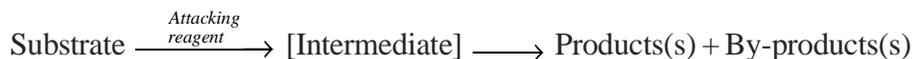


Section - 6

MECHANISM IN ORGANIC REACTIONS

A general organic reaction may be depicted as:



As we can see, there are two reactants: substrate and reagent. Substrate is the reactant that supplies carbon to the newly formed bond. The other reactant is called the reagent.

In case, both reactants supply carbon to the new bond, the molecule on which attention is focussed is arbitrarily chosen as the substrate.

Mechanism is the actual process by which the reaction takes place. It tells us which bonds are broken, which new bonds are formed, the order in which bond fission-formation takes place, the steps involved etc.

In most of the organic reactions that we will encounter, bonds are broken. This can occur in either of two ways:

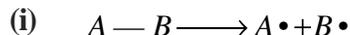
- (i) Homolytic fission
- (ii) Heterolytic fission

Bond fission leads to formation of reactive intermediates and the nature of these intermediates depends on the mode of bond cleavage. In other words, what type of intermediate species (carbocation, carbanion etc.) are formed will depend upon the way a particular bond breaks.

Further, reagents and intermediates, together, decide the type of reaction a given substrate will undergo e.g. addition, substitution etc.

(a) BOND CLEAVAGE

A knowledge of how bond cleavage takes place in molecules is important to understand the various transient intermediate structures formed during reactions. There are three ways in which a covalent bond can be broken:



This sort of cleavage is termed **homolytic fission** because each group separates with one electron. The entities so formed are very reactive and are known as radicals. Such cleavage generally occurs in the gas phase or in non-polar solvents. It can be catalysed by light (as in the substitution of methane which will be discussed suitably under free radical reactions) or by the addition of other radicals



In the process of cleavage, it could happen that one group separates with both the electrons of the covalent bond. This will result in the formation of an ion pair. Note that it can happen in two ways as in (ii) and (iii) above. Such cleavage is termed **heterolytic fission**. This generally occurs in solution in polar solvents. There are two reasons for this.

(a) a polar solvent aids in the separation of charge (by favouring the bond cleavage process)

(b) the resultant ion pair so formed can be stabilised through solvation (by the molecules of the polar solvent.)

Further, an electron-withdrawing substituent intensifies the positive charge on the already electron-deficient C-atom, making it less stable. Refer Fig.... (b) above.

Hence, we can say that the higher is the number of electron-releasing substituents, more stable is the carbocation. Such a phenomenon of availability (release or withdrawal) of electrons at the reaction site is called as **polar effect**.

Carbanions: We shall now move onto another kind of transient intermediates carbanions. As the name itself suggests, this kind of intermediate has a negative charge being carried by the C-atom. This negatively charged C-atom could be either sp^3 hybridised (resulting into a pyramidal configuration Fig... (a)) or sp^2 hybridised (yielding planar trigonal arrangement, Fig.... (b)). Examine the following possible configurations.

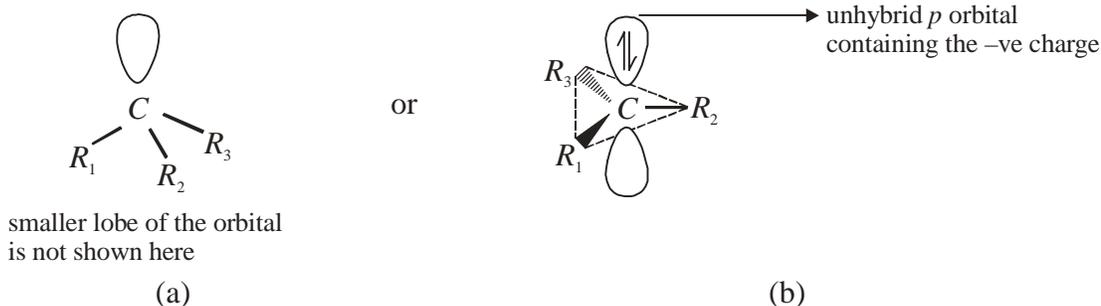
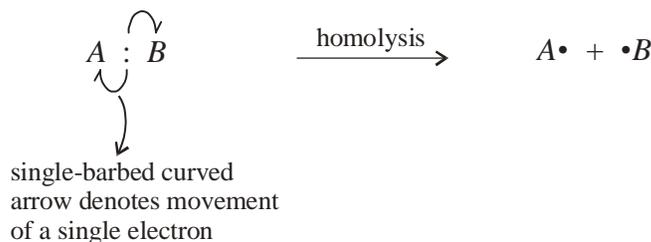


Fig - 29

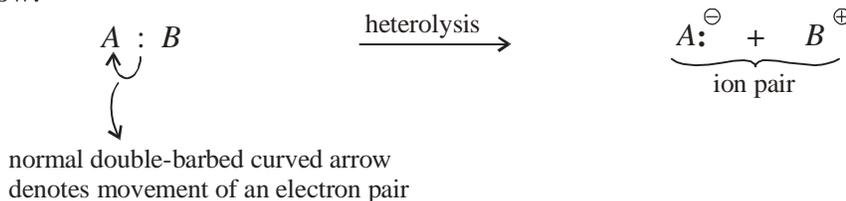
In the above figure, 'R' (R_1, R_2, R_3) is any hydrocarbon group. Now, of the two possible configurations shown in Fig...., which one actually exists in a given organic reaction depends on the nature of R_1, R_2 and/or R_3 . For the time being, it is sufficient for you to understand that a carbanion may have any of the two possible configurations. In fact, the actual configuration may be intermediate between the two.

The stability of a carbanion is judged on grounds similar to those applicable to carbocations. The higher the number of electron-withdrawing substituents on the negatively charged C-atom, the more is the dispersal of the negative charge and hence, increased stability of the carbanion.

Free Radicals: We now move onto understand free radicals one of the most reactive transient intermediates. By definition, an atom or group of atoms having an *odd* electron (an electron which is not paired; it does not have a partner of opposite spin) is called a free radical. Its symbolic representations includes a dot (\bullet) to indicate an odd electron. Further, when a free radical participates in a reaction, the movement of the single electron (or even in cases where no free radical is involved, but we need to exclusively depict the movement of one single electron and not one pair of electrons) is indicated by a single - barbed curved arrow, as shown below:



Note: Movement of a pair of electrons in an organic reaction is shown by the normal double - barbed curved arrow as drawn below:



Structurally, the case of a free radical is somewhat similar to that of carbanions as far as location of the odd electron is concerned. Two configurations are possible: one, the unpaired electron is present in an unhybrid p orbital (with rest of the sp^2 hybrid orbitals forming planar trigonal configuration); and second, the odd electron could be present in a sp^3 hybrid orbital (thus giving a pyramidal shape to the radical). The two possibilities are as shown below:

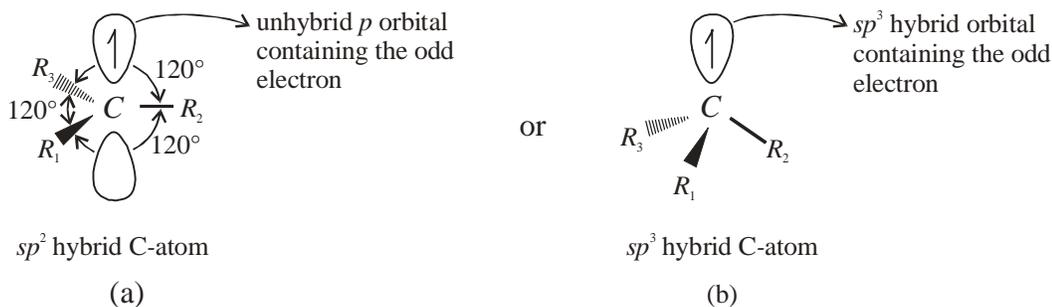


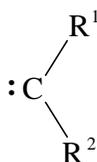
Fig - 30

Experimentally, it has been found that most simple alkyl radicals are planar trigonal at the carbon having the unpaired electron. The simplest alkyl radical is $CH_3\cdot$ called as methyl radical. However, an experimentally observed exception is that of $CF_3\cdot$ which has essentially sp^3 hybrid C-atom. Hence $CF_3\cdot$ has a pyramidal geometrical shape.

Let us now discuss the stability aspects relating to a free radical. Although alkyl radicals are uncharged, the carbon that bears the odd electron is electron-deficient (as its octet in the valence shell is not complete). Hence, electron-releasing substituents (recall 'polar effects') bonded to such a C-atom would stabilize it, and the more such substituents are, the more stable the radical would be.

Carbenes: Carbenes are neutral species in which carbon atom forms only two bonds (C is bonded to only 2 atoms) and has only 6 valence electrons. Out of these 6 electrons, 2 are present in each bond and the remaining 2 are non-bonding electrons.

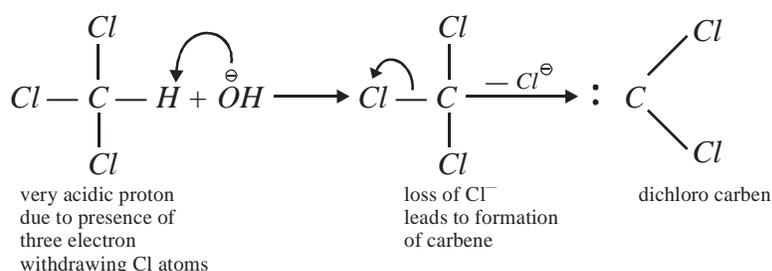
A carbene may be represented as:



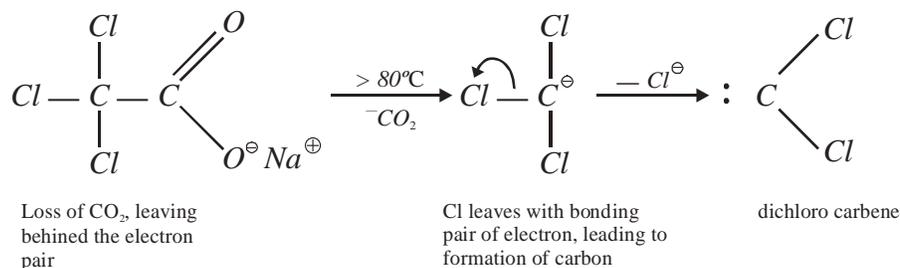
Carbenes are very reactive species and have a lifetime of less than 1 second. They can only be isolated by trapping them in matrices at low temperature.

Generation of carbenes:

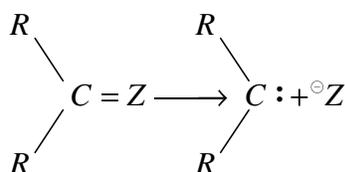
- (i) α -elimination: In these types of eliminations, both leaving groups are from the same atom. e.g. When chloroform is treated with a base, it leads to the formation of dichlorocarbene.



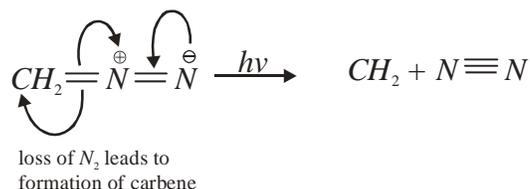
e.g. Decarboxylation of sodium trichloro acetate.



(ii) Disintegration of compounds containing certain types of double bonds.



e.g. Decomposition of diazomethane.

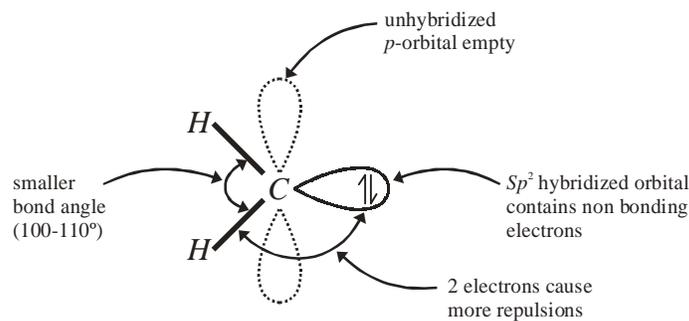


Types of carbenes:

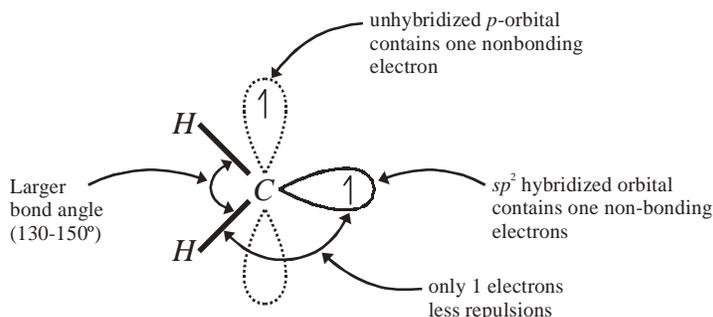
There are two types of carbenes: (i) Singlet (ii) Triplet.

Both singlet and triplet carbenes are sp^2 hybridised and the two differ only in the way the non-bonded electrons occupy the orbitals.

(i) *Singlet carbene*: In case of singlet carbenes, the two non-bonded electrons are present in the sp^2 hybridized orbital. The unhybridized p-orbital remains vacant.



(ii) *Triplet carbene*: The two non-bonding electrons in triplet carbenes occupy different orbitals. One electron is present in sp^2 hybrid orbital and the other is present in unhybridized p-orbital



All carbenes can exist either as singlet or triplet. However, most carbenes are stable as triplet states because the energy that can be gained by bringing the electron to more stable sp^2 orbital is insufficient to overcome the repulsion that arises due to pairing of electron.

Section - 7

ELECTRONIC EFFECTS IN MOLECULE

A number of factors operate in molecules that govern the charge density available at different sites in the molecule. We will discuss these effects in the context of organic molecules in particular.

(a) INDUCTIVE EFFECT:

This effect takes place whenever two atoms/groups of different electronegativities are bonded to each other. The more electronegative atom/group of the two will tend to draw the shared electron pair more towards itself, resulting in a skewed rather than a symmetrical electron charge distribution.

Consider two atoms A and B bonded to each other, with B being more electronegative. B will tend to pull the electron pair of the covalent bond towards itself. This means that overall, the electron pair of the covalent bond will spend more time near B than A , resulting in a slight negative charge (δ^-) on B and a slight positive charge (δ^+) on A :



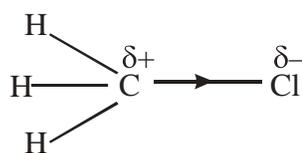
B is more electronegative than A , so its pull on the electron pair is greater than A



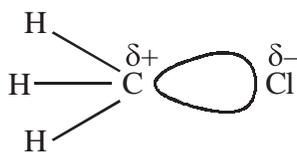
An approximate orbital picture showing the skewed electron charge density between A and B

Fig - 31

Consider the compound CH_3Cl (methyl chloride). Chlorine is more electronegative than carbon. Thus, methyl chloride shows the inductive effect : electron density is greater near the chlorine atom



Inductive effect in methyl chloride

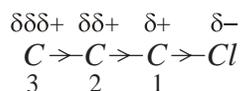


An approximate orbital picture showing the skewed charge distribution between carbon and chlorine

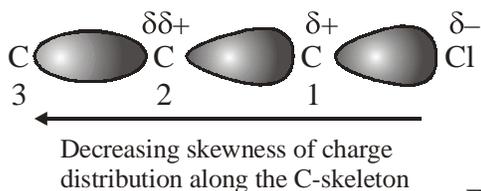
Fig - 32

Thus, it should be noted that inductive effect in a molecule is a state of permanent polarisation of the molecule. This will show up in the physical properties of the molecule like its dipole moment.

Inductive effect can be propagated down a chain. Consider the following carbon chain, with chlorine at one end. Observe how the inductive effect propagates down the chain:



It should be clear that the strength of the inductive effect falls as we proceed down the chain. For all purposes, the transmission of the inductive effect after the second carbon atom is negligible.

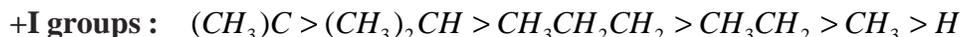


A crude orbital picture showing how the inductive effect dies down along the chain

Fig - 33

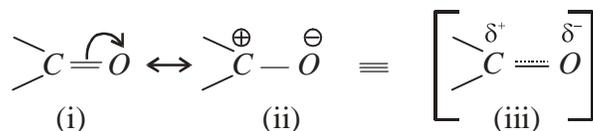
Inductive effect is abbreviated as the **I-effect**

Further, any atom or group which attracts electrons more strongly than hydrogen, is said to be showing -I (negative-inductive / electron - withdrawing) effect. On the other hand, any atom or group attracting electrons less strongly than hydrogen is said to be showing +I (positive inductive / electron-releasing) effect. Following are two sequences in decreasing order of their effects:



(b) MESOMERIC EFFECTS:

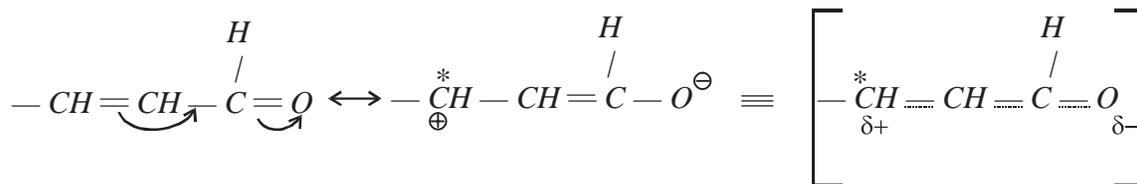
Consider an organic compound in which the linkage $\text{>C}=\text{O}$ is present. We can write two canonical forms for this linkage so that the actual linkage will be a hybrid of these two canonical forms :



You might say that (ii) is not a stable canonical form since it involves the separation of charge and therefore will be of a higher energy content. However, the negative charge being on electronegative oxygen atom will stabilise this form to an extent. Thus, (ii) will not have a negligible contribution to the hybrid (iii).

Thus, we should actually expect that the linkage will be in a state of permanent polarisation due to the resonance possible. There will be an electron withdrawing inductive effect of the oxygen atom too, but since the σ electrons are much less polarisable than the π electrons, we can expect the polarisation in (iii) to be mostly due to the π electrons.

Lets see another example in which such redistribution is possible. We consider a conjugated system in which the $\text{>C}=\text{O}$ linkage is conjugated to a carbon - carbon double bond. For this compound, we can write two canonical forms, and the actual structure will be a hybrid of these two forms:

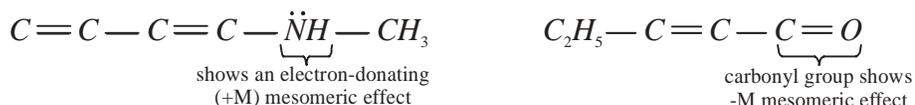


Thus, the actual structure is in a state of permanent polarisation, with the oxygen atom being slightly negatively charged and the (starred) carbon atom being slightly positively charged. Notice that this polarisation has been transmitted through the π electrons only.

Having seen these two examples, we can now properly define the mesomeric effect : it is essentially an electron redistribution that can take place in unsaturated systems (especially in conjugated systems) via the π orbitals.

Since transmission of this effect occurs via the π orbitals while inductive effect operates through the sigma orbitals (which are much less polarisable than the π orbitals), the mesomeric effect suffers much less attenuation in its transmission, with the result that this effect can operate across long carbon chains (the polarity of adjacent carbon atoms will alternate along the chain due to this effect). Electron-donating mesomeric effect is represented as the +M effect while the electron withdrawing mesomeric effect is represented as -M effect.

Consider the following two examples:



Following is a list of +M and -M atom or group of atom:

+M groups: $-\text{Cl}, -\text{Br}, -\text{I}, -\text{NH}_2, -\text{NR}_2, -\text{OH}, -\text{OCH}_3$

-M groups: $-\text{NO}_2, -\text{C}\equiv\text{N}, >\text{C}=\text{O}$

Like the inductive effect, mesomeric effect is a permanent polarisation state of the molecule and would thus, show up in physical properties of the molecule like its dipole moment. For the sake of emphasis, inductive and mesomeric effects have been compared in the table below:

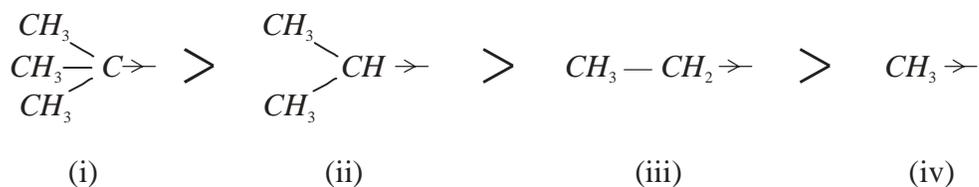
Table-2: Comparison between inductive and mesomeric effects

	Inductive effects	Mesomeric effects
1.	Operate in both saturated and unsaturated compounds	Operate only in unsaturated compounds (and especially in conjugated compounds)
2.	Involve σ bond electrons	Involve π electrons and orbitals
3.	Can be transmitted only over very short distances due to low polarisability of the σ orbitals	Can be transmitted across large carbon chains (provided, of course, that conjugation is present across the carbon chain)

(c) HYPERCONJUGATION:

In part (a), we discussed the inductive effect as an electron donating or withdrawing effect of a group depending on the relative electronegativity of the other group with which it is bonded.

It is known that alkyl groups have the following order of electron donating inductive effect (which we'll denote as $+I$ effect):



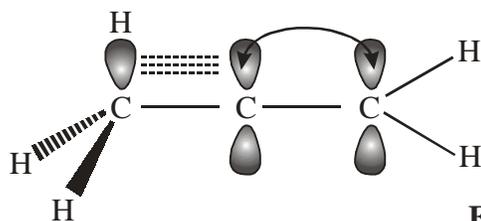
Thus, tertiary alkyl groups as in (i) above have the highest $+I$ effect while methyl group (in (iv) above) will have the lowest $+I$ effect.

However, this order of electron donating effect does not hold true when the alkyl group is attached to an unsaturated system like a double bond or a benzene ring. In some cases, this order might even be reversed, so that the methyl group will have the highest and the tertiary alkyl group the lowest electron releasing effect.

Obviously, some other mechanism of electron donation is at work when alkyl groups are connected to unsaturated systems. This mechanism is termed hyperconjugation and is a sort of an extension of the mesomeric effect. In hyperconjugation, the delocalisation of electrons occurs through σ - π overlap of orbitals.

Let us discuss this effect in detail in the case of $\text{CH}_3 - \text{CH} = \text{CH}_2$. First, let us understand the physical picture of how the σ - π overlap occurs. Then we'll understand how to represent the process of hyperconjugation on paper, through canonical forms.

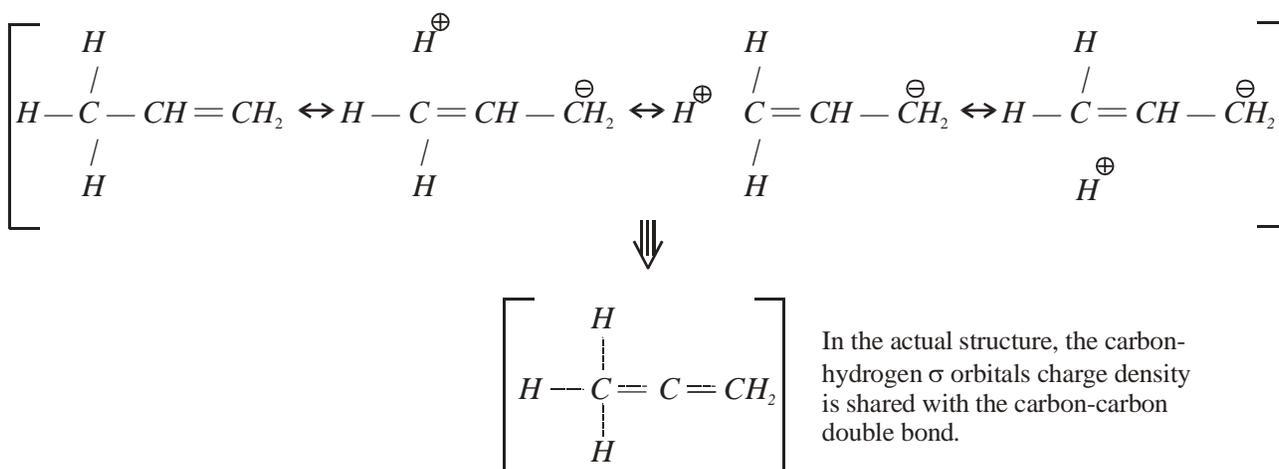
Consider the following approximate orbital picture of $\text{CH}_3 - \text{CH} = \text{CH}_2$.



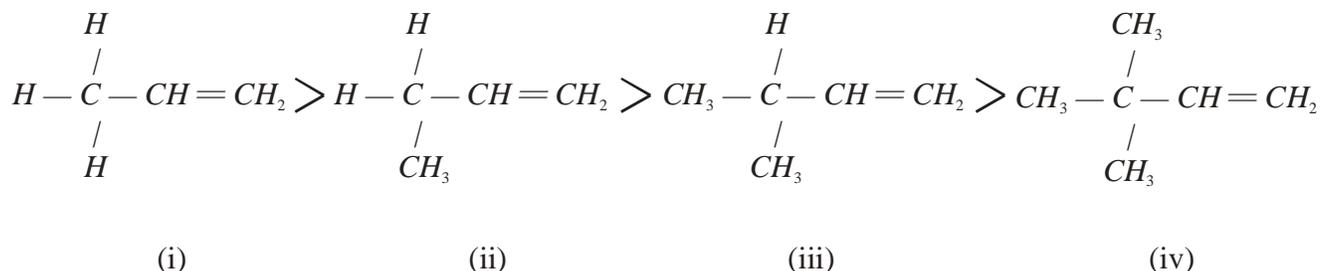
Only one of the three carbon-hydrogen σ molecular orbital has been drawn. Note that in addition to the 2p-2p unhybridised orbital overlap, an overlap can also take place of the carbon-hydrogen σ orbital with the orbital system of the double bond. This is represented by the three dotted lines

Fig - 34

As is evident in the figure above, (each of) the carbon hydrogen sigma molecular orbital can overlap with the π -orbital system of the carbon-carbon double bond, resulting in a sharing of electron charge density of the carbon-hydrogen single bonds with the carbon-carbon double bond. This explains the electron donating effect of the methyl group when attached to a double bond (or any unsaturated system). We can represent hyperconjugation in this case using canonical forms as follows:

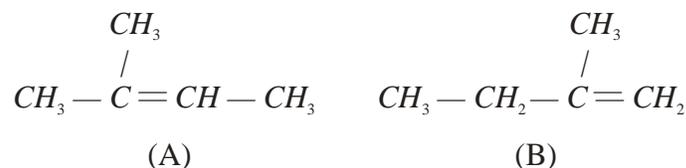


We can now explain the observed reversal of the electron donating effects of alkyl groups when attached to unsaturated systems using hyperconjugation



In (i), we have three 'hyperconjugable' hydrogen atoms, because all three of the carbon-hydrogen σ orbitals can overlap with the π molecular orbital system. In (iv), for example, there is no hyperconjugable H -atom and thus electron-donating effect of the alkyl group, here, through hyper conjugation is the lowest.

Hyperconjugation explains a lot of phenomenon which could not otherwise be explained. It tells us, for example, why (A) is thermodynamically more stable than (B) below:

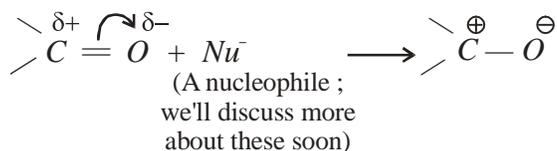


(A) has nine hyperconjugable H -atoms while (B) has only five. Thus, the effective delocalisation of charge is more in (A) than in (B) (due to hyperconjugation) and hence (A) is more stable.

(d) TIME VARIABLE EFFECTS (ELECTROMERIC EFFECT) :

The three effects discussed above are permanent in the sense that they represent permanent polarisations in the compound. They would thus show up in the physical properties of the molecule, like its dipole moment. Molecules can also show time-variable effects, which occur only on some external stimuli, like the approach of a reagent, for example.

We will discuss here one of the more important time variable effects, the electromeric effect. This effect occurs via π - electrons. On the approach of some external reagent, the π - electron pair shifts entirely to the more electronegative atom. Consider the following example



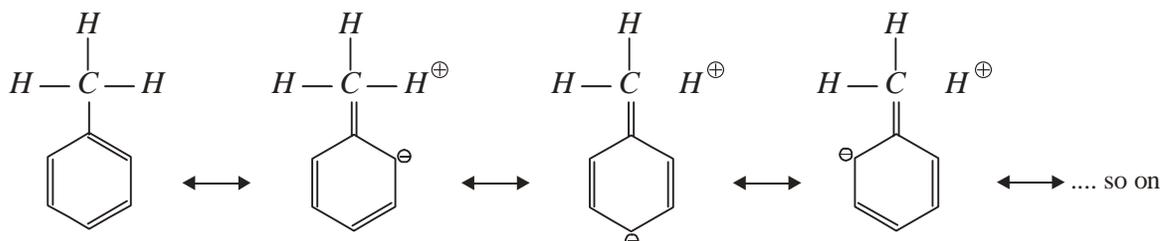
The approach of Nu^- above causes the π - electron pair to shift entirely to oxygen. Electromeric effect is a temporary effect. If the attacking reagent is removed, the molecule will revert back to its ground state. Thus, this effect will not show up in the physical properties of the molecule.

Electromeric effect is the time-variable counterpart of the mesomeric effect. Like wise, there's a time-variable inductomeric effect which corresponds to the (permanent) inductive effect

Example 29

Draw the hyperconjugation possible in toluene ($Ph-CH_3$) by sketching various possible canonical forms.

Solution: Following canonical forms depict hyperconjugation in toluene:

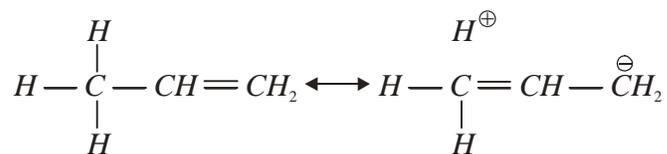


for the other two H atoms on the C atom bonded to the phenyl group. Hence, there would be a total of 10 such canonical forms.

Note: While writing such canonical forms, try to explicitly show all hyperconjugable H atoms(s) so that you don't miss out drawing any possible canonical form.

Example 30

A student represents the hyperconjugation possible in propane as follows:



Can we infer from the second canonical form that a proton separates from the main carbon chain? What is the significance of this second structure?

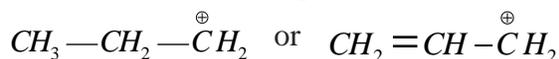
Solution: No, the second canonical form does not imply that a proton becomes free. Separation from the main carbon chain would mean movement of the proton from its original position - a situation inhibiting delocalisation whose basic pre-requisite is that all the constituent atoms must occupy essentially the same relative positions in each canonical form.

(The significance of the second structure lies in clarifying how alkyl groups here), CH_3- are capable of giving rise to electron release, thus, enabling delocalisation.

TRY YOURSELF - II

Q. 1 Explain why reactions involving ionic intermediates take place more easily in solution in polar solvents than in non-polar solvents.

Q. 2 Which carbocation is expected to be more stable:



Q. 3 What should be the direction of the inductive effect exerted on carbon by magnesium in the compound H_3C-MgX where X is a halogen atom? (This compound is an example of a Grignard reagent which we will encounter later in organic chemistry).

Section - 8

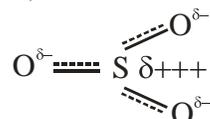
TYPES OF REAGENTS

In this section we will formally categorise the types of reagents that we encounter in the course of our study of organic chemistry.

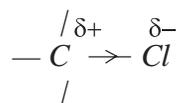
(a) Electrophiles (electron-seeking reagents)

These are species which tend to attack electron rich sites. For example, a site like the oxygen atom in the $\text{>C}=\text{O}$ linkage will tend to be attacked by an electrophile. Substitution on the benzene ring will be almost always by an electrophile because of the high electron charge density on the ring.

Electrophiles can be positively charged cations like NO_2^+ . They might also be species that are actually not cations but possess an atom or centre that is electron deficient and will tend to react with an electron rich site. For example the sulphur atom SO_3 will act as an electrophile, due to the electron deficient sulphur atom, (even though SO_3 is not a full blown cation):

**(b) Nucleophiles (“nucleus” - seeking reagents)**

These are reagents which will tend to attack electron deficient sites. For example, in the following compound

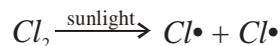


the carbon atom acquires a slightly positive charge due to the $-I$ effect of the chlorine atom. This carbon atom will tend to be attacked by nucleophiles.

As in electrophiles, nucleophiles can either be negatively charged anions like OH^- , Cl^- etc, or they can be species which are not actually anions but which possess an atom or a centre that is electron rich. For example, the nitrogen atom in ammonia, NH_3 , will tend to act as a nucleophile.

(c) Free radicals

These are highly reactive reagents (intermediates) which are not charged, and thus they are much less prone to variations in electron density in the substrate (which they attack) than reactions which involve polar intermediates (electrophiles or nucleophiles). An example of a free radical is the chlorine free radical, which can be formed by the action of sunlight on the chlorine molecule :



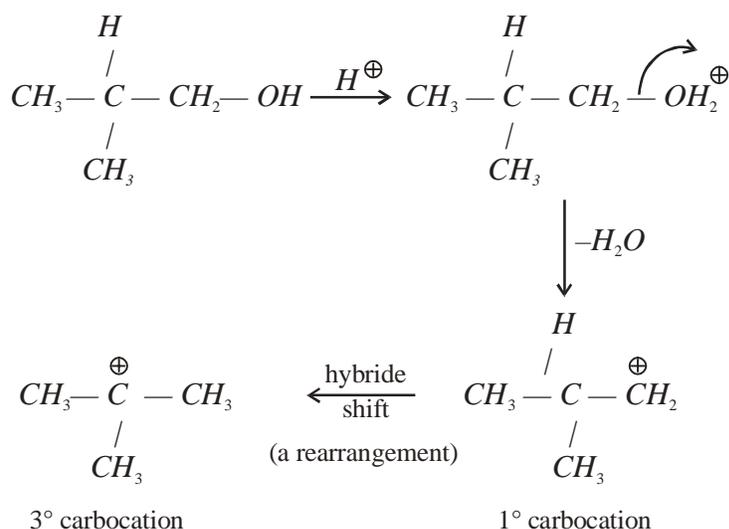
We will discuss more about the properties of these reagents (like their hybridisation states etc) as and when we encounter them. For the time being, this introduction should suffice.

Example 31

Classify the following as electrophiles or nucleophiles.

- | | | |
|----------------------|--------------------|---------------------|
| (i) NO_2^+ | (ii) RO^- | (iii) OH^- |
| (iv) AlCl_3 | (v) SO_3 | (vi) CO_2 |

(Note that electrophilicity of Al, S and C atoms are being referred to wherever present)



This example illustrates that rearrangements do take place. Details of this reaction will be dealt with later. Rearrangements can also proceed through intermediates that can be cations (electrophiles), anions (nucleophiles) or radicals. The most common intermediates in rearrangements are carbocations.

Section - 10

ACIDS AND BASES

(A) DEFINITIONS

We will, in our course of the study of organic chemistry, frequently encounter acids and bases. Questions might be posed as to which of a given set of organic compounds is the most acidic or most basic, and so on. It is thus of significant importance to study the concept of acidity and basicity, the various theories involved and the factors influencing acidity and basicity.

The three theories of acidity / basicity that we'll discuss are as follows in increasing order of generality :

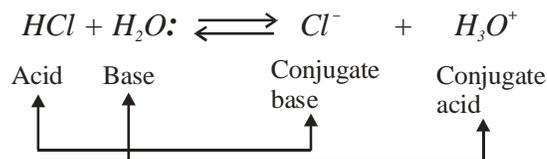
(i) Arrhenius definition

Acids are compounds that yield hydrogen ions (H^+) in solution. Bases are compounds that yield hydroxide ions (OH^-) in solution. This was one of the first definitions proposed and it sufficiently covers reactions in which water is the reaction medium.

As an example of an Arrhenius acid and base, you can think of HCl which would be an acid since it can yield H^+ ion in solution ; $NaOH$ is a possible base since it can yield OH^- in solution. However, this definition cannot account for acidity and basicity in certain compounds and thus it has become more generalised.

(ii) Bronsted definition

Acids are proton (H^+) donors while bases are proton acceptors. For example, consider the following reaction:



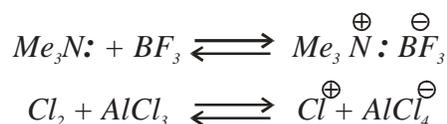
Observe that HCl acts as a Bronsted acid since it can donate an H^+ ion to the water molecule; it thereby gets converted into Cl^- which is termed its **conjugate base**. H_2O acts as a Bronsted base since it can accept the H^+ ion from HCl ; doing so converts H_2O into H_3O^+ which is its **conjugate acid**.

The Bronsted definition is an improvement over the Arrhenius definition in terms of more generality, but it can be further generalised to include even more compounds. This is what the Lewis definition does.

(iii) Lewis definition

Acids are molecules or ions which can co-ordinate with unshared electron pairs provided to them by other molecules or ions. Bases are molecules or ions which have unshared electron pairs available for co-ordination with other molecules or ions.

To understand how this definition is more generalised, consider the following reactions

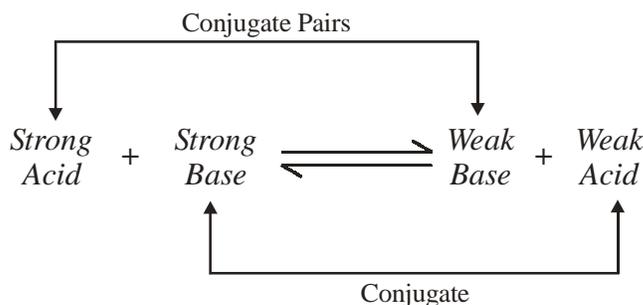


In these reactions, there is no involvement of protons (H^+ ions)/hydroxide ions (OH^- ions). Even then, we can use the Lewis definition to say that BF_3 and AlCl_3 , for example, are Lewis acids because each of them are capable of co-ordinating with (accepting) an unshared electron pair.

(B) ACID - BASE REACTIONS

Can we predict whether a given pair of acid and base will react to give appreciable amounts of products or not?

Let us see how to do so. It is said that initially acid-base reactions exist in equilibrium .



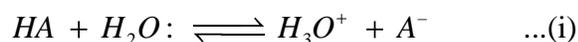
The products of the reaction are determined by the position of equilibrium. We know that equilibrium reactions always favour formation of most stable species. Since weaker acids and bases are more stable than stronger acids and bases, the equilibrium shifts towards formation of weaker acid and base.

Thus, we should always keep in mind the following rule: “Acid-base reactions always favour the formation of weaker acid and weaker base”.

(C) MEASURE OF ACIDITY/BASICITY

As has been discussed in the chapter on equilibrium, the strength of acids and bases is measured in terms of pK_a and pK_b respectively (We will be concerned with only proton acids and bases for the time being) K_a and K_b are equilibrium constants for the following equilibrium (considered in an aqueous solution)

Acids



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$pK_a = -\log_{10} K_a$$

Bases

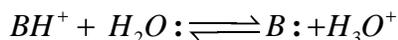


$$K_b = \frac{[BH^+][OH^-]}{[B:]}$$

$$pK_b = -\log_{10} K_b$$

It is evident from these relations that stronger acids/bases imply higher corresponding values of K_a/K_b and therefore lower corresponding values of pK_a/pK_b . Thus, for example, an acid with a pK_a of 1 will be stronger than an acid with a pK_a of 2. A similar analogy would hold for such a pair of bases.

Conventionally, the strength of bases is also described in terms of K_a (and pK_a) instead of K_b and (pK_b). Doing so will result in a single scale/measure for the strength of both acids and bases and will thus be more convenient. To do so, we consider, instead of the reaction (ii), the following reaction as our reference reaction for bases :



For this reaction, we can write the K_a (and pK_a) as :

$$K_a = \frac{[B:] \cdot [H_3O^+]}{[BH^+]}$$

$$pK_a = -\log_{10} K_a$$

Thus, K_a (pK_a) here would be a measure of the strength of the conjugate acid BH^+ of the base $B:$. A lower pK_a value will imply a stronger conjugate acid BH^+ and thus a weaker conjugate base $B:$. Similarly, a higher pK_a value implies a stronger base $B:$

\Rightarrow Lower pK_a value \Rightarrow Stronger acid BH^+ \Rightarrow Weaker base $B:$

\Rightarrow Higher pK_a value \Rightarrow Weaker acid BH^+ \Rightarrow Stronger base $B:$

For example, $\overset{\cdot\cdot}{N}H_3$ has a pK_a value of 9.25 while $CH_3\overset{\cdot\cdot}{N}H_2$ has a pK_a value of 10.64. Thus, $CH_3\overset{\cdot\cdot}{N}H_2$ is a stronger base.

One point must be emphasised here : the pK_a scale is logarithmic and you must appreciate this. Thus, an acid with a pK_a value of 2 will be 10 times weaker than an acid with a pK_a value of 1. In fact, acids with $pK_a > 16$ will not even be detectable as acids at all in water, because their ionisation will be less than the autolysis of water itself.

For very stronger acids, full ionisation will be achieved in water, and thus all strong acids will appear to be of the same strength in water. This **levelling effect** of water will be reduced to an extent in case the solvent is other than water and is a weaker base than water (because for a weaker base, ionisation of the acid will be 100% complete).

This means that relative strengths of strong acids can be compared in a solvent that is a weaker base than water. Similarly, relative strengths of very weak acids can be compared in bases stronger than water.

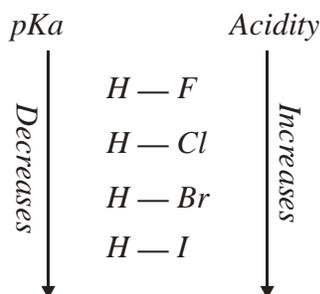
(D) FACTORS AFFECTING ACIDITY

In this section, we will discuss the factors which affect the strength of acids in the form of HA . If HA gives up its proton easily, it will be a stronger acid than in the case when it is reluctant to give up the proton.

Also, the acid which gives up its proton easily results in formation of a weaker base than when it is reluctant to give up the proton.

The factors which can affect acidity/basicity are:

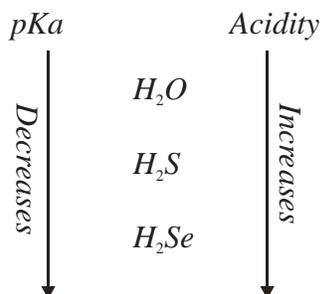
- (i) Strength of $H—A$ bond : The general rule is: The stronger the $H—A$ bond, the weaker the acid.” Amongst the compound, of the same group of the periodic table, bond strength to proton decreases on moving down the group.



This is because, as we move down the group, the effective overlap between hydrogen and the halogen atom decreases. Thus, overlap is minimum in HI which results in formation of weaker $H—I$ bond. Weaker bond implies stronger acid.

Now let us compare the basic strength of the conjugate bases of these acids. Since HI is the strongest acid amongst them, its conjugate base (I^-) will be the weakest one. On the other hand, F^- will be a stronger base because it is the conjugate base of a weaker acid ($H—F$).

The same holds true for compounds of other groups of periodic table.



Here, H_2O is the weakest acid and H_2Se is the strongest one.

- (ii) **Electronegativity:** On moving left to right across a periodic table, bond strength varies but the predominant factor is the increase in electronegativity. Recall that electronegativity is a measure of an atom's attraction for electrons. The higher the electronegativity, the greater the attraction. Electronegativity has the following two effects on the acidity

- (a) Polarity of the bond.
 (b) Stability of the anion formed (conjugate base) after the loss of proton

High electronegativity increases the polarity of the bond. Let us examine the compounds of any one period. e.g. CH_4 , NH_3 , H_2O , HF .

electronegativity $\xrightarrow[\text{C N O F}]{\text{Increases}}$

Thus, we can say, F being most electronegative causes most polarization of the $H—F$ bond. In other words, H acquires maximum positive charge in HF and least in CH_4 . Thus, HF can readily lose a proton to a base and hence, is most acidic.



Polarity $\xrightarrow{\text{Increases}}$

pK_a $\xrightarrow{\text{Decreases}}$

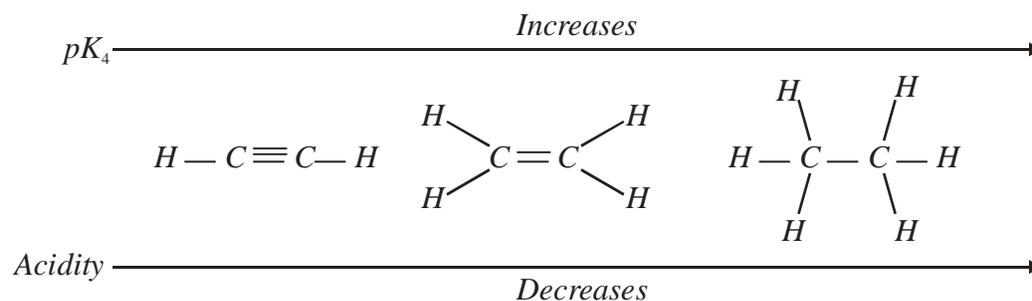
Acidity $\xrightarrow{\text{Increases}}$

Now let us compare the strength of their conjugate bases.

HF being the strongest acid forms the weakest base F^- . This is because fluorine is most electronegative and can most readily accommodate the negative charge. Thus, F^- is most stable and least reactive and hence, least basic.

On the other hand, CH_4 is the weakest acid so leads to formation of strongest base $^-CH_3$. Carbon being the least electronegative atom is least ready to accept the negative charge and is most unstable and reactive. Thus, it is most basic.

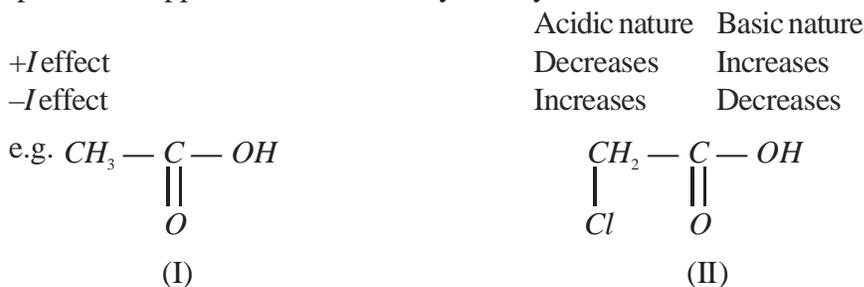
- (iii) **Hybridization:** We have already studied about the effect of hybridization on the acidity of the molecule. Recall that more s-character increases the electronegativity. Thus,



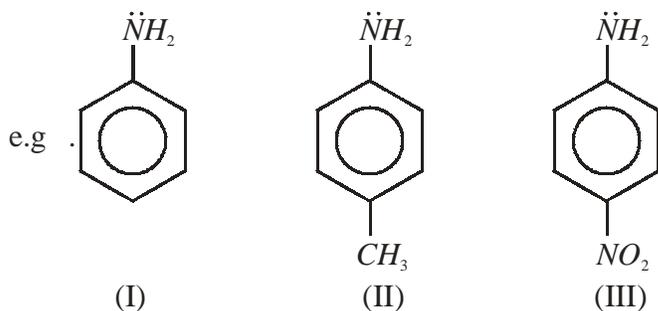
- (iv) **Inductive effect:** We studied about inductive effect and the types of inductive effects in section-7. We know that $+I$ group (electron releasing group) increases the electron density around the atoms to which it is attached. If it is attached to a base, it will increase the electron density around it making it more unstable and hence, more reactive or more basic.

On the other hand, $-I$ group (electron withdrawing group) decreases the electron density around the atom to which it is attached. $-I$ group attached to a base decreases electron density of the base making it less reactive and less basic.

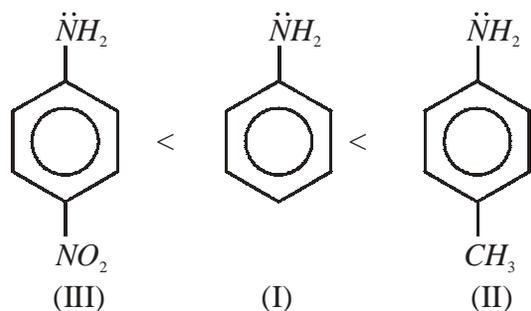
$-I$ groups attached to an acid facilitate release of proton by withdrawing electrons. On the other hand, $+I$ groups have an opposite effect on acidity i.e. they decrease acidic character.



Amongst the two compounds, (II) will be more acidic because of presence of a $-I$ group at α -carbon.



The increasing order of basicity of the above compounds is:



(III) is least basic because it has an electron withdrawing ($-I$ group) attached which decreases basicity. On the other hand, (II) has an electron-donating ($+I$ group) which increases basicity.

Inductive effect: We studied about inductive effect in Section -7. The application of inductive effect and its influence on acidity of a molecule is explained using example 37.

- (v) **Effect of stability of A^- with respect to HA :** This factor is very important in determining the strengths of acids. If the conditions are such that A^- (the conjugate base of HA) can be stabilised with respect to HA itself, we will find that HA will tend to be more acidic.

The reason for this is clear. A stable conjugate base A^- because of its stability, will be reluctant to gain a proton to form back the acid HA . Thus, a stable A^- will be a weak base and consequently, HA will be a strong acid. You can think of it this way : if A^- can be stabilised somehow, it will be 'energetically favorable' for HA to give up a proton to form A^- can ; thus, HA will lose its proton with ease, and will therefore be a strong acid.

All factors that can possibly stabilise A^- will have something to do with dispersion/delocalisation of charge. Let us consider the various factors through examples :

Example 32

The order of acidity of the hydrogen halides in aqueous solution is $HF < HCl < HBr < HI$. Explain.

Solution: Observe this order carefully. Do you realise that this order is contrary to what we should expect due to the affect of electronegativity described earlier ? For example, since fluorine is the most electronegative of all the halides, we should expect HF to be the strongest acid. However, as it turns out, it is the weakest. (Before proceeding on, one point requires attention here. The order of acidity is being talked about in water as a solvent, since this is the most common solvent used for organic reactions). One factor to which we can attribute the reversal of the expected acidity order is the relative stability order of the halide anions (the conjugate bases) formed on the loss of a proton. This stability order is as follows:

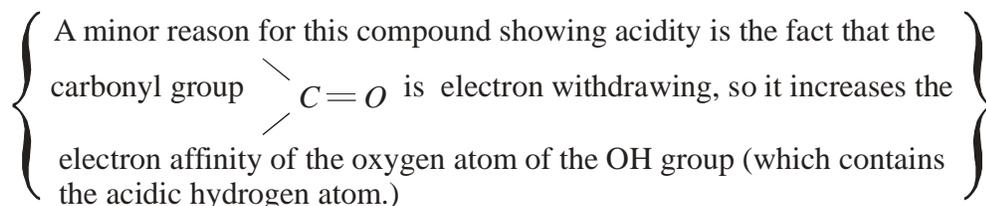


The reason for this stability order is that the larger the atomic radius of an anion, the more the volume of the region over which the negative charge can spread and thus more stable that anion will be. Since atomic radii of the halide atoms are in the order $F < Cl < Br < I$, stability of the anions will also follows this order. Consequently, as described earlier, acidity of the hydrogen halides will also follow this order.

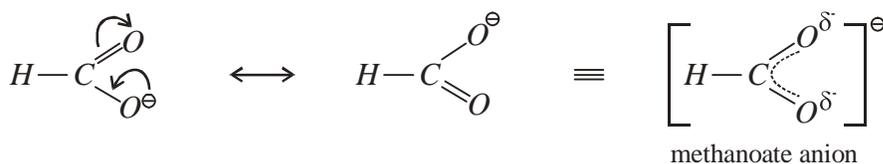
Example 33

The compound $HCOOH$ is by organic standards, a moderately strong acid. It has pK_a of of 3.77 (The name of this compound is methanoic acid). Explain.

Solution: We must again look into the possibility of the conjugate base of this acid being somehow stabilised.

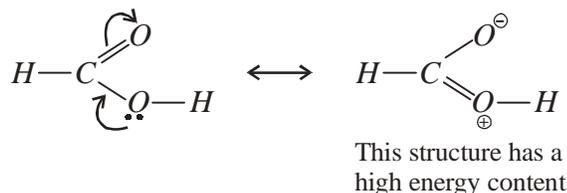


The major reason for methanoic acid showing strong acidity is that the conjugate base is resonance stabilised.



The delocalisation of the negative charge is in fact extremely effective since the two canonical forms are of identical energy content. Thus, the methanoate anion is quite stable.

Observe that although delocalisation through resonance can take place in methanoic acid itself, it will not be really effective since it will involve charge separation in the canonical forms.



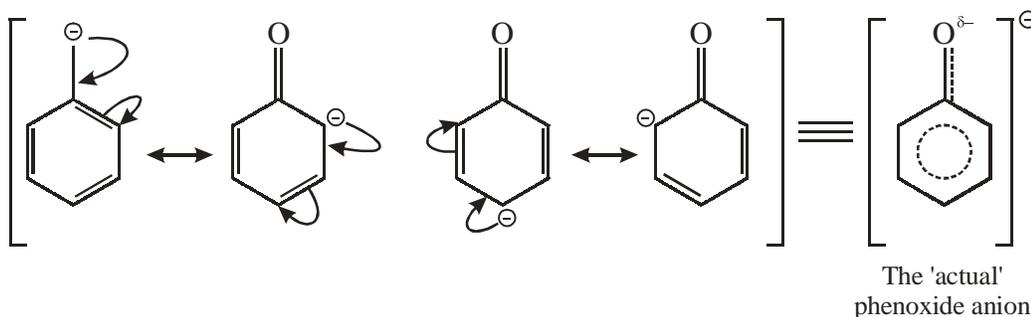
Thus, resonance will tend to stabilise the methanoate anion with respect to the methanoic acid, which results in the acidity of the latter.

Example 34

The alcohol ROH (where R is an alkyl group) is a much weaker acid than phenol, $PhOH$, although both contain the same functional group ($-OH$). Explain.

Solution: Again, we look into factors stabilising the conjugate base of phenol and which do not work for the alcohol

Consider the conjugate base of phenol, PhO^- . Observe that there is a possibility of resonance stabilisation in this anion :



Observe that in the phenoxide anion, the negative charge is delocalised over the entire benzene ring and thus this anion is stabilised.

Resonance can occur in the undissociated phenol molecule also but that will involve charge separation and will therefore be less effective than resonance in the conjugate base.

This discussion justifies why phenol shows an acidity stronger than alcohols (where no such resonance stabilisation is possible in the conjugate base RO^-).

As an example, the pK_a of CH_3OH is 16 while that of phenol is around 10, indicating that phenol is a considerably stronger acid than CH_3OH .

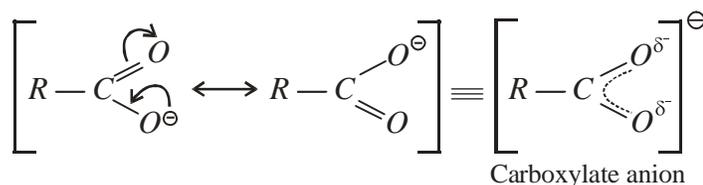
Example 35

Phenol ($PhOH$) is a considerably weaker acid than the carboxylic acids (in which the acidic part is the functional

group $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C} \\ \backslash \\ \text{OH} \end{array}$). Explain.

Solution: As discussed in the previous case study, the phenoxide anion PhO^- is stabilised by resonance and thus $PhOH$ is acidic. Here we need to look into how carboxylic acids should be even stronger acids.

Consider the conjugate base of a general carboxylic acid ($RCOOH$) and observe that it will be resonance stabilised too:



However, resonance stability in the carboxylate anion will be much more than that in the phenoxide anion. This is due to two reasons:

- (i) For the carboxylate anion, both the canonical forms are of identical energy content
- (ii) In the canonical forms of the carboxylate anions, the negative charge is on the highly electronegative oxygen atoms and therefore we can expect these forms to be stable.

In the canonical forms of the phenoxide anion drawn earlier, there is a negative charge on a carbon atom in three of the four structures, and hence these forms are likely to be of a higher energy content (and therefore less stable) than the structure in which the negative charge is on oxygen.

These two reasons justify why carboxylic acids are stronger acids than phenol. As an example, the

pK_a of phenol is around 10, while that of methanoic acid, $CH_3-C(=O)OH$ is 4.76.

Note: The inductive effect of the groups connected to the acidic group in a molecule can have a significant effect on the acidic properties of that molecule. We first discuss as an example, inductive effects in carboxylic acids. Consider a general carboxylic acid of the form $G-COOH$, where G could be any group. If G has an electron withdrawing inductive effect, it will tend to stabilise the carboxylate anion by aiding in the dispersion of charge on the $-COO^-$ group. On the other hand, a $+I$ effect of G would tend to destabilise the carboxylate anion.



We can thus conclude that groups with $-I$ effect will increase the acidity of the carboxylic acid while groups with $+I$ effect will decrease the acidity. This is what is actually observed, as the data in the table below proves.

Methanoic acid, $H-COOH$ ($pK_a = 3.77$) has been used as a reference. On the left hand side are carboxylic acids weaker than methanoic acid due to the $+I$ effect of the group attached to the carboxylic group; on the right hand side are carboxylic acids stronger than methanoic acid due to the $-I$ effect of the group attached to the carboxylic group.

These acids have been arranged in increasing order of acidity.

Table 3 : Major acids in increasing order of acidity

	Acids weaker than methanoic acid	pK_a		Acids stronger than methanoic acid	pK_a
(1)	$\begin{array}{c} \text{CH}_3 \\ \downarrow \\ \text{CH}_3 \rightarrow \text{C} \rightarrow \text{COOH} \\ \uparrow \\ \text{CH}_3 \end{array}$	5.05	(12)	$\begin{array}{c} \text{O} \\ \\ \text{C}_2\text{H}_5\text{O} - \text{C} - \text{CH}_2 \leftarrow \text{COOH} \end{array}$	3.35
(2)	$\text{CH}_3\text{CH}_2 \rightarrow \text{COOH}$	4.88	(13)	$\text{I} \leftarrow \text{CH}_2 \leftarrow \text{COOH}$	3.16
(3)	$\begin{array}{c} \text{CH}_3 - \text{CH} \rightarrow \text{COOH} \\ \\ \text{CH}_3 \end{array}$	4.86	(14)	$\text{Br} \leftarrow \text{CH}_2 \leftarrow \text{COOH}$	2.90
(4)	$\text{CH}_3\text{CH}_2\text{CH}_2 \rightarrow \text{COOH}$	4.82	(15)	$\text{Cl} \leftarrow \text{CH}_2 \leftarrow \text{COOH}$	2.86
(5)	$\text{CH}_3 \rightarrow \text{COOH}$	4.76	(16)	$\text{F} \leftarrow \text{CH}_2 \leftarrow \text{COOH}$	2.57
(6)	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2 - \text{COOH} \\ \\ \text{Cl} \end{array}$	4.52	(17)	$\text{NC} \leftarrow \text{CH}_2 \leftarrow \text{COOH}$	2.47
(7)	$\text{CH}_2 = \text{CH} - \text{COOH}$	4.25	(18)	$(\text{CH}_3)_3\overset{\oplus}{\text{N}} \leftarrow \text{CH}_2 \leftarrow \text{COOH}$	1.83
(8)	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{COOH} \\ \\ \text{Cl} \end{array}$	4.06	(19)	$\text{NO}_2 \leftarrow \text{CH}_2 \leftarrow \text{COOH}$	1.68
(9)	$\text{H}\ddot{\text{O}} \leftarrow \text{CH}_2 - \text{COOH}$	3.83	(20)	$\begin{array}{c} \text{Cl} \leftarrow \\ \text{Cl} \leftarrow \text{CH} \leftarrow \text{COOH} \end{array}$	1.25
(10)	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 \leftarrow \text{COOH} \end{array}$	3.58	(21)	$\begin{array}{c} \text{Cl} \\ \uparrow \\ \text{Cl} \leftarrow \text{C} \leftarrow \text{COOH} \\ \downarrow \\ \text{Cl} \end{array}$	0.65
(11)	$\text{CH}_3 - \ddot{\text{O}} - \text{CH}_2 \leftarrow \text{COOH}$	3.53			

*Data quoted from "Peter Sykes : A Guidebook..."

You are urged to go through this table and observe carefully how the pK_a varies as the group attached to the carboxylic group is varied.

It would in fact be a good exercise to compare two different compounds of the same (or similar) molecular formula or similar structure and try to reason out why their acidities differ. We will now do this in a few examples.

{ As mentioned at the end of case study 1, here also the justification of the acidity order based only on the inductive effect is only partially complete. The actual scenario requires a more detailed and complete justification. You can refer to the appendix for that purpose. However, for our current needs, the justification provided above would suffice. }

Example 36

(a) Why is $F-CH_2-COOH$ a stronger acid than $I-CH_2-COOH$?

(b) Why is $\begin{array}{c} Cl \\ \diagdown \\ CH \\ \diagup \\ Cl \end{array} - COOH$ a stronger acid than $Cl-CH_2-COOH$?

Solution : You should find this question very straightforward since it requires simple reasoning based on the inductive effect.

(a) F is more electronegative than I ; the electron withdrawing inductive effect ($-I$ effect) of F will therefore be more than I , and thus stabilisation of conjugate bases will be greater in the case of $F-CH_2-COOH$ than in the case of $I-CH_2-COOH$. This explains the observed greater acidity of $F-CH_2-COOH$.

(b) The $-I$ effect of two chlorine atoms will obviously be more than that of just a single chlorine atom. This explains why the dichloro-substituted acid is stronger.

Example 37

Why is $CH_2=CH-COOH$ a stronger acid than CH_3-CH_2-COOH ?

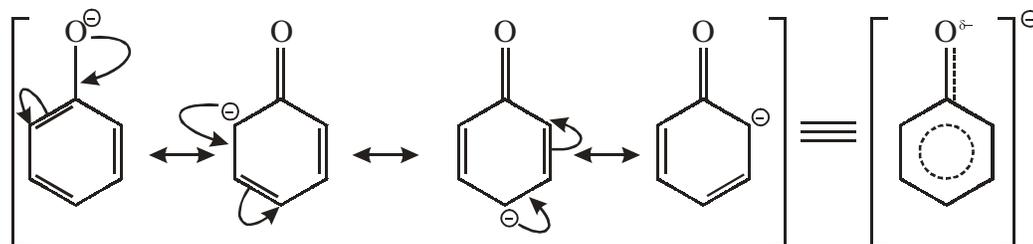
Solution : The α -carbon (the C-atom immediately next to the carboxylic C-atom) in the first compound is sp^2 hybridised. Electrons in an sp^2 hybrid orbital will be drawn closer to the carbon nucleus than in an sp^3 hybrid orbital. The reason for this has already been discussed. sp^2 orbitals contain a greater s -character. Thus, an sp^2 hybridised carbon atom will be less electron donating than an sp^3 hybridised carbon atom.

Thus, the $+I$ effect on the carboxylic group will be lesser in the case of the first compound than in the second in which the α -carbon is sp^3 hybridised. This explains why $CH_2=CH-COOH$ is a stronger acid

Note: Let us now understand the effect of inductive/mesomeric electron withdrawal/donation on acidity in aromatic compounds.

Inductive and mesomeric effects can have significant influence on acidity in aromatic compounds too, as in the case of aliphatic compounds.

For a start, we'll discuss acidity in substituted phenols. Our reference compound for discussion will be phenol ($pK_a = 9.95$). The conjugate base of phenol is phenoxide anion which is stabilised by resonance :

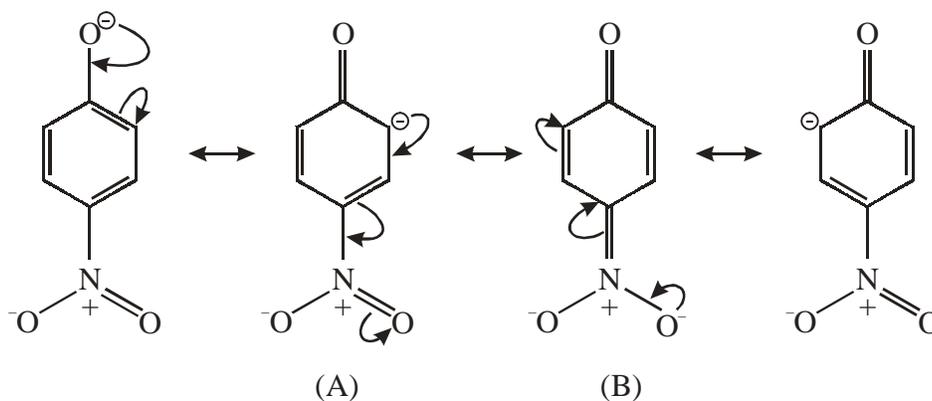


Although resonance to an extent delocalises the negative charge over the benzene ring, any group which has an electron withdrawing effect, when attached to the benzene ring, will further increase the stability of the phenoxide anion by aiding in further delocalisation of the negative charge. Such a substituted phenol will be more acidic than phenol itself.

On the contrary, any group which has an electron donating effect, when attached to the benzene ring, will tend to destabilize the phenoxide ion, and hence the substituted phenol will be less acidic than phenol itself.

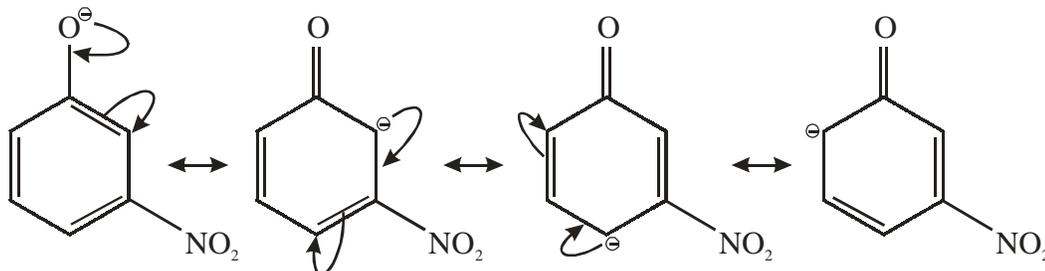
- * If the substituted group has an inductive effect, we can expect the inductive influence of this group to fall off with distance as we go from ortho \rightarrow meta \rightarrow para substituted phenol.
- * If the substituted group has a mesomeric effect, it will have an influence when the group is attached to the ortho or para position but not at the meta position. This will become clear when we draw the canonical structures possible for each of the three positions and observe that only if the group is at the ortho or the para position can it promote ionisation by stabilisation of the anion.

We do this as an example for NO_2 attached at para position, i.e., for *p*-nitrophenoxide ion.



Observe the form (A) – (B) and note that it was because of the fact that the nitro group is at the *p*-position that it could exert $-M$ effect and aid in the stabilisation of the phenoxide anion.

This would not have been possible had the nitro group been on the meta position, as should be evident from the following canonical forms:

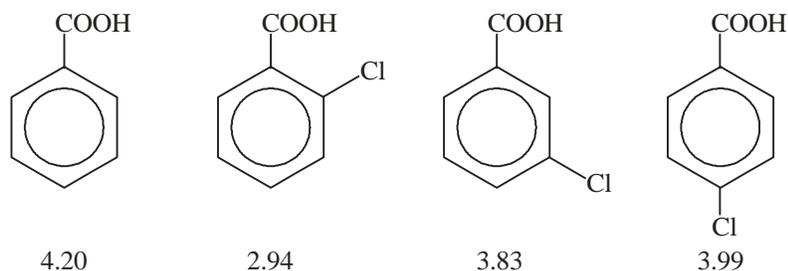


In the canonical forms above, the negative charge never appears at the meta position ; therefore, the nitro group does not have a possibility of delocalising the negative charge over itself through its $-M$ effect.

Let us now discuss other cases of acidity through examples.

Example 38

Justify the following observed values of pK_a :

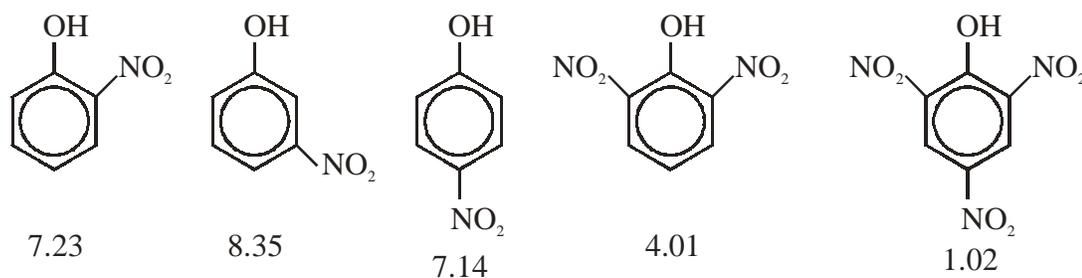


Solution: We must first of all focus our attention on the substituent which is Cl here. Cl has a power $-I$ effect because of its high electronegativity. However, Cl can also exert a $+M$ effect due to the lone pair when attached at the ortho or para position. This means that there are two opposing effects here : Cl will tend to stabilise the system by its $-I$ effect but at the same time tend to destabilise the system by its $+M$ effect

- * o -chlorobenzoic acid is the strongest of the four given acids because of the extremely short distance over which the powerful $-I$ effect of Cl operates (this more than compensates for the $+M$ effect of Cl). As we go from o - \rightarrow m - \rightarrow p - chlorobenzoic acid, the strength of this $-I$ effect falls off very quickly.
- * p -chlorobenzoic acid is weaker than m -chlorobenzoic acid due to a weaker $-I$ effect in the former (because of the larger distance) and the possibility of the $+M$ effect due to chlorine being at the para position.

Example 39

Explain the observed values of pK_a for the following nitro-substituted phenols (phenol itself has a pK_a of 9.95) :



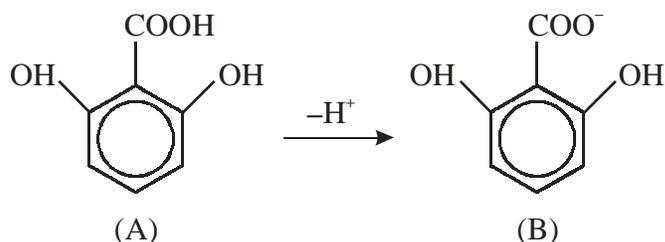
Solution: Here we present a point - by - point analysis of these observed values of pK_a .

- * All nitro-substituted phenols are stronger acids than phenols due to the $-I$ effect of NO_2 and $-M$ effect of NO_2 if it is at the ortho or para position
- * o - and p -nitrophenol are stronger acids than m -nitrophenol due to the $-M$ effect the NO_2 can exert at the ortho and para positions

- * Although in *o*-nitrophenol, the $-I$ effect of NO_2 operates over a shorter distance than in *p*-nitrophenol (and we should therefore expect *o*-nitrophenol to be stronger than *p*-nitrophenol), it actually turns out that *p*-nitrophenol is the stronger acid (albeit only marginally). This happens because there are a lot of (complicated) factors contributing to acidity, like the solvation patterns etc (and which we do not consider here for the sake of simplicity).
- * 2,4-dinitrophenol will obviously be a still stronger acid due to two reasons: the powerful $-I$ effect of the two nitro groups and also their $-M$ effect since they are at the ortho positions.
- * 2,4,6-trinitrophenol is a very strong acid due to the effect of the three nitro groups which will exert both $-I$ effect and $-M$ effect to stabilise the conjugate base to a large extent.

Example 40

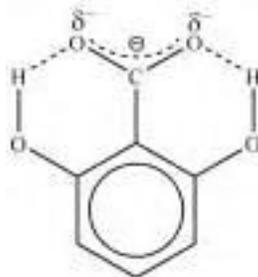
2,6-dihydroxybenzoic acid is found to be highly acidic by organic standards ($pK_a = 1.30$)



Such high acidity cannot be accounted for by the $-I$ effect of the OH groups alone. What could be the other possible factors?

Solution: This is an example of a general trend: the behaviour of ortho-substituted acids many times turns out to be significantly greater than expected because of direct interaction possible between the adjacent groups.

It turns out that here a direct interaction is possible between the carboxylic group ($-\text{COO}^-$) and the two hydroxyl groups ($-\text{OH}$) in the form of hydrogen bonding, which stabilises the anion (B) to a very large extent.



This stability is the reason that the acid (A) readily gives up its acidic proton to form the anion (B). It should be pointed out here that intramolecular H -bonding will also be possible in the undissociated acid (A) itself but it will not be as effective as in (B) in which there is a negative charge and hence stronger H -bonding.

(iv) **Effect of solvent:** A mention was made earlier about the levelling effect of water. All strong acids get 100% dissociated in water and thus appear to be equally strong in water. To compare the relative strengths of these strong acids, a base weaker than water can be used as the solvent. This is one of the many examples which show that the nature of the solvent can have a profound determining effect on the acidity of the solvent. As the example above shows, this is particularly the case when water is the solvent.

We can divide organic solvents into two broad classes :

- (a) polar solvent - like water
- (b) non-polar solvent - like toluene (methylbenzene)

We might find cases where a particular molecule shows acidic properties in a particular solvent but is totally non-acidic in another. The next example considers this scenario.

Example 41

HCl is a very strong acid in water. In fact, it exists almost fully dissociated in water. In alcohols also, like methanol (CH_3OH) for example, *HCl* is a moderately strong acid. However, in a non-polar solvent like toluene (methyl benzene), *HCl* is almost totally non-acidic i.e. it occurs almost totally undissociated in toluene. Justify these observations.

Solution: For any acid, the stronger the solvent as a base, the more the dissociation of that acid in the solvent will be observed and correspondingly, the weaker the solvent as a base, the lesser the dissociation of that acid will be observed. Water and alcohol are good solvents in this sense. In fact, water is a very good polar solvent :

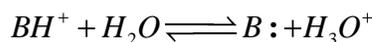
- (a) it has a high dielectric constant which aids in the formation of the ion pairs from the acid
- (b) it aids in the stabilisation of the ion pair because it has a very strong ion-solvating power due to its ability to form hydrogen bonds.

Alcohols share these properties to an extent and thus *HCl* is found to be a moderately strong acid in methanol also.

However, toluene is non-polar (and non-basic) and has none of the ion-pair stabilisation abilities that water and alcohol have. Thus, it is energetically unfavorable for the *HCl* molecule to dissociate in toluene. This explains the observations.

(D) FACTORS AFFECTING BASICITY

As discussed earlier, the reference reaction for bases is the following equilibrium :



with K_a and pK_a now being given by

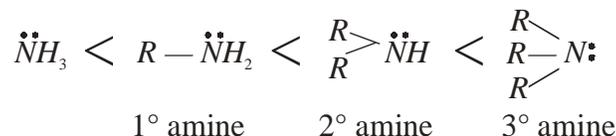
$$K_a = \frac{[B:][H_3O^+]}{[BH^+]} \quad ; \quad pK_a = -\log_{10} K_a$$

Thus, higher the pK_a , stronger is the base *B*: In physical terms, the strength of a base is the measure of ease with which *B*: can accept a proton, or equivalently, the measure of the availability of the unshared electron pair on *B*. Factors which increase this availability of electrons will tend to increase the basicity of *B*: while factors which decrease this availability of electrons will tend to reduce its basicity.

However, as in acidity, the solvent also has an effect on the basicity. We will now discuss the various factors through examples.

Example 42

The basicity order of ammonia (NH_3) and alkyl-substituted ammonia (amines) in a non-polar solvent is found to be in the following order

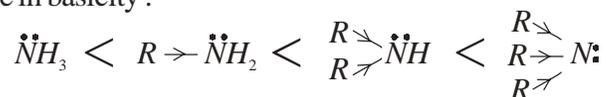


Explain.

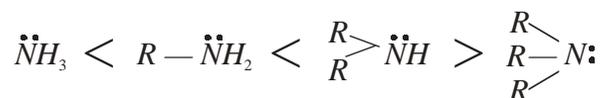
Solution: The basicity order being talked about has been measured in a non-polar solvent which means that we can safely neglect any effects of solvent molecules on the basicity order (such as H -bonding) and concentrate only on structural reasons that give rise to this order.

Recall that basicity will increase as the unshared electron pair availability on the nitrogen atom increases. Recall also that alkyl groups have a $+I$ effect.

This is the reason behind the observed basicity order. As we go from 1° amine to 3° amine, the increasing $+I$ effect of the substituted alkyl groups increases the electron pair availability on nitrogen, causing an increase in basicity :

**Example 43**

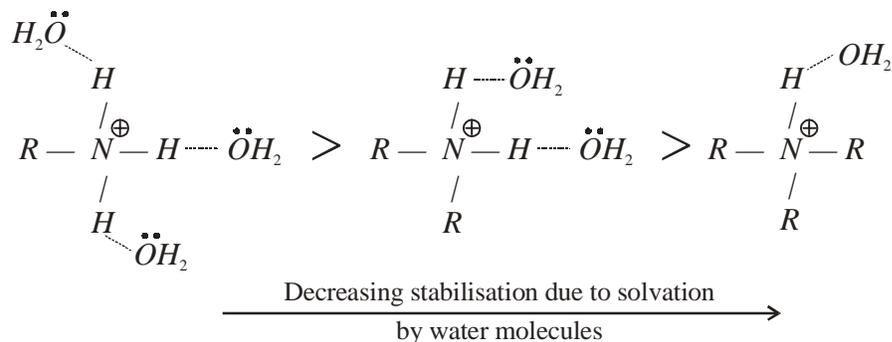
The basicity order of NH_3 and the amines in water follows the order:



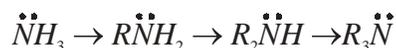
This means that basicity increases up to the 2° amine but then decreases in the 3° amine! Explain.

Solution: Obviously, apart from the $+I$ effect of the alkyl groups, there's another factor at work now, which must be due to the solvent, water. This factor is that water due to its polar nature, has the ability of ion solvation. The amine, after the uptake of a proton, can become solvated by water molecules through hydrogen bonding and can thus get stabilised.

If you observe the structures of the amines carefully, you will realise that after protonation, a 1° amine is capable of forming 3 H -bonds, a 2° amine can form 2 H -bonds while a 3° amine can form only 1 H -bond :

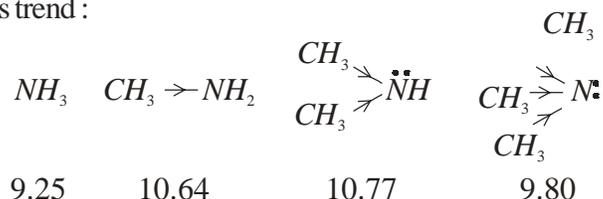


Thus, while progressing along the series



the inductive effect increases the basicity but lesser stabilisation of the cation formed after protonation by the water molecules through solvation decreases the basicity. The net result is that the effect of introducing alkyl groups becomes progressively smaller and from $2^\circ \rightarrow 3^\circ$ amine, a reversal takes place because the solvation factor becomes stronger than the inductive factor.

This explains the observed basicity order. As an example, consider the following pK_a values which clearly confirm this trend :

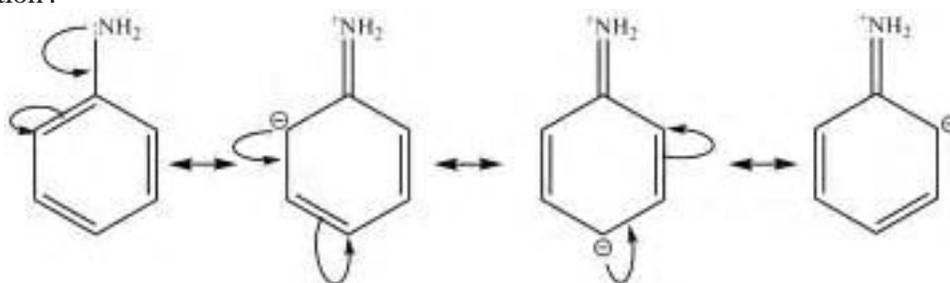


Example 44

Aniline, $Ph\ddot{N}H_2$ ($pK_a = 4.62$) is a very weak base compared to ammonia, $\ddot{N}H_3$ ($pK_a = 9.25$). Explain.

Solution: We must look into the factors affecting the unshared electron pair availability on the nitrogen atom. Obviously, for aniline to be a weaker base, there must be a factor (s) at work which is reducing the e^- - pair availability on nitrogen. If we analyse the structure of aniline, we'll be able to identify two such factors:

- (a) The unshared electron pair on nitrogen can interact with the π -molecular orbital system on the benzene ring, and get delocalised over the benzene ring to an extent, reducing its availability for protonation :

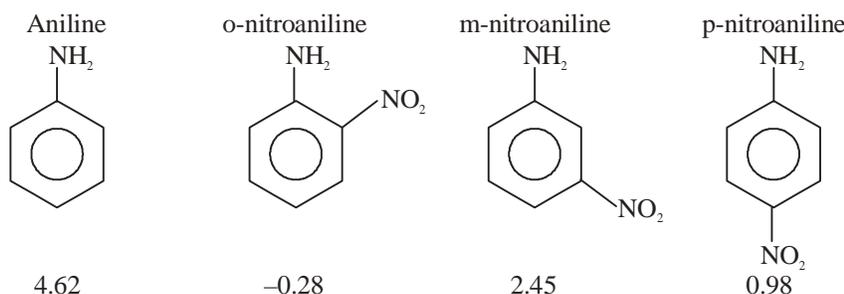


Thus, it would be energetically unfavorable for aniline to gain a proton since then the lone pair will no longer be available for delocalisation

- (b) Nitrogen atom is attached to an sp^2 - hybridised carbon atom, which also plays a role (how significant is difficult to say) in making the unshared pair lesser available for protonation.

Example 45

Nitro-substituted anilines are extremely weak bases. This should be evident from the following pK_a values



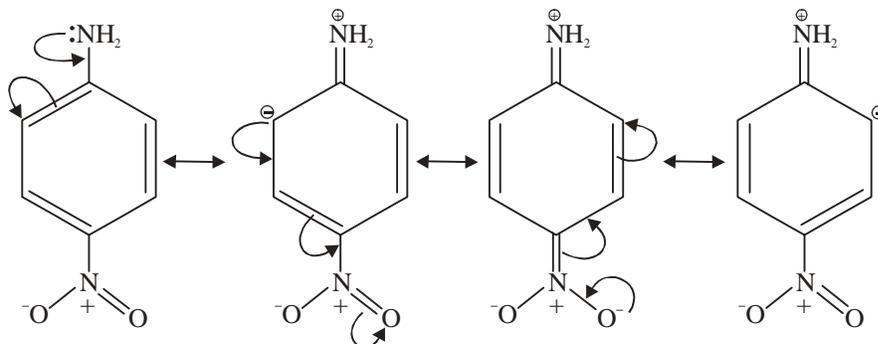
Explain.

Solution: As discussed earlier, the NO_2 group will have two effects :

(a) $A-I$ effect which decreases with distance as $o- \rightarrow m- \rightarrow p-$.

(b) $A-M$ effect which operates if NO_2 is at the $o-$ or the $p-$ positions.

The point (b) explains why $o-$ and $p-$ nitro aniline are weaker bases than $m-$ nitro aniline. For the sake of emphasis, let us draw the canonical forms for $p-$ nitro aniline and see the $-M$ effect of the NO_2 group:



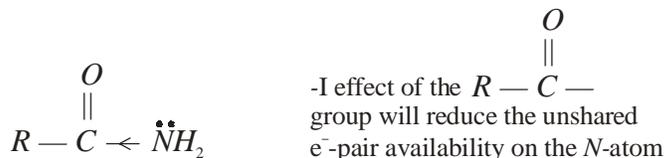
Forms (A) – (B) should make it clear to you how NO_2 exerts $a-M$ effect being at the $p-$ position.

The point (a) partially explains why $o-$ nitroaniline is a much weaker base than $p-$ nitroaniline. Another reason is the stabilising effect of the intra-molecular H -bonding possible between the NO_2 and NH_2 groups when NO_2 is at the $o-$ position.

Example - 46

Amides, of the general structural form $R - \overset{\overset{\text{O}}{\parallel}}{\text{C}} - \overset{\cdot\cdot}{\text{N}}\text{H}_2$, are very weak bases. Justify.

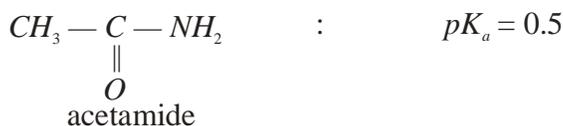
Solution: One possible reason for this observation is that the nitrogen atom is bonded to a group with an overall electron-withdrawing inductive effect through the sp^2 - hybridised carbonyl carbon :



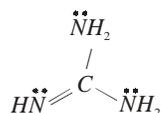
A more significant reason is that the $R - \overset{\overset{\text{O}}{\parallel}}{\text{C}} -$ group can give rise to an electron-withdrawing mesomeric effect ($-M$ effect) :



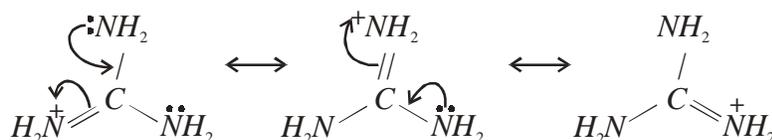
Thus, amides are weak bases for these two reasons. As an example, consider the pK_a of acetamide :



Example - 47

Guanidine, with the structure:  is an extremely strong organic base, with a pK_a of 13.6. Explain.

Solution: Observe that the guanidine molecule exhibits a certain sort of symmetry. This symmetry is more evident when we consider the protonated form of guanidine. For the protonated cation, we find that three identical canonical forms (of equal energy content) can be drawn :

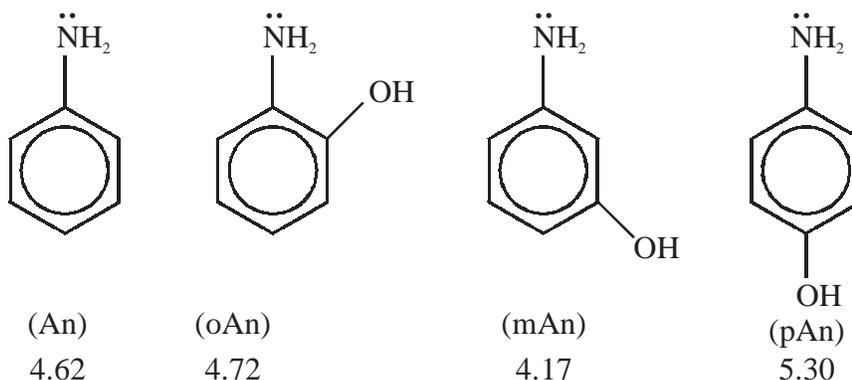


The outcome of the fact that three identical canonical forms can be drawn is that this cation is extremely stable, with the positive charge being delocalised over the entire molecule. Thus, it is energetically favorable for the guanidine molecule to accept a proton, which justifies its strong basicity.

Observe that the non-protonated guanidine molecule will also show resonance but not as effective as that possible in the protonated cation.

Example 48

Compare to aniline, the pK_a values of the OH -substituted anilines are found to be as follows:



Explain.

Solution: Let us first discuss what effect(s) the substituent OH can have :

- (a) a base strengthening $+M$ effect from the ortho and para positions
- (b) a base weakening $-I$ effect which falls off with distance as $o- \rightarrow m- \rightarrow p-$.

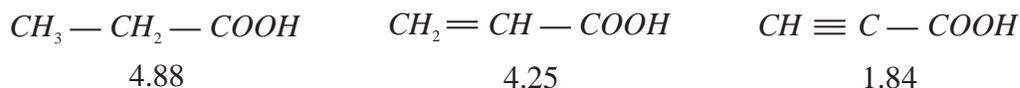
In mAn , there can be no base strengthening $+M$ effect. However, the $-I$ effect operates and this explains why mAn is a weaker base than An .

Both oAn and pAn are stronger bases than An due to the $+M$ effect possible in these two molecules. However, between oAn and pAn , oAn is a weaker base because of

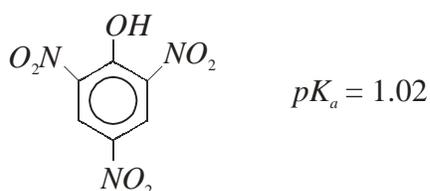
- (a) powerful $-I$ effect of OH which is a short distance away from NH_2 in oAn .
- (b) other steric and polar effects possible in oAn due to direct interaction between NH_2 and OH group.

TRY YOURSELF - III

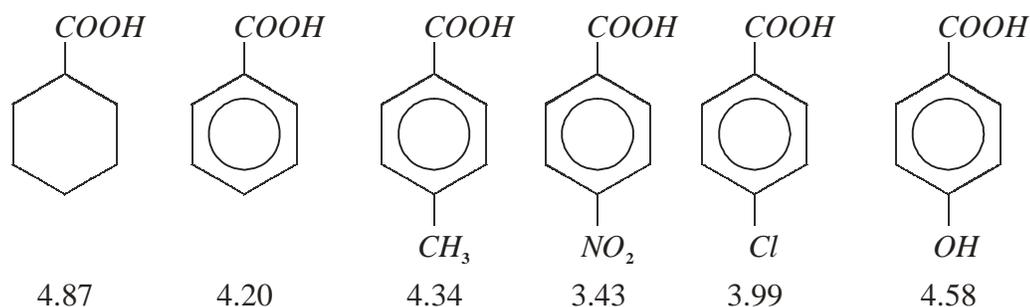
Q. 1 Explain the following observed pK_a values :



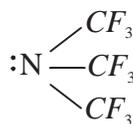
Q. 2 2, 4, 6-trinitrophenol (below) is a very strong acid. Explain the possible reason(s).



Q. 3 Explain the following observed pK_a values:

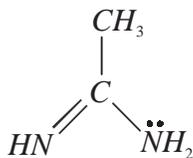


Q. 4 The following compound is found to be non-basic even though it contains a nitrogen atom

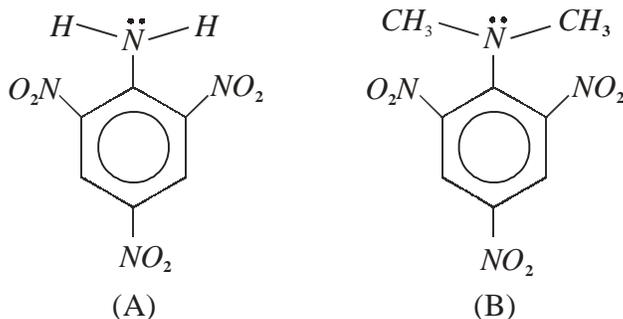


Explain.

Q. 5 Ethanamidine (drawn below) is an extremely basic compound, with $pK_a = 12.4$. What is (are) the possible reason(s)?



Q. 6 Consider the following two compounds:



It is observed that (B) is about 40000 times more basic than (A). What could be the possible reason(s)?

Section - 11

DIPOLE MOMENT

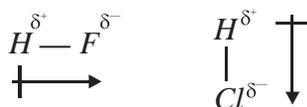
- (i) **Polarity of bond:** We know that a covalent bond is formed by sharing of electrons between two atoms. The electrons are shared equally when the two atoms forming the covalent bond have, approximately, the same tendency to attract electrons. However, when one of the atoms, forming the covalent bond, is more electronegative than the other, the electron cloud shifts towards the atom with higher attracting power.

This results in increase in electron density around one atom and a decrease in electron density around the other making the bond negative at the electronegative end and positive at the other. Or we can say, there develops a positive and a negative pole. In other words, the molecule constitutes a dipole due to separation of two opposite poles in space.

It is symbolized as:



Such bonds are said to be polar and they possess polarity. Polarity is indicated using symbols δ^+ and δ^- which imply partial (or slight) positive and negative charge.



Remember, the greater the difference in electronegativities of the atoms forming covalent bonds, the more polar the bond will be.

The polarity of bond affects various physical and chemical properties of the molecule like solubility, melting point, boiling point, the type of reaction that it undergoes etc.

Dipole moment is a physical property which can be measured experimentally. It may be defined as the product of magnitude of charge (in electrostatic units, esu) and the distance between the charges (in cm).

Dipole moment = charge \times distance

$$\mu = e \times d$$

Thus, its unit will be esu cm.

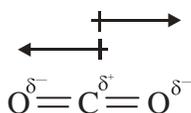
Since the charge of most molecules is of the order 10^{-10} esu and separation between them is approximately 10^{-8} cm, ($\mu = 10^{-10}$ esu $\times 10^{-8}$ cm = 10^{-18} esu cm) for convenience 10^{-18} esu cm is taken to be one debye, D.

So far we have only discussed diatomic molecules. We concluded that any diatomic molecule in which two atoms have different electronegativities will be polar and will necessarily have a dipole moment.

What if a molecule consists of more than one polar bond? Will it necessarily be polar? We will see that it may or may not be polar. Lets see how.

- (ii) **Polarity of molecule:** As an example, we will discuss the polarity of the carbon dioxide molecule. We know carbon and oxygen have appreciable difference in electronegativity values. Thus, carbon-oxygen bond will be polar with slight positive charge on carbon and slight negative charge on oxygen. Hence, we should expect CO_2 , having two polar bonds, to be polar.

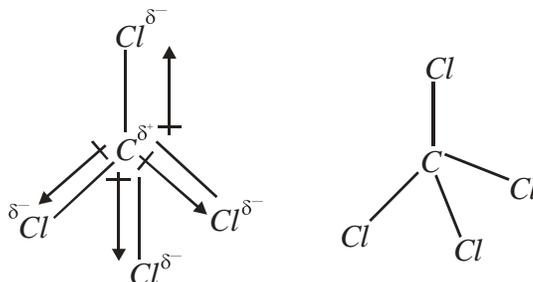
But actually, CO_2 has zero dipole moment. If we look at the structure of CO_2 , we see that it is linear (carbon being sp hybridized). The two carbon-oxygen bonds are definitely polar but the two dipoles act in opposite direction.



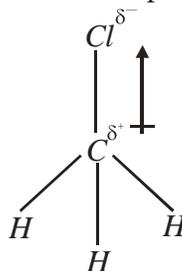
Since the individual dipoles are equal in magnitude, they cancel each other and result in no net dipole moment.

Let us take another molecule CCl_4 . Obviously, the C—Cl bond will be polar due to large difference in electroegativities of carbon and chlorine. But just like CO_2 , CCl_4 also doesn't possess any dipole moment and is non polar.

This is because CCl_4 is tetrahedral and if we consider the direction of individual bond moments, we will see that they cancel each other.



If on the other hand, we consider another molecule CH_3Cl , we will find that it possesses considerable amount of dipole moment. This is because it has three carbon–hydrogen bonds which have negligible individual dipole moments (C and H have nearly the same electronegativities). However, the carbon–chlorine bond is highly polar and accounts for the dipole moment of $CHCl_3$.



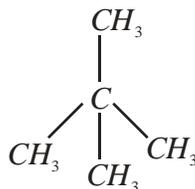
Example 49

Predict whether the given molecules will possess net dipole moment or not:



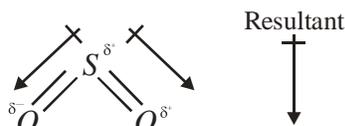
Solution: (i) $C(CH_3)_4$

This case is similar to CCl_4 . Being a symmetric molecule, it doesn't possess any overall dipole moment.



(ii) SO_2

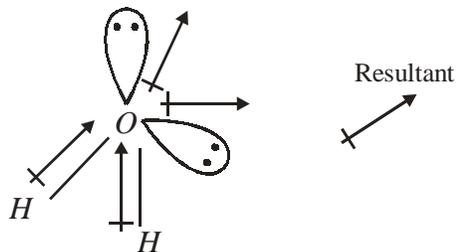
According to VSEPR theory, the shape of SO_2 molecule is angular (Unlike CO_2 which has linear as geometry).



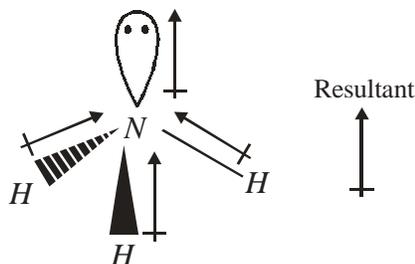
Thus, it possesses dipole moment.

(iii) H_2O

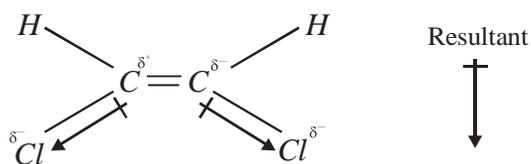
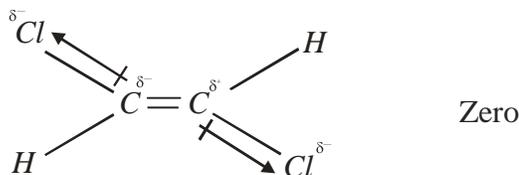
Water also has angular shape with two lone pair of electrons on oxygen. Lone pairs contribute more to the dipole moment because they are not bonded to any atom.

(iv) NH_3

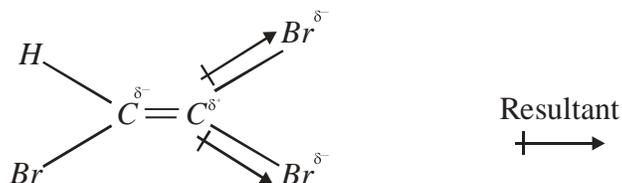
Like H_2O , NH_3 also possesses dipole moment. The shape of NH_3 is pyramidal with one lone pair on nitrogen.

**Example 50**

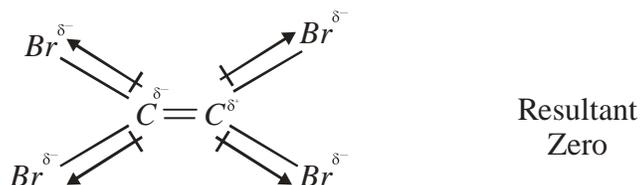
Predict whether the following molecules possess net dipole moment or not. Also give the direction of net dipole moment for the molecule.

(i) *cis* $CHCl = CHCl$ (ii) *trans* $CHCl = CHCl$ (iii) $CH_2 = CBr_2$ (iv) $CBr_2 = CBr_2$ **Solution:** (i) *cis* $CHCl = CHCl$ (ii) *trans* $CHCl = CHCl$ 

(iii)



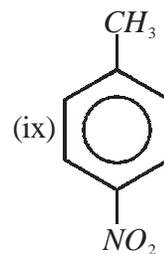
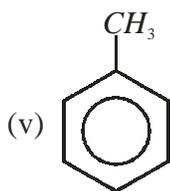
(iv)



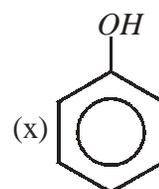
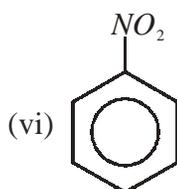
TRY YOURSELF - IV

1. Indicate the direction of dipole moment if any.

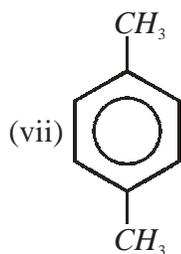
(i) diethyl ether



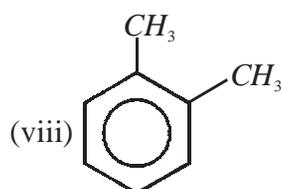
(ii) $N(CH_3)_3$



(iii) ICl



(iv) Methanol



EXERCISE

- Q. 1** Given that benzene contains an annular electron cloud above and below the plane of the ring, what type of reagents are expected to attack benzene most readily?
- Q. 2** What are the important criteria for delocalisation of electrons through orbital overlap to take place?
- Q. 3** Explain how conjugation takes place in the following compound (draw the possible canonical forms):

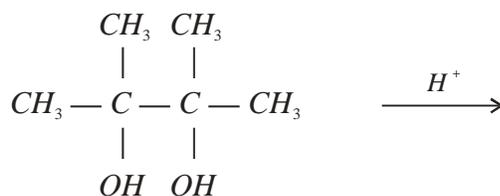


- Q. 4** Classify the following as electrophiles or nucleophiles:



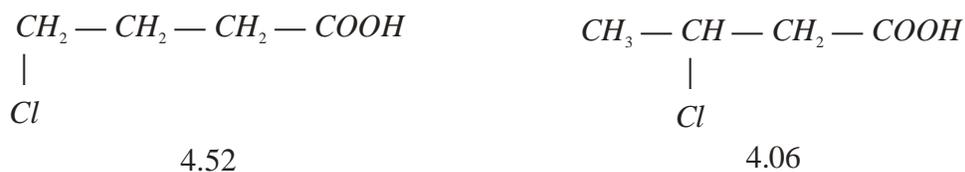
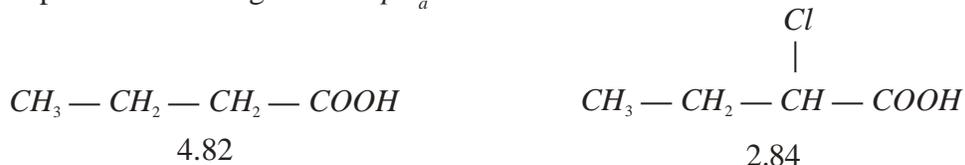
(A starred atom means electrophilicity / nucleophilicity is being talked about for that particular atom)

- Q. 5** What do you expect should happen when the following compound is treated with an acid?

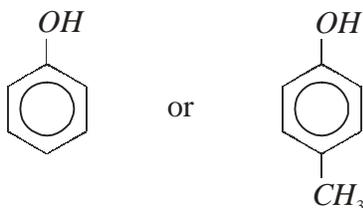


Think as freely as you can, and remember that one of the most important factors driving a reaction is the stability of its end products.

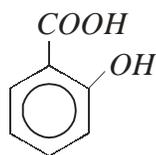
- Q. 6** Explain the following observed pK_a values:



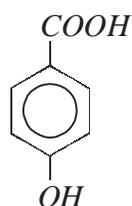
- Q. 7** Which of the following compounds will be more acidic?



Q. 8 Explain why *o*-hydroxybenzoic acid is found to be much more acidic than *p*-hydroxybenzoic acid.



o-hydroxy benzoic acid



p-hydroxy benzoic acid

Q. 9 Explain the following observed pK_a values:



Q. 10 The basicity of butyl amines in chlorobenzene is found to follow the following order:

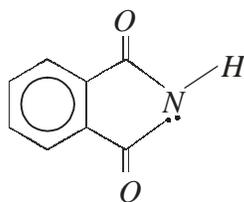


while in water, it follows the following order:



Explain

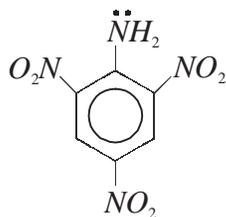
Q. 11 Consider the following compound (which is known as phthalimide):



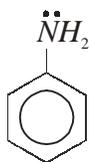
Do you expect this compound to be acidic or basic?

Q. 12 The compound diphenylamine, Ph_2NH , is an extremely weak base, with $pK_a = 0.8$. Explain the possible reason.

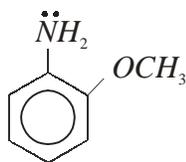
Q. 13 Do you expect the following compound to be extremely basic



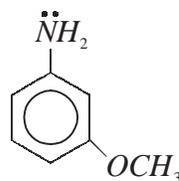
Q. 14 Explain the following observed pK_a values:



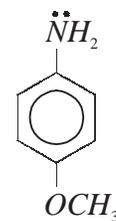
4.62



4.49



4.20

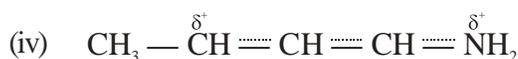
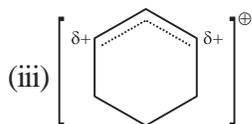
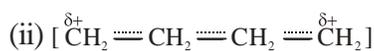


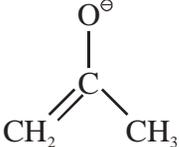
5.29

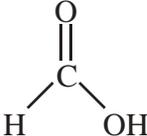
[ANSWER]

TRY YOURSELF - I

- (a) Hint: $C_3 - C_4$ bond has a partial double bond character
 (b) Hint: delocalisation of electrons would require the four p atomic orbitals to be essentially parallel, thus, restricting rotation about the $C_3 - C_4$ single bond.
- Benzene being flat has an aromatic character due to cyclic overlap of p orbitals and fulfillment of the $4n + 2 \pi$ electrons as per the Hückel's rule. Aromaticity imparts extra stability than the hypothetical 'cyclohexatriene'.
- The conjugate base PhO^- of $PhOH$ is resonance stabilised while it is not so in case of an aliphatic alcohol of the general form ROH .
- Resonance hybrids are as follows:



- (i)  because negative charge on highly electronegative atom makes the structure more stable.

- (ii)  because charge separation decreases stability. Also, more covalent bonds a structure has, more stable it is

- (iii) $CH_3 - CH = \overset{+}{O}H$ because all atoms have a complete octet of electrons.

- Cyanic acid and isocyanic acid differ in position of hydrogen atom
Loss of proton from.

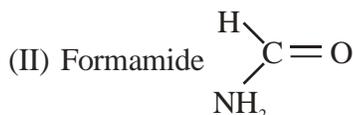
Cyanic acid yield. $\overset{-}{O} - C \equiv N$

and from isocyanic acid yields: $\overset{-}{N} - C = O$

They are resonating structures.



- (I) Methylamine $CH_3 - NH_2$



Carbon in (I) is sp^3 hybridized and in (II) is sp^2 hybridized. Thus, carbon in (II) has more s-character than in (I) and hence forms a shorter and a stronger bond with nitrogen.

TRY YOURSELF - II

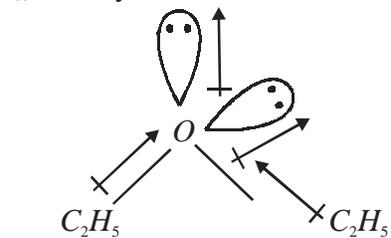
- Hint: due to greater ease of separation of charge and stabilisation of the resultant ion pairs through solvation.
- $\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{C}}\text{H}_2$ is more stable
- $\text{H}_3\text{C} \leftarrow \text{MgX}$

TRY YOURSELF - III

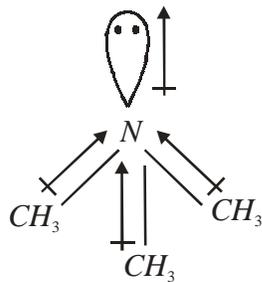
- Higher is the degree of *s*-character in the hybridization of the α -carbon atom, more closely electrons are held to the carbon nucleus. Hence, *sp* hybridised α -carbon is less electron-donating (thus, corresponding carboxylic acid is more acidic) than *sp*² and similar order of decreasing electron-donation follows from *sp*² to *sp*³ hybridized α -carbon atom.
- Due to the following reasons:
 - -M effect of nitro substituents in the ortho and para positions
 - -I effect of all the three nitro groups (though it falls off rapidly with distance on moving from *o*- → *m*- → *p*-).
 - the pattern of negative charge increases stability of the anion via solvation.
- Use the following hints to explain the *pK_a* values:
 - phenyl group has lower +I effect (than a saturated C-atom) due to the *sp*² hybridized C-atom to which the carboxyl group is attached.
 - +I substituents (e.g. alkyl groups) decrease acidity
 - -M groups at *o*- and *p*- position (e.g. -NO₂) increase acidity
 - Groups with -I but +M effect when located at *o*- and *p*-positions (here, -OH, -Cl) have an overwhelming electron-donating mesomeric effect, thus reducing the acidity.
- Hint: presence of three powerful electron-withdrawing CF₃ groups.
- Delocalisation stabilises both the neutral (given) molecule as well as the cation resulting from its protonation. Further unlike the given neutral molecule, the cation has two exactly equivalent canonical forms, thus, making protonation energetically profitable.
- The -NMe₂ group sterically interferes with the two very large -NO₂ groups at *o*-position, thus, preventing the *p* orbitals of the N-atom from being parallel to the *p* orbitals of the ring-carbon atoms, Hence +M effect of -NMe₂ is inhibited. Also, -M effect of -NO₂ groups does not take place and their base-weakening influence is restricted to their inductive effects. Thus, N-atom in -NMe₂ is more electron-rich than that in -NH₂.

TRY YOURSELF - IV

1. (i) diethyl ether



Resultant

(ii) $N(CH_3)_3$ 

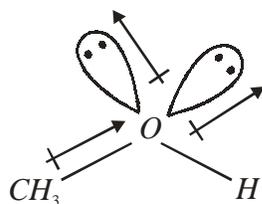
Resultant

(iii) $I^{\delta-} - Cl^{\delta-}$

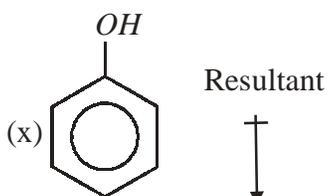
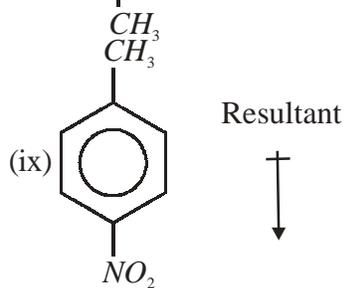
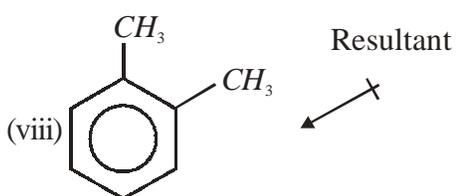
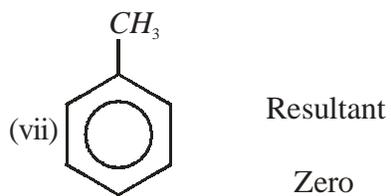
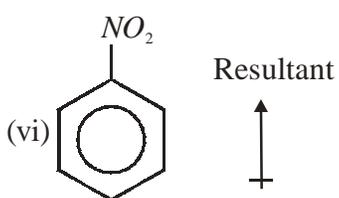
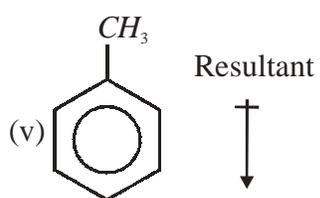
Resultant



(iv) Methanol



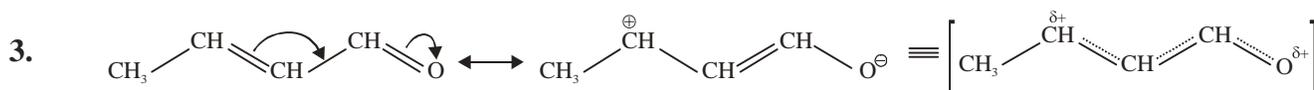
Resultant



EXERCISES

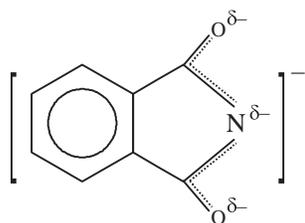
[ANSWER]

1. Electron-seeking or electrophilic reagents.
2. For delocalisation, all participating atomic orbitals should essentially be parallel by virtue of planarity of the molecule. This planarity may get effected due to steric factors. Further, a large increase or decrease in compound's energy content and/or charge separation discourages delocalisation.



4. Electrophiles : O_3, H^+
Nucleophiles : $RC\equiv C^-, H^-$
5. The product (mechanistic details would be learnt later under pinacol-pinacolone rearrangement) is as shown below:

$$(CH_3)_3C - \overset{\overset{O}{\parallel}}{C} - CH_3$$
6. Farther located is the halogen atom from the carboxyl group, its $-I$ effect dies down more rapidly along a saturated chain. Hence, the negative charge in carboxylate anion becomes progressively spread.
7. C_6H_5OH is more acidic.
8. Formation of intramolecular hydrogen bonding stabilises the anion from o-hydroxybenzoic acid by delocalising its charge. This is not possible in p-hydroxybenzoic acid.
9. Ponder upon the following hints:
 - the $-I$ effect of carboxylic group as a substituent falls off rapidly with saturated C-atom(s) separating the two $-COOH$ groups
 - phenyl group has lower electron-donating nature than saturated α -carbon as in CH_3- group.
10. In solvents such as water where stabilisation by solvation via the hydrogen-bonding can occur, introduction of a second alkyl group increases the basic strength. However, the introduction of a third alkyl group decreases the basic strength as it is also determined by the extent to which the cation, formed by uptake of a proton, can be solvated and hence, stabilised.
In a solvent such as chlorobenzene where there is no scope for hydrogen-bonding, the higher the number of alkyl groups, the more is the basicity of the butylamines as here, basicity is determined exclusively by electron availability on the nitrogen atom.
11. Compound is acidic as loss of proton would lead to the following resonance stabilised anion.



12. Reasons are as follows:
- N-atom is bonded to two sp^2 hybridised C-atom
 - Unshared electron pair on nitrogen get protonated, the resultant cation does not have unshared electron pair for delocalisation. Thus, the neutral molecule is stabilised with respect to the cation (or protonation of the neutral molecule is energetically unfavorable).
13. The given compound has very low basicity due to effective +M effect of $-NH_2$ group (hardly any steric repulsion as $-NH_2$ is a sufficiently small group) and hydrogen bonding between the oxygen atoms of the o - NO_2 groups and the hydrogen atoms of the NH_2 group (this hydrogen-bonding assists in holding the groups in the required planar orientation).
14. Use the following hints:
- $-OMe$ group has +M effect (at o - and p - position) and $-I$ effect.
 - o -substituent has both steric and polar effects apart from the usual +M and $-I$ effect