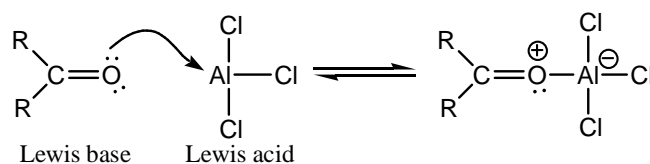


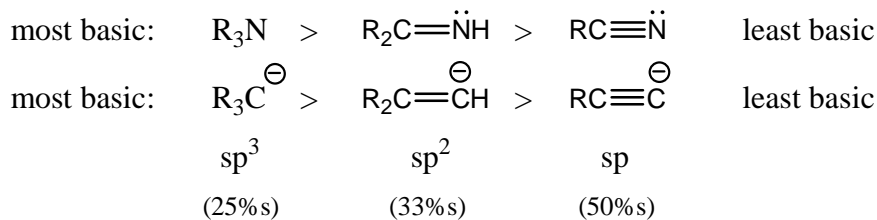
pairs.

- A Lewis base is any substance that donates an electron pair in forming a coordinate bond. Examples include  $\text{H}_2\text{O}$ ,  $\text{ROH}$ ,  $\text{RCHO}$ ,  $\text{R}_2\text{CO}$ ,  $\text{R}_3\text{N}$  and  $\text{R}_2\text{S}$ . They all have a lone pair(s) of electrons on the hetero atom (O, N or S)

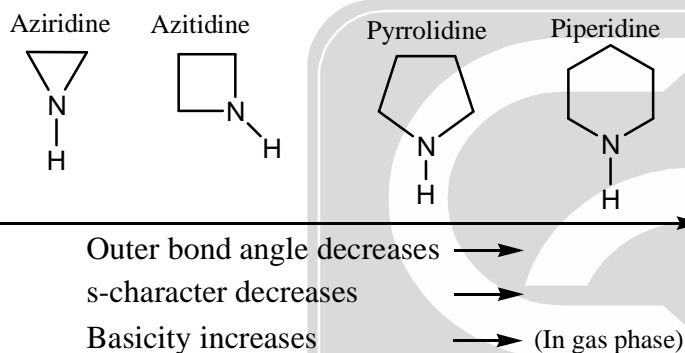


### (f) Basicity and hybridisation:

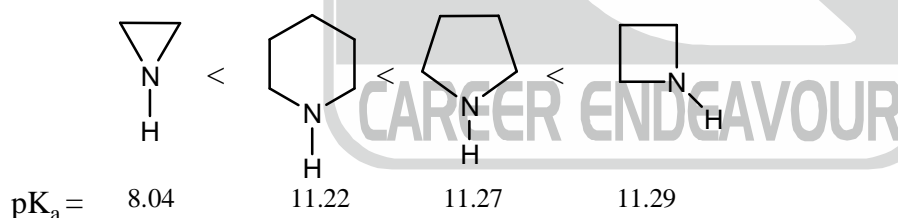
The greater the 's' character of an orbital, the lower is energy the electrons and the more tightly the electrons are held to the nucleus. The electrons in an  $sp$ -orbital are therefore less available for protonation than those in an  $sp^2$ - or  $sp^3$ -hybrid orbital and hence the compounds are less basic.



### Exceptional example:



**Note:** In aqueous solution phase, the basicity trend is opposite except aziridine due to very high s-character (Banana bond)

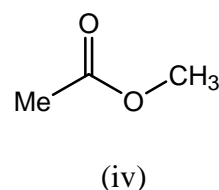
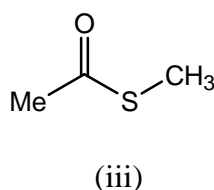
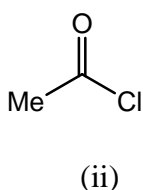
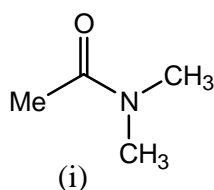


**Compound with different functional groups and their acidic strength order:**

$R-SO_3H$	Sulphonic acids	
$R-CO_2H$	Carboxylic acids	
	1, 3-diketones	
	Phenols	
$R-CH_2-NO_2$	Nitro alkanes	
	1, 3-Diesters	
$CH_3OH$	Methanol ( $pK_a = 15.5$ )	
$H_2O$	Water ( $pK_a = 15.74$ )	
$R-OH$	Alcohols ( $R \neq CH_3$ )	
	Acetone	
$R-C \equiv C-H$	Alkynes	
$NH_3$	Ammonia	
$H_2C=CH_2$	Alkenes $\approx$ Arenes	
$H_3C-CH_3$	Alkanes	
		Weak acid

## 1.08. PREVIOUS YEAR SOLVED PROBLEMS

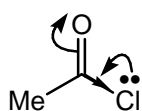
1. Rank the following molecules in order of electrophilicity (from most to least electrophilic):



- (a) ii > iii > iv > i      (b) i > iv > iii > ii      (c) ii > iv > iii > i      (d) i > iii > iv > ii

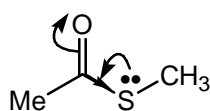
**Soln.** As the +M/+R and +I effect of the substituent attached with the carbonyl group increases, the electrophilicity decreases.

Since,



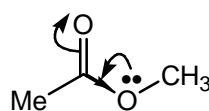
-I (High)  
+R(low)2p-3p

(II)



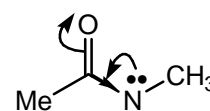
-I (low)  
+R(low)2p-3p

(III)



-I (High)  
+R(High)2p-2p

(IV)



-I (medium)  
+R(Very high)2p-2p

(I)

Therefore, (II) > (III) > (IV) > (I) will be electrophilicity order.

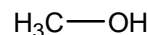
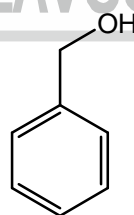
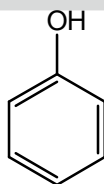
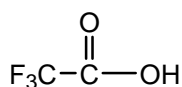
**Correct option is (a)**

2. Arrange the  $pK_a$  values of the hydroxy groups of methanol, trifluoroacetic acid, phenol and benzyl alcohol in ascending order:

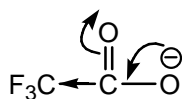
- (a) Trifluoroacetic acid < phenol < benzyl alcohol < methanol  
 (b) Trifluoroacetic acid < benzyl alcohol < phenol < methanol  
 (c) Phenol < trifluoroacetic acid < benzyl alcohol < methanol  
 (d) Trifluoroacetic acid < methanol < phenol < benzyl alcohol

**Soln.** Stronger the acid lower the value of  $pK_a$  and the strength of an acid depends upon the stability of its conjugate base

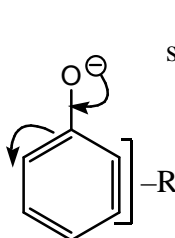
**Acids:**



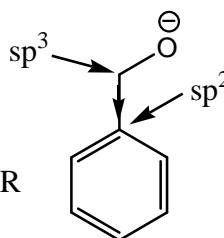
**Conjugate bases:**



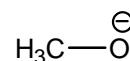
Stabilized by strong (-I) and delocalization



stabilized by delocalization

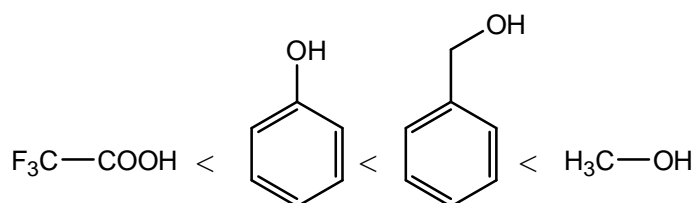


weak (-I) less stable



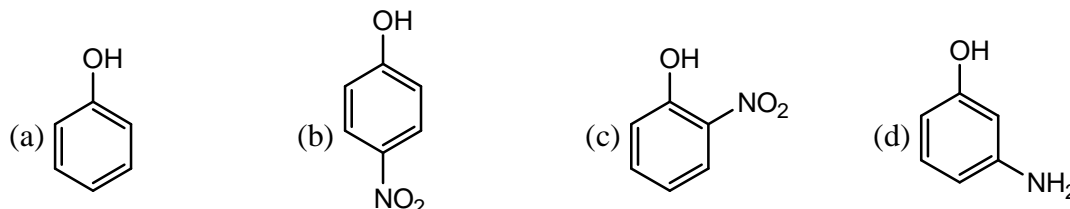
Least stable  
No electron withdrawing factor like (-I) or (-R)

Therefore, order of  $pK_a$  values is

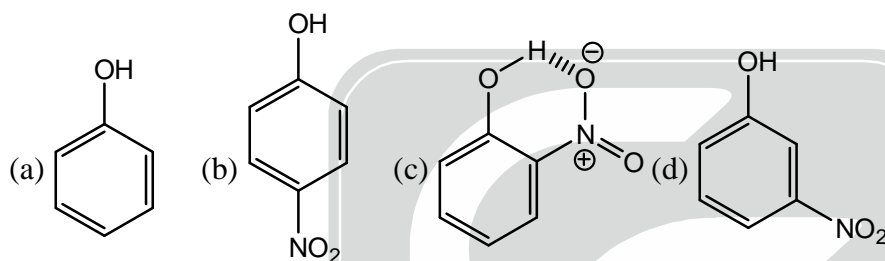


**Correct option is (a)**

3. Acidic strength is greater in



**Soln.** Acids:



Due to strong  $-I$  and  $-M$  effects,  $-NO_2$  group stabilizes the conjugate base in cases of (b) and (c). But, hydrogen in (c) which is to be released for acidic character is under extra bonding i.e. intramolecular H-bonding. Therefore, (b) is strongest acid.

**Correct option is (b)**

4. The order of ease of hydrogenations is

- (a) anthracene > naphthalene > benzene      (b) benzene > anthracene > naphthalene  
(c) benzene > naphthalene > anthracene      (d) naphthalene > anthracene > benzene

**Soln.** Higher the resonance energy or aromaticity, more stable will be compound and can not be hydrogenated easily. The resonance energy/aromaticity per benzene ring follows order as



Therefore, reactivity order for hydrogenation reaction is



**Correct option is (a)**

5. Which one of the following reagents is a nucleophile?

- (a)  $BF_3$       (b)  $SO_3$       (c)  $\ddot{C}Cl_2$       (d)  $NH_3$

**Soln.** Molecule or moieties that are having high electron density and can donate electrons called nucleophiles

- (a)  $BF_3$ : electron deficient due to incomplete octet (Electrophile) and having vacant p-orbital.  
(b)  $SO_3$ : accepts electrons due to three O-atoms, (electrophile) and vacant d-orbital in S-atom.  
(c)  $\ddot{C}Cl_2$ : incomplete octet in carbenes (electrophile) and having vacant p-orbital

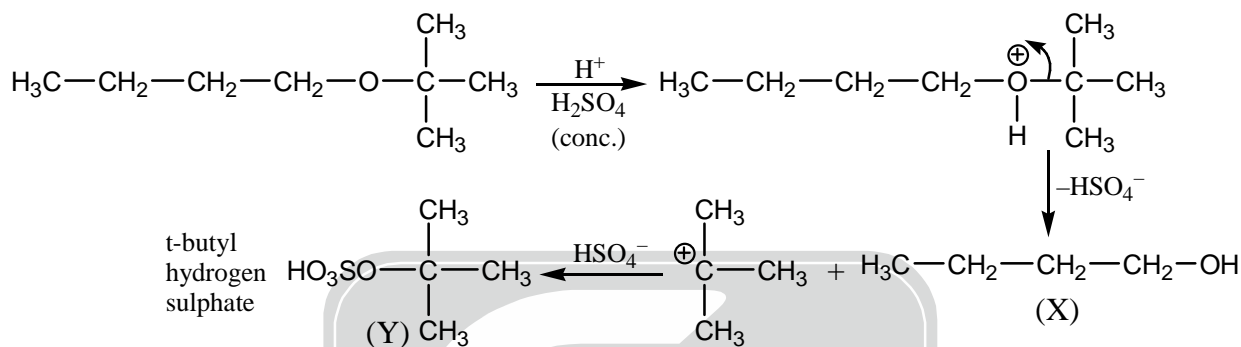
- (d)  $\ddot{N}H_3$ : complete octet and can donate its lone pair (Nucleophile)

**Correct option is (d)**

6. Like other oxygen-containing compounds, *n*-butyl *tert*-butyl ether dissolves in cold conc.  $\text{H}_2\text{SO}_4$ . On standing, an acid-insoluble layer, made up of high-boiling hydrocarbon material slowly separates from the solution. What this material is likely to be?

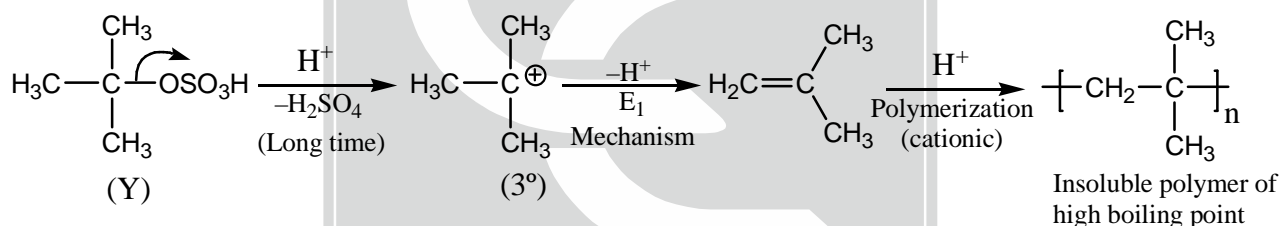
- (a)  $\sim\sim\text{CH}_2-\underset{\text{CH}_2\text{CH}_3}{\text{CH}_2}\sim\sim$  (b)  $\sim\sim\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}\sim\sim$
- (c)  $\sim\sim\underset{\text{CH}_3}{\text{CH}_2}-\underset{\text{CH}_3}{\text{C}}\sim\sim$  (d) All of the above

**Soln. Step-I:**



(X) and (Y) are soluble in acidic medium.

**Step-I: (Polymerization)**



**Correct option is (c)**

7. Arrange the following compounds in order of decreasing ease of nucleophilic substitution reactions
- (I) 4-Nitrochlorobenzene (II) 2, 4-Dinitrochlorobenzene
- (III) 2, 4, 6-Trinitrochlorobenzene (IV) Benzyl chloride

Answer codes:

- (a) IV > III > II > I (b) I > II > III > IV
- (c) III > II > I > IV (d) III > IV > II > I

**Soln.**

