IIT-JEE 2004 Mains Questions & Solutions – Chemistry – Version 2

(The questions are based on memory)

Break-up of marks:

Physical	Inorganic	Organic
30	10	20

1. One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. The volume decreases by 1 ml. Find ΔU and ΔH.

[2]

Solution

Since the process is under adiabatic condition,

$q_p = 0$

$\therefore \Delta H = q_p = 0$

Now, $\Delta U = \Delta W$ since $q_p = 0$

$= - P_{ext}\Delta V$

$= - 100 bar \times -1 ml$

$= 10$ J

2. Using VSEPR theory, draw the molecular structures of OSF_4 and XeF_4, indicating the location of lone pair(s) of electrons and hybridization of central atoms.

[2]

Solution

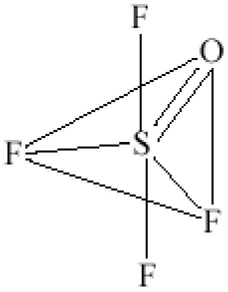
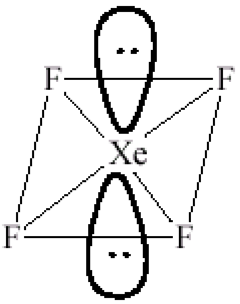
Consider OSF_4

$H = \frac{1}{2}(V + M - C + A)$

$= \frac{1}{2}(6+4) = 5$, i.e. sp^3d

Consider XeF_4

$H = \frac{1}{2}(8+4) = 6$, i.e. sp^3d^2

 Shape: Distorted trigonal bipyramidal No lone pair of electron	 Shape: Square planar 2 lone pairs of electron

3. For the reaction, A + B $\longrightarrow$ Products, the following initial rates were obtained at various given initial concentrations

S. No.	[A]	[B]	Rate(mol L^{-1} sec^{-1})
1.	0.1	0.1	0.05
2.	0.2	0.1	0.10
3.	0.1	0.2	0.05

Write rate law and find the rate constant of the above reaction.

[2]

Solution

From the given data it is evident that the reaction is of first order with respect to reactant A and is of zero order with respect to reactant B. Therefore, the rate law of the reaction is

$$rate = k[A]^1[B]^0$$

On putting the value of concentration of reactant A and rate of reaction from set of data first (S. No.–1), we get

$$\text{Rate constant, k} = \frac{0.05}{0.1} = 5 \times 10^{-1}\ s^{-1}$$

4. (i) AB crystallizes in a rock salt structure with A : B = 1 : 1. The shortest distance between A and B is $y^{1/3}$ nm. The formula mass of AB is 6.023 Y amu where Y is any arbitrary constant. Find the density in kg m^{-3}.

(ii) If measured density is 20 kg m^{-3}. Identify the type of point defect.

[2]

Solution

(i) Edge length of FCC unit cell $= 2 \times$ shortest distance between A and B

$$= 2 \times Y^{1/3}$$

Density of the crystal of AB

$$= \frac{Z \times M}{N_o \times a^3} = \frac{4 \times (6.023\ Y)}{6.023 \times 10^{23} \times (2Y^{1/3} \times 10^{-9})^3}$$

$$= 5 \times 10^3\ \text{g m}^{-3}$$

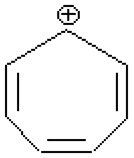
$$= 5\ \text{kg m}^{-3}$$

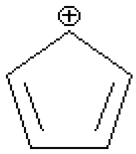
(ii) There is huge difference in theoretically calculated density and observed density. It is only possible if some foreign species occupies interstitial space i.e. substitution defect.

5. 7–bromo–1,3,5–cycloheptatriene exists as an ion whereas 5–bromo–1,3–cyclopentadiene does not form an ion even in the presence of Ag^+. Explain

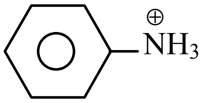
[2]

Solution

On ionization, 7–bromo–1,3,5–cycloheptatriene gives  which is highly stable due to aromatic character.

On the other hand, 5–bromo–1,3–cyclopentadiene gives  which involves cyclic resonance of 4π electrons making it highly unstable antiaromatic cation.

6. Which one is more acidic? Explain.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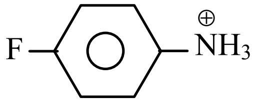
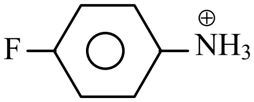
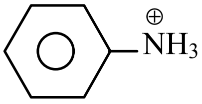
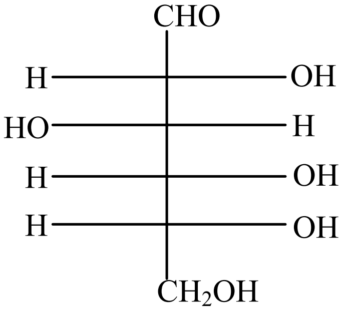


[2]

Solution

Due to the presence of electron withdrawing F group in , it is more acidic than  (-I effect).

7. The Fischer projection formula of D–glucose is



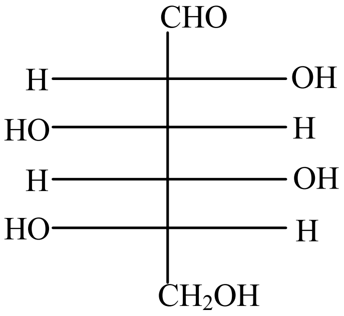
(i) Give Fischer projection formula of L–glucose.

(ii) Give the product of reaction of L–glucose with Tollen's reagent.

[2]

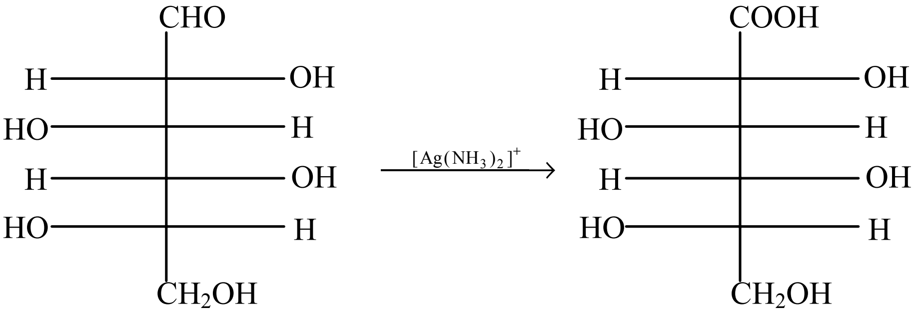
Solution

(i)



L–Glucose

(ii)



L–Glucose

L–Gluconic acid

8. Arrange the following in the decreasing order of Bronsted basicity:
$BaO, Cl_2O_7, SO_3, B_2O_3, CO_2$. Justify in not more than two sentences. **[2]**

Solution

$BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$. $HClO_4$ is stronger acid than H_2SO_4 which is stronger than H_2CO_3. B_2O_3 like water is amphoteric. BaO is basic.

9. AlF_3 does not dissolve in anhydrous HF but dissolves in KF.
(i) Explain the reason
(ii) When BF_3 is added to the above solution containing KF, aluminium trifluoride is precipitated. Give balanced chemical equation.

[2]

Solution

(i) AlF_3 does not dissolve in HF because fluorine of HF molecule is not available for coordination due to hydrogen bonding, while AlF_3 dissolves in KF due to formation of double salt $3KF.AlF_3$.

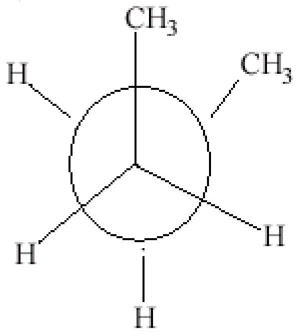
$$3KF + AlF_3 \longrightarrow 3KF.AlF_3$$

(ii) $3KF.AlF_3 + 3BF_3 \longrightarrow AlF_3(s) + 3KBF_4$

10. Give the Newmann configuration of the least stable staggered form of n–butane. Due to which of the following strain it is destabilised.
(i) Torsional strain
(ii) Van der Waal's strain
(iii) Combination of the two.

[2]

Solution

The reason of unstability is Van der Waal's strain. The electrostatic force of repulsion acting between the two methyl groups present in close proximity is responsible for making it the least stable.	

11. (i) 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K_b for acetone = 1.7) and (ii)100 g benzene (K_b for benzene = 2.6). The elevation in boiling points ΔT_b is 0.17°C and 0.13°C respectively.
(a) What are the molecular weights of benzoic acid in both the solutions?
(b) What do you deduce out of it in terms of structure of benzoic acid?

(ii) 0.1 M HA is titrated against 0.1 M NaOH. Find the pH at the end point. Dissociation constant for the acid HA is 5×10^{-6} and the degree of hydrolysis, h <<1

[4]

Solution

(i) (a) Let M and M′ be the molecular weight of benzoic acid (C_6H_5COOH) in acetone and benzene respectively.

We know

$$\Delta T_b = k_b \times m$$

$$0.17 = 1.7 \times \frac{1.22 \times 1000}{M \times 100}$$

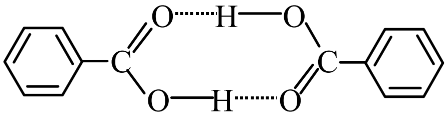
Molecular weight of benzoic acid in acetone, M = 122

and $$0.13 = 2.6 \times \frac{1.22 \times 1000}{M' \times 100}$$

Molecular weight of benzoic acid in benzene, M′ = 244

The formula weight of benzoic acid = (7 × 12) + (6 × 1) + (16 × 2) = 122

(b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene as



(ii) $HA + NaOH \longrightarrow NaA + H_2O$

At end point their equal equivalents react together.

$\therefore$ [NaA] = 0.05 M

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$pH = -\log\sqrt{\frac{K_w.K_a}{c}}$$

$$pH = -\log\sqrt{\frac{10^{-14} \times 5 \times 10^{-6}}{0.05}}$$

$\therefore$ pH = 9

12. DMG (Dimethyl glyoxime) is added to alcoholic solution of $NiCl_2$. When ammonium hydroxide is slowly added to it a rosy red precipitate of a complex appears.

(i) Give the structure of complex showing hydrogen bonds.

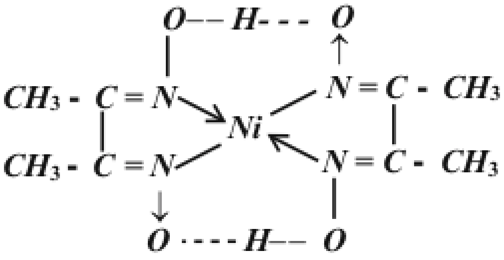
(ii) Give oxidation state and hybridization of central metal ion.

(iii)Identify whether it is paramagnetic or diamagnetic.

[4]

Solution

(i)



(ii) The oxidation state of nickel is (II) in complex and its hybridization is dsp^2.
(iii)This complex is diamagnetic in nature.

13. There are two ores (A_1) and (A_2) of metal (M). When ore (A_1) is calcinated a black solid (S) is obtained along with the liberation of CO_2 and water. The ore (A_1) on treatment with HCl and KI gives a precipitate (P) and iodine is liberated. Another ore (A_2) on roasting gives a gas (G) and metal (M) is set free. When gas (G) is passed through $K_2Cr_2O_7$ it turns green. Identify (M), (A_1), (A_2), (S), (P) and (G).

[4]

Solution

Metal (M) is Cu and its two ores are
(A_1) is malachite $CuCO_3.Cu(OH)_2$
(A_2) is copper glance Cu_2S.

Reactions involved are

$$\underset{(A_1)}{CuCO_3.Cu(OH)_2} \xrightarrow{\text{Calcination}} \underset{\text{(S) black}}{2CuO\downarrow} + CO_2\uparrow + H_2O$$

$$CuCO_3.Cu(OH)_2 + 4HCl \longrightarrow 2CuCl_2 + CO_2\uparrow + 3H_2O$$

$$2CuCl_2 + 4KI \longrightarrow \underset{(P)}{Cu_2I_2\downarrow} + 4KCl + I_2$$

$$\underset{(A_2)}{2Cu_2S + 3O_2} \xrightarrow{\text{Roasting}} 2Cu_2O + \underset{(G)}{2SO_2\uparrow}$$

$$Cu_2S + 2Cu_2O \longrightarrow \underset{(M)}{6Cu\downarrow} + SO_2\uparrow$$

$$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + 4H_2O$$

14. (a) (i) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

This reaction is carried out at 298 K and 20 bar. 5 mol each of N_2O_4 and NO_2 are taken initially.

Given: $\Delta G^o_{N_2O_4} = 100 \text{ kJ mol}^{-1}$; $\Delta G^o_{NO_2} = 50 \text{ kJ mol}^{-1}$

Find ΔG for reaction at 298 K under given condition.

(ii) The reaction proceeds at a initial pressure of 20 bar. Find the direction in which the reaction proceeds to achieve equilibrium.

(b) For a real gas obeying van der Waal's equation a graph is plotted between PV_m (y–axis) and P(*x*–axis) where V_m is molar volume. Find y–intercept of the graph.

[4]

Solution

(a) (i) Standard Gibbs free energy change for the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$\Delta G^\circ = \Delta G^o_{\text{Product}} - \Delta G^o_{\text{Reactant}}$$

$$= 2 \times 50 - 100 = 0$$

$$\Delta G^\circ = -2.303 \, RT \log K_p = 0$$

$$K_p = 1$$

Initially,

$$P_{N_2O_4} = P_{NO_2} = 10 \text{ bar}$$

So, $$Q_{P_{\text{Initial}}} = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = 10$$

Initial Gibbs free energy of the above reaction,

$$\Delta G = \Delta G^\circ + 2.303 \, RT \log Q_P$$

$$\Delta G = 0 + 2.303 \times 8.314 \times 298 \log 10$$

$$= 5.705 \times 10^3 \text{ kJ mol}^{-1}$$

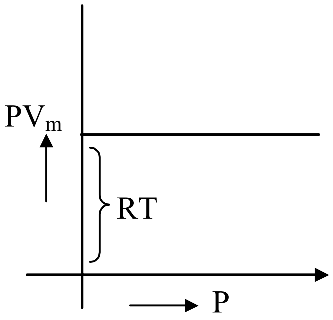
(ii) Since initial Gibbs free energy change of the reaction is positive, so the reverse reaction will take place

(b) At the point of intercept P = 0 and at very low pressure van der Waal's equation reduces to ideal gas equation

$$PV = nRT$$

$$PV_m = RT$$

So, y–intercept of the graph = RT



15. Find the equilibrium constant at 298 K for the reaction,

$$Cu^{2+}(aq) + In^{2+}(aq) \rightleftharpoons Cu^{+}(aq) + In^{3+}(aq)$$

Given that

$$E^{o}_{Cu^{2+}|Cu^{+}} = 0.15\ V$$
$$E^{o}_{In^{3+}|In^{+}} = -0.42\ V$$
$$E^{o}_{In^{2+}|In^{+}} = -0.40\ V$$

[4]

Solution

$$Cu^{2+}(aq) + In^{2+}(aq) \rightleftharpoons Cu^{+}(aq) + In^{3+}(aq)$$

$$E^{o}_{cell} = E^{o}_{Cu^{2+}|Cu^{+}} - E^{o}_{In^{3+}|In^{2+}}$$

$$E^{o}_{cell} = 0.15 - E^{o}_{In^{3+}|In^{2+}} \qquad \ldots(i)$$

For $E^{o}_{In^{3+}|In^{2+}}$:

$$In^{3+} + 2e^{-} \longrightarrow In^{+};\quad E° = -0.42\ V$$
$$In^{+} \longrightarrow e^{-} + In^{2+};\quad E° = +0.40\ V$$

$$In^{3+} + e^{-} \longrightarrow In^{2+};\quad E° = ?$$

Applying,

$$\Delta G° = \Delta G^{o}_{1} + \Delta G^{o}_{2}$$
$$-nFE° = -2\ F\ (-0.42) - 1\ F\ (0.40)$$
$$-E° = 0.84 - 0.40$$
$$E^{o}_{In^{3+}|In^{2+}} = -0.44\ V$$
$$\therefore\ E^{o}_{cell} = 0.15 + 0.44 = 0.59\ V$$
$$\because\ E^{o}_{cell} = \frac{2.303\ RT}{nF}\log K_c$$
$$\therefore\ 0.59 = \frac{0.059}{1}\log K_c$$
$$K_c = \text{Antilog } 10$$
$$\therefore\ K_c = 10^{10}$$

16. Arrange the following compounds in the increasing order of bond length of O–O bond: O_2, $O_2[AsF_6]$, KO_2 . Explain on the basis of ground state electronic configuration of dioxygen in these molecules.

[4]

Solution

For O_2:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma\, 2s^2\ \sigma^* 2s^2,\ \sigma 2p_z^2 \left[\begin{matrix}\pi 2p_x^2\\ \pi 2p_y^2\end{matrix}\right. \left[\begin{matrix}\pi^* 2p_x^1\\ \pi^* 2p_y^1\end{matrix}\right.$$

Bond order = $\frac{1}{2}(10-6) = 2$

For O_2^+ :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma\, 2s^2\ \sigma^* 2s^2,\ \sigma 2p_z^2 \left[\begin{matrix}\pi 2p_x^2\\ \pi 2p_y^2\end{matrix}\right. \left[\begin{matrix}\pi^* 2p_x^1\\ \pi^* 2p_y^o\end{matrix}\right.$$

Bond order = $\frac{1}{2}(10-5) = 2.5$

For O_2^-:

$$\sigma 1s^2, \sigma^* 1s^2, \sigma\, 2s^2\ \sigma^* 2s^2,\ \sigma 2p_z^2 \left[\begin{matrix}\pi 2p_x^2\\ \pi 2p_y^2\end{matrix}\right. \left[\begin{matrix}\pi^* 2p_x^{1+1}\\ \pi^* 2p_y^1\end{matrix}\right.$$

Bond order = $\frac{1}{2}(10-7) = 1.5$

Higher the bond order smaller the bond length.
Hence, $O_2[AsF_6] < O_2 < KO_2$

17. (i) The wave function of 2s electron is given by

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)e^{-\frac{r}{a_o}}$$

It has a node at $r = r_o$, find relation between r_o and a_o.

(ii) Find wavelength for 100 g particle moving with velocity 100 ms^{-1}.

(iii) ${}^{234}_{90}Th$ emits 7 α and 6 β particles. Find the atomic no. and mass no. of the resulting nuclear specie. Also identify it.

[4]

Solution

(i) The probability of finding of 2s electron at a point,

$$\psi_{2s}^2 = \frac{1}{32\pi}\left(\frac{1}{a_o}\right)^3\left(2-\frac{r}{a_o}\right)^2 e^{-\frac{2r}{a_o}}$$

Node is the point at which probability of finding an electron is zero. It means the value of ψ_{2s}^2 is zero when r = r_o.

$$\frac{1}{32\pi}\left(\frac{1}{a_o}\right)^3\left(2-\frac{r_o}{a_o}\right)^2 e^{-\frac{2r_o}{a_o}} = 0$$

$$\Rightarrow \quad 2-\frac{r_o}{a_o} = 0$$

$\therefore$ $r_o = 2a_o$

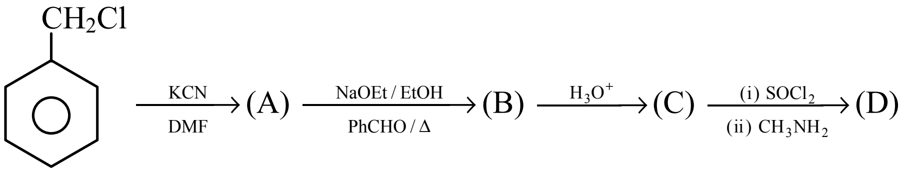
(ii) Applying de–Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}}{100\times10^{-3}\times100} = 6.626\times10^{-35} \text{ m}$$

(iii)On balancing the mass number and charge of the nuclear reaction, we get

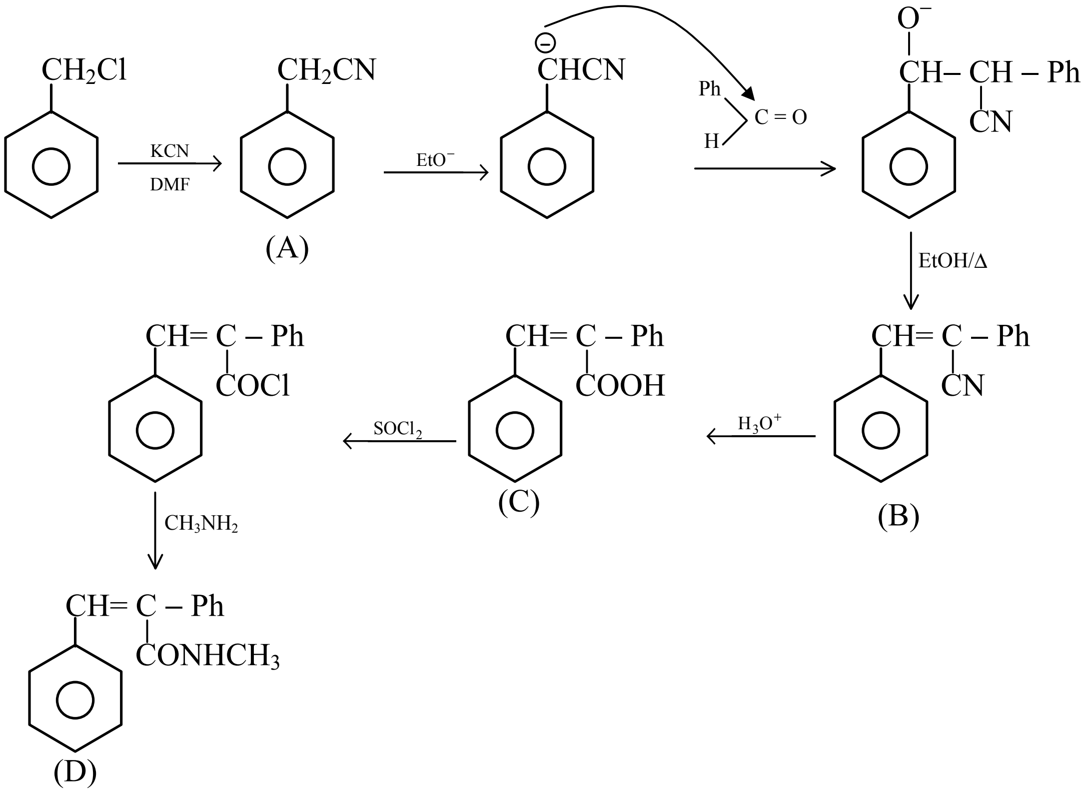
$$^{234}_{90}\text{Th} \longrightarrow 7\,^{4}_{2}\text{He} + 6\,^{0}_{-1}\text{e} + ^{206}_{82}\text{Pb}$$

18. Identify the compounds (A), (B), (C) and (D) in given reaction sequence.

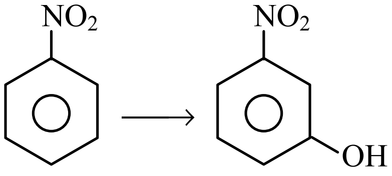


[4]

Solution



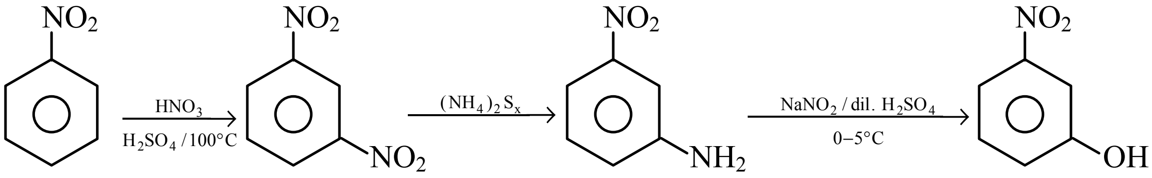
19. Convert



in not more than 4 steps. Clearly show the reagents, reaction condition and intermediates in the above conversion.

[4]

Solution



20. An organic compound (P), $C_5H_{10}O$ reacts with dil. H_2SO_4 to give (Q) and (R). Both (Q) and (R) give positive iodoform test. The reactivity of organic compound (P) is 10^{15} times more than ethylene with respect to dil. H_2SO_4.

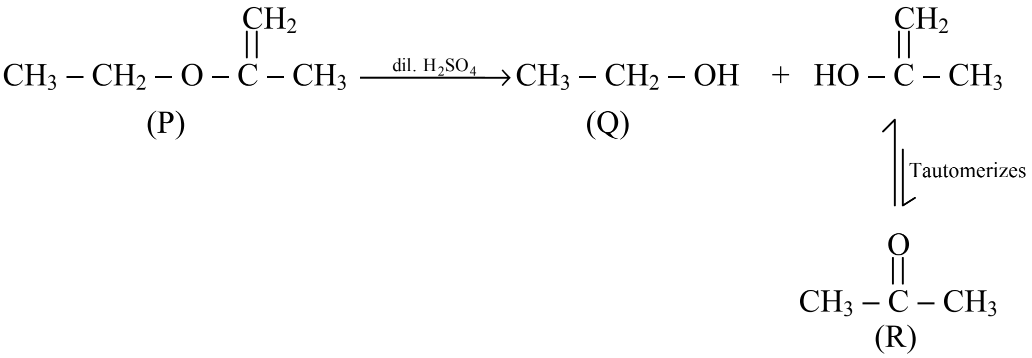
(i) Identify the compounds (P), (Q) and (R).

(ii) Give reason for the extraordinary reactivity of compound (P).

[4]

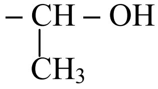
Solution

(i) The compound (P), $C_5H_{10}O$ have 1° unsaturation.



$$\underset{(P)}{CH_3-CH_2-O-\overset{\overset{\displaystyle CH_2}{||}}{C}-CH_3} \xrightarrow{\text{dil. } H_2SO_4} \underset{(Q)}{CH_3-CH_2-OH} + HO-\overset{\overset{\displaystyle CH_2}{||}}{C}-CH_3 \underset{\text{Tautomerizes}}{\rightleftharpoons} \underset{(R)}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}$$

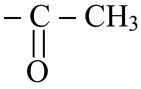
Compound (Q) and (R) both gives the iodoform test since (Q) contain



$$-\underset{\underset{\displaystyle CH_3}{|}}{CH}-OH$$

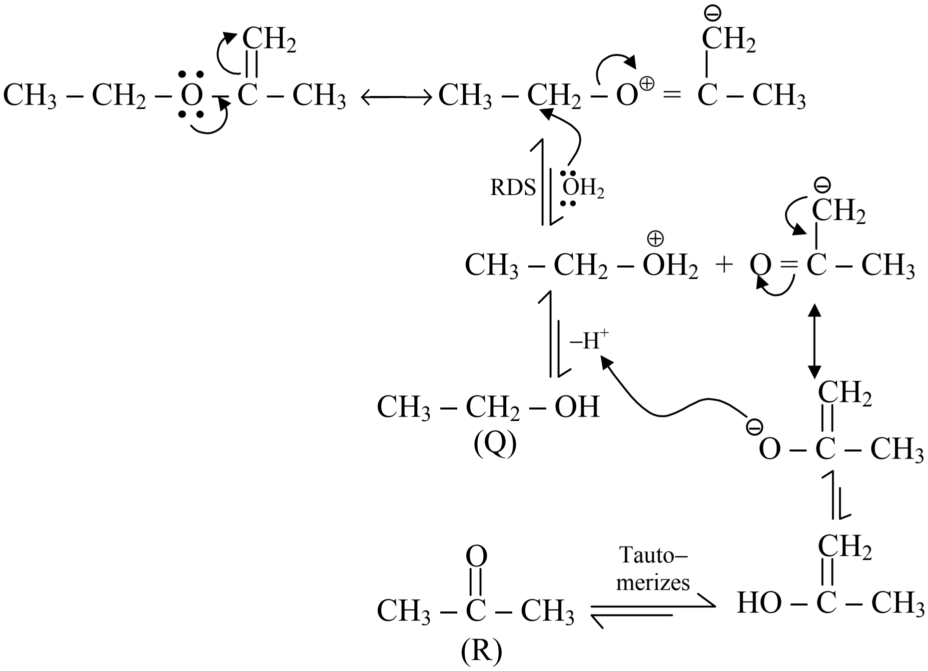
group,

while (R) is methyl ketone having

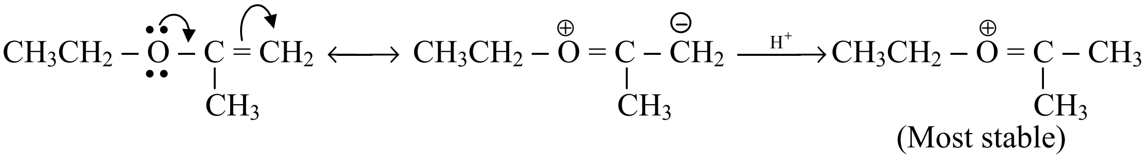


$$-\underset{\underset{\displaystyle O}{||}}{C}-CH_3$$

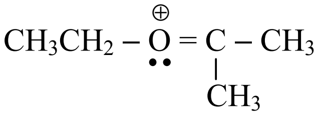
group.



(ii)



The compound (P) on reaction with dil. H_2SO_4 gives most stable cationic intermediate which is stabilized by completion of octet. Hence its rate of formation is higher while $CH_2 = CH_2$ gives 1° carbocation i.e. $CH_3-\overset{\oplus}{C}H_2$ with dil. H_2SO_4, which is not so greatly stabilized by resonance. Hence $CH_2 = CH_2$ is very less reactive than compound (P).



$$CH_3CH_2-\overset{\oplus}{\underset{\cdot\cdot}{O}}=\underset{\substack{|\\CH_3}}{C}-CH_3$$