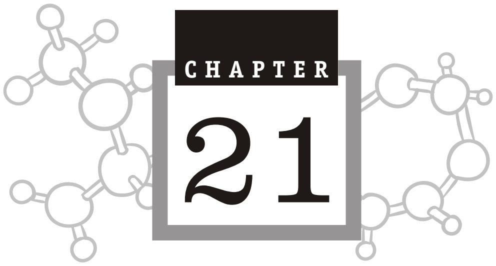


CHAPTER

21

Acidic and Basic Strength

ACID-BASE REACTIONS

To appreciate the reason for teaching acid-base chemistry early in the course, we need to first have a very simple understanding of what acid-base chemistry is all about. Let's summarize with a simple equation:

$$HA \rightleftharpoons H^{+} + A^{-}$$

In the equation above, we see an acid (HA) on the left side of the equilibrium and the conjugate base (A) on the right side. HA is an acid by virtue of the fact that it has a proton (H) to give. A is a base by virtue of the fact that it wants to take its proton back (acids give protons and bases take protons). Since A is the base that we get when we deprotonate HA, we call A the conjugate base of HA.

> ► **Acid and conjugate base strength**
> - The stronger the acid HA, the weaker its conjugate base, A^{-}
> - The stronger the base A^{-}, the weaker its conjugate acid AH

Acids

Regarding **anionic stability,** there are many relevant factors. Among these are external influences such as **solvent effects.** Specifically, a **polar solvent** has the ability to stabilize ionic species through charge – charge interactions or charge – heteroatom interactions. Conversely, a nonpolar solvent generally inhibits formation of charged species because it cannot interact with the ions.

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

General representation of acid dissociation

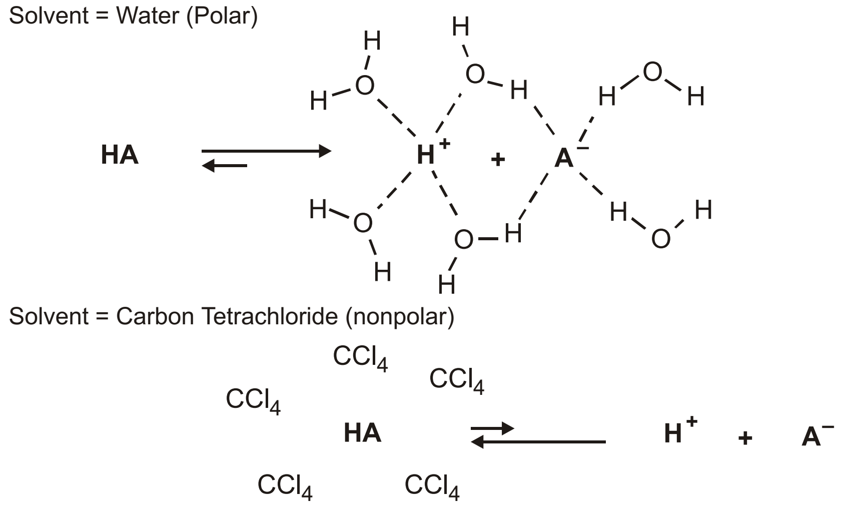
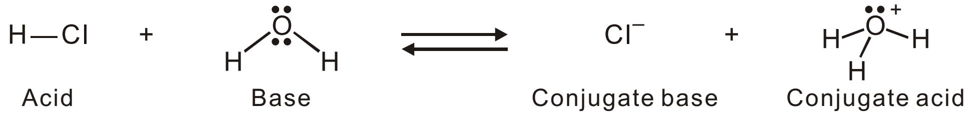


Figure 21.1 : Solvent effects on acid dissociation.

ACIDS AND BASES : THE BRONSTED-LOWRY DEFINITION

Perhaps the most important of all concepts related to electronegativity and polarity is that of acidity and basicity. We'll soon see, in fact, that the acid–base behavior of organic molecules explains much of their chemistry. You may recall from a course in general chemistry that two definitions of acidity are frequently used : the Bronsted–Lowry definition and the Lewis definition. We'll look at the Brønsted–Lowry definition in this and the following three sections and then discuss the Lewis definition.

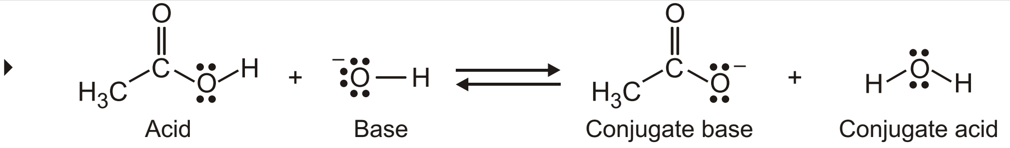
A **Brønsted–Lowry acid** is a substance that donates a hydrogen ion, H and a Brønsted–Lowry base is a substance that accepts a hydrogen ion. When gaseous hydrogen chloride dissolves in water, for example, a polar HCl molecule acts as an acid and donates a proton, while a water molecule acts as a base and accepts the proton, yielding chloride ion (Cl) and hydronium ion (H_3O). This and other acid–base reactions are reversible, so we'll write them with double, forward-and-backward arrows.

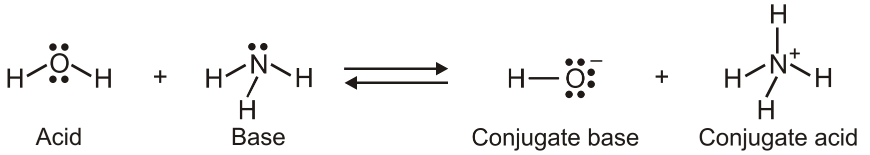


Chloride ion, the product that results when the acid HCl loses a proton, is called the **conjugate base** of the acid, and hydronium ion, the product that results when the base H_2O gains a proton, is called the conjugate acid of the base. Other common mineral acids such as H_2SO_4 and HNO_3 behave similarly, as do organic acids such as acetic acid, CH_3CO_2H. In a general sense,

$$\underset{\text{Acid}}{\text{H—A}} + \underset{\text{Base}}{:\text{B}} \rightleftharpoons \underset{\text{Conjugate base}}{:\text{A}^-} + \underset{\text{Conjugate acid}}{\text{H—B}^+}$$

Solved Example





► **For any acid and any base**

$$AH + B \rightleftharpoons BH^+ + A^-$$

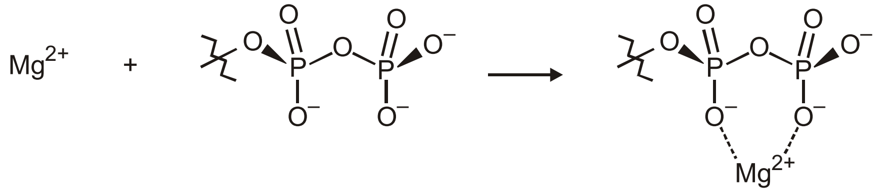
where AH is an acid and A^- is its conjugate base and B is a base and BH^+ is its conjugate acid, that is, *every acid has a conjugate base associated with it and every base has a conjugate acid associated with it.*

For example, with ammonia and acetic acid

$$CH_3COOH \quad NH_3 \rightleftharpoons NH_4 \quad CH_3COO$$

ACIDS AND BASES : THE LEWIS DEFINITION

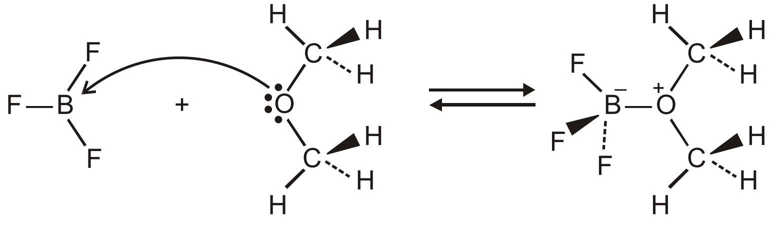
The Lewis definition of acids and bases is broader and more encompassing than the Brønsted–Lowry definition because it’s not limited to substances that donate or accept just protons. A **Lewis acid** is a substance that accepts an electron pair and a **Lewis base** is a substance that donates an electron pair. The donated electron pair is shared between the acid and the base in a covalent bond.



Lewis acid

Lewis base
(an organodiphosphate ion)

Acid–base complex



Boron
trifluoride
(Lewis acid)

Dimethyl
ether
(Lewis base)

Acid–base
complex

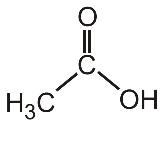
Dimethyl ether is the lewis base in the above written reaction which donates the electron pair to the valence orbital of the boron atom in BF_3, a lewis acid. Curved arrow shows the electron flow.

SOME FURTHER EXAMPLES OF LEWIS ACIDS FOLLOW

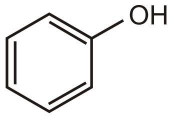
Some Lewis acids

Some neutral proton donors:

H_2O HCl HBr HNO_3 H_2SO_4



A carboxylic acid



A phenol

CH_3CH_2OH

An alcohol

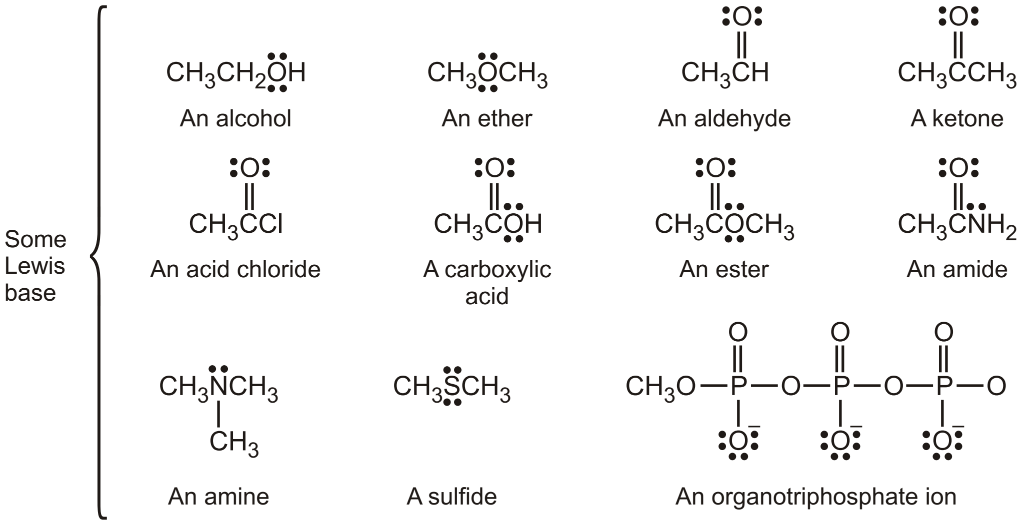
Some cations :

Li^+ Mg^{2+}

Some metal compounds :

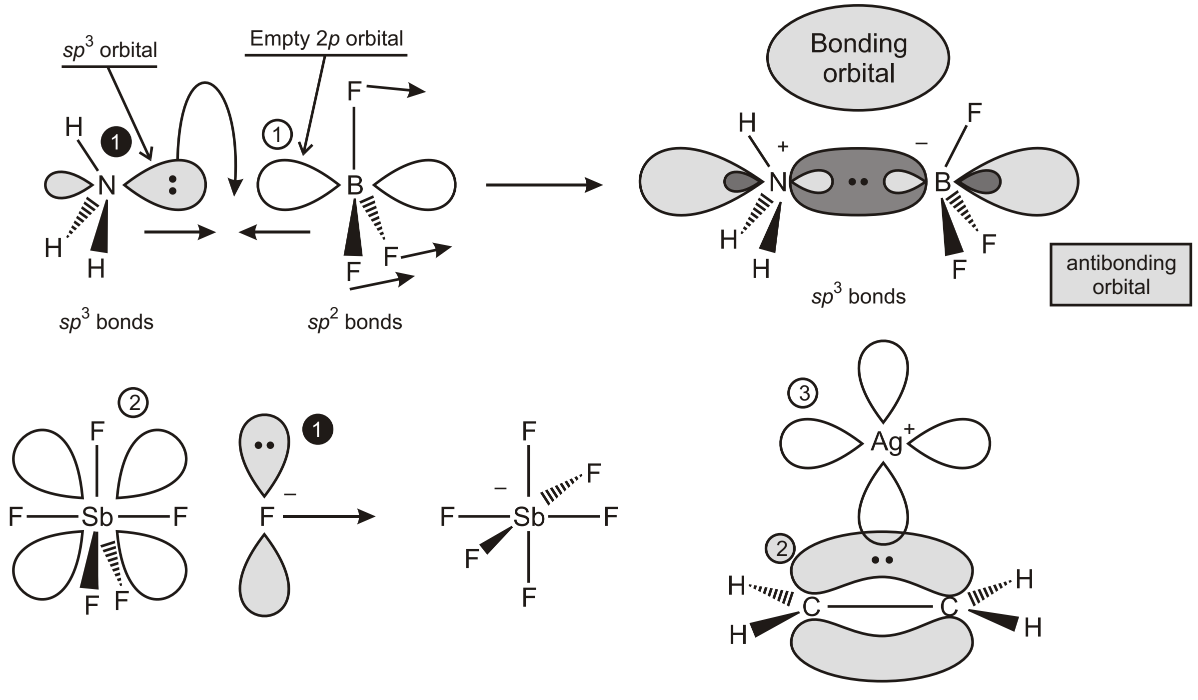
$AlCl_3$ $TiCl_4$ $FeCl_3$ $ZnCl_2$

- ☞ Compounds with open sextets (Empty *p* orbitals) [BF_3, BH_3] and with expandable valence shells [SbF_5, $FeBr_3$, $AlCl_3$] and Cation with vacant d orbitals [Ag , Zn^{2}].



- ☞ Compounds with atoms carrying unshared pair electron for example NH_3, H_2O and compound with multiple bonds CH_2 CH_2, CH CH are lewis base.

Lewis Acids and Lewis Bases



Lewis Bases

❶ Unshared pairs of electrons [NH_3, H_2O, F^{1}]

❷ orbitals [CH_2 CH_2]

Lewis Acid

① Open sextets (Empty *p* orbitals) [BF_3, BH_3]

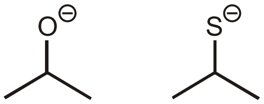
② Expandable valence shells (low-lying empty *d* orbitals) [SbF_5, $FeBr_3$, $AlCl_3$]

③ Positive ions with low-lying empty *d* orbitals [Ag , Zn^{2}, but not NH_4, Na]

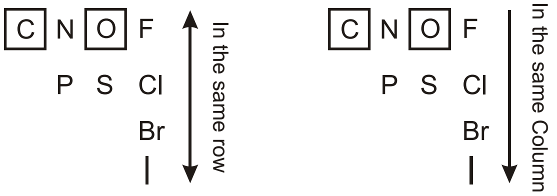
FACTOR AFFECTING THE ACIDIC STRENGTH

Factor-1 : Atom Carrying the Charge

The most important factor for determining charge stability is to ask what atom the charge is on. For example, consider the two charged compounds below :

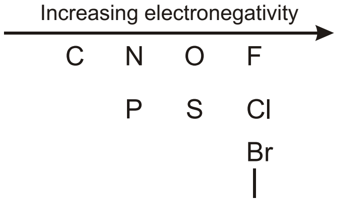


The one on the left has a negative charge on oxygen, and the one on the right has the charge on sulfur. How do we compare these? We look at the periodic table, and we need to consider two trends: comparing atoms in the same row and comparing atoms in the same column :



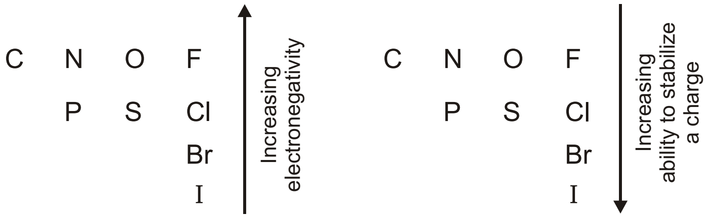
Let's start with comparing atoms in the same row. For example, let's compare carbon and oxygen :

The compound on the left has the charge on carbon, and the compound on the right has the charge on oxygen. Which one is more stable? Recall that electronegativity increases as we move to the right on the periodic table :



Since electronegativity is the measure of an element's affinity for electrons (how willing the atom will be to accept a new electron), we can say that a negative charge on oxygen will be more stable than a negative charge on carbon.

Now let's compare atoms in the same column, for example, iodide (I^-) and fluoride (F). Here is where it gets a little bit tricky, because the trend is the opposite of the electronegativity trend :

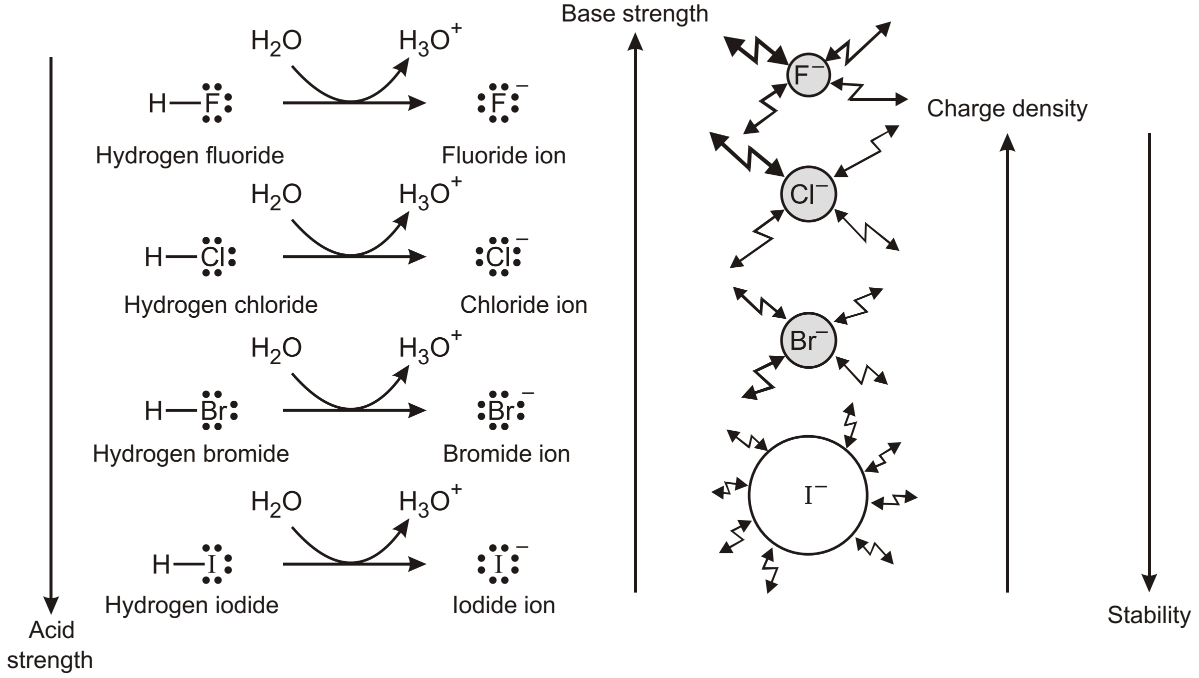


It is true that fluorine is more electronegative than iodine, but there is another more important trend when comparing atoms in the same column : the size of the atom. Iodine is huge compared to fluorine. So when a charge is placed on iodine, the charge is spread out over a very large volume. When a charge is placed on fluorine, the charge is stuck in a very small volume of space:

Even though fluorine is more electronegative than iodine, nevertheless, iodine can better stabilize a negative charge. If I^- is more stable than F , then HI must be a stronger acid than HF, because HI will be more willing to give up its proton than HF.

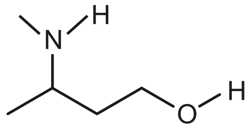
- ☞ To summarize, there are two important trends : electronegativity (for comparing atoms in the same row) and size (for comparing atoms in the same column). The first factor (comparing atoms in the same row) is a much stronger effect. In other words, the difference in stability between C and F is much greater than the difference in stability between I^- and F .

Solved Example

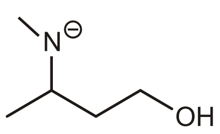


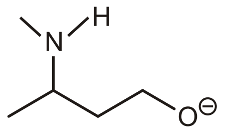
Solved Example

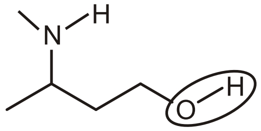
- Compare the two protons in the following compound. Which one is more acidic?



Ans. We begin by pulling off one proton and drawing the conjugate base that we get. Then, we do the same thing for the other proton :







Now we need to compare these conjugate bases and ask which one is more stable. In other words, which negative charge is more stable? We are comparing a negative charge on nitrogen with a negative charge on oxygen. So we are comparing two atoms in the same row of the periodic table, and the important trend is electronegativity. Oxygen can better stabilize the negative charge, because oxygen is more electronegative than nitrogen. The proton on the oxygen will be more willing to come off, so it is more acidic:

Relative acid strengths :

NH_3	<	H_2O	<	HF
pKa = 36		pKa = 15.7		pKa = 3.2

Relative elecronegativities of carbon atoms :

$sp > sp^2 > sp^3$

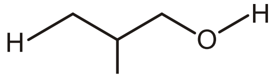
increasing electronegativity ←

Relative electronegativities :

N < O < F

Solved Example

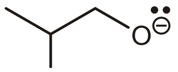
- Compare the two protons clearly shown in the following compound. (There are more protons in the compound, but only two are shown.) Which of these two protons is more acidic? Remember to begin by drawing the two conjugate bases, and then compare them.



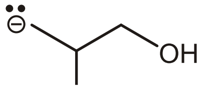
Conjugate base 1

Conjugate base 2

Ans.



Conjugate base 1

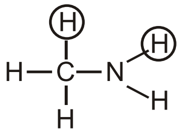


Conjugate base 2

; 1 is more stable than 2

Solved Example

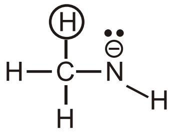
- Compare the two protons clearly shown in the following compound. Which of these two protons is more acidic?



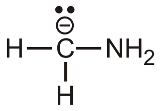
Conjugate base 1

Conjugate base 2

Ans.



Conjugate base 1

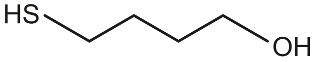


Conjugate base 2

; 1 is more stable than 2

Solved Example

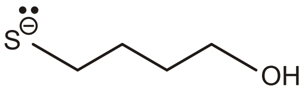
- Compare the two protons shown in the following compound and identify which proton is more acidic:



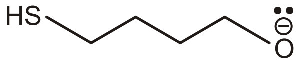
Conjugate base 1

Conjugate base 2

Ans.



Conjugate base 1

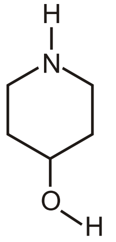


Conjugate base 2

; 1 is more stable than 2

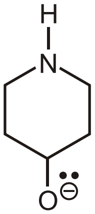
Solved Example

- Compare the two protons shown in the following compound, and identify which proton is more acidic:

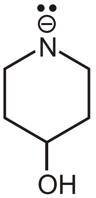


Conjugate base 1   Conjugate base 2

Ans.



Conjugate base 1



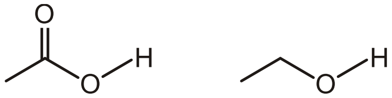
Conjugate base 2

; 1 is more stable than 2

Factor-2 (Resonance) :

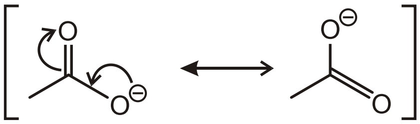
The last chapter was devoted solely to drawing resonance structures. If you have not yet completed that chapter, do so before you begin this section. We said in the last chapter that resonance would find its way into every single topic in organic chemistry. And here it is in acid-base chemistry.

To see how resonance plays a role here, let's compare the following two compounds:

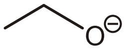


In both cases, if we pull off the proton, we get a charge on oxygen:

So we cannot use factor 1 (what atom is the charge on) to determine which proton is more acidic. In both cases, we are dealing with a negative charge on oxygen. But there is a critical difference between these two negative charges. The one on the left is stabilized by resonance:



A delocalized negative charge is more stable than a localized negative charge (stuck on one atom) :

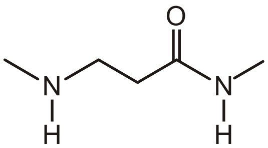


Charge is stuck on one atom ("localized")

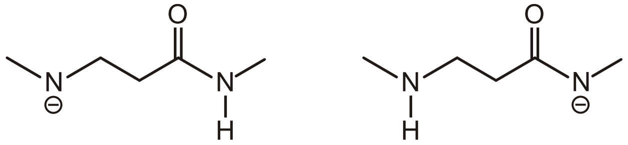
we have one molecule losing its proton for every 10,000 molecules that do not give up their proton. In the world of acidity, this is not very acidic, but everything is relative.

Solved Example

- Compare the two protons shown in the following compound. Which one is more acidic?



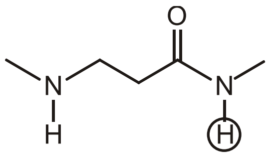
Ans. We begin by pulling off one proton and drawing the conjugate base that we get. Then we do the same thing for the other proton:



Now we need to compare these conjugate bases and ask which one is more stable. In the compound on the left, we are looking at a charge that is localized on a nitrogen atom. For the compound on the right, the negative charge is delocalized over a nitrogen atom and an oxygen atom (draw resonance structures).

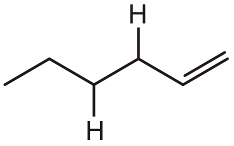
It is more stable for the charge to be delocalized, so the second compound is more stable.

The more acidic proton is that one that leaves to give the more stable conjugate base.



Solved Example

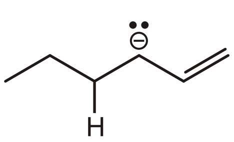
- Compare the two protons identified below. There are more protons in the compound, but only two of them are shown.



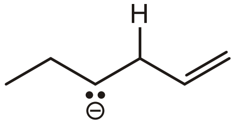
Conjugate base 1

Conjugate base 2

Identify which of these protons is more acidic, and explain why by comparing the stability of the conjugate bases.

Ans. 

Conjugate base 1

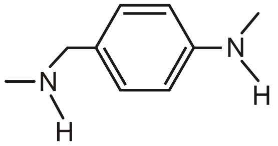


Conjugate base 2

; 1 is more stable than 2

Solved Example

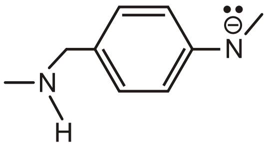
- Compare the two protons identified below :



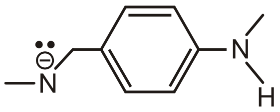
Conjugate base 1

Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

Ans. 

Conjugate base 1

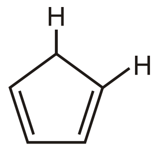


Conjugate base 2

; 1 is more stable than 2

Solved Example

- Compare the two protons identified below : H

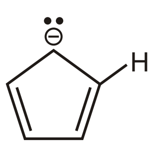


Conjugate base 1

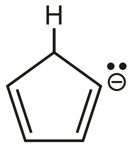
Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

Ans.



Conjugate base 1

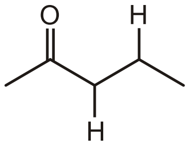


Conjugate base 2

; 1 is more stable than 2

Solved Example

- Compare the two protons identified below :

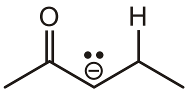


Conjugate base 1

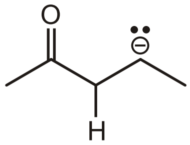
Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

Ans.



Conjugate base 1

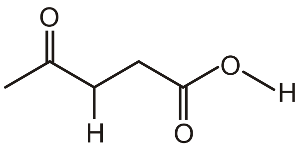


Conjugate base 2

; 1 is more stable than 2

Solved Example

- Compare the two protons identified below :

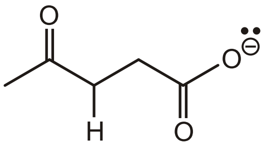


Conjugate base 1

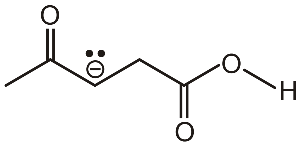
Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

Ans.



Conjugate base 1

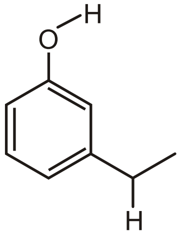


Conjugate base 2

; 1 is more stable than 2

Solved Example

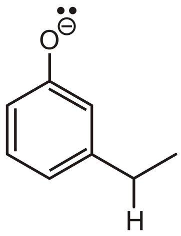
- Compare the two protons identified below :



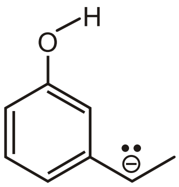
Conjugate base 1

Conjugate base 2

Ans.



Conjugate base 1



Conjugate base 2

; 1 is more stable than 2

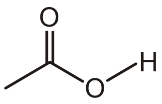
► **Get a feel of *p*K_a*s*!**

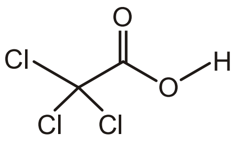
Notice that these oxygen acids have *p*K_a*s* that conveniently fall in units of 5 (approximately).

Acid	RSO_2OH	RCO_2H	PhOH	ROH
Approx. *p*K_a	0	5	10	15

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

Let's compare the following compounds :



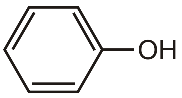


Which compound is more acidic? The only way to answer that question is to pull off the protons and draw the conjugate bases :

Let's go through the factors we learned so far. Factor 1 does not answer the problem: in both cases, the negative charge is on oxygen. Factor 2 also does not answer the problem: in both cases, there is resonance that delocalizes the charge over two oxygen atoms. **NOW WE NEED FACTOR 3.**

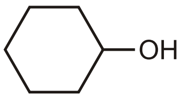
Some important acidic strength comparisons :

1.



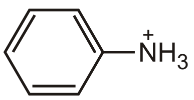
phenol
pK_a = 10

>



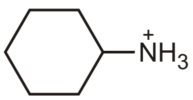
cyclohexanol
pK_a = 16

2.



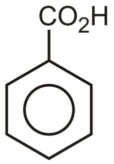
protonated aniline
pK_a = 4.60

>



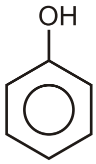
protonated cyclohexylamine
pK_a = 11.2

3.



Benzoic acid
pK_a = 4.2

>



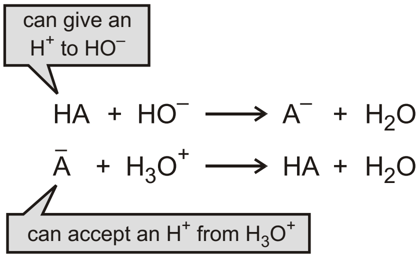
Phenol
pK_a = 10

☑ SPECIAL TOPIC

Buffer Solutions

A solution of a weak acid (HA) and its conjugate base (A) is called a buffer solution.

A buffer solution will maintain nearly constant pH when small amounts of acid or base are added to it, because the weak acid can give a proton to any HO added to the solution, and its conjugate base can accept any H that is added to the solution.



$$HA + HO^- \longrightarrow A^- + H_2O$$

$$\overset{-}{A} + H_3O^+ \longrightarrow HA + H_2O$$

acid's pK_a is 3.75, the majority of the buffer will be in the basic form at pH = 4.2. Acetic acid with pK_a 4.76, will have more buffer in the acidic form than in the basic form. Thus, it would be better to use acetic acid/acetate buffer for your reaction.

Blood : A buffered solution

Blood is the fluid that transports oxygen to all the cells of the human body. The normal pH of human blood is ~7.4. Death will result if this pH decreases to less than ~6.8 or increases to greater than ~8.0 for even a few seconds.

Oxygen is carried to cells by a protein in the blood called haemoglobin (HbH). When haemoglobin binds O_2, hemoglobin loses a proton, which would make the blood more acidic if it did not contain a buffer to maintain its pH.

$$HbH \quad O_2 \rightleftharpoons HbO_2 \quad H$$

A carbonic acid/bicarbonate (H_2CO_3 / HCO_3) buffer controls the pH of blood. An important feature of this buffer is that carbonic acid decomposes to CO_2 and H_2O, as shown below :

$$\underset{\text{bicarbonate}}{HCO_3} \quad H \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3} \rightleftharpoons CO_2 \quad H_2O$$

During exercise our metabolism speeds up, producing large amounts of CO_2. The increased concentration of CO_2 shifts the equilibrium between carbonic acid and bicarbonate to the left, which increases the concentration of H . Significant amounts of lactic acid are also produced during exercise, which further increases the concentration of H . Receptors in the brain respond to the increased concentration of H by triggering a reflex that increases the rate of breathing. Haemoglobin then relases more oxygen to the cells and more CO_2 is eliminated by exhalation. Both processes decrease the concentration of H in the blood by shifting the equilibrium of the top reaction to the left and the equilibrium of the bottom reaction to the right.

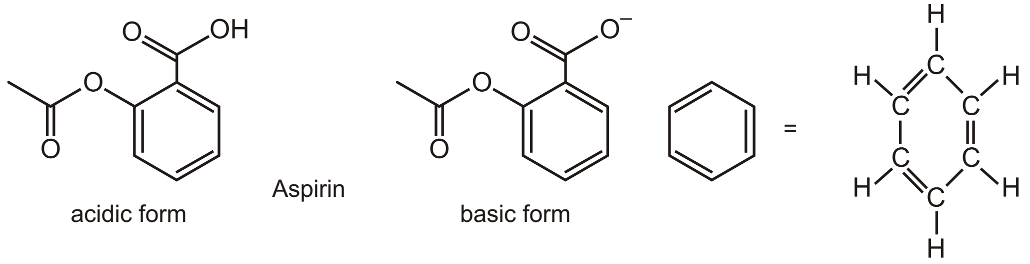
Thus, any disorder that decreases the rate and depth of ventilation, such as emphysema, will decrease the pH of the blood–a condition called acidosis. In contrast, any excessive increase in the rate and depth of ventilation, as with hyperventilation due to anxiety, will increase the pH of blood – a condition called alkalosis.

☑ SPECIAL TOPIC

Aspirin Must be in its basic form to Be physiologically active.

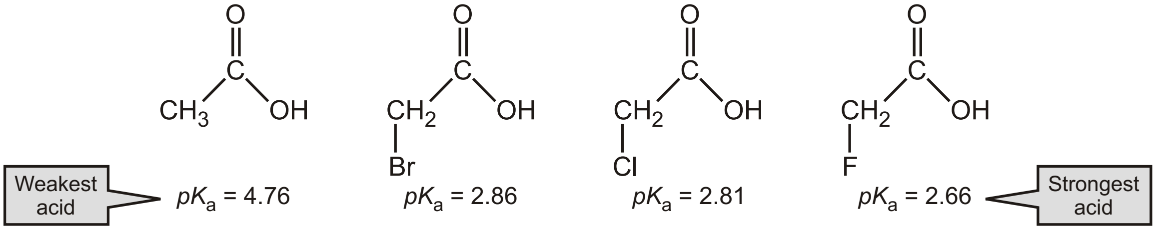
Aspirin has been used to treat fever, mild pain, and inflammation since it first became commerically available in 1899. It was the first drug to be tested clinically before it was marketed. Currently one of the most widely used drugs in the world, aspirin is one of a group of over-the-counter drugs known as NSAIDs (non steroidal anti-inflammatory drugs).

Aspirin is a carboxylic acid. The carboxylic acid group must be in its basic form to be physiologically active.



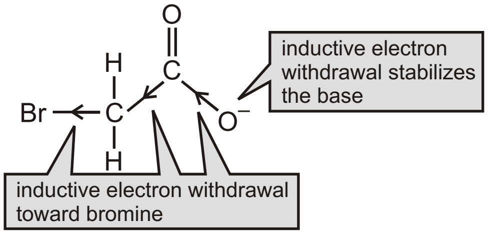
Factor-3 : How Substituents Affect the Strength of an Acid

Although the acidic proton of each of the following carboxylic acids is attached to the same atom (an oxygen), the four compounds have different pK_a values :



The different pK_a values indicate that there must be another factor that affects acidity other than the nature of the atom to which the hydrogen is bonded. From the pK_a values of the four carboxylic acids, we see that replacing one of the hydrogens of the CH_3 group with a halogen increases the acidity of the compound. (The term for replacing an atom in a compound is substitution , and the new atom is called a substituent.) The halogen is more electronegative than the hydrogen it has replaced, so the halogen pulls the bonding electrons toward itself more than a hydrogen would. Pulling electrons through sigma (s) bonds is called inductive electron withdrawal.

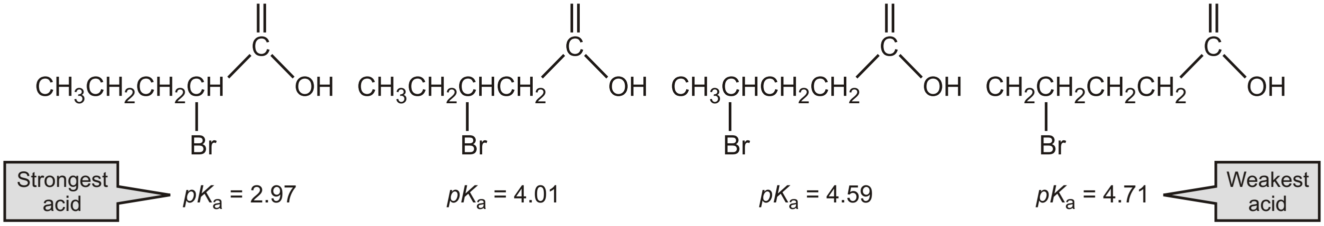
If we look at the conjugate base of a carboxylic acid, we see that inductive electron withdrawal decreases the electron density about the oxygen that bears the negative charge, thereby stabilizing it. And we know that stabilizing a base increases the acidity of its conjugate acid.



The pK_a values of the four carboxylic acids shown above (become more acidic) as the electron-withdrawing ability (electronegativity) of the halogen increases.

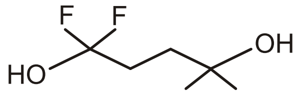
Thus, the fluoro-substituted compound is the strongest acid because its conjugate base is the most stabilized (is the weakest).

The effect a substituent has on the acidity of a compound decreases as the distance between the substituent and the acidic proton increases.

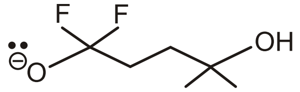


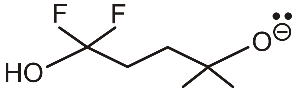
Solved Example

- Compare two protons shown in the following compound. Which proton is more acidic?



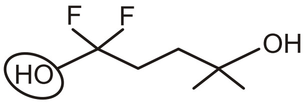
Ans. Begin by drawing the conjugate bases:





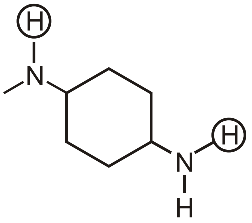
In the compound on the left, the charge is somewhat stabilized by the inductive effects of the two neighboring fluorine atoms. In contrast, the compound on the right is destabilized by the presence of two carbon atoms (methyl groups) that donate electron density. Therefore, the compound on the left is more stable.

The more acidic proton is the one that will leave to give the more stable negative charge. So the circled proton is more acidic:



Solved Example

- Compare the two protons identified below :

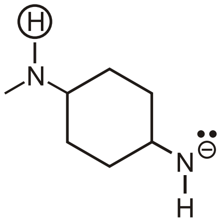


Conjugate base 1

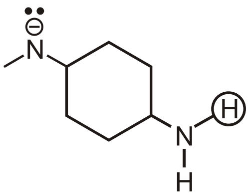
Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

Ans.



Conjugate base 1

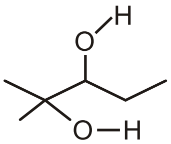


Conjugate base 2

; 1 is more stable than 2

Solved Example

- Compare the two protons identified below :

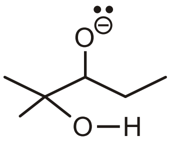


Conjugate base 1

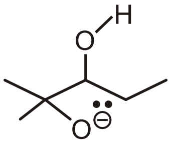
Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

Ans.



Conjugate base 1

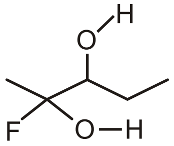


Conjugate base 2

; 1 is more stable than 2

Solved Example

- Compare the two protons identified below :

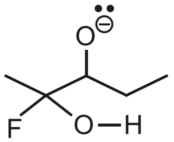


______________ Conjugate base 1

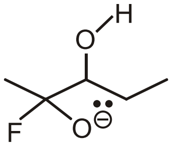
______________ Conjugate base 2

Identify which proton is more acidic, and explain why by comparing the stability of the conjugate bases.

Ans.



Conjugate base 1

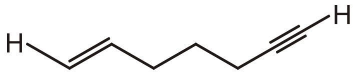


Conjugate base 2

; 2 is more stable than 1

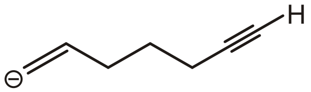
FACTOR-4 (Orbitals)

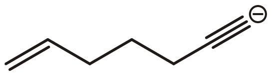
The three factors we have learned so far will not explain the difference in acidity between the two identified protons in the compound below :



If we pull off the protons and look at the conjugate bases to compare them, we see this:

So a negative charge on an sp hybridized carbon is more stable than a negative charge on an sp^3 or sp^2 hybridized carbon:



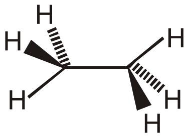


More stable

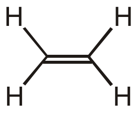
Determining which carbon atoms are sp, sp^2 or sp^3 is very simple: a carbon with a triple bond is sp, a carbon with a double bond is sp^2, and a carbon with all single bonds is sp^3. For more on this topic, turn to the next chapter (covering geometry).

Hybridization can also affect the pK_a

The hybridization of the orbital from which the proton is removed also affects the pK_a. Since *s* orbitals are held closer to the nucleus than are *p* orbitals, the electrons in them are lower in energy, that is, more stable. Consequently, the more s character an orbital has, the more tightly held are the electrons in it. This means that electrons in an *sp* orbital (50% s character) are lower in energy than those in an sp^2 orbital (33% s character), which are, in turn, lower in energy than those in an sp^3 orbital (25% s character). Hence the anions derived from ethane, ethene, and ethyne increase in stability in this order and this is reflected in their pK_as. Cyanide ion, –CN, with an electronegative element as well as an *sp* hybridized anion, is even more stable and HCN has a pK_a of about 10.

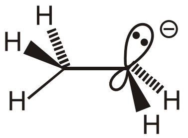


pK_a ca. 50

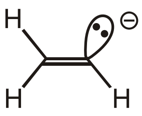


pK_a ca. 44

pK_a ca. 26



lone pair of CHCH
in sp orbital



lone pair of CHCH
in sp orbital

lone pair of
in sp orbital

SUMMARY OF ACIDIC STRENGTH

1. **1.** What atom is the charge on? (Remember the difference between comparing atoms in the same row and comparing atoms in the same column.)
2. **2.** Are there any resonance effects making one conjugate base more stable than the others?
3. **3.** Are there any inductive effects (electronegative atoms or alkyl groups) that stabilize or destabilize any of the conjugate bases?
4. **4.** In what orbital do we find the negative charge for each conjugate base that we are comparing?

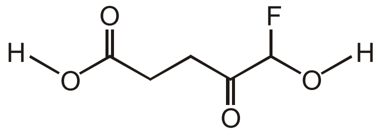
There is an important exception to this order. Compare the two compounds below :

If we wanted to know which compound was more acidic, we would pull off the protons and compare the conjugate bases :

When comparing these two negative charges, we find two competing factors : the first factor (what atom is the charge on?) and the fourth factor (what orbital is the charge in?). The first factor says that a negative charge on nitrogen is more stable than a negative charge on carbon. However, the fourth factor says that a negative charge in an sp orbital is more stable than a negative charge in an sp^3 orbital (the negative charge on the nitrogen is an sp^3 orbital).

Solved Example

- Compare the two protons identified below :



Identify which proton is more acidic, and explain why.

Now we can compare them and ask which negative charge is more stable, using our four factors :

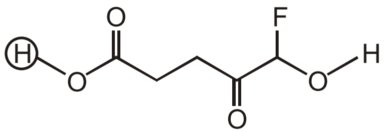
(i) Atom In both cases, the charge is on an oxygen, so this doesn't help us.

(ii) Resonance The compound on the left has resonance stabilization and the compound on the right does not. Based on this factor alone, we would say the compound on the left is more stable.

(iii) Induction The compound on the right has an inductive effect that stabilizes the charge, but the compound on the left does not have this effect. Based on this factor alone, we would say the compound on the right is more stable.

(iv) ***Orbital*** This does not help us.

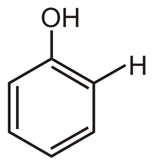
So, we have a competition of two factors. In general, resonance will beat induction, so we can say that the negative charge on the left is more stable. Therefore, the more acidic proton is the one circled here :



Solved Example

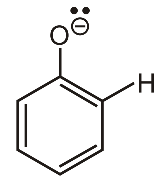
- For each compound below, two protons have been identified. In each case, determine which of the two protons is more acidic.

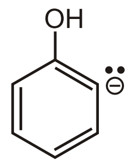
(i)



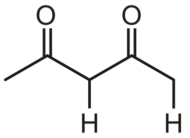
Conjugate base 1

Conjugate base 2

Ans. 
Conjugate base 1

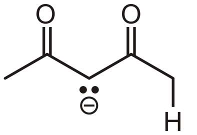

Conjugate base 2

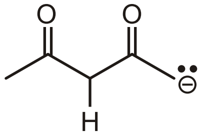
; 1 is more stable than 2

(ii) 

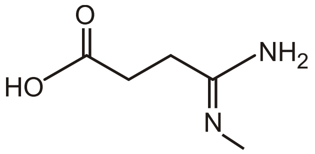
Conjugate base 1

Conjugate base 2

Ans. 
Conjugate base 1

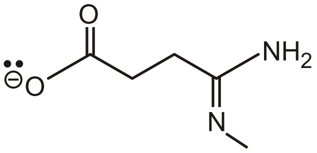

Conjugate base 2

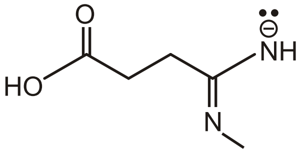
; 1 is more stable than 2

(iii) 

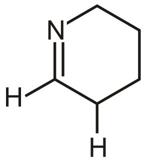
Conjugate base 1

Conjugate base 2

Ans. 
Conjugate base 1

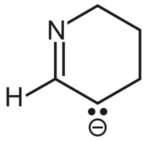

Conjugate base 2

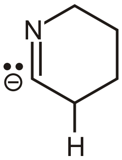
; 1 is more stable than 2

(iv) 

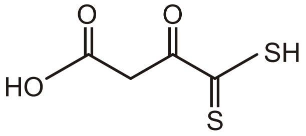
Conjugate base 1

Conjugate base 2

Ans. 
Conjugate base 1

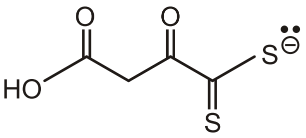

Conjugate base 2

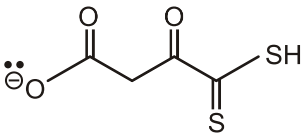
; 1 is more stable than 2

(v) 

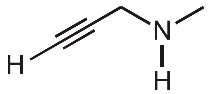
Conjugate base 1

Conjugate base 2

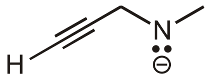
Ans. 
Conjugate base 1


Conjugate base 2

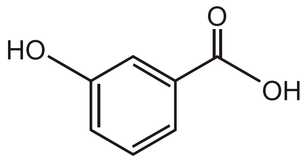
; 1 is more stable than 2

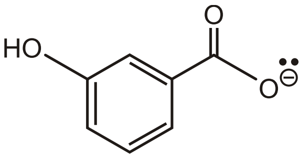
(vi)  ________ Conjugate base 1 ________ Conjugate base 2

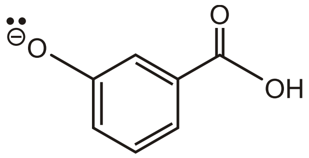
Ans. 
Conjugate base 1


Conjugate base 2

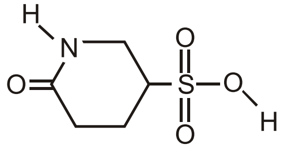
; 1 is more stable than 2

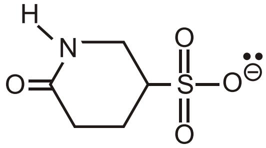
(vii)  ________ Conjugate base 1 ________ Conjugate base 2

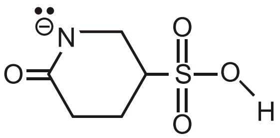
Ans. 
Conjugate base 1


Conjugate base 2

; 1 is more stable than 2

(viii)  ________ Conjugate base 1 ________ Conjugate base 2

Ans. 
Conjugate base 1


Conjugate base 2

; 1 is more stable than 2

Solved Example

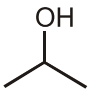
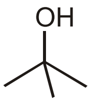
- For each pair of compounds below, predict which will be more acidic.

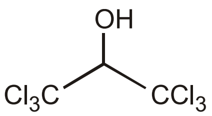
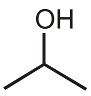
(i) HCl ; HBr

(ii) H_2O; H_2S

(iii) NH_3; CH_4

(iv)  ; 

(v)  ; 

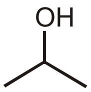
(vi)  ; 

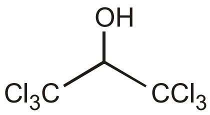
Ans. (i) HBr

(ii) H_2S

(iii) NH_3

(iv) 

(v) 

(vi) 

☑ SPECIAL TOPIC

Derivation of the Henderson-Hasselbalch equation

The Henderson-Hasselbalch equation can be derived from the expression that defines the acid dissociation constant:

$$K_a \quad \frac{[H_3O\ \ ][A\ \ ]}{[HA]}$$

Take the logarithms of both sides of the equation and remember that when expressions are multiplied, their logs are added. Thus, we obtain

$$\log K_a \quad \log[H_3O\ \ ] \quad \log\frac{[A\ \ ]}{[HA]}$$

Multiplying both sides of the equation by   1 gives us

$$\log K_a \qquad \log[H_3O\ \ ] \quad \log\frac{[A\ \ ]}{[HA]}$$

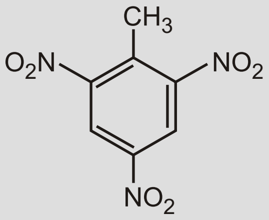
Substituting pKa for $\log K_a$, pH for $\log[H_3O\ \ ]$, and inverting the fraction (which means the sign of its log changes), we get

$$pK_a \quad pH \quad \log\frac{[HA]}{[A\ \ ]} \quad \text{or} \quad pH \quad pK_a \quad \log\frac{[HA]}{[A\ \ ]}$$

☑ SPECIAL TOPIC

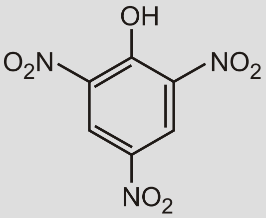
► **Picric acid is a very acidic phenol**

Electron-withdrawing effects on aromatic rings will be covered in more detail in Chapter 22 but for the time being note that electron-withdrawing groups can considerably lower the *pKas* of substituted phenols and carboxylic acids, asillustrated by picric acid.



trinitrotoluene, TNT

2, 4, 6-Trinitrophenol's more common name, picric acid, reflects the strong acidity of this compound (pK_a 0.7 compared to phenol's 10.0). Picric acid used to be used in the dyeing industry but is little used now because it is also a powerful explosive (compare its structure with that of TNT!).

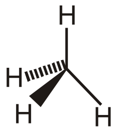


picric acid

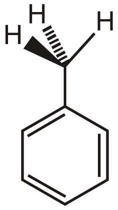
FACTOR-5 (Steric Factor)

Highly conjugated carbon acids

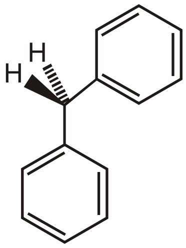
If we can delocalize the negative charge of a conjugate anion on to oxygen, the anion is more stable and consequently the acid is stronger. Even delocalization on to carbon alone is good if there is enough of it, which is why some highly delocalized hydrocarbons have remarkably low pKas for hydrocarbons. Look at this series.



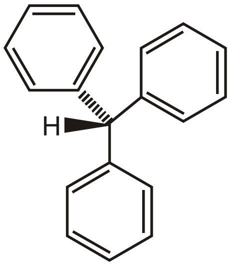
pK_a ca. 48



pK_a ca. 40

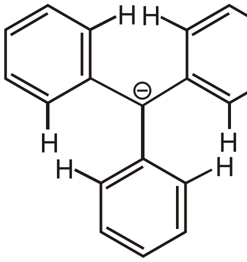


pK_a ca. 33

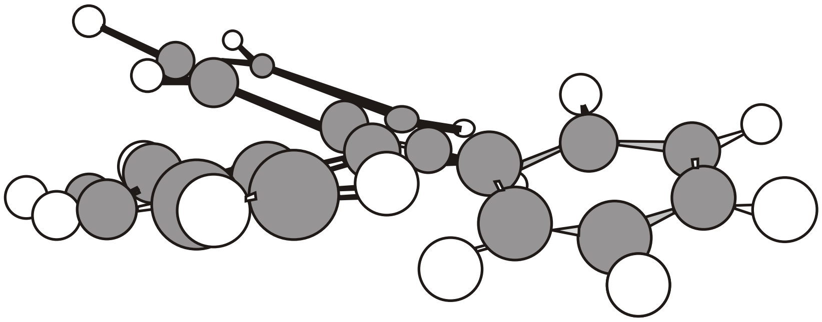


pK_a ca. 32

Increasing the number of phenyl groups decreases the pK_a—this is what we expect, since we can delocalize the charge over all the rings. Notice, however, that each successive phenyl ring has less effect on the pK_a: the first ring lowers the pK_a by 8 units, the second by 7, and the third by only 1 unit. In order to have effective delocalization, the system must be planar. Three phenyl rings cannot arrange themselves in a plane around one carbon atom because the ortho-hydrogens clash with each other (they want to occupy the same space) and the compound actually adopts a propeller shape where each phenyl ring is slightly twisted relative to the next.

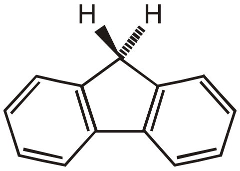


the hydrogens in the *ortho* positions try to occupy the same plane

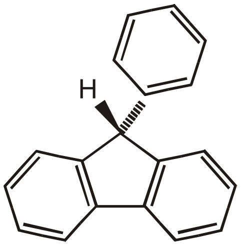


each phenyl ring is staggered relative to the next

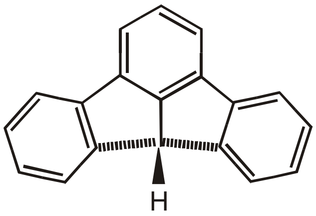
Even though complete delocalization is not possible, each phenyl ring does lower the pK_a because the sp^2 carbon on the ring is electron-withdrawing. If we force the system to be planar, as in the compounds below, the pK_a is lowered considerably.



fluorene, pK_a 22.8
in the anion, the whole
system is planar



9-phenylfluorene, pK_a 18.5
in the anion, only the two
fused fings can be planar

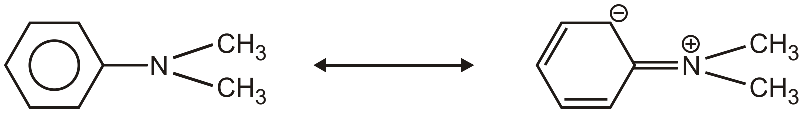


fluoradene pK_a 11
in the anion, the whole
system is planar

☑ SPECIAL TOPIC

Steric Inhibition of Resonance (S.I.R effect) :

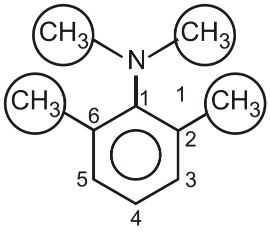
Restriction of resonance due to steric hindrance is known as S.I.R effect



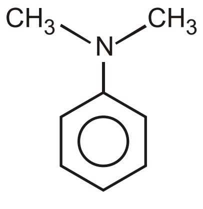
(X) (Y)

For instance in the above compound carbon atom of the Phenylring and Nitrogen are in same plane. If substituents are present in 2, 6 position, this coplanarity is inhibited and lone pair of Nitrogen is not involved in Resonance.

In compound (*P*) due to steric hindrance across Nitrogen. Bond rotation across C and Nitrogen will take place and lonepair of Nitrogen is perpendiculars to ring thereafter it will not involve in resonance with Phenylring, this is known as S.I.R. effect.



(*P*)

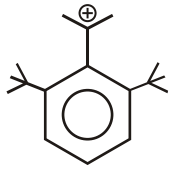


(*Q*)

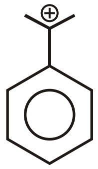
P is more basic than Q, because in (*P*) lonepair of Nitrogen is not involved in resonance.

Solved Example

- Compare carbocation stability in given pairs,



(*A*)

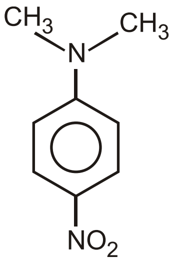


(*B*)

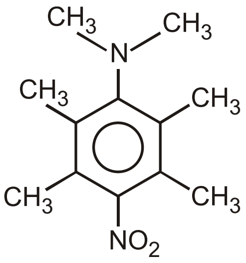
Sol. *B* is more stable than (*A*) because carbocation (*B*) is resonance stabilizer. In compound (*A*) resonance does not take place because of S.I.R. effect.

S.I.R. effect can also affect dipole of the compound for example.

Solved Example

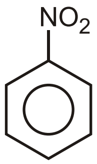


$\mu = 6.87$D

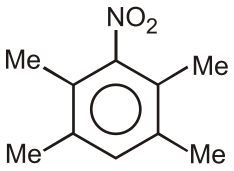


$\mu = 4.11$D

Solved Example



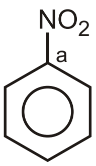
$\mu = 3.95$D



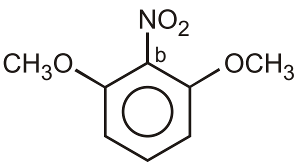
$\mu = 3.39$D

S.I.R. effect can also affect bond length

Solved Example



(*X*)



(*Y*)

Bond length of Carbon-Nitrogen are **b > a.**

Due to S.I.R. effect in (*Y*), NO_2 will not participate in resonance with phenyl ring, therefore has single bond character (b).

While in compound (*X*). Nitrogen and phenyl ring are co-planar, therefore resonance will take place.

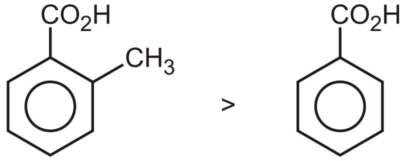
☑ SPECIAL TOPIC

Ortho and Para effect :

Classic concept of resonance, steric effect and steric inhibition of resonance have been widely used when interpreting reactivites of crowded conjugated molecules.

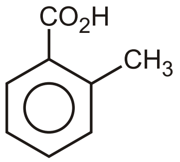
Ortho effect is used in following case

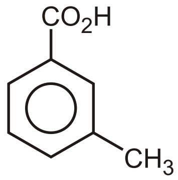
(1) Benzoic acid (ortho - substituted benzoic acid is stronger acidic than benzoic acid)

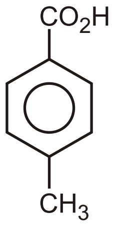


Compare acidic strength

(1)


(a)

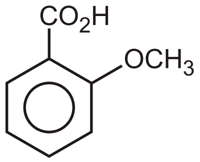

(b)

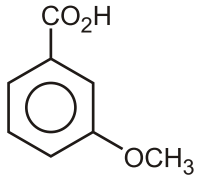

(c)

Ans. **a** > **b** > **c**

ortho effect I effect + H effect

(2)


(a)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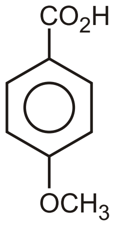
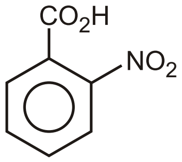
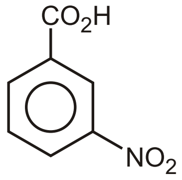

(c)

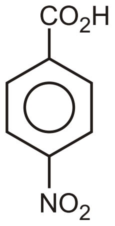
Ans. **a** > **b** > **c**

ortho effect –I effect of $-OCH_3$ + m effect of $(-OCH_3)$

(3)


(a)


(b)


(c)

Ans. **a** > **c** > **b**

ortho effect Due to –m effect of $-NO_2$, para is more acidic –I effect

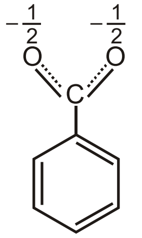
FACTOR-6 (Hydrogen Bonding) :

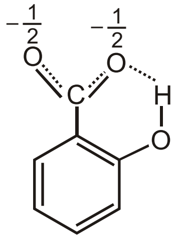
o-Hydroxybenzoic acid (salicylic acid) is far stronger than the corresponding m- and p-isomers.

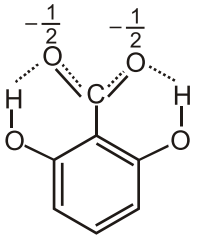
The explanation offered is hydrogen bonding; H of the o-OH group can form a hydrogen bond with the carboxyl group. The carboxylate ions of o-hydroxybenzoic acids are stabilised by intramolecular hydrogen bonding and support for this is given by the following order of acidic strength :

2, 6-di-OH benzoic acid (pK_a 2.30) > 2-OH benzoic acid(pK_a 2.98) > benzoic acid (pK_a 4.17)

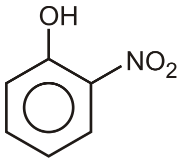
It can be seen that two hydrogen bonds would be expected to bring about more stabilisation than one hydrogen bond.



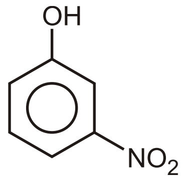




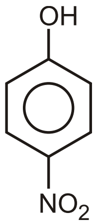
Acidic strength comparison of nitrophenol :



(a)
ortho-nitrophenol



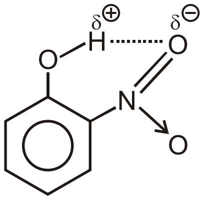
(b)
meta-nitrophenol



(c)
para-nitrophenol

Acidic strength : c > a > b

Reason : Intramolecular H-bonding in orthonitrophenol decreases it's acidic strength a bit.

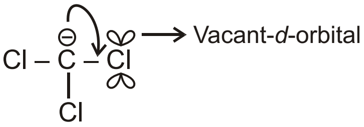


FACTOR-7 (*d*-orbital Resonance) :

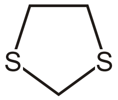
Due to *d*-orbital resonance the stability of conjugate base increases which results in the increase of acidic strength.

(1) Acidic strength : $CHCl_3 > CHF_3$

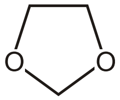
Explanation :



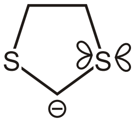
(2) Acidic strength :



>



Explanation :



is *d*-orbital resonance stabilised anion.

☑ SPECIAL TOPIC

► Acids as preservatives

Acetic acid is used as a preservative in many foods, for example, pickles, mayonnaise, bread and fish products, because it prevents bacteria and fungi growing. However, its fungicidal nature is not due to any lowering of the pH of the foodstuff. In fact, it is the *undissociated* acid that acts as a bactericide and a fungicide in concentrations as low as 0.1–0.3%. Besides, such a low concentration has little effect on the pH of the foodstuff anyway.

Although acetic acid can be added directly to a foodstuff (disguised as E260), it is more common to add vinegar which contains between 10 and 15% acetic acid. This makes the product more 'natural' since it avoids the nasty 'E numbers'. Actually, vinegar has also replaced other acids used as preservatives, such as propionic (propanoic) acid (E280) and its salts (E281, E282 and E283).

FACTOR-8 (Aromatic and Non-aromatic) :

Aromatic nature of conjugate base increases it's stability which results in the increase acidic strength.

(1) Acidic strength :

Explanation :

FACTOR-9 (Combined effect of resonance, hyperconjugation and inductive effect) :

Remember the 8 factors, and what order they come in :

1. Atom
2. Resonance
3. Induction
4. Orbital
5. Steric effects
6. Hydrogen bond
7. d-orbital resonance
8. Aromaticity

☞ If you have trouble remembering the order, try remembering this acronym: **ARIOSHDA.**

Acid Base Equilibrium : An acids pKa depends on the stability of its conjugate base

$$HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^{\ominus} \qquad Ka \quad 10^{7}$$

$$CH_3COOH + H_2O \rightleftharpoons H_3O^{\oplus} + CH_3COO^{\ominus} \qquad Ka \quad 1.74 \quad 10^{\ 5}$$

The stronger the acid HA, the weaker its conjugate base $A^{\ominus}$

The stronger the base A , the weaker its conjugate acid HA

$$\underset{\boxed{\text{stronger acid}}}{RC\equiv CH} + \underset{\boxed{\text{stronger base}}}{\underset{\text{amide anion}}{{}^{-}NH_2}} \rightleftharpoons \underset{\boxed{\text{weaker base}}}{\underset{\text{acetylide anion}}{RC\equiv C^{-}}} + \underset{\boxed{\text{weaker acid}}}{NH_3}$$

$$\underset{\boxed{\text{weaker acid}}}{RC\equiv CH} + \underset{\boxed{\text{weaker base}}}{\underset{\text{hydroxide anion}}{HO^{-}}} \rightleftharpoons \underset{\boxed{\text{stronger base}}}{\underset{\text{acetylide anion}}{RC\equiv C^{-}}} + \underset{\boxed{\text{stronger acid}}}{H_2O}$$

- **Reactions with metals and alkalies:**

$$2R-COOH + 2Na \qquad \underset{\text{sodium carboxylate}}{2RCOONa} \quad H_2$$

$$R-COOH + NaOH \qquad R-COONa + H_2O$$

$$R-COOH + NaHCO_3 \qquad RCOONa + H_2O + CO_2$$

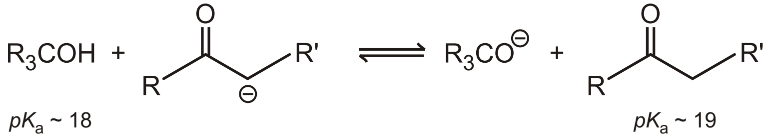
Solved Example

- Predict the direction of the equillibrium of the following :

(a) $NH_3 + {}^{\ominus}OH \rightleftharpoons {}^{\ominus}NH_2 + H_2O$ Keq – $10^{17.26}$ (left side favoured)
pK_a 33 pK_a 15.74

(b) $CH_3CO_2H + CO_3^{\ominus} \rightleftharpoons CH_3CO_2^{\ominus} + HCO_3^{\ominus}$ Keq ~ $10^{5.33}$ (right side favoured)
pK_a ~ 5 pK_a 10.33

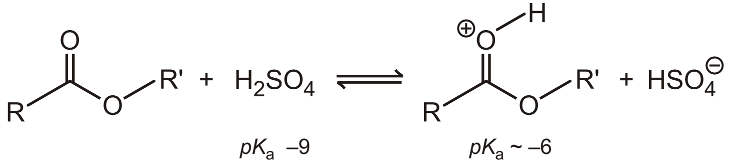
(c) $RCO_2H + R_2NH \rightleftharpoons RCO_2^{\ominus} + R_2NH_2^{\oplus}$ Keq ~ 10^6 (right side favoured)
pK_a ~ 5 pK_a 11

(d) 

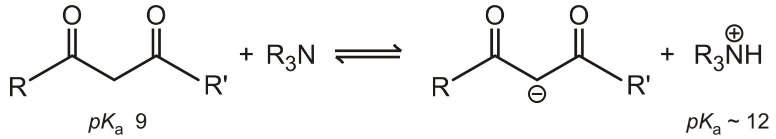
Keq ~ 10 (right side favoured)

(e) $NaF + HCl \rightleftharpoons NaCl + HF$ Keq ~ $10^{9.22}$ (right side favoured)
pK_a ~ 6 pK_a 3.22

(f) $ArOH + RNH_2 \rightleftharpoons Ar\overset{\ominus}{O} + \overset{\oplus}{R}NH_3$ Keq ~ 1 (niether side favoured)
pK_a 10 pK_a 10

(g) 

Keq ~ 10^3 (right side favoured)

(h) 

Keq ~ 10^3 (right side favoured)

(i) $R{-}C{\equiv}C^{\ominus} + RCH_2OH \rightleftharpoons R{-}C{\equiv}C{-}H + RCH_2O^{\ominus}$ Keq ~ 10^9 (right side favoured)
pK_a 16 pK_a 25

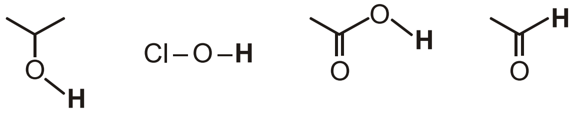
(j) $CH_3Li + (CH_3)_2C{=}CH_2 \rightleftharpoons CH_4 + (CH_3)_2C{=}\overset{\ominus}{C}H\ Li^{\oplus}$ Keq ~ 10^6 (right side favoured)
pK_a 44 pK_a 50

Solved Example

- Compare the acidic strength of the following :

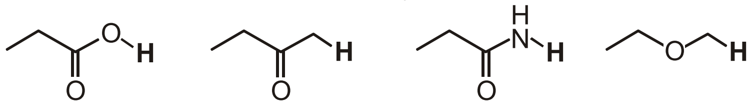
(a) CH_3CH_2-**H** CH_3O-**H** **H**$-F$ CH_3CH_2NH-**H** (1 = least acidic, 4 = most acidic)
1 3 4 2

(b) **H**$-Cl$ **H**$-F$ **H**$-Br$ **H**$-I$ (1 = least acidic, 4 = most acidic)
2 1 3 4

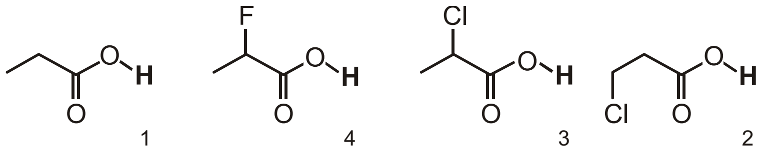
(c) 

(1 = least acidic, 4 = most acidic)
3 2 4 1

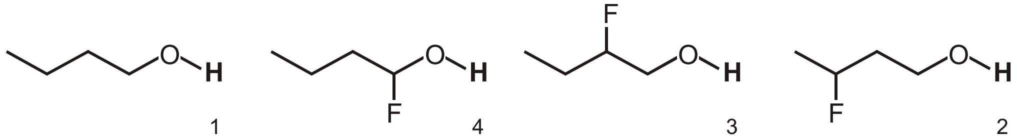
(ClOH less acidic than the alcohol since the conjugate base Cl-O- will have neighbouring lone pairs and therefore be less stable than RO-)

(d) 

(1 = least acidic, 4 = most acidic)
4 2 3 1

(e)  (1 = least acidic, 4 = most acidic)

(f)  (1 = least acidic, 4 = most acidic)

(g) 

(1 = least acidic, 4 = most acidic)

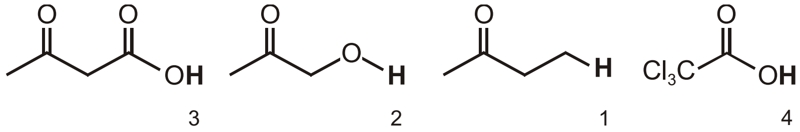
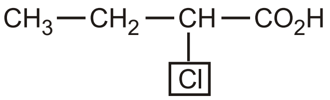
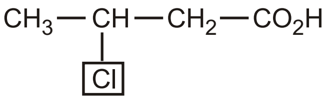
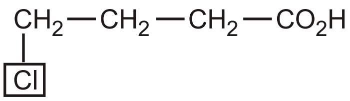
(h)  (1 = least acidic, **4** = most acidic)

Table 1 : Inductive effects of substituent groups of some substituted acetic acids

Acid	pK_a	I effect of the substitutent
$\boxed{H}-CH_2-CO_2H$	4.75	H reference point
$\boxed{CH_3}-CH_2-CO_2H$	4.90	+I
$\boxed{CH_3-O}-CH_2-CO_2H$	4.30	−I
$\boxed{I}-CH_2-CO_2H$	3.00	−I
$\boxed{Br}-CH_2-CO_2H$	2.90	−I
$\boxed{Cl}-CH_2-CO_2H$	2.80	−I
$\boxed{(CH_3)_3N^+}-CH_2-CO_2H$	1.80	−I

Here, —I effect Acid strength

Table 2 : Position of the substituent and inductive effect

Acid	pK_a	I effect of the substitutent
 $CH_3-CH_2-\underset{\boxed{Cl}}{CH}-CO_2H$	2.84	−I
 $CH_3-\underset{\boxed{Cl}}{CH}-CH_2-CO_2H$	4.06	−I
 $\underset{\boxed{Cl}}{CH_2}-CH_2-CH_2-CO_2H$	4.52	−I

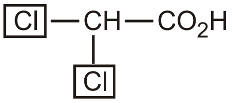
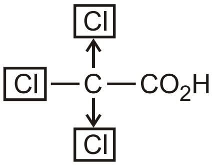
Substituent at the position exerts the maximum effect.

Table 3 : Distance between the groups and the extent of inductive effect.

Acid	*pK*$_a$	I effect of the substitutent
$\boxed{HO_2C}-CO_2H$	1.23	–I
$\boxed{HO_2C}-CH_2-CO_2H$	2.88	–I
$\boxed{HO_2C}-CH_2-CH_2-CO_2H$	4.19	–I

Inductive effect is distance dependent; as distance increases, inductive effect decreases.

Table 4 : Additive nature of inductive effect

Acid	*pK*$_a$	I effect of the substitutent
$\boxed{H}-CH_2-CO_2H$	4.75	H = reference point
$\boxed{Cl}-CH_2-CO_2H$	2.86	One (–I) effect
 $\boxed{Cl}-\underset{\underset{\boxed{Cl}}{\mid}}{CH}-CO_2H$	1.25	Two (–I) effect
 $\boxed{Cl}-\underset{\underset{\boxed{Cl}}{\downarrow}}{\overset{\overset{\boxed{Cl}}{\uparrow}}{C}}-CO_2H$	0.65	Three (–I) effect

Inductive effect is an additive effect.

Table 5 : Aromatic acids and inductive effect

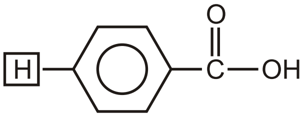
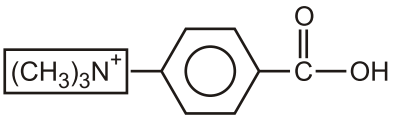
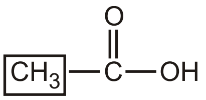
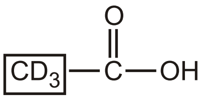
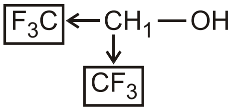
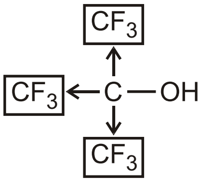
Acid	*pK*$_a$	I effect of the substitutent
	4.2	H = reference point
	3.9	–I effect

Table 6 : Isotopic substituents and inductive effect

Acid	*pK*$_a$	I effect of the substitutent
 $\boxed{CH_3}-\overset{\overset{O}{\|}}{C}-OH$	4.75	+I
 $\boxed{CD_3}-\overset{\overset{O}{\|}}{C}-OH$	4.6	+I

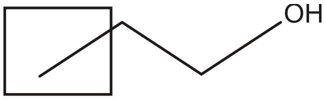
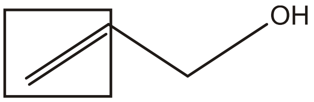
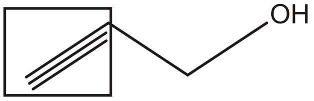
+I effect of deuterium is stronger than that of hydrogen. $+I(-CD_3 \quad -CH_3)$

Table 7 : Electron withdrawing groups and inductive effects

Acid	*pK*$_a$	I effect of the substitutent
$\boxed{CH_3}-OH$	15.5	+I
$\boxed{F_3C}\leftarrow CH_2-OH$	12.4	–I
 $\boxed{F_3C}\leftarrow \underset{\underset{\boxed{CF_3}}{\downarrow}}{CH_1}-OH$	9.3	–I
 $\boxed{CF_3}\leftarrow \overset{\overset{\boxed{CF_3}}{\uparrow}}{\underset{\underset{\boxed{CF_3}}{\downarrow}}{C}}-OH$	5.4	–I

Electron withdrawing groups lower the *pK*$_a$ of alcohols.

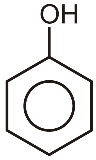
Table 8 : Hybridization state of the carbon atom in the substituent and inductive effect

Acid	*pK*$_a$	I effect of the substitutent
	16	+I
	15.5	–I effect
	13.5	–I effect

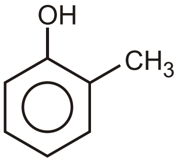
Solved Example

- Compare acidic strength :

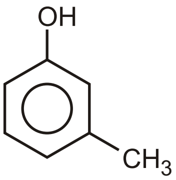
(a)



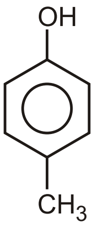
(b)



(c)

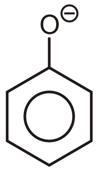


(d)

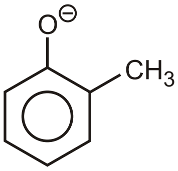


Ans. a > c > d > b

Exp. (a)

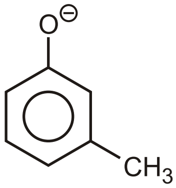


(b)



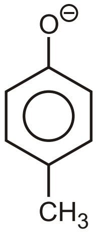
De-stabilized by +H
and
+I and (+I) is maximum

(c)



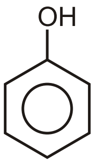
De-stabilized by +I only

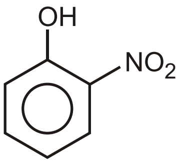
(d)

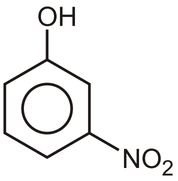


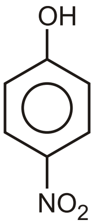
De-stabilized by +H
and
+I and (+I) is minimum

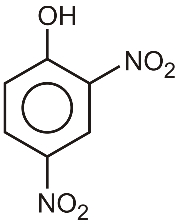
- Compare the acidic strength :

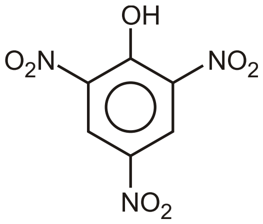
(a)


(b)


(c)


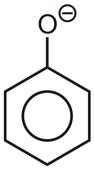
(d)


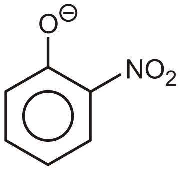
(e)


(f)


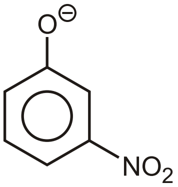
Sol. f > e > d > b > c > a

Due to intramolecular hydrogen bonding ortho isomer (b) is less acidic than Para isomer(d).

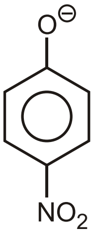
Exp. (a)


(b)


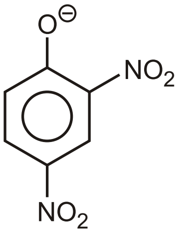
Stabilised by –M and –I effect of NO_2

(c)


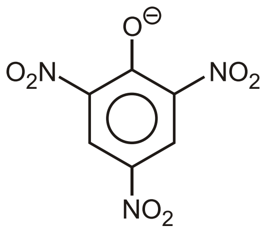
Stabilised by –I effect only

(d)


Stabilised by –M and –I effect of NO_2

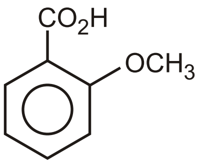
(e)


Stabilised by –M and –I effect of two NO_2 groups

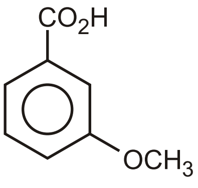
(f)


Stabilised by –M and –I effect of three NO_2 groups

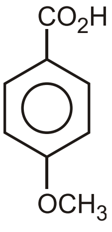
- Compare acidic strength :



(a)



(b)

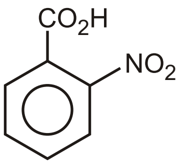


(c)

Ans. a > b > c

ortho effect – I effect of $–OCH_3$ + m effect of $(–OCH_3)$

- Compare acidic strength :

(a)


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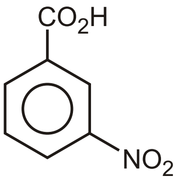

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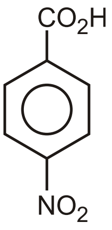


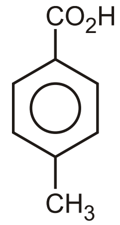
Ans. a > c > b

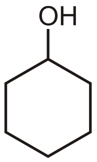
ortho effect

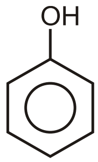
Due to –m effect of $-NO_2$, para is more acidic

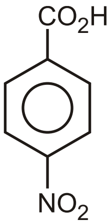
I effect

- Correct order of acidic strength of given compounds will be?


(I)

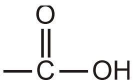

(II)


(III)

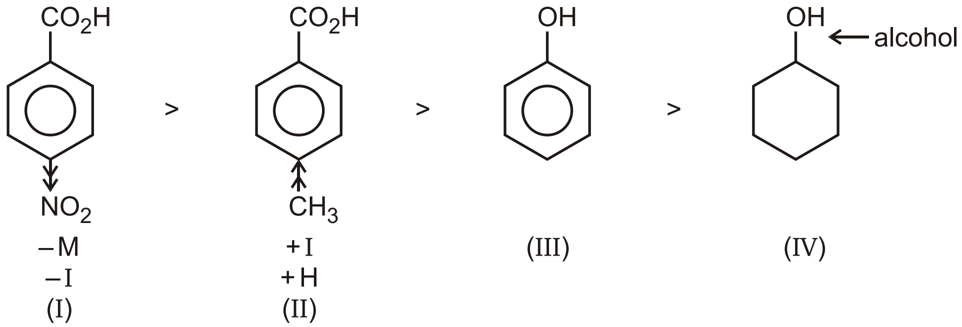

(IV)

(A) IV II I III
(B) IV III I II
(C) IV I II III
(D) IV I III II

Ans. (D)

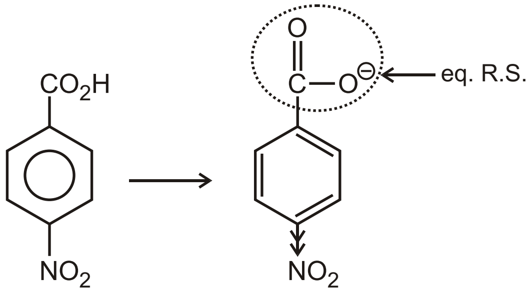
Sol. **Strategy** (I) 
$-\overset{O}{\overset{\|}{C}}-OH$ group is always more acidic than alcohol and phenol

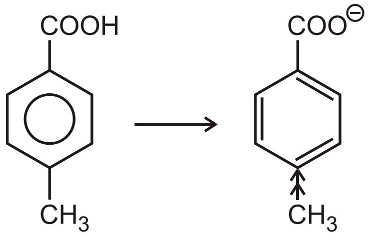
(II) Always check **Acidic strength by stability of conjugate base**

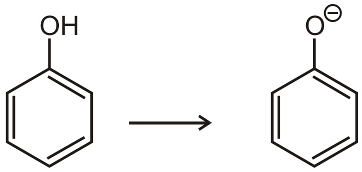


Always check Acidic strength by stability of conjugate base

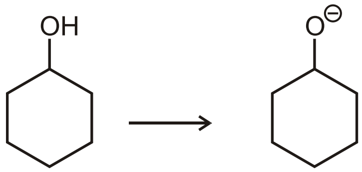
Order of acidic strength (I > II > III > IV)

(I) 

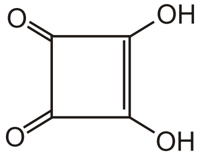
(II) 

(III) 

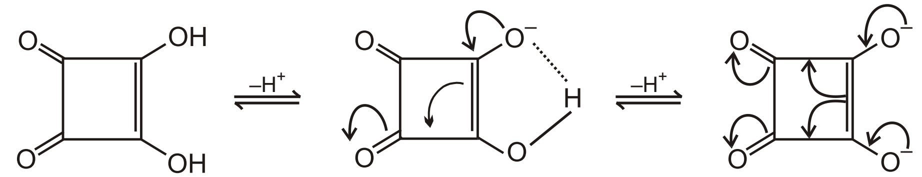
(Reso. stabalised)

(IV) 

(Not Reso.
stabalised)

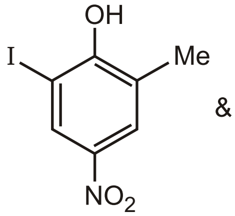
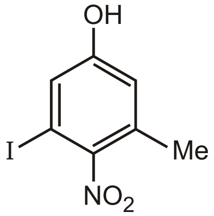
- Squaric acid  is a diprotic acid with both protons being more acidic than acetic acid. In the di-anion after the loss of both protons all of the C-C bonds are the same length as well as all of the C-O bonds. Provide a explanation for these observations.

Sol.

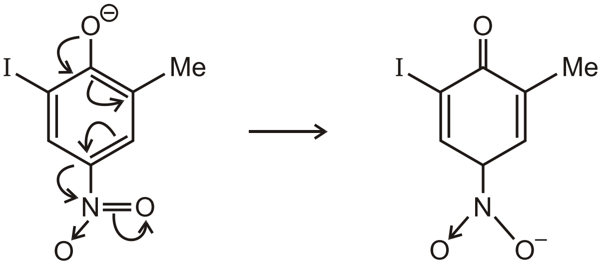


R-stablized & intra H-bonding

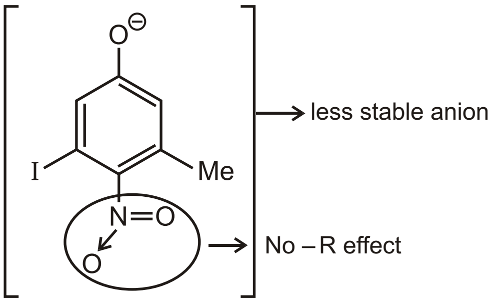
4 Eq. R.S.

- Among  &  which is more acidic & why? Explain through canonical forms.

Sol.

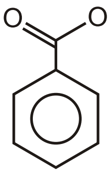


stable anion

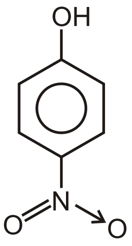


Out of plane

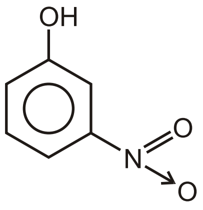
- In the following compound



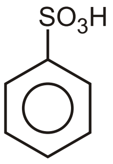
(I)



(II)



(III)



(IV)

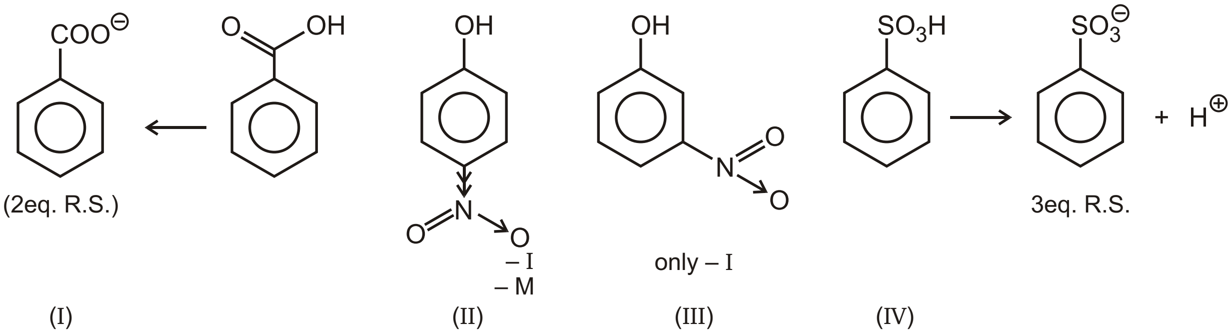
the decreasing order of acidic strength :

(A) I II IV III (B) II I IV III

(C) II IV I III (D) IV I II III

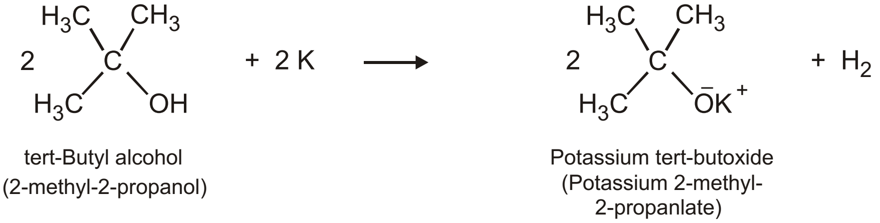
Ans. (D)

Sol.



REACTION OF ACTIVE METAL

Because alcohols are weak acids, they don't react with weak bases, such as amines or bicarbonate ion, and they react to only a limited extent with metal hydroxides, such as NaOH. Alcohols do, however, react with alkali metals and with strong bases such as sodium hydride (NaH), sodium amide ($NaNH_2$), and Grignard reagents (RMgX). Alkoxides are themselves bases that are frequently used as reagents in organic chemistry. They are named systematically by adding the -ate suffix to the name of the alcohol. Methanol becomes methanolate, for instance.



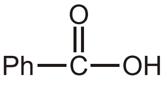
CH_3OH NaH CH_3O Na H_2

Methanol Sodium methoxide (sodium methanolate)

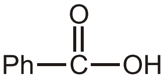
CH_3CH_2OH $NaNH_2$ CH_3CH_2O Na NH_3

Ethanol Sodium ethoxide (sodium ethanolate)

Solved Example



$Ph-\overset{\overset{O}{\|}}{C}-OH$ $NaNH_2$ (*A*) gas

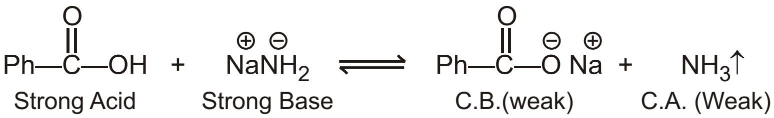


$Ph-\overset{\overset{O}{\|}}{C}-OH$ NaH (*B*) gas

(*A*) & (*B*) are molecular mass of gas so the value of *A* *B* 10

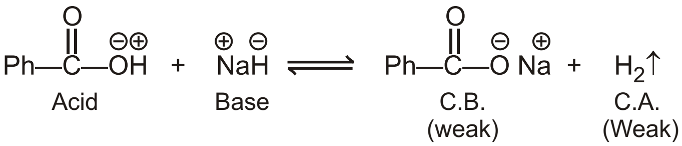
Ans. 9

Sol. **Strategy** Acid - Base reaction always **favour** the formation of **weaker acid and weaker base**



$$\underset{\text{Strong Acid}}{Ph-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Strong Base}}{\overset{\oplus\ \ominus}{NaNH_2}} \rightleftharpoons \underset{\text{C.B.(weak)}}{Ph-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}\ \overset{\oplus}{Na}} + \underset{\text{C.A. (Weak)}}{NH_3\uparrow}$$

(A) NH_3 gas



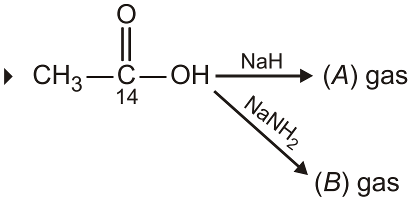
$$Ph-\overset{O}{\overset{\|}{C}}-\overset{\ominus\oplus}{OH} + \overset{\oplus\ \ominus}{NaH} \rightleftharpoons Ph-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\,\overset{\oplus}{Na} + H_2\uparrow$$

(B) H_2 gas

		Mol. wt.
(A)	NH_3	17
(B)	H_2	2

A B 19 A B 10 9

Solved Example

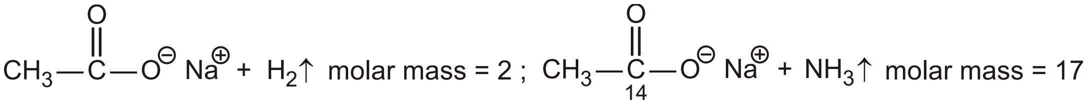


$$CH_3-\underset{14}{\overset{O}{\overset{\|}{C}}}-OH \xrightarrow{NaH} (A)\text{ gas};\quad \xrightarrow{NaNH_2} (B)\text{ gas}$$

Sum of molar mass of (A B) is suppose (X) so the value of (X 15) is :

Ans. A H_2 ; B NH_3 ; $x = 2 + 17 - 15 = 4$

Sol.



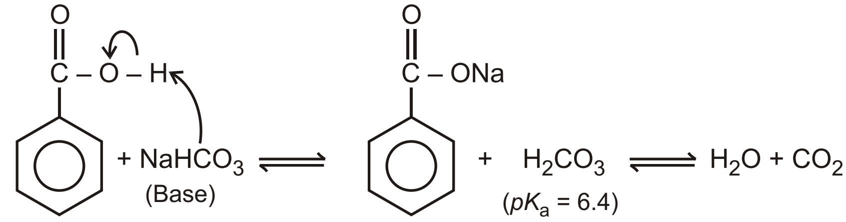
$$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}\,Na^{\oplus} + H_2\uparrow \text{ molar mass} = 2\ ;\ CH_3-\underset{14}{\overset{O}{\overset{\|}{C}}}-O^{\ominus}\,Na^{\oplus} + NH_3\uparrow \text{ molar mass} = 17$$

A B 19 ; 19 – 15 = 4

Separation of binary mixture

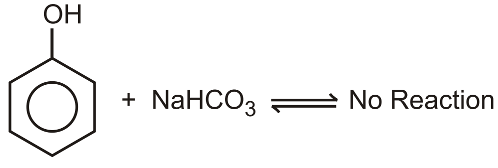
$NaHCO_3$ is used to separate a binary Mixture of Phenol and benzoic acid. Phenol will not react with $NaHCO_3$ because of weak acidic hydrogen of Phenol.

(1)

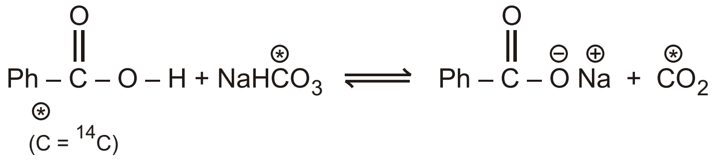


(Acid)
($pK_a = 4.2$)

(2)

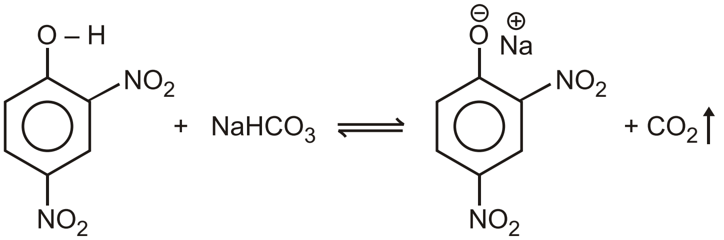


(Phenol)
(pH = 10)

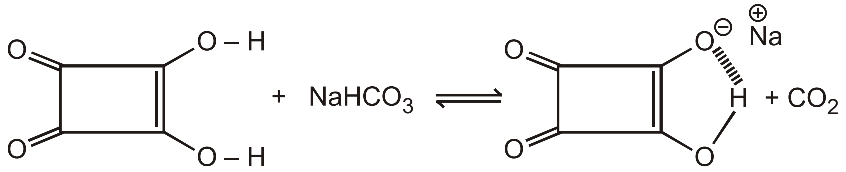
(3) 

$$\text{Ph}-\overset{\overset{\displaystyle O}{\|}}{C}-O-H+\text{NaH}\overset{\circledast}{C}O_3 \rightleftharpoons \text{Ph}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}\,\overset{\oplus}{Na}+\overset{\circledast}{C}O_2$$

$(\overset{\circledast}{C} = {}^{14}C)$

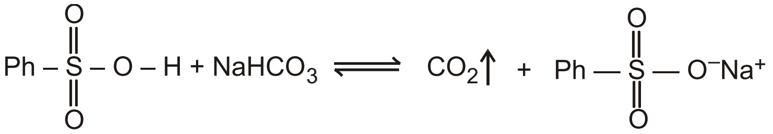
(4) 

(5) Squaric acid will also react with $NaHCO_3$ because both acidic hydrogens are more acidic than carboxylic acid.

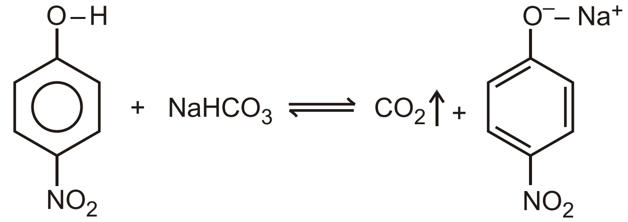


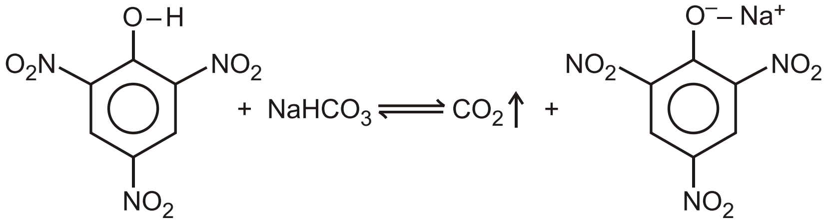
Solved Example

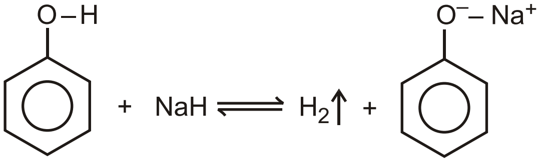
- Which gas is evolved in each reactions?

(1) 

$$\text{Ph}-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-O-H+NaHCO_3 \rightleftharpoons CO_2\uparrow+\text{Ph}-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-O^-Na^+$$

(2) 

(3) 

(4) 

Separation of cyclohexanamine and cyclohexanol by an extraction procedure :

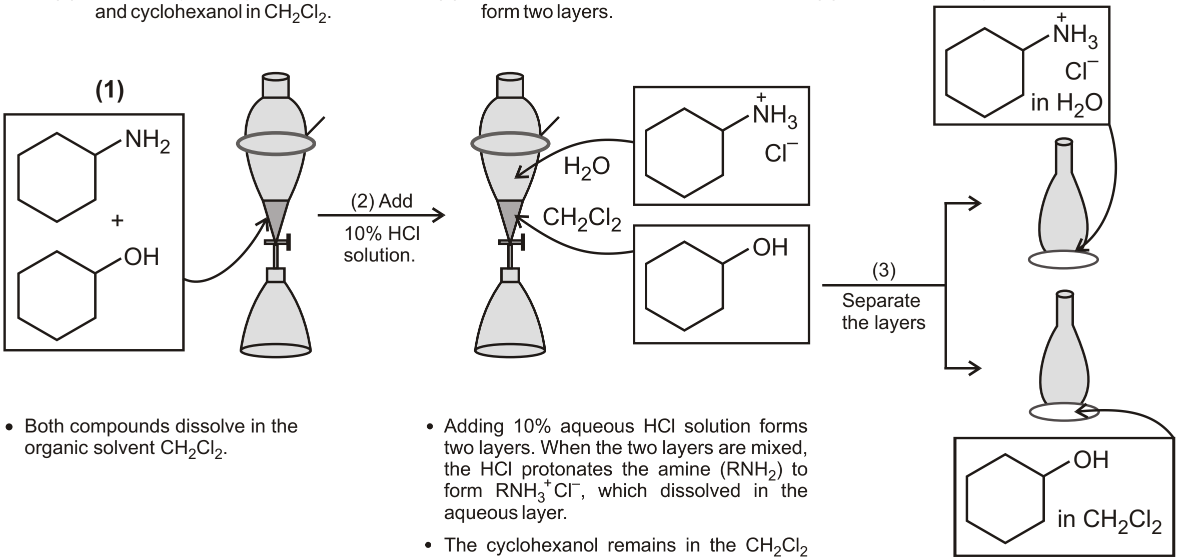
Because amines are protonated by aqueous acid, they can be separated from other organic compounds by extraction using a separatory funnel. **Extraction separates compounds based on solubility differences.** When an amine is protonated by aqueous acid, its solubility properties change.

For example, when cyclohexylamine is treated with aqueous HCl, it is protonated, forming an ammonium salt. Because the ammonium salt is ionic, it is soluble in water, but insoluble in organic solvents. A similar acid-base reaction does not occur with other organic compounds like alcohols, which are much less basic.

Step (1) Dissolve cyclohexylamine and cyclohexanol in CH_2Cl_2.

Step (2) Add 10% HCl solution to form two layers.

Step (3) Separate the layers.



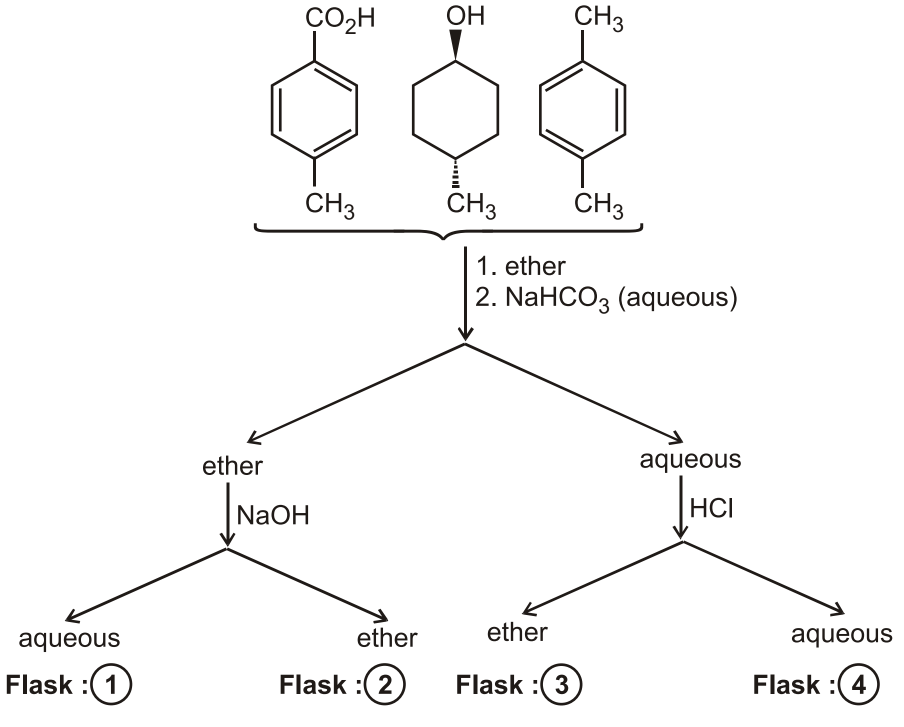
- Both compounds dissolve in the organic solvent CH_2Cl_2.

- Adding 10% aqueous HCl solution forms two layers. When the two layers are mixed, the HCl protonates the amine (RNH_2) to form $RNH_3^+Cl^-$, which dissolved in the aqueous layer.
- The cyclohexanol remains in the CH_2Cl_2 layer.

- Draining the lower layer out the bottom stopcock separates the two layers and the separation process is complete.
- Cyclohexanol (dissolved in CH_2Cl_2) is in one flask. The ammonium salt, $RNH_3^+Cl^-$ (dissolved in water), is in another flask.

Solved Example

SCHEME/PATTERN

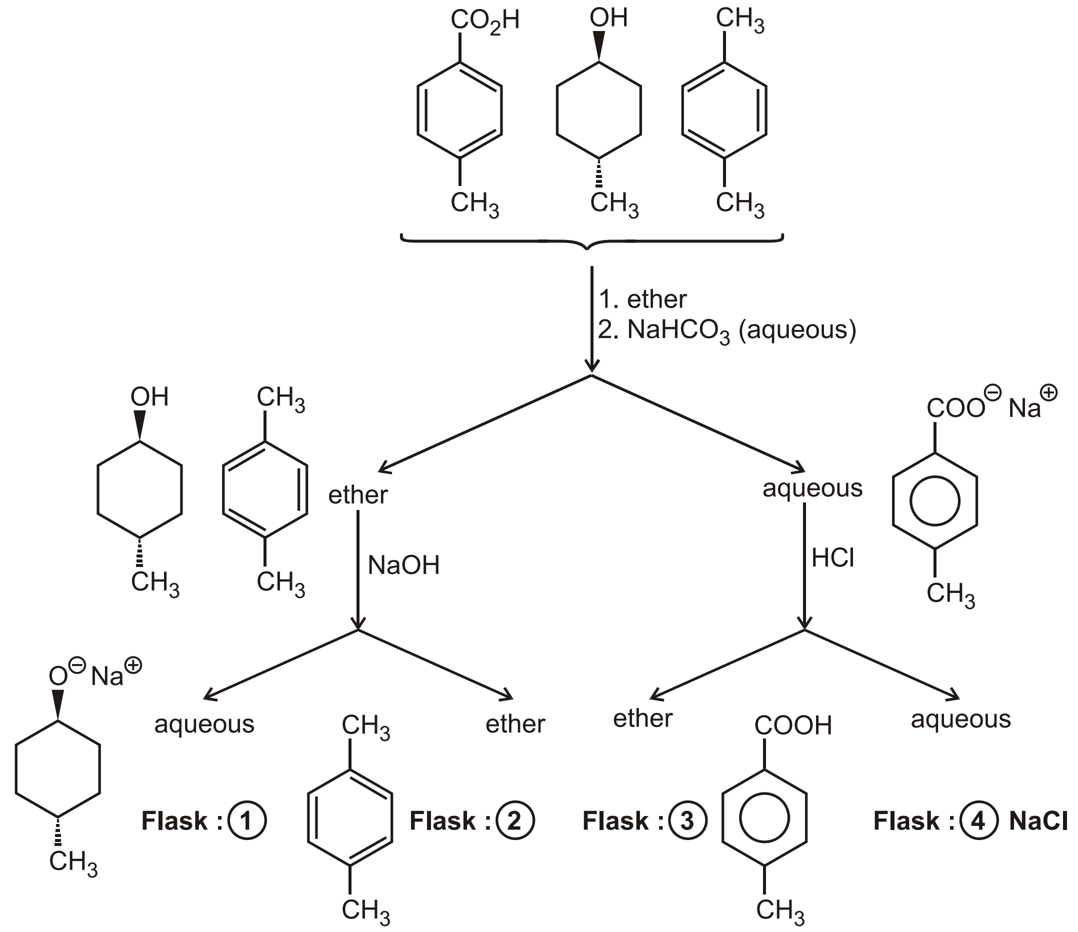


Which flask contains the 4-methyl benzoic acid?

(A) 1 (B) 2 (C) 3 (D) 4

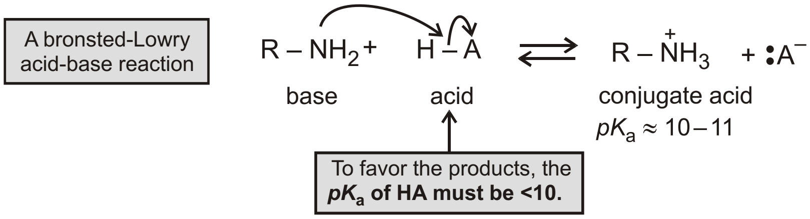
Sol.

SCHEME



BASIC STRENGTH COMPARISON

Amines as Bases : Amines react as Bases with a variety of organic and inorganic acids.



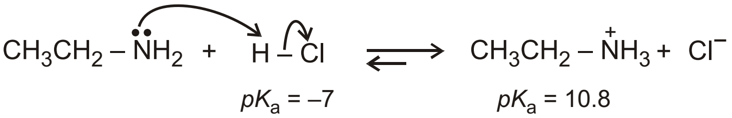
A bronsted-Lowry acid-base reaction

$$R-NH_2 + H-A \rightleftharpoons R-\overset{+}{N}H_3 + :A^-$$

base acid conjugate acid

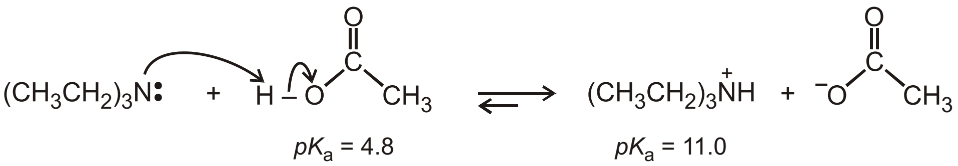
$pK_a \approx 10-11$

To favor the products, the ***pK*$_a$ of HA must be <10.**



$$CH_3CH_2-\ddot{N}H_2 + H-Cl \rightleftharpoons CH_3CH_2-\overset{+}{N}H_3 + Cl^-$$

$pK_a = -7$ $pK_a = 10.8$



$$(CH_3CH_2)_3N: + H-O-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons (CH_3CH_2)_3\overset{+}{N}H + {}^-O-\overset{O}{\overset{\|}{C}}-CH_3$$

$pK_a = 4.8$ $pK_a = 11.0$

Equilibrium favours the products

Table 1 : State of hybridization and base strength

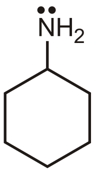
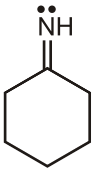
Base		Base strength	Comment
(a)		↓ Decreases	Lone pair on *sp*^{3} hybridized atom is more protonating
(b)			

Table 2 : Carbon chain length and base strength

Base		Base strength	Comment
(a)	$CH_3 — NH_2$	↓ increase	I effect increases with the length alkyl chain and so does base strength.
(b)	$CH_3 — CH_2 — CH_2 — NH_2$		

Table 3 : Center atom and base strength

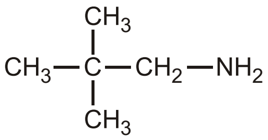
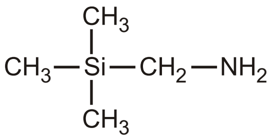
Base		Base strength	Comment
(a)	 $CH_3—C(CH_3)_2—CH_2—NH_2$	↓ increase	Here, the central atom silicon being more electro-positive than carbon, pushes the electron density more.
(b)	 $CH_3—Si(CH_3)_2—CH_2—NH_2$		

Table 4 : Extent of inductive effect and base strength

Base		Base strength	Comment
(a)	$Cl_3C — CH_2 — NH_2$	↓ increase	I effect (1/basic strength) I effect of Cl_3C group in less effective in (b) than in (a).
(b)	$Cl_3C — CH_2 — CH_2 — NH_2$		

Table 5 : Inductive effect and base strength

Base		Base strength	Comment
(a)	$F_3C — CH_2 — NH_2$	↓ increase	I effect of $–CF_3$ $–CCl_3$
(b)	$Cl_3C — CH_2 — NH_2$		

Table 6. Delocalization of lone pair and base strength

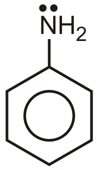
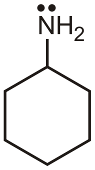
Base		Base strength	Comment
(a)	 Aniline	↓ Increase	Lone pair of electrons on nitrogen in aniline is delocalized
(b)	 Cyclohexylamine		

Table 7 : Delocalization of negative charge and base strength

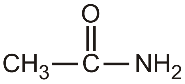
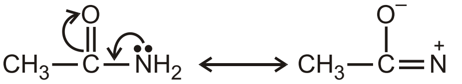
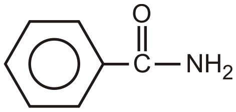
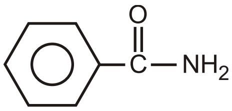
Base		Base strength	Comment
(a)	 $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ Acetamide	↓ Increase	 Effective delocalization of negative charge on oxygen.
(b)	 Benzamide		 −I effect decreases basic strength

Table 8 : Basic strength of pyridine and pyrrole

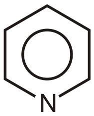
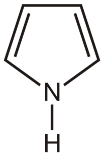
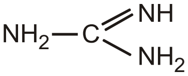
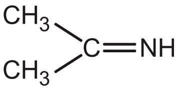
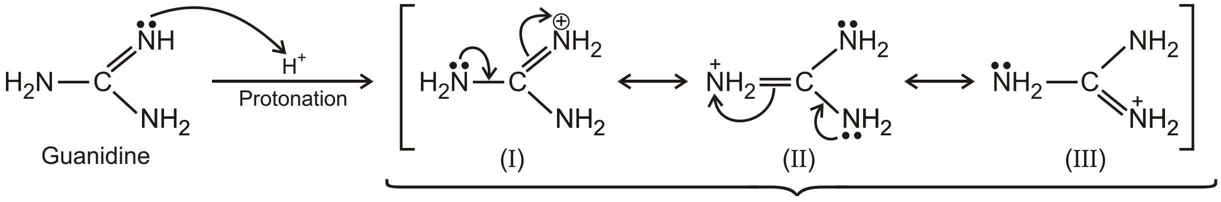
Base		Base strength	Comment
(a)	 Pyridine	↓ Decreases	Lone pair of nitrogen is delocalized in pyrrole because it is conjugated to the *p* bond. Therefore, it is not available for protonation.
(b)	 Pyrrole		

Table 9 : Basic strength of guanidine and imine

Base		Base strength	Comment
(a)	 Guanidine	↓ Decreases	Guanidine is the strongest organic nitrogen base. On protonation, the positive charge can be delocalized over three nitrogen atoms to give a very stable cation.
(b)	 Isopropyl		



All three have equal contribution in resonance hybrid. This makes Guanidine the strongest base.

Table 10 : Amine inversion and base strength

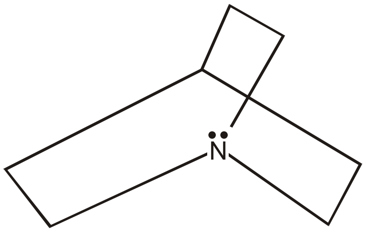
Base		Base strength	Comment
(a)	 Quinuclidene	Decreases ↓	Quinuclidene will not undergo amine inversion.
(b)	$Et_3\ddot{N}$ Triethylamine		

Table 11 : Bredt's rule and base strength

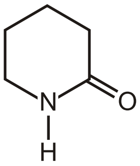
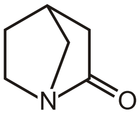
Base		Base strength	Comment
(a)		Increase ↓	Lone pair is not delocalized in (b) because it violates Bredt's rule.
(b)			

Table 12 : Mesomeric effect and base strength

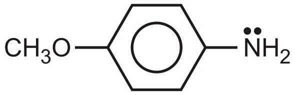
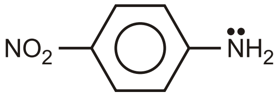
Base		Base strength	Comment
(a)		Decreases ↓	*M* basic strength *M* $\frac{1}{\text{basic strength}}$
(b)			

Table 13 : Delocalization of lone pair and base strength

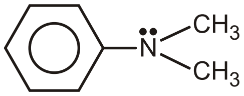
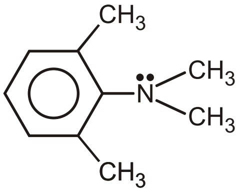
Base		Base strength	Comment
(a)		↓ Increase	Lone pair of electrons is not delocalized in (b) due to SIR and so it is more basic.
(b)			

Table 14 : Ortho effect and base strength

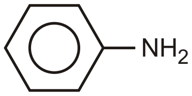
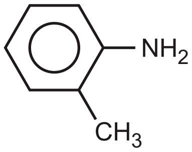
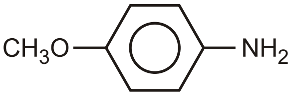
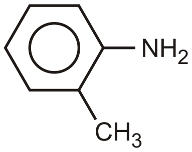
Base		Base strength	Comment
(a)		↓ Decreases	Base strength decreases due to ortho effect.
(b)			

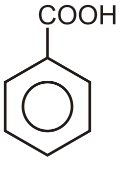
Table 15 : Para effect and base strength

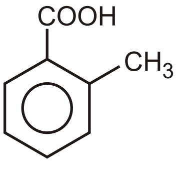
Base		Base strength	Comment
(a)		↓ Decreases	Base strength decreases due to para effect.
(b)			

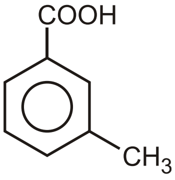
EXERCISE

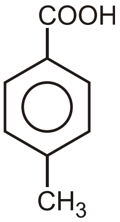
SINGLE CHOICE QUESTIONS

1. Which of the following is most acidic in nature.

(I) 

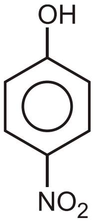
(II) 

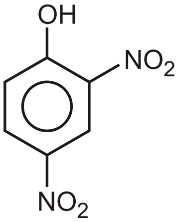
(III) 

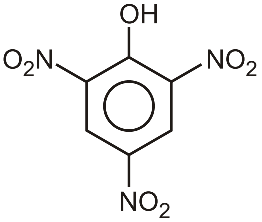
(IV) 

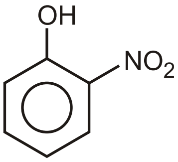
(A) I (B) II (C) III (D) IV

2. Which of the following substituted phenol is most acidic in nature?

(I) 

(II) 

(III) 

(IV) 

(A) I (B) II (C) III (D) IV

3. Which of the following substituted carboxylic acid has the highest Ka value?

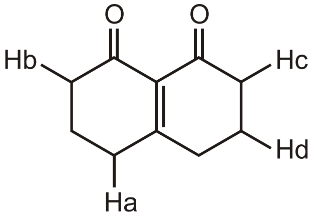
(A) -chlorobutyric acid

(B) -chlorobutyric acid

(C) -fluorobutyric acid

(D) -fluorobutyric acid

4. Which of the following indicated H-atom is most acidic in nature.



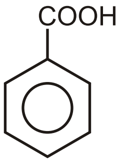
(A) Ha

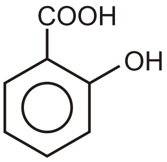
(B) Hb

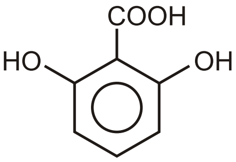
(C) Hc

(D) Hd

5. Write the correct order for the acidic strength of the following?

(a) 

(b) 

(c) 

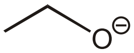
(A) a > b > c

(B) b > c > a

(C) c > b > a

(D) None of these

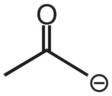
6. Which bases are strong enough to deprotonate H_2O?

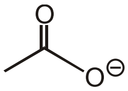
(a) 

(b) 

(c) $Cl^{\ominus}$

(d) $\overset{\ominus}{N}H_2$

(e) 

(f) 

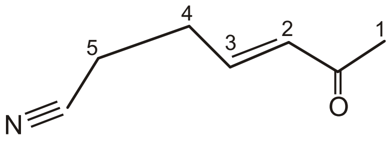
(A) a,b,c,d,e

(B) b,c,d,e,f

(C) a,b,d,e

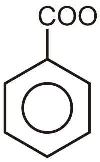
(D) b,c,d,e

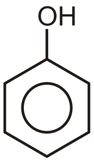
7. Which of the following carbon will be deprotonated first on treatment with base.

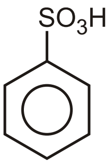


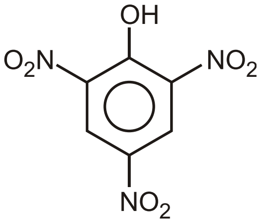
(A) 4 (B) 5 (C) 2 (D) 3

8. Which of the following compound do not react with $NaHCO_3$ to evolve CO_2 gas?

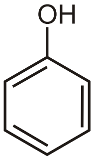
(A)


(B)


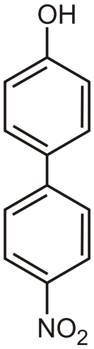
(C)


(D)


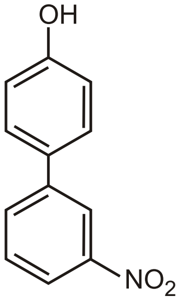
9. Correct order of Acidic strength among the following compounds :



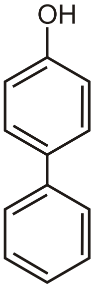
(I)



(II)



(III)



(IV)

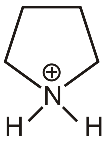
(A) I II III IV

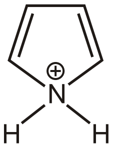
(B) II III IV I

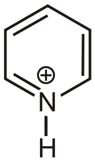
(C) II III I IV

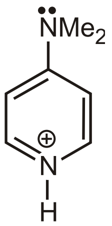
(D) III II IV I

10. The Most acidic species is :

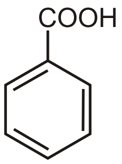
(A)


(B)


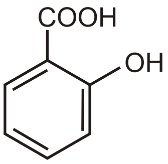
(C)


(D)


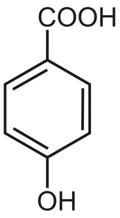
11. Among the following given compounds



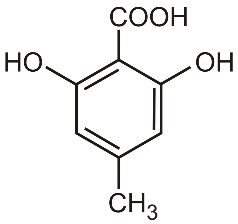
(I)



(II)



(III)

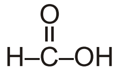


(IV)

The decreasing order of their acidity is :

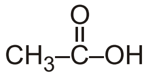
(A) I II III IV (B) I III II IV (C) IV II III I (D) IV II I III

12. What is the correct order of acidic strength?



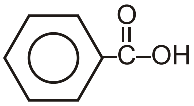
$\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}OH}$

I



$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH}$

II



III

H_2CO_3

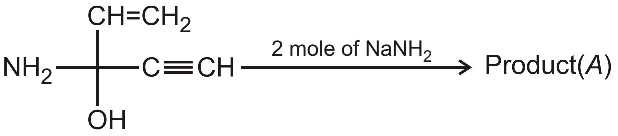
IV

(A) I II III IV (B) IV I II III (C) III IV I II (D) I III II IV

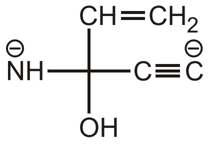
13. Which compounds release CO_2 gas on reaction with $NaHCO_3$(aq)?

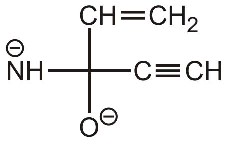
(A) Phenol (carbolic acid) (B) Cyclohexanol

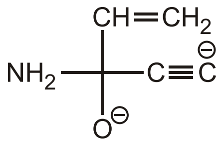
(C) Benzoic acid (D) Benzamide

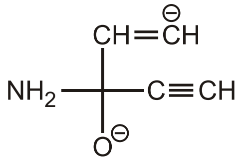
14. 

The product (*A*) will be :

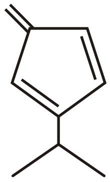
(A) 

(B) 

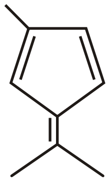
(C) 

(D) 

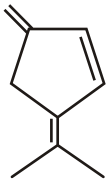
15. Which of the given compounds is the strongest acid?



1

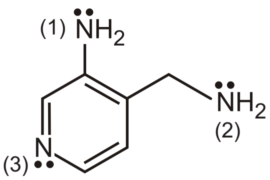


2



3

(A) 1 (B) 2 (C) 3 (D) Both 1 & 2

16. 

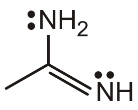
Find the basic strength order among nitrogen atoms :

(A) 2 > 1 > 3 (B) 2 > 3 > 1 (C) 3 > 2 > 1 (D) 3 > 1 > 2

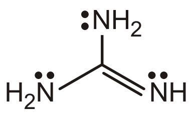
17. Correct order of Basic Strength (K_b order) is :

1

2



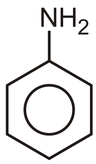
3

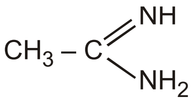


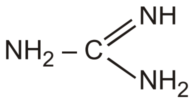
4

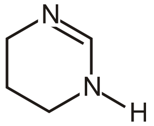
(A) 4 > 3 > 2 > 1 (B) 1 > 2 > 3 > 4 (C) 4 > 3 > 1 > 2 (D) 1 > 4 > 3 > 2

18. Which of the following base is weaker than $CH_3 — CH_2 — NH_2$ (ethyl amine) :

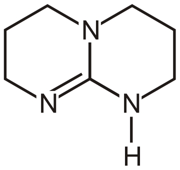
(A)


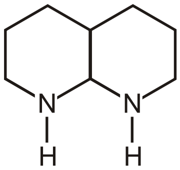
(B)

$CH_3 - C\begin{smallmatrix}{=}NH\\ NH_2\end{smallmatrix}$

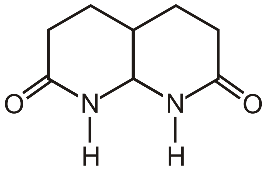
(C)

$NH_2 - C\begin{smallmatrix}{=}NH\\ NH_2\end{smallmatrix}$

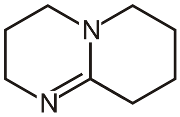
(D)


19. Compare the Basic strength :

(1)


(2)


(3)


(4)


(A) 1 > 4 > 2 > 3 (B) 2 > 1 > 4 > 3 (C) 2 > 4 > 1 > 3 (D) 1 > 2 > 4 > 3

20. The most basic compound among the following is :

(A) Benzylamine (B) Aniline

(C) Acetaniline (D) *p*-nitro aniline

21. The correct decreasing order of basic strength of the following species is ________.

$H_2O, NH_3, OH\ , NH_2$

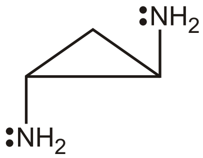
(A) NH_2 OH NH_3 H_2O (B) OH NH_2 H_2O NH_3

(C) NH_3 H_2O NH_2 OH (D) H_2O NH_3 OH NH_2

SUBJECTIVE TYPE QUESTIONS

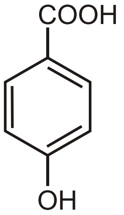
1. -Aminoacids have greater dipole moments that expected. Explain.

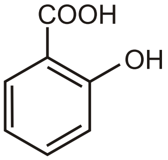
2. Which one of the following two compounds is more basic and why?

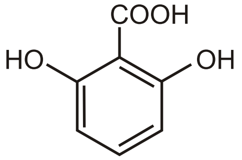
(a)


(b)


3. Arrange the following compounds in order of increasing acid strength with explanation.

(a)


(b)


(c)


4. What is squaric acid. Why is it a very strong acid?

Answers

Single Choice Questions

1. (B) **2.** (C) **3.** (C) **4.** (A) **5.** (C) **6.** (C) **7.** (A) **8.** (B)
9. (B) **10.** (B) **11.** (D) **12.** (D) **13.** (C) **14.** (C) **15.** (B) **16.** (B)
17. (C) **18.** (A) **19.** (A) **20.** (A) **21.** (A)

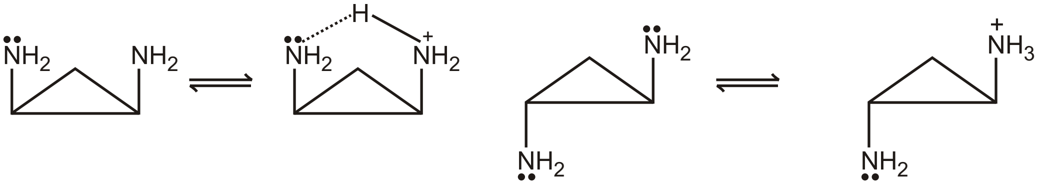
Subjective Type Questions

1. An -amino acid remains as a dipolar zwitter ion and that enhances polarity. That is why amino acids have higher dipole moments than expected.

$$H_2\overset{\bullet\bullet}{N}-CH_2-COOH \rightleftharpoons H_2\overset{+}{N}-CH_2-COO^-$$

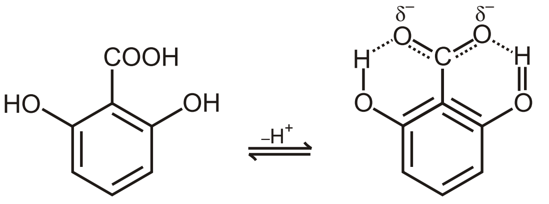
Glycene Zwitter ion (More polar)

2. The above mentioned compounds are rigid molecules. The compound (b) is more basic, because monoprotonated form gets stabilized by intramolecular hydrogen bonding. In the case of compound (a). such intramolecular hydrogen bonding is not possible after monoprotonation.

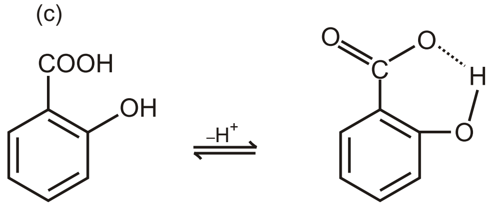


Not stabilized by Intramolecular hydrogen bonding

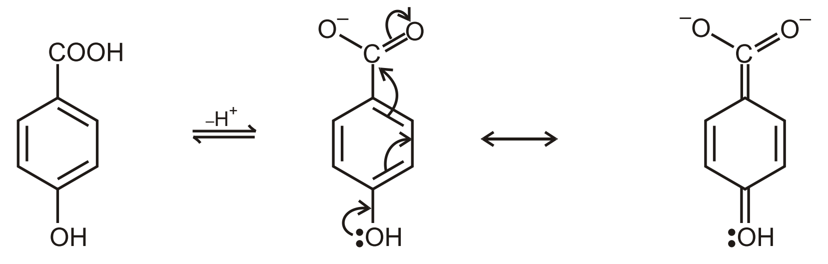
3. The decreasing aciding order is (c) > (b) > (a). In case of (c), the corresponding carboxylate anion is stabilized by intramolecular hydrogen bonding from the two ortho — OH groups. In case of (b), the stabilization comes from intramolecular hydrogen bonding from one ortho — OH group. In case of (a), carboxylate ion is destabilized by resonance involving *p* — OH group.



(c)

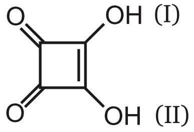


(b)

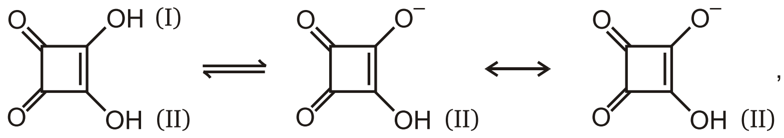


Electron density increases on the carboxylate group making the acid weaker

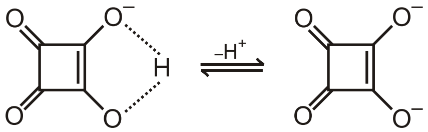
4. The structure of squaric acid is given here.



Structurally it is symmetrical. Its two acidic hydrogen atoms are associated with two OH groups identified as (I) and (II). The first ionization is found to give a more acidic hydrogen ion, because of vinylogous effect. Second ionization becomes slightly difficult because of the formation of a weak intramolecular hydrogen bonding.



, $pK_a = 1.5$



, $pK_a = 3.5$

❑❑❑