

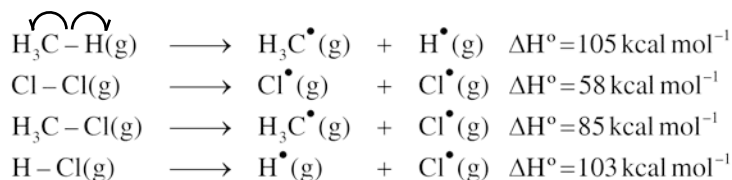
ORGANIC CHEMISTRY

GENERAL ORGANIC CHEMISTRY

Paragraph for Q.1 and Q.2

The amount of energy required to break a bond is same as the amount of energy released when the same bond is formed. In gaseous state, the energy required for *homolytic cleavage* of a bond is called Bond Dissociation Energy (BDE) or Bond Strength. BDE is affected by *s*-character of the bond and the stability of the radicals formed. Shorter bonds are typically stronger bonds. BDEs for some bonds are given below:

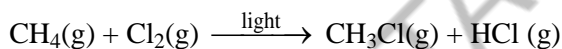
[JEE(Advanced) 2021]



1. Correct match of the **C-H** bonds (shown in bold) in Column **J** with their BDE in Column **K** is

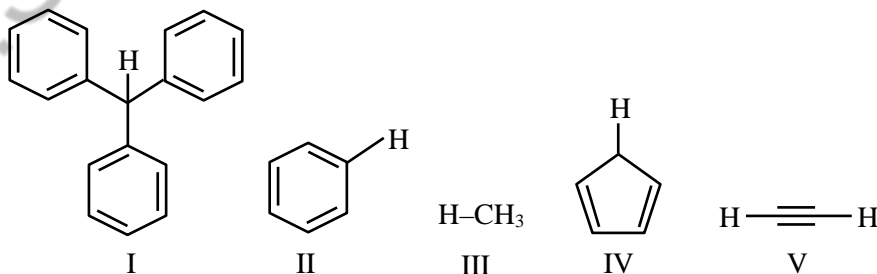
Column-J Molecule	Column-K BDE (kcal mol ⁻¹)
(P) H-CH (CH ₃) ₂	(i) 132
(Q) H- CH ₂ Ph	(ii) 110
(R) H-CH=CH ₂	(iii) 95
(S) H- C ≡ CH	(iv) 88

- (A) P – iii, Q – iv, R – ii, S – i
 (B) P – i, Q – ii, R – iii, S – iv
 (C) P – iii, Q – ii, R – i, S – iv
 (D) P – ii, Q – i, R – iv, S – iii
2. For the following reaction



the correct statement is

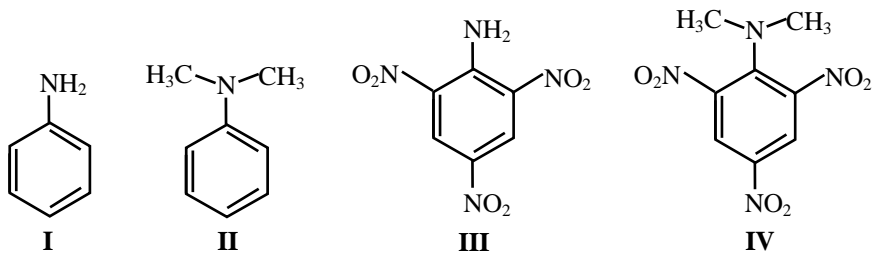
- (A) Initiation step is exothermic with $\Delta H^\circ = -58 \text{ kcal mol}^{-1}$.
 (B) Propagation step involving $\cdot\text{CH}_3$ formation is exothermic with $\Delta H^\circ = -2 \text{ kcal mol}^{-1}$.
 (C) Propagation step involving CH_3Cl formation is endothermic with $\Delta H^\circ = +27 \text{ kcal mol}^{-1}$.
 (D) The reaction is exothermic with $\Delta H^\circ = -25 \text{ kcal mol}^{-1}$.
3. With respect to the compounds **I-V**, choose the correct statement(s). [JEE(Advanced) 2020]



- (A) The acidity of compound **I** is due to delocalization in the conjugate base.
 (B) The conjugate base of compound **IV** is aromatic.
 (C) Compound **II** becomes more acidic, when it has a -NO₂ substituent.
 (D) The acidity of compounds follows the order **I** > **IV** > **V** > **II** > **III**.

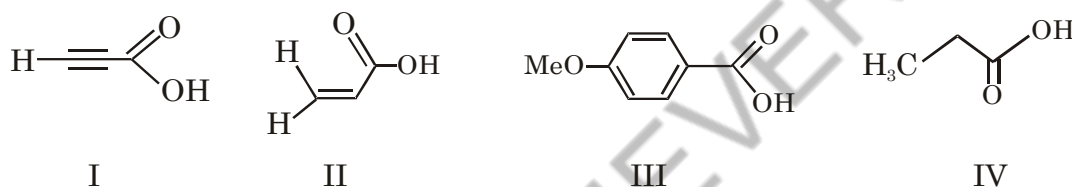
4. Consider the following four compounds **I**, **II**, **III**, and **IV**.

[JEE(Advanced) 2020]



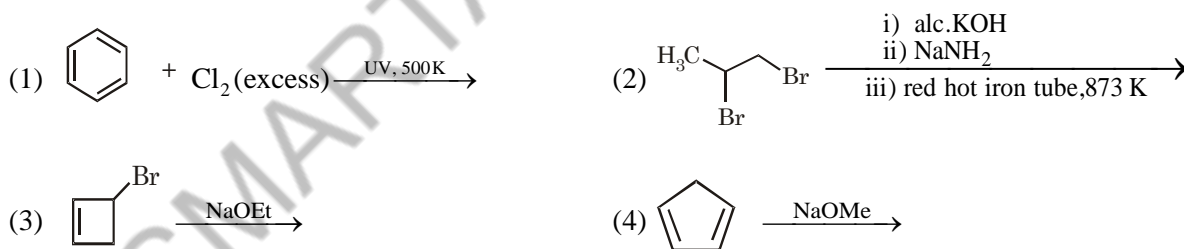
Choose the correct statement(s).

- (A) The order of basicity is **II** > **I** > **III** > **IV**.
 (B) The magnitude of pK_b difference between **I** and **II** is more than that between **III** and **IV**.
 (C) Resonance effect is more in **III** than in **IV**.
 (D) Steric effect makes compound **IV** more basic than **III**.
5. The correct order of acid strength of the following carboxylic acids is - [JEE(Advanced) 2019]



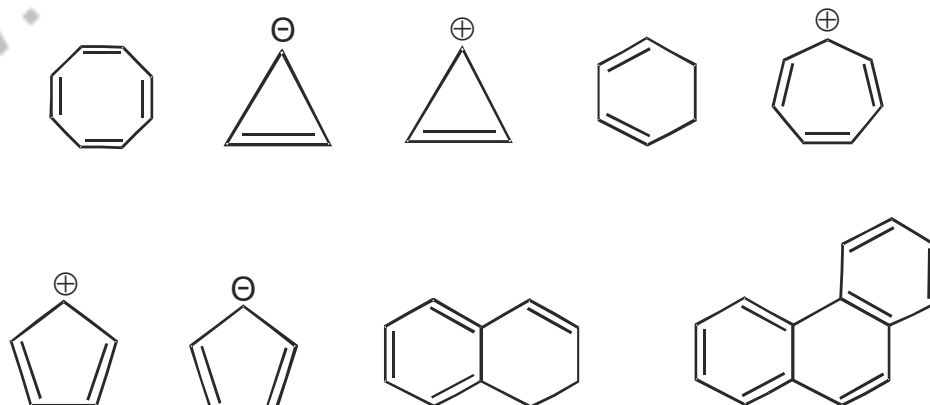
- (A) **I** > **III** > **II** > **IV**
 (B) **III** > **II** > **I** > **IV**
 (C) **II** > **I** > **IV** > **III**
 (D) **I** > **II** > **III** > **IV**
6. Choose the correct option(s) that give(s) an aromatic compound as the major product.

[JEE(Advanced) 2019]

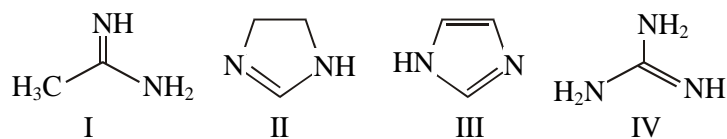


7. Among the following, the number of aromatic compound (s) is-

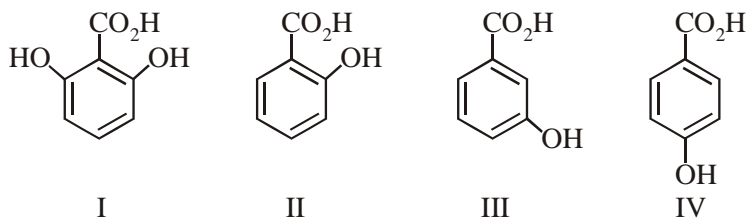
[JEE(Advanced) 2017]



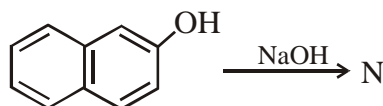
8. The order of basicity among the following compounds is [JEE(Advanced) 2017]



9. The correct order of acidity for the following compounds is: [JEE(Advanced) 2016]



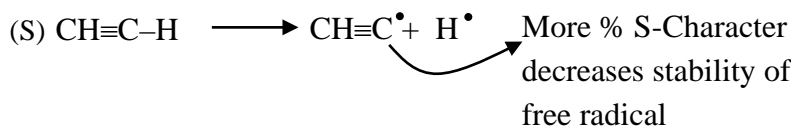
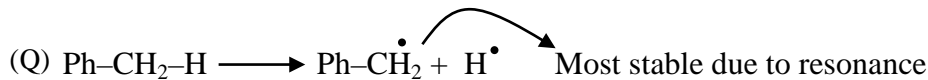
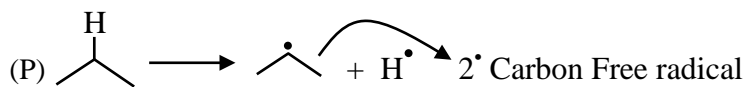
10. The number of resonance structures for N is : [JEE(Advanced) 2015]



SOLUTIONS

1. Ans. (A)

Sol. Most stability of radical, less is the bond energy



Q require least BDE and S Required maximum BDE

Max BDE

So, Order of BDE $Q < P < R < S$

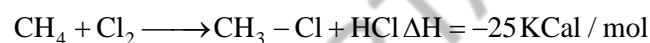
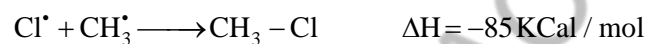
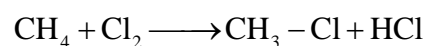
2. Ans. (D)

Sol. Initiation step is endothermic hence option (A) is wrong.

Propagation step involving $\dot{\text{C}}\text{H}_3$ formation is endothermic hence option (B) is wrong.

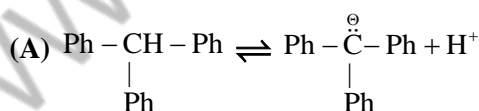
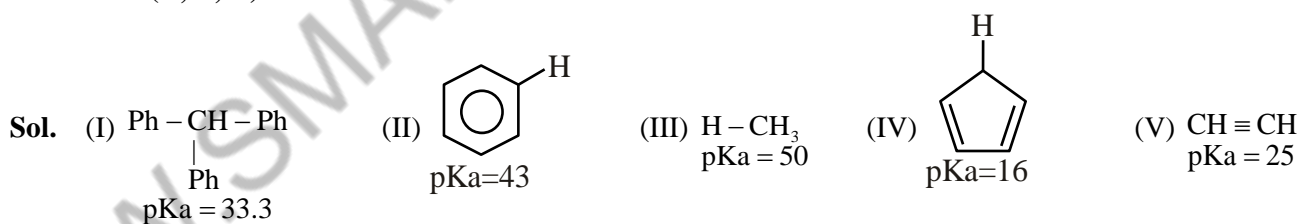
Propagation step involving CH_3Cl formation is exothermic hence option (C) is wrong.

Reaction

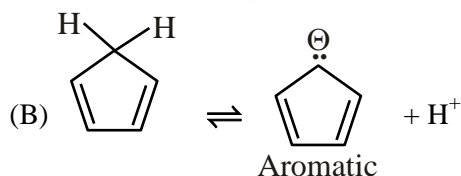


Overall reaction is exothermic with $\Delta H^\circ = -25 \text{ KCal/mol}$, hence option (D) is correct.

3. Ans. (A, B, C)



(Resonance stabilised)

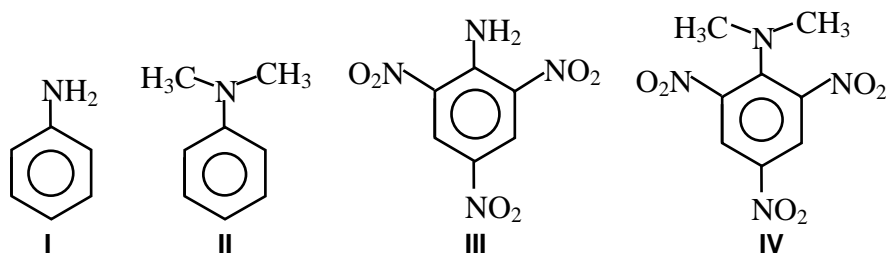


(C) $-\text{NO}_2$ is $-I$ group (electron withdrawing group). It increases acid strength.

(D) Acid strength order : $\text{IV} > \text{V} > \text{I} > \text{II} > \text{III}$

4. Ans. (C, D)

Sol.



pK_b different between I and II is 0.53 and that of III and IV is 4.6.

So, option (B) is incorrect

Correct Statement (C), (D)

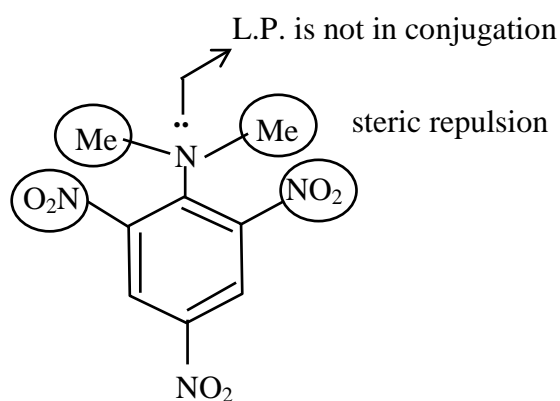
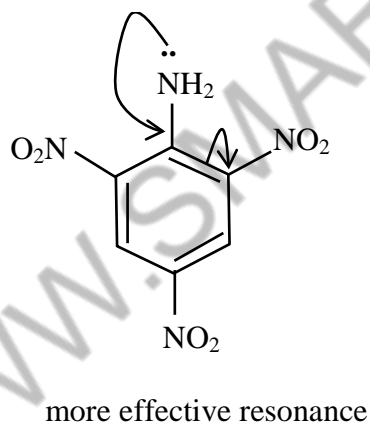
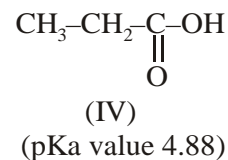
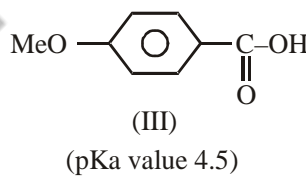
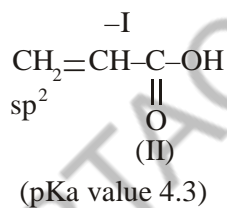
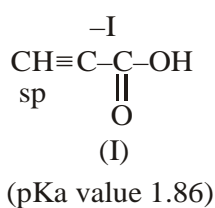
The most basic compound in the given option is (II) and least basic compound is (III)

In 2,4,6-trinitro aniline (III) due to strong $-R$ effect of $-NO_2$ groups, the $l.p.$ of $-NH_2$ is more involved with benzene ring hence it has least basic strength.

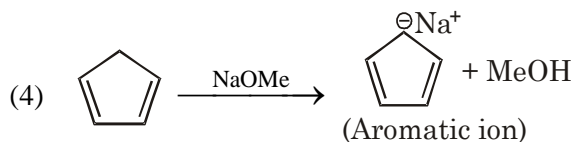
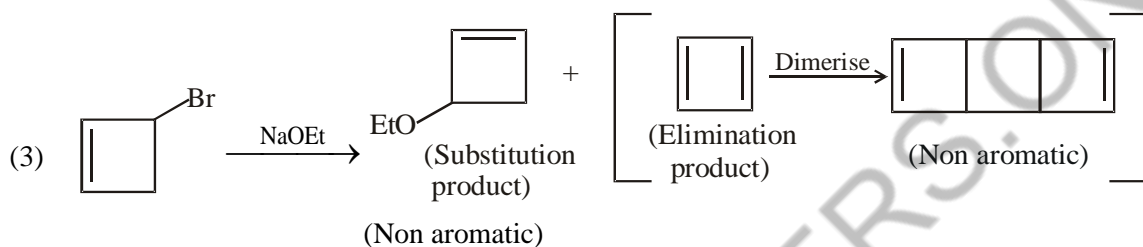
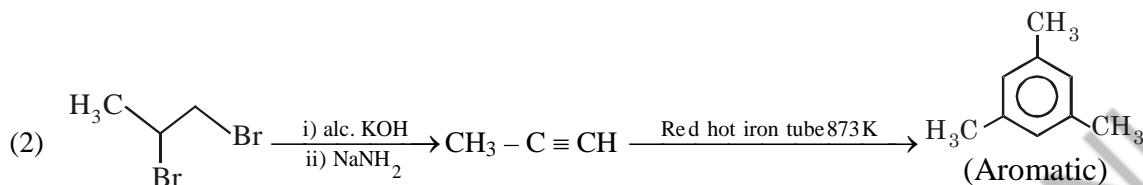
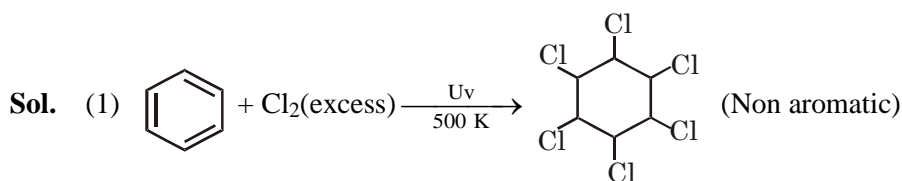
Whereas (IV) N,N-Dimethyl 2,4,6-trinitro aniline, due to steric inhibition to resonance (SIR) effect; the lone pair of nitrogen is not in the plane of benzene, hence make it ($l.p.$) more free to protonate

5. Ans. (D)

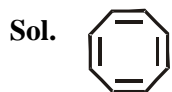
Sol. $I > II > III > IV$



6. Ans. (B, D)



7. Ans. (5)



Cyclooctatetraene ; **non aromatic**

Due to nonplanarity of ring the π-electrons are not delocalised.



Cyclopropenyl anion ; **Anti aromatic**

4π-electrons delocalised.

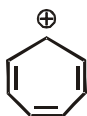


Cyclopropenyl cation ; **Aromatic**

2π-electrons delocalised.



Cyclohexadiene : **Non-aromatic**



Tropylium ion : **Aromatic**

6π-electrons delocalised.



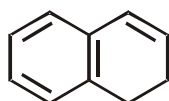
Cyclopentadienyl cation ; **Anti-aromatic**

4π -electrons delocalised.

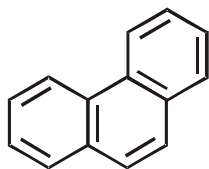


Cyclopentadienyl anion ; **Aromatic**

6π -electrons delocalised.



aromatic



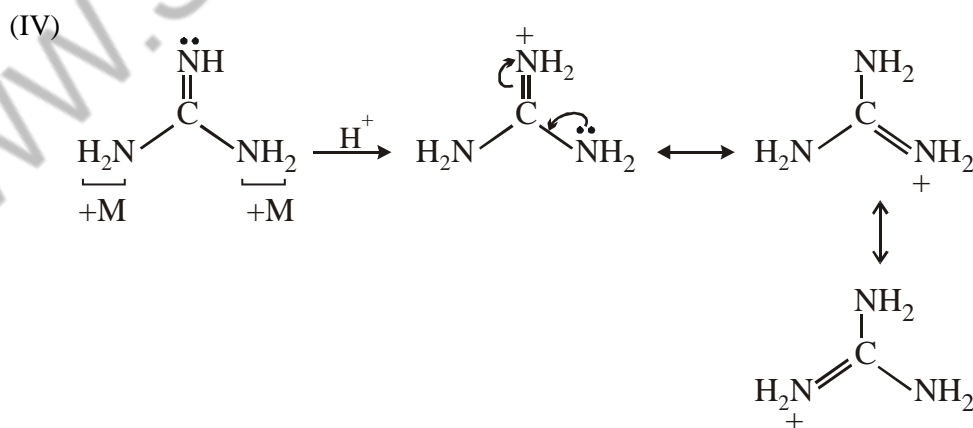
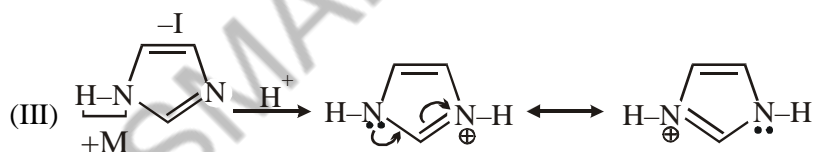
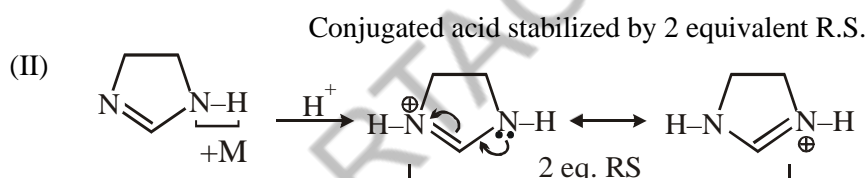
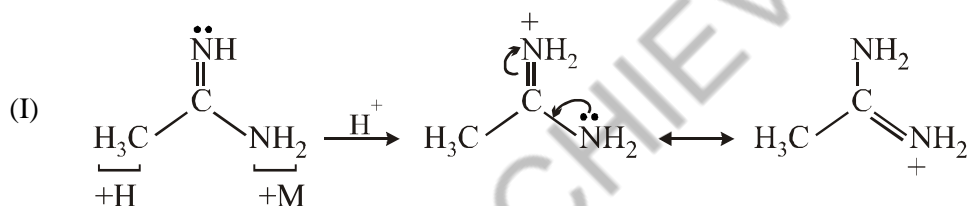
aromatic

$14\pi e^-$ s
(delocalised)

8. **Ans. (D)** IV > I > II > III

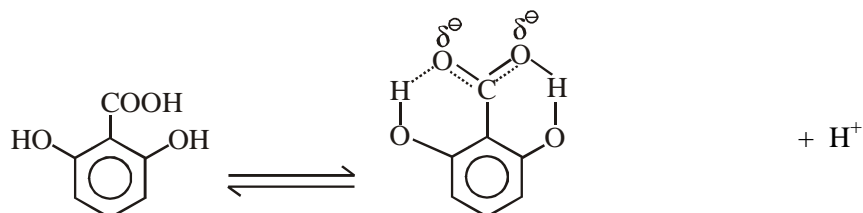
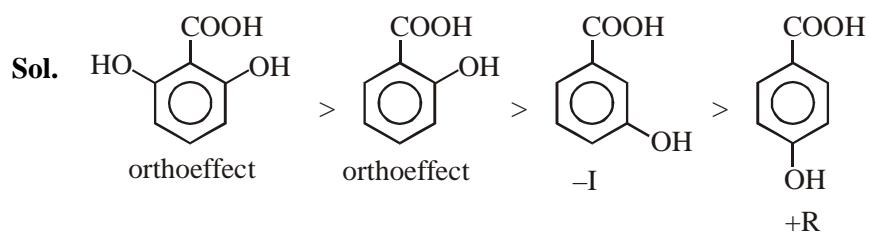
Sol. Basic strength \propto stability of conjugated acid.

$\propto +M / +H / +I$

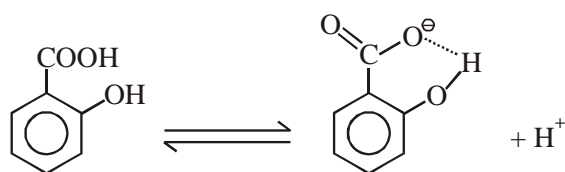


Conjugated acid stabilized by 3 equivalent R.S.

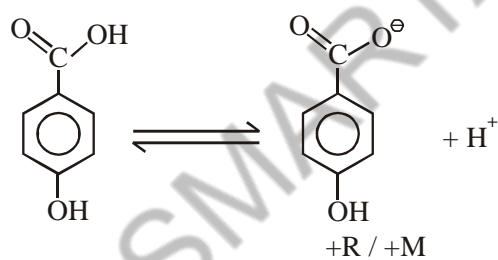
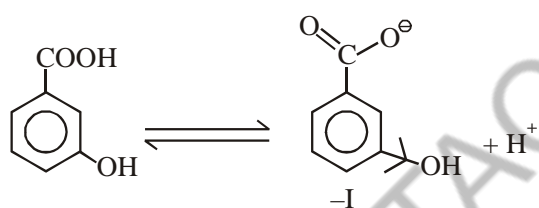
9. Ans. (A)



Most stable due to chelation of two
-OH group with $-\text{COO}^-$ group



Stable due to chelation of one
-OH group with $-\text{COO}^-$ group



10. Ans. (9)

Sol.

