US04CCHE21: ORGANIC CHEMISTRY

UNIT – IV : Chemical Reactivity and Molecular Structure

(Acid- Base Properties)

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Acid-Bases, scale of acidity-basicity, Resonance effect, drawing of structures and the condition for resonance, Effect of change of hybridization on acidity and basicity, Inductive and electronic effects, steric effect and hydrogen bonding, Lewis acid and bases, Keto – enol tautomerism. Difference between resonance and tautomerism.

Arrhenius Acids and Bases :

- An Arrhenius acid is a compound that increases the H^+ ion concentration in aqueous solution.
- An Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution.
- The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.

The Brønsted-Lowry Theory of Acids and Bases :

In this theory, acids are defined as proton donors; whereas bases are defined as proton acceptors.

A Brønsted-Lowry acid is a proton (hydrogen ion) donor. A Brønsted-Lowry base is a proton (hydrogen ion) acceptor. Acids are Proton Donors and Bases are Proton Acceptors.

CH_3COOH	+ NH_3	<=> CH_3COO^-	+ NH_4^+
(Brønsted Acid)	(Brønsted Base)	(Brønsted Base)	(Brønsted Acid)

The stronger an acid, the weaker is its conjugate base, the stronger the base, the Weaker is its conjugate acid.

Lewis Acids and Bases:

Lewis base can donate a pair of electrons and Lewis acid can accept a pair of electrons. It forms a product containing a coordinate covalent bond.

$$\mathbf{H_3N: \quad + \quad BF_3 \qquad <=> \qquad H_3N:^{+} ---BF_3^{--}}$$

IONISATION CONSTANT :

The strength of acids and bases :

Acid dissociation

$HA_{(aq)} \quad \rightleftharpoons \quad A^-_{(aq)} \quad + \quad H^+_{(aq)}$

Acid Ionization Constant:

$K_a \; = \; [A^-] \; [H^+] / [HA]$

Base dissociation:

$B_{(aq)} \quad + \quad H_2O_{(l)} \quad \rightleftharpoons \quad HB^+_{(aq)} \quad + \quad OH^-_{(aq)}$

Base Ionization Constant :

$K_b \; = \; [HB^+] \; [OH^-] / [B]$

Relationship between Ka, pKa and acid strength:

$$\text{p}Ka \; = \; --\log_{10} Ka$$

$$\text{p}Ka \quad + \quad \text{p}Kb \quad = \quad 14$$

stronger an acid, the lesser is its **p*Ka*** value and the stronger a base, the greater is its **p*Ka*** .

Acid :	H_2O	C_6H_5OH	C_2H_5COOH	CH_3COOH
p*Ka* :	14	10	4.87	4.75

in the series, as the strength of the acid increases, the pKa progressively decreases.

The concentration of hydrogen ions is expressed in terms of pH

$pH \; = \; -\log [H^+] \quad = \quad \log 1/ H^+$

The smaller the value of **Ka**, the larger the value of **pKa**, the weaker the acid. If the pH of a solution of a weak acid and the **pKa** are known, the ratio of the concentration of the conjugate base to the concentration of the acid may be calculated

The larger the K_a means acid is stronger and small value of K_a means acid is weak. The larger the pK_a means the weaker is the acid. The smaller the pK_a means the stronger is the acid. pK_a is a constant for each conjugate acid and its conjugate base pair.

In case of acetic acid, trifluoroacetic acid, and hydrochloric acid.

CH_3COOH	**<**	**CF_3COOH**	**<**	**HCl**
pKa = 4.76		pKa = 0		pKa = -- 7
weak acid				very weak acid

Increasing acid strength ----------------------→

Similarly, the stronger the acid, the weaker will be its conjugate base and vice versa.

The **acidic properties** of **oxyacids** of the same element which is in different oxidation states increase with an increase in oxidation number.

+ 1 +3 +5 +7

$HClO < HC1O_2 < HC1O_3 < HClO_4$

+4 +6 +3 +5

$H_2SO_3 < H_2SO_4$; $HNO_2 < HNO_3$

But this rule fails in **oxyacids** of phosphorus.

$H_3PO_2 > H_3PO_3 > H_3PO_4$

The **acidic properties** of the **oxyacids** of different elements which are in the same oxidation state decreases as the atomic number increases. This is due to increase in size and decrease in electronegativity.

$$HClO_4 > HBrO_4 > HIO_4$$

$$H_2SO_3 > H_2SeO_3$$

But there are a number of acid-base reactions in which no proton transfer takes place, e.g.,

$$SO_2 + SO_2 \leftrightarrow SO^{2+} + S$$

$$\text{Acid}_1 \quad \text{Base}_2 \quad \text{Acid}_2 \quad \text{Base}_1$$

Thus, the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as $COCl_2$, SO_2, N_2O_4, etc.

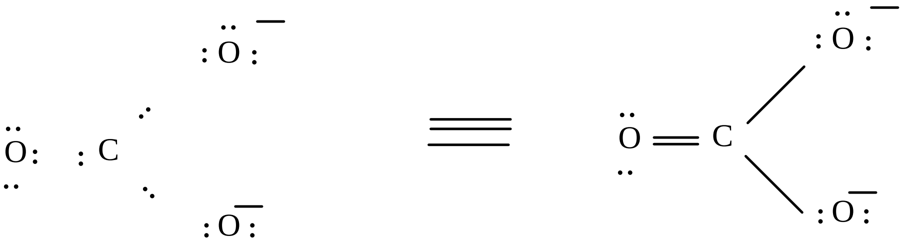
Resonance effect :

The concept of resonance effect tells about the polarity induced in a molecule by the reaction between a lone pair of electron and a pi bond. It also occurs by the interaction of 2 pi bonds in the adjacent atoms. Resonance in simple is the molecules with multiple Lewis structures.

Resonance in chemistry helps in understanding the stability of a compound along with the energy states.

Definition – The resonance effect can be defined as a chemical phenomenon which is observed in the characteristic compounds having double bonds in the organic compounds. The organic compounds contain these double bonds in the structures and usually have the overlapping of the p-orbitals on the two adjacent sides of carbon atoms.

In the Lewis structure of carbonate ion (CO_3^{--}), position of electrons is fixed, shows that there are two C—O single bonds and one C==O double bond.

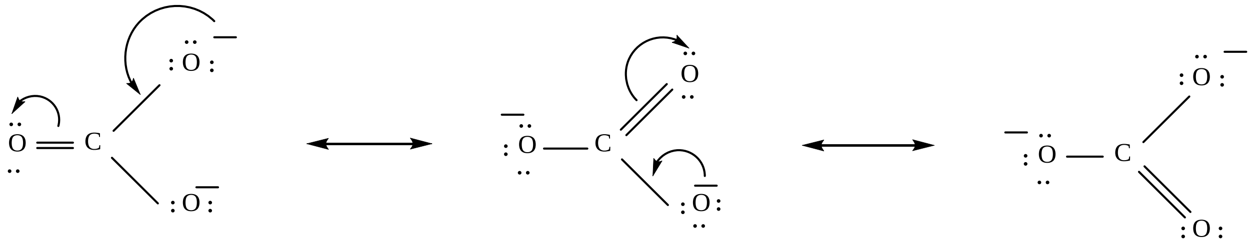


Electron dot structure

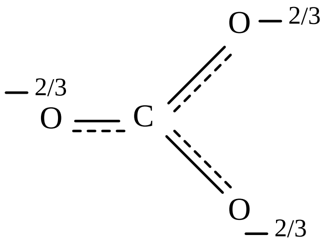
Lewis structure

Experimentally it has been determined that the three carbon-oxygen bond lengths in carbonate ion are equal and the bond distance is also equal to 1.28 A^0 i.e. it is symmetrical.

All the three structure can be written as shown below :

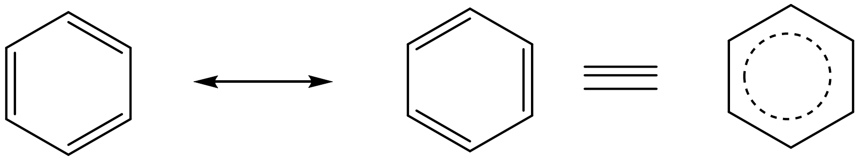


Therefore, different structures of a molecule which differ in the position of electrons only are called resonance or canonical structures and this phenomenon is known as resonance. Resonance structure are alternate structures of the same molecules and are called resonance contributing structures. Its true structure is called resonance hybrid. Resonance hybrid of carbonate ion is :

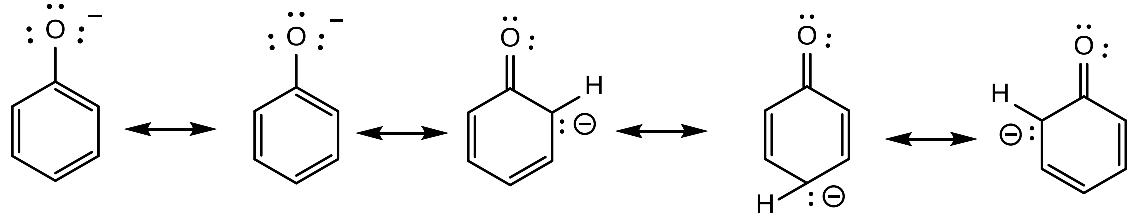


In the resonance hybrid structure, the negative charge is distributed equally among the three oxygen atoms. The dispersal of charge leads to a greater stability of the ion or molecule.

Benzene is an aromatic hydrocarbon, it have two resonance structure.

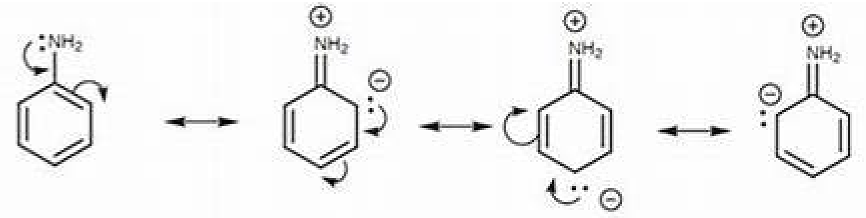


Resonance structure of phenoxide ion :



Phenoxide ion

Resonance structure of aniline :



Delocalization of electrons in a molecules decreases the energy and enhance its stability. Resonance energy is thus a measure of the stability of a system.

Effect of change of hybridization on acidity and basicity :

Acidity means ability to donate proton and basicity to accept proton. These properties also relates to hybridization which involve mixing of s- and p-orbitals. Greater the s character greater the chances of proton donation thus greater the acidity. For example,

$H_3C\text{-}CH_3$ has 25% s-character, $H_2C=CH_2$ has 33.3% and HC $\equiv$ CH is 50% ...so order of acidity is

$$H_3C\text{-}CH_3\ (sp^3) < H_2C=CH_2\ \ sp^2 < HC\equiv CH\ \ sp$$

$$25\%\ s < 33.33\%\ s < 50\%\ s$$

While the order of basicity increases with decrease in s character.

$$HC \equiv CH < H_2C = CH_2 < H_3C - CH_3$$

$$50\%\ s < 33.33\%\ s < 25\%\ s$$

Inductive and electronic effects :

This is the electron-withdrawing inductive effect, also known as the -I effect. In short, alkyl groups tend to donate electrons, leading to the +I effect.

Comparison between inductive effect and electromeric effect.

Inductive Effect	**Electromeric Effect**
It is a permanent effect.	It is a temporary effect.

Inductive effect : The inductive effect is a permanent state of polarization. The electron density in a sigma σ - bond between two unlike atoms is not uniform. The electron density is more dense toward the more electronegative of the two atoms.

The inductive effect operates through polarization of single bonds, and is associated with the electronegative of a group. For instance, in a bond between carbon and an electronegative atom ‘X’, the electron cloud will be closure to X end of the bond. The bond is thus polarized. This polarizing effect of ‘X’, is called the inductive effect.

The inductive effect is a distance-dependent phenomenon:

$C\ \delta+\ -\ X\delta-$

$C^{\delta+}\ \text{-}\rightarrow C^{\delta+} \rightarrow C^{\delta+}\ -\ X\delta-$

There are two categories of inductive effects:

the electron-withdrawing (- I effect) and the electron-releasing (+ I effect).

The latter is also called the *electron-donating effect.* In general, symbol ‘X’ is electron-withdrawing and ‘Y’ is electron-donating.

Among formic acid, acetic acid and chloroacetic acid, which one is stronger acid and why ?

The decreasing order of acid strength is

Chloroacetic acid > formic acid > acetic acid

Ka : 1.75×10^{-5} 21.4×10^{-4} 1.4×10^{-3}

Carboxylic acids are the most acidic compounds among the organic compounds.

Chloroacetic acid is more acidic than formic acid due to --I effect (the group attached to the chain is *electron-withdrawing*) of chloro group. While acetic acid is weaker acidic than formic acid due to + I effect (the group attached to the chain is *electron-donating*) of methyl group.

[Chloroacetic acid > benzoic acid > acetic acid > Phenol]

These relative inductive effects are measured with reference to hydrogen:

NO_2 > COOH > F > Cl > Br > I > OR > OH > C_6H_5 (Benzene) > H > Me_3C- > Me_2CH- > $MeCH_2-$ > CH_3-.

- I effect :

The -I effect is seen around a more electronegative atom or group, and electron density is higher there than elsewhere in the molecule.

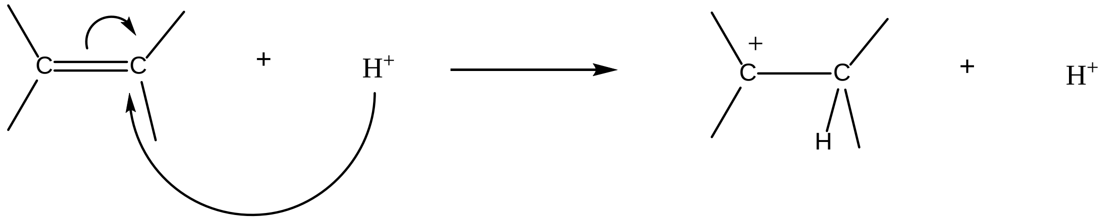
Electron-withdrawing groups include halogen, nitro (-NO_2), cyano (-CN), carboxy (-COOH), ester (-COOR), and aryloxy (-OAr).

+ I effect:

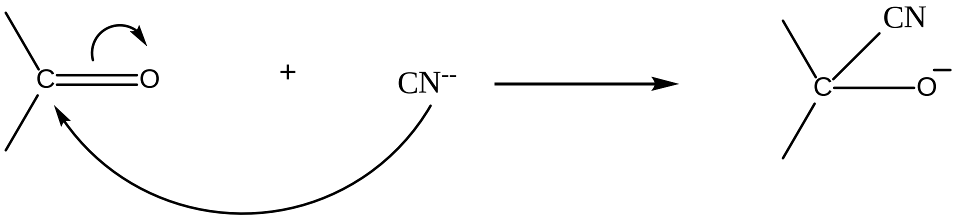
The +I effect is observed among the less electronegative atoms of the molecule by electron-releasing (or electron-donating) groups. The alkyl groups are usually considered electron-releasing (or electron-donating) groups.

The electromeric effect is an intramolecular movement of electrons from a pi-bond to another atom in the molecule due to attack by a reagent. It is temporary and reversible.

Positive electromeric effect : In this effect the pi-electrons of the multiple bond are transferred to that atom to which the reagent gets attached.



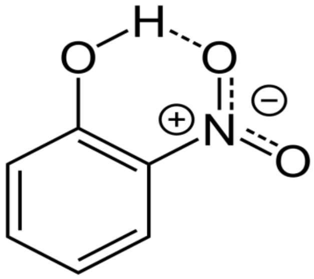
Negative electromeric effect : In this effect the pi-electrons of the multiple bond are transferred to that atom to which the attacking reagent do not gets attached.



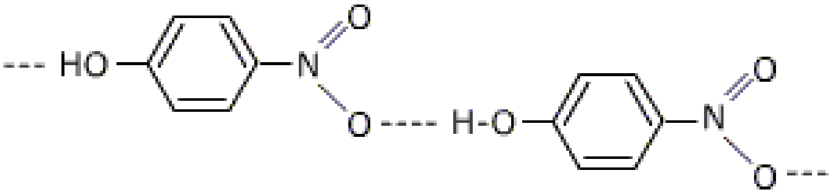
Steric effect and H- (hydrogen) bonding :

O-nitrophenol and p-nitrophenol can be separated by steam distillation.

Due to Intramolecular hydrogen bonding O-nitrophenol is water insoluble and will evaporate faster upon steam distillation.



While due to intermolecular hydrogen bonding between p-nitrophenol and water, p-nitrophenol is water soluble, and is not able to evaporate and it remains inside water.

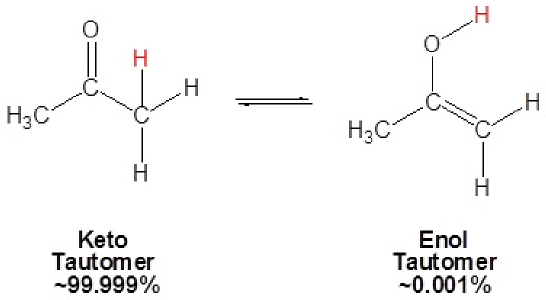


P- Nitrophenol with inter molecular hydrogen bonding

Keto – enol tautomerism :

In organic chemistry, **keto–enol tautomerism** refers to a chemical equilibrium between a **keto form** (a **ketone** or an aldehyde) and an **enol** (an alcohol).
The **keto** and **enol** forms are said to be **tautomers** of each other.

Because of the acidity of α-hydrogens carbonyls undergo keto-enol tautomerism. Tautomers are rapidly interconverted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom and a differently located double bond. The equilibrium between tautomers is not only rapid under normal conditions, but it often strongly favors one of the isomers. Even in such one-sided equilibria, evidence for the presence of the minor tautomer comes from the chemical behavior of the compound. Tautomeric equilibria are catalyzed by traces of acids or bases that are generally present in most chemical samples.



Difference between resonance and tautomerism :

Resonance is the displacement of lone pair and double bonds of molecules without changing the position of the atoms.

Tautomerization is the change in position of lone pair and double bonds to yield two different constitutional isomers.

There are following difference between tautomerism and resonance -

1. In resonance, resonating structure is hypothetical i.e. it doesn't exist. So we can't isolate. While tautomers are real. So we can isolate.
2. In resonance, only the movement of electron cloud takes place. While in tautomerism movement of atoms also takes place.
3. Resonance takes place for short distance of atom, while tautomerism for long distance.

Q. Arrange the following on the basis of their acidity and explain in detail:

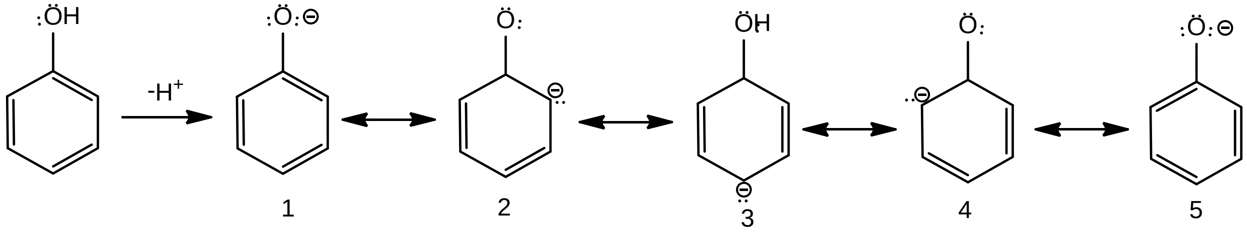
i) Picric acid
ii) o/p-nitrophenol
iii) 2,4- dinitrophenol
iv) Phenol

The acidity order of above structures is :

Picric acid > 2,4-dinitro phenol > o/p nitro phenol > phenol

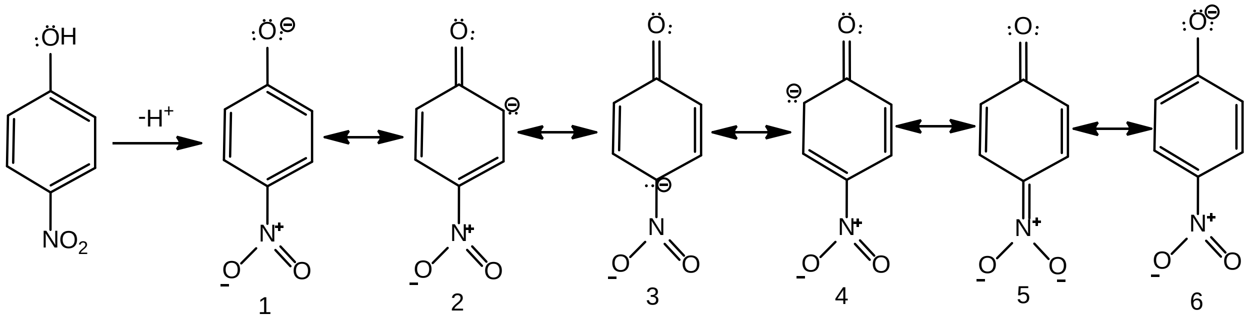
Q. Explain: Phenol is acidic in nature.

When H^+ ion is released from the phenol and it forms phenoxide ion. As phenol releases H^+ ion, and phenoxide ion becomes resonance stabilized anion, according to Brønsted-Lowry concept it is acidic in nature.



If electron attracting group such as $–NO_2$, enters to the o- or p- positron then o/p-nitro phenol is formed, and due to the attachment of the $–NO_2^+$ group, there are resonance stabilized structures as seen in phenoxide ion.

Q. Explain: p-Nitrophenol is acidic in nature.



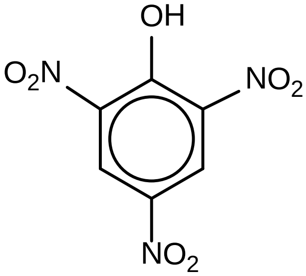
As $–NO_2^+$ group also takes part in resonance, six resonance structures are formed in p-Nitrophenol. In nitro-phenoxide ion, $–NO_2^+$ takes part in the resonance, hence its resonance stability is more and is more acidic then phenol. If two $–NO_2^+$ groups are present in the phenoxide ion than seven resonating structures are formed.

Means, as the number of $–NO_2^+$ group is increases, the stability of phenoxide ion also increases, consequently the acidity also increases.

Hence, there is rapid increase in acidity of the phenoxide ion, after adding of 3 $–NO_2^+$ group and hence it is more acidic than the phenol although it doesn't contains –COOH group.

Q. Explain : Picric acid doesn't contains –COOH group even though it is acidic in nature.

The structure formula for Picric acid is as under :



In case of Picric acid, the phenolic -OH group readily give away proton as the resulting phenoxide ion is significantly stabilized by delocalization over three nitro groups situated at 2-, 4-, 6- positions of Picric acid.

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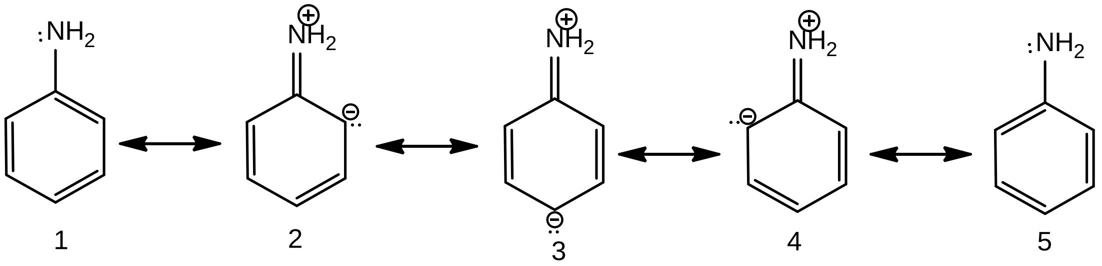
Q. Explain : The basicity of aliphatic amines is 10^6 times more than Aniline?

The basicity of methyl amine is more than aniline? Why



The basicity of any organic (inorganic) substance is due to the presence of lone pair on it. The lone pair of electron on 'N' is responsible for its basicity. But, here, this lone pair of electron takes part in the resonance and five such resonance structures are obtained. And due to the resonance, this electron pair doesn't stay steadily on benzene ring and hence aniline can't donates its electron pair easily. And the protonation of aniline is not easy. Thus, the basicity of aniline is less.

Now, when protonation of aniline takes place, we get anilinium ion which doesn't exhibits such resonance hence there is a loss of resonance stabilization and hence it is least basic.

In aliphatic amine, the lone pair of electron are stayed steady as they don't shows resonance and hence aliphatic amines can easily donates their electron pair. Thus, the protonation of aliphatic amine is easily performed. Hence, they are more basic in nature than aniline.

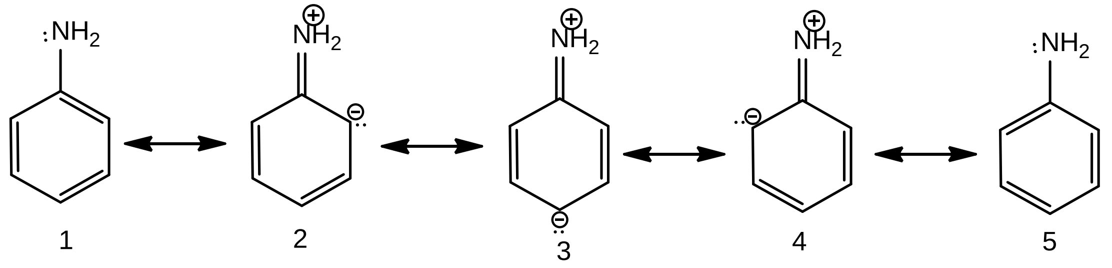
Arrange the following according to their basicity.

1) Aniline

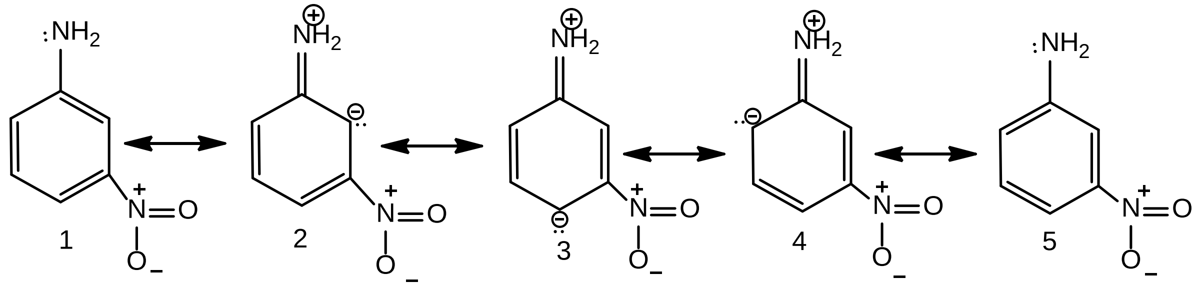
2) 2,4-dinitroaniline
3) 2-Nitroaniline/4-nitroaniline, m- nitroaniline
4) 2,4,6-Trinitroaniline

According to Lewis- Acid base principle, the basicity of the substance is due to the lone pair of electrons present on them. Such substance donate electron easily is basic.

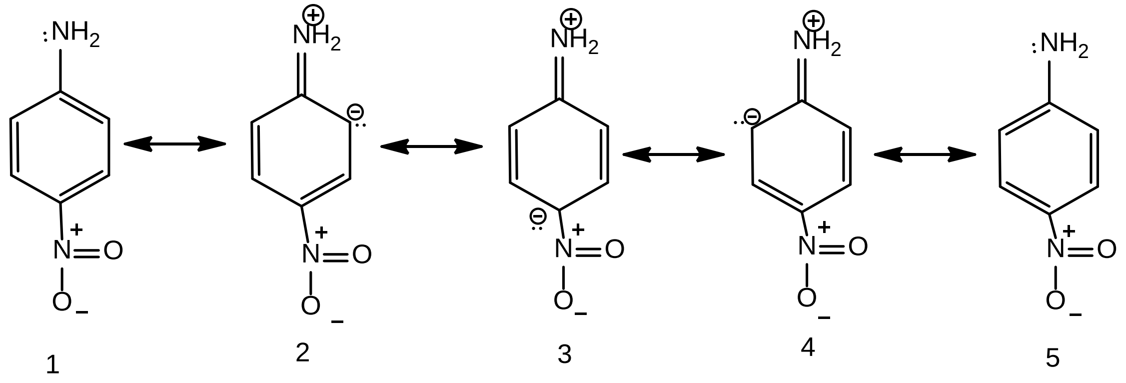
The basicity of Aniline is due to the lone pair of electrons, it contains



m-Nitroaniline



p-Nitroaniline



Due to resonance effect, the basicity of aniline decreases, due to increase in the stability of anilinium ion. When we add strong electron attracting group such as $-NO_2^+$ to the aniline, it attract lone pair of the electron towards it self.

As, we adds $–NO_2^+$ group in aniline, the number of resonance structure is increases and basicity decreases.

In o-/p-Nitroaniline, six resonance structures are seen because $–NO_2^+$ group takes part in resonance, similarly, resonance structures are seen in 2,4-dinitroaniline, while in 2,4,6-trinitroaniline, there are eight resonance structures.

Hence the basicity order of such compound is as :

Aniline > o-/p-Nitroaniline > 2,4- dinitroaniline > 2,4,6-Trinitroaniline

But, in m-nitroaniline, $–NO_2^+$ group doesn't take part in resonance and hence only five resonance structure are possible while in o/p-nitroaniline 6 structures 4 possible as $–NO_2^+$ group takes part in resonance.

(The electron of N are less provided) hence basicity of m-nitro-Aniline is more than 0/p nitro Aniline.

m- Nitroaniline > o-nitroaniline > of resonance between π-electron of (>C=O) ketone group and lone pair of electrons of N-atom and two resonance structures are found.

Due to the resonance stability increases, basicity decreases.

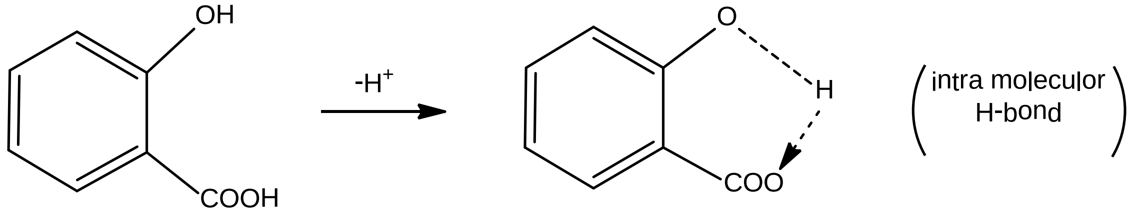
Electrostatic effect is also seen in amides. Due to this effect the lone pair of electrons of 'N' atom is attracted towards 'O' as 'O' is more electron negative than nitrogen and hence possibility of finding electrons on N-atom is least.

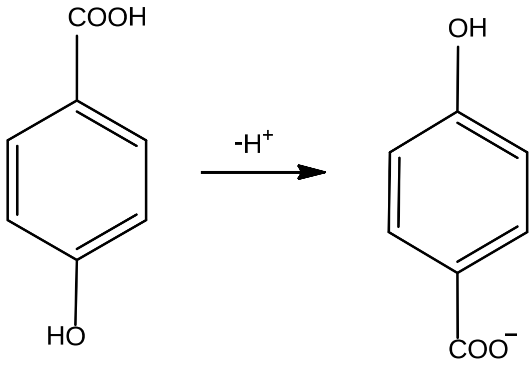
Due to the resonance effect and static effect the electron on N-atom are not easily attracted and protonation of such electrons is easily performed means such electrons are not easily donated and hence aqueous solution of amides are neutral.

Effect of hydrogen:

In certain compound, the acidic proton from H-bond with the other atom of the molecule which is knows as intra molecular H-bond and due to its impact the stability of anion increase and the acidity of appropriate acid increases

Explain : The acidity of salicylic acid is more than p-hydroxybenzoic acid.





In salicylic acid –COOH and –OH groups are nearer to each other on benzene ring. And hence in salicylate ion these two group forms intra- molecular H-bond with each other and the anion becomes stable. Thus, the stability of salicylate ion increases. Hence, the original acid salicylic acid is stronger acid.

Now, in p-hydroxybenzoic acid the –COOH and –OH groups are far away from each other and hence in it, benzoate ion –COOH and –OH group doesn't form intera molecular H-bond and the anion doesn't possess stability and hence the main acid p-hydroxy benzoic acid is least stable.

And, hence if in anion (related base) of acid there is a formation of intramolecular H-bond than the stability of anion increase and also acidity of many acid increases