orbital giving following configuration.



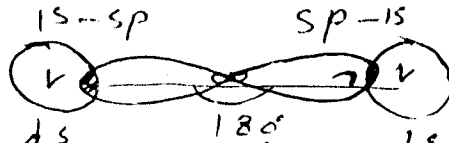
If it is considered that ~~bonds~~ in BeH_2 ~~exists~~ one Be-H bond is formed due to $2s - 1s$ overlap and other due to $2p_x - 1s$ overlap then two Be-H bonds should not be equivalent (they should have different stabilities and different bond lengths) But in fact the two Be-H bonds are exactly equivalent in their stabilities and bond lengths etc.

Thus it is considered that $2s$ and $2p_x$ combine to produce two hybrid orbitals each one of them called sp -hybrid.

The $2sp$ are situated at an angle of 180° from each other. Each hybrid has 50% 's' and 50% 'p' character. "sp" indicates that 's' and 'p' has combined in 1:1 ratio



The "1s" orbital of hydrogen overlaps with "sp" hybrid orbital to form a sigma bond. Thus two sigma bonds are equivalent (each due to sp-1s overlap)



Thus BH_2 has linear structure (bond angle 180°) which is in accordance with V.S.E.P.R. THEORY

The hybrid orbitals have slightly higher energy than combining orbitals and energy is absorbed during hybridization process. Thus hybrid orbitals are slightly unstable than atomic orbitals. However this decreased stability is compensated due to greater stability of bonds formed due to sp-1s overlap. (more energy is released due to two sp-1s overlap than released due to ~~sp~~ 1s-2s, & 1s-p_x overlap) (this is also called DIAGONAL HYBRIDIZATION).

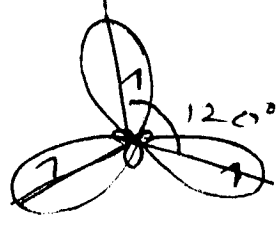
$3sp^2$ HYBRIDIZATION IN BORON.

Boron with atomic number "5" has following electronic configuration = $1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$. According to this configuration Boron should be monovalent but Boron is trivalent in most of its compounds. Let us consider that in excited state one electron from $2s^2$ is promoted to an empty $2p_z^0$ giving following configuration

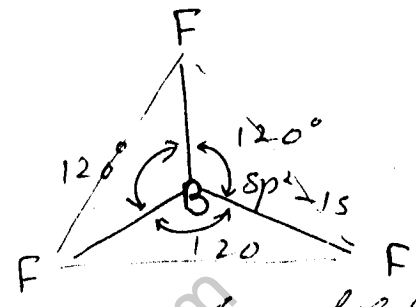
$$B^* = 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$$

One "2s" and two "2p" orbitals ($2p_x^1 2p_y^1$) combine to produce three hybrid orbitals each hybrid is called sp^2 hybrid. sp^2 indicates that "s" and p have combined in 1:2 ratio. Each hybrid has $\frac{1}{3}$ s and $\frac{2}{3}$ p-character.

The three sp^2 hybrid orbitals are situated at an angle of 120° from each other. The three sp^2 are co-planar directed towards corners of an equilateral triangle. This is called trigonal hybridization.



In BF_3 , each B-F bond is formed due to linear overlap of sp^2-2p_z overlap. Thus 3 bonds are identical in all respects.

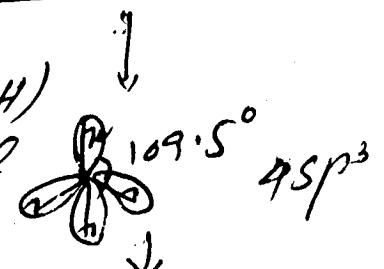


The shapes of ammonia and H_2O can also be explained on the basis of hybridization.

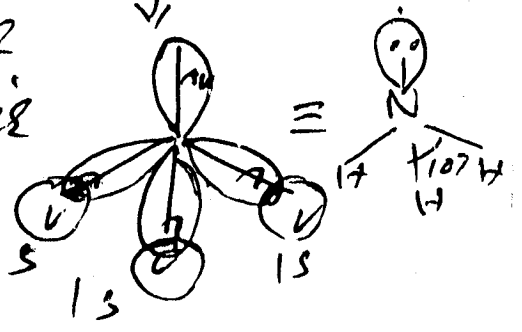
SHAPE OF NH_3 Nitrogen has following electronic configuration

$$N = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$$

If it is considered that three hydrogens are attached to three 'p' orbitals then bond angle should be 90° each. But in actual it is 107° . Thus it is considered that in nitrogen sp^3 hybridization occurs. There are 5 electrons to be placed in the four sp^3 hybrid orbitals. One hybrid orbital has paired electron and it remains as lone pair. Three hydrogens each having 1s-orbital overlaps with sp^3 hybrid orbitals having unpaired electron. Thus three (N-H) sigma bonds are formed due to sp^3-1s overlap. The bond angle is reduced to 107.5° due to greater repulsion of lone pair.



NH_3 has trigonal pyramidal structure.



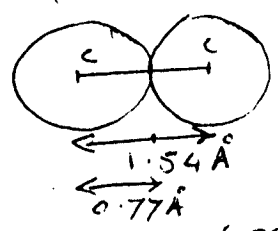
BOND LENGTHS : : & COVALENT RADII : :

The mean distance between nuclei of two atoms bonded by a covalent bond is called BOND LENGTH.
 When two atoms are bonded by a bond, the distance between their nuclei is ^{not} constant because the atoms are always vibrating about a mean position.

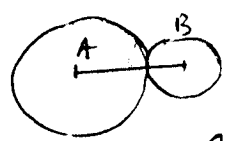
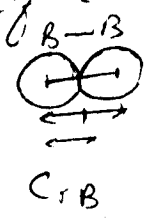
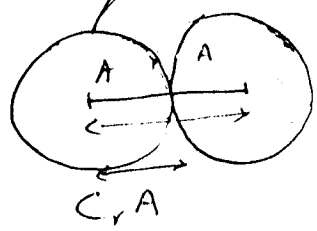
This in bond length consideration average distance between their centres is considered. Although bond length is slightly different in different molecules yet variation is less than 1%. For example C-C bond length is very close to 1.54 Å in most of compounds.

COVALENT RADIUS :-

One half of the distance between centres of two atoms bonded by a single covalent bond is called Covalent Radius. For example when "C" and "C" are bonded by a single covalent bond, the distance between their centres is 1.54 Å. The ~~bond~~ covalent radius of carbon is $\frac{1.54}{2} = 0.77 \text{ \AA}$.



The covalent radii can be used to find out the bond lengths between two unlike atoms. The bond length of such a bond is equal to sum of covalent radii of two atoms.



$$\text{Bond length} = r_A + r_B$$

For example the "C-Cl" bond length in methyl chloride is 1.76 Å which is equal to sum of covalent radius of Carbon (0.77) and covalent radius of chlorine (0.99).

But in most of cases the rule does not hold good.

For example sum of covalent radii of carbon and nitrogen is 1.52 \AA whereas actual bond length is of $C-N$ is 1.47 in methylamine. Similarly sum of covalent radii of two carbon and oxygen is 1.51 \AA while actual bond length is 1.42 \AA . This difference may be due to following factors:

(i) Ionic character of covalent bond due to difference of electronegativity between two bonded atoms. The difference between expected and actual bond lengths increases with increase in A.E.N. of two bonded atoms.

Further bond length ^{also} depends upon the "s" character present in hybrid orbital. For example $C-H$ bond length in methane is 1.11 \AA (sp^3-1s bond) in ethane it is 1.10 (sp^2-1s overlap) and 1.08 in ethyne ($sp-1s$ overlap). It can be noticed that bond length decreases with increasing "s" character.

Double bond length and triple bond length is shorter than single bond length. This is due to the fact that there is one electron pair in single bond, two in d.b. and three electron pairs in triple bond. The extra electrons bring two atoms more and more closer to each other.

IONIC CHARACTER OF COVALENT BOND.
When covalent bond is formed between identical atoms, the shared electron pair is equally attracted by two atoms. Thus shared electron pair is equally shared by two atoms. Thus such a bond is non polar bond.

However when a covalent bond is formed between two dissimilar atoms, one atom attracts shared electron pair more powerfully to itself than the other. This power of an atom to attract shared electron pair to itself is called Electronegativity. The more E.N. atom acquires partial negative charge and less E.N. atom acquires partial positive charge. Such a bond is called polar bond.

For example consider a bond between Hydrogen and Chlorine in "H-Cl". Chlorine attracts shared electron pair to itself more powerfully than hydrogen. Thus chlorine acquires partial negative charge and hydrogen acquires partial positive charge. $\overset{+s}{H} \rightarrow \overset{-s}{Cl}$. Such a bond is called polar bond. Similarly $\overset{+s}{H} - \overset{-s}{Cl}$ also has some ionic character.

The ionic character increases with increase in difference of E.N. between two atoms. When difference of E.N. between two atoms is greater than 1.7 then the bond has more than 50% ionic character. The electronegativities of atoms cannot be measured directly. However some of E.N. scales have been based upon I.P., Electron affinities, atomic radii, n.m.f. etc. A particularly convenient scale has been devised by Pauling from bond energies of diatomic molecules.

The bond energy of a bond between two dissimilar atoms 'A-B' is always greater than the geometric mean of the energies of bonds A-A and B-B (The difference between actual and expected bond energy (mean B.E.) is called Δ).

Fluorine has been given maximum E.N. = 4. Other elements has been assigned E.N. relative to fluorine by using following formula.

$$X_K - X_U = \sqrt{\frac{\Delta}{965}}$$

X_K = E.N. of known atom

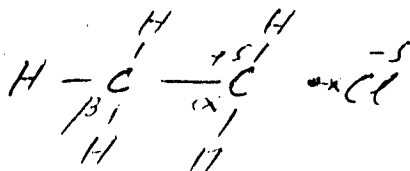
X_U = E.N. of unknown atom (to be determined)

DEFINITION:-

The permanent dipole at one position induces charge separation of an adjacent bond and further along the chain.

For example consider an Ethylchloride molecule.

$\overset{+\delta}{\text{H}}-\overset{+\delta}{\text{C}}-\overset{+\delta}{\text{C}}-\overset{-\delta}{\text{Cl}}$. Chlorine being more electronegative attracts electron pair more powerfully than carbon. Hence chlorine acquires partial negative charge and carbon has partial positive charge. Thus it is called a polar bond with some dipole.



The α -carbon with δ^+ ve charge attracts electron pair between itself and β -carbon more powerfully and β carbon also acquires δ^+ ve charge. No doubt this δ^+ ve is greater lesser than δ^+ ve of α -carbon.

The β -carbon attracts electron pairs between itself and hydrogens more powerfully and β -hydrogens also bear δ^+ ve charge. This process goes on further along the chain. It is called **INDUCTIVE EFFECT**.

The charge separation has been produced due to greater electronegativity of chlorine. Thus chlorine is an electron withdrawing group.

The functional groups responsible for inductive effect are divided into two categories.

ELECTRON WITHDRAWING GROUPS **"-I EFFECT"**

The groups which are more E.N. as compared to "H" are called electron withdrawing groups. They

are said to have -I effect. Some common electron withdrawing groups are given below.

- I EFFECT :- $-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{N}H_3$, $-NO_2$, $-CN$
 $-COOH$, $-F$, $-Cl$, $-Br$, $-I$
 $-COR$, $-CH=CR_2$ etc,

ELECTRON DONATING INDUCTIVE EFFECT :-

The groups which are electron releasing with respect to hydrogen are called Electron donating groups. They are said to have +I effect. Some common electron releasing groups are given below.

- $-O^-$, $-C(=O)O^-$, $-CR_3$, $-CH_2R$, $-CH_3$, $-D$

Alkyl groups are considered as electron donating groups but latest research has shown that it may have +I or -I effect depending on situation.

The inductive effect operates through sigma bond and decreases with increasing distance from permanent dipole. There is no actual shifting of electron from one atom to another but electron pair gets closer to one atom than the other due to difference of E.N. between two bonded atoms.

Inductive effect plays a very important role in determining acids strength of various carboxylic acids. Let us consider following examples.

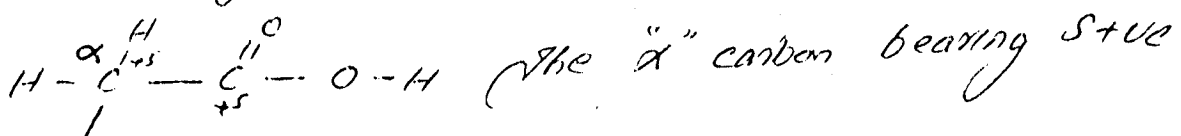
CHLOROACETIC ACID IS STRONGER THAN ACETIC ACID

The strength of acid depends upon two factors

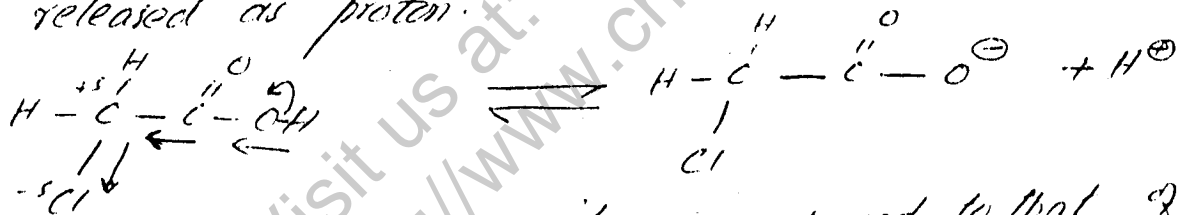
- (i) The ease with which proton is donated
- (ii) The stability of anion formed after removal of proton.

The acid which easily gives its proton is a stronger acid and vice versa. Similarly acid whose anion is stable is stronger acid.

In case of chloroacetic acid one hydrogen of acetic acid has been replaced by $-Cl$. Chlorine being more E.N. attracts electron pair between itself and carbon more powerfully. Thus a δ^+ charge is produced on "C" and δ^- charge on chlorine.



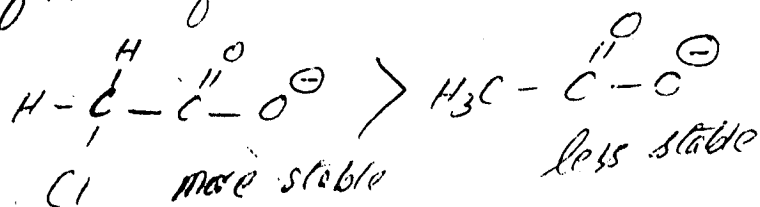
charge δ^+ , attracts electron pair between itself and carbonyl carbon more powerfully. Hence carbonyl carbon also acquires extra positive charge. This carbonyl carbon in turn attracts electron pair between itself and oxygen more powerfully. Oxygen in turn takes up the electron pair between itself and hydrogen. Thus hydrogen is released as proton.



Thus proton is released as easily as compared to that of acetic acid. Thus chloroacetic acid is stronger acid as compared to acetic acid.

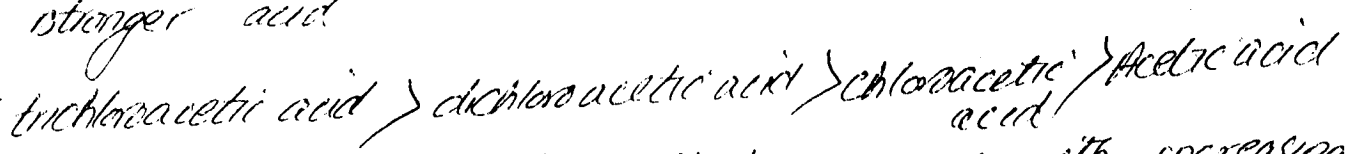
The greater acidity of chloroacetic acid can also be explained on the basis stability of anion formed by removal of proton from two acids.

The anion formed by removal of proton from chloroacetic acid is more stable as compared to anion formed from acetic acid.



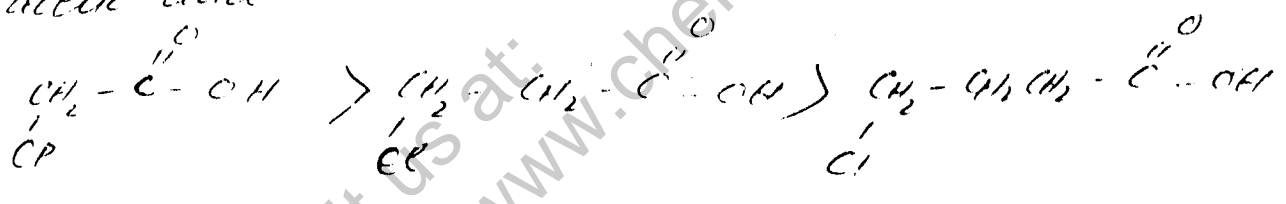
It is due to the fact ^{that} at oxygen electron density is decreased due to electron withdrawing nature of Chlorine in chloroacetic acid. Hence anion is stabilized.
 (The greater the stability of anion, the stronger is the acid.)

Dichloroacetic acid is still more acidic than chloroacetic acid & Acetic acid. Because there are two electron withdrawing groups, and proton is removed even more easily. Further dichloroacetate ion is much more stable than acetate ion. Trichloroacetic acid is even stronger acid.

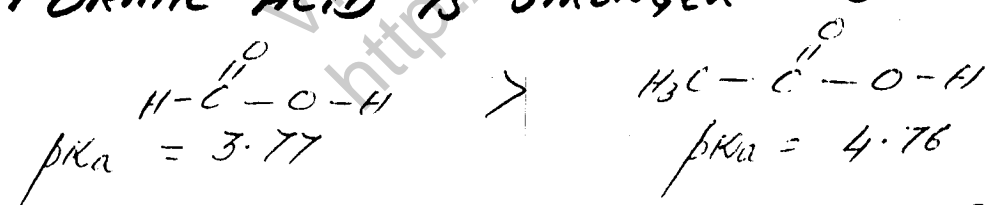


The inductive effect decreases with increasing distance from permanent dipole.

For example 2-Chloroacetic acid is stronger than 3-Chloroacetic acid and 4-Chloroacetic acid.



FORMIC ACID IS STRONGER ACID THAN ACETIC ACID.

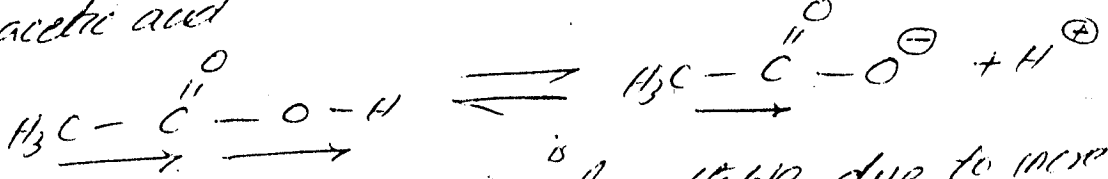


It can be explained on the basis of electron donating inductive effect of methyl group.

Methyl group is electron donating group, it pushes electron density towards carbonyl carbon which in turn increases electron density on oxygen. Thus oxygen is not "WILLING" to take electron pair between itself and hydrogen. Thus hydrogen is not released easily from oxygen.

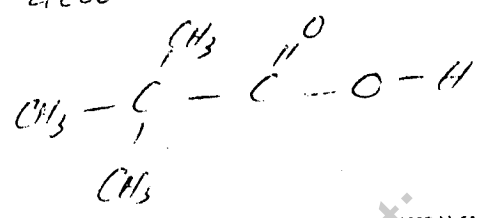
of acetic acid. And even if it is released it is recaptured by acetate ion. Thus acetic cannot give its proton easily. Thus it is weaker acid than formic acid.

Formic acid do not have any electron donating group. So it is ~~most~~ almost ten times stronger than acetic acid.



Further anion of acetic acid is less stable due to increased electron density of oxygen bearing negative charge.

Following acid are stronger weaker acids than acetic acid. The additional methyl groups decrease acidity of this acid.



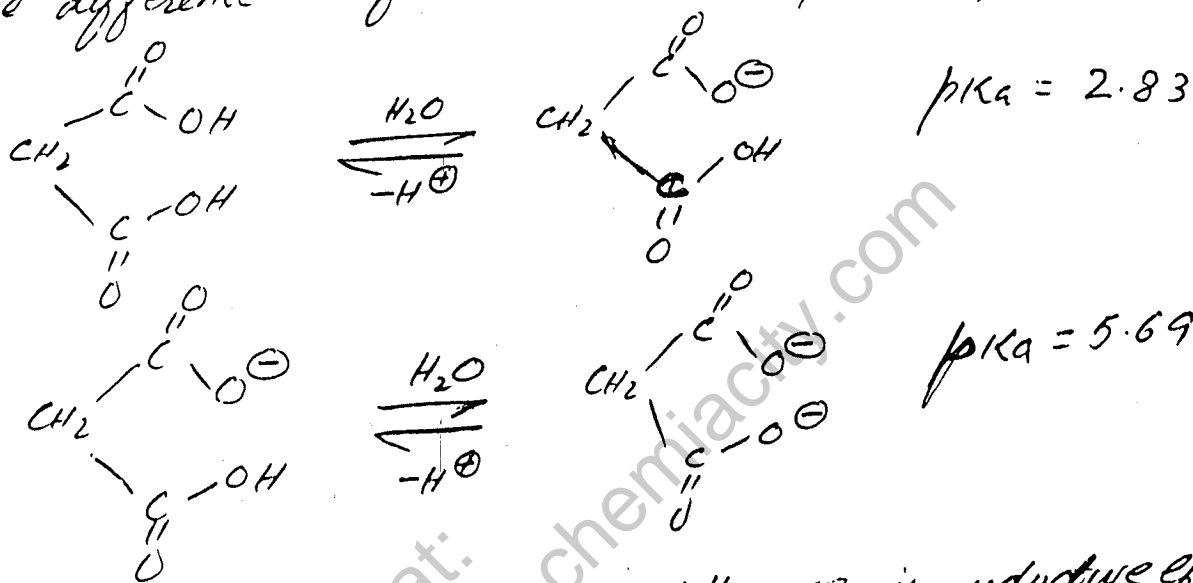
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WRITE A NOTE ON FIELD EFFECT:

The factors which decrease the second ionization of a diprotic acid, through space, solvent or other medium is called FIELD EFFECT. Contrary to inductive effect, it operates through medium or space and not through sigma bond.

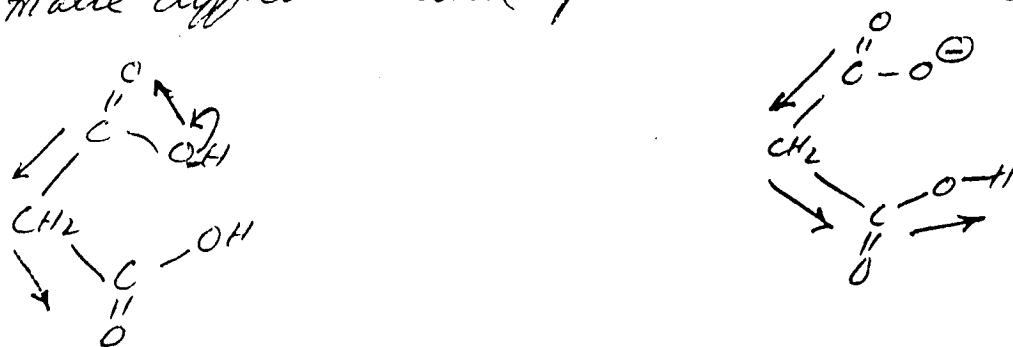
EXPLANATION:- Let us consider first and second ionization of malonic acid (A diprotic acid $\text{CH}_2(\text{COOH})_2$).
The first pK_a is 2.83 and second pK_a is 5.69.
The difference in first and second pK_a is approx = 3



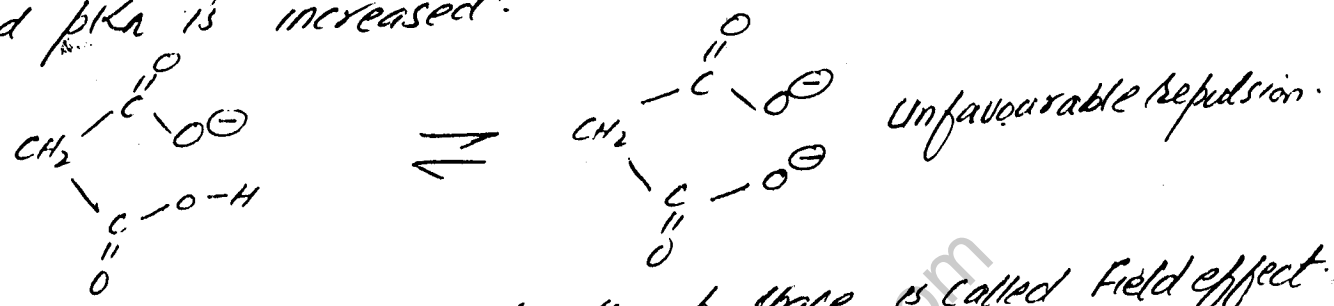
One factor responsible for this difference is inductive effect

The $-\text{COOH}$ group in malonic acid is electron withdrawing group, and it makes first pK_a smaller than acetic acid ($-\text{COOH}$ electron withdrawing group).

For removal of second proton, the $-\text{COO}^-$ group acts as electron donating group, and makes removal of proton difficult. Thus removal of second proton is made difficult and pK_a is increased ($pK_a = 5.69$)



But only this factor cannot explain the very large difference of pK_a . Actually the ionization of second proton leads to an unfavourable repulsion between charges of resulting dianion. Thus dianion is much more UNSTABLE than monoanion. The strength of acid depends upon stability of anion. Due to instability of dianion the second proton is not removed easily and pK_a is increased.



This effect which operates through space is called Field effect.

This effect depends upon geometry of molecule.

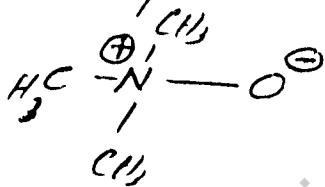
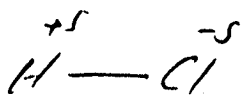
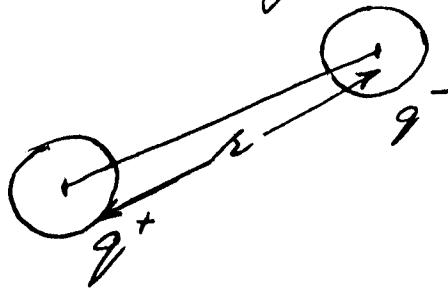
Actually polarization is a combined action of two effects and it is often difficult to separate these two effects. In most of cases these are considered together under the name field effect.

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DIPOLE MOMENT:-

Dipole moment measures concentration of positive and negative charges in different parts of molecule. It is denoted by " μ " and mathematically, it is equal to charge and distance between the charges. If charge is denoted by " q " and distance between charges is denoted by " r " then $\mu = q \cdot r$

These charges may be due to difference of E.N. between two atoms or due to presence of formal charges.



The magnitude of positive and negative charge is always equal but with different charge. Thus charge on either end is considered.

The charge on either end is of the order of 10^{-10} e.s.u. and distance between charges is of the order of 10^{-8} cm. Thus usual value of dipole moment is 10^{-18} esu-cm. The value is commonly called Deby denoted by "D".

For example in a molecule charge on either end is 0.8×10^{-10} e.s.u. and distance between charges is 1.5×10^{-8} cm then dipole moment is

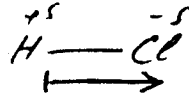
$$\mu = (0.8 \times 10^{-10} \text{ e.s.u.}) \times (1.5 \times 10^{-8} \text{ cm})$$

$$\mu = 1.2 \times 10^{-18} \text{ esu} \cdot \text{cm}$$

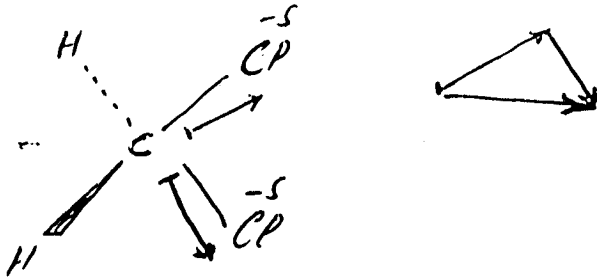
$$\mu = 1.2 \text{ D}$$

Dipole moment is a vector quantity and its direction is always ~~pos~~ from positive to negative end.

It is represented by an arrow directed from positive to negative end.

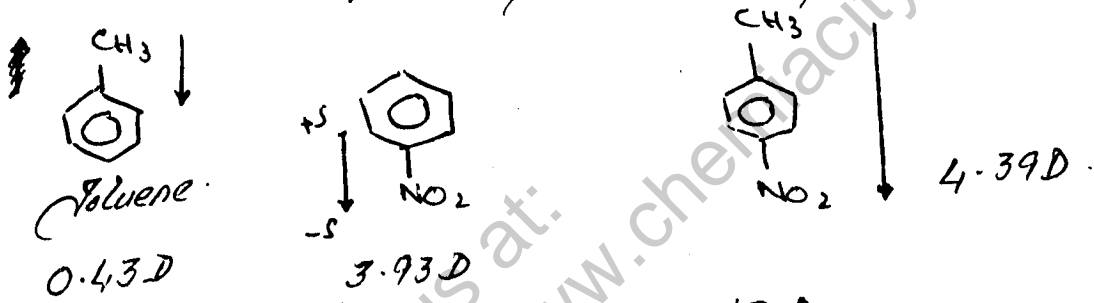


In some polyatomic molecules, there are more than one bond moments and total dipole moment is vectorial sum of individual dipoles.



The value of bond moments is roughly same in different molecules. So total dipole moment of a molecule can be determined if individual dipole moments are known.

For example consider *p*-Nitrotoluene



Dipole moment of toluene = 0.43 D
 " " " Nitrobenzene = 3.93 D
 Expected dipole = 4.36 D

This expected dipole is very close to actual value (4.39 D).

C-H has a slight dipole in the direction of hydrogen. It is due to directional hybrid orbital. The electron density of carbon is not evenly distributed but it is located away from carbon.

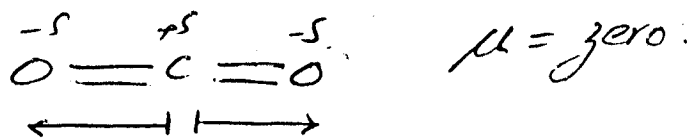
This dipole decreases with increase in "s"-character of hybrid orbital.



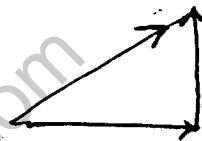
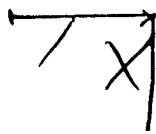
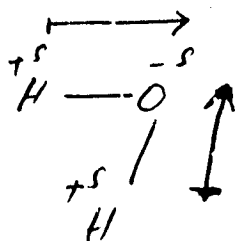
The decreasing order of E.N. is $sp > sp^2 > sp^3$

STRUCTURE DETERMINATION:-

Dipole moment value can be used to determine structure of some molecules. For example linear structure of "CO₂" is supported by its zero dipole. The individual dipoles are oriented at such a distance from an angle that they cancel each other out.



The bent structure of water is supported by its dipole moment ~~1.4 D~~ 1.84 D



Had it linear structure, it should have zero dipole moment.

Similarly cis and trans ~~isomers~~ dichloroethene can be distinguished on the basis of its dipole moment.

Trans-dichloroethene has zero dipole moment because individual dipoles cancel each other out. The cis isomer has dipole moment 1.9 D.

