PAPER : IIT-JAM 2005

CHEMISTRY-CY [PAPER]

NOTE: Attempt ALL the **44 questions.** Questions 1-30 **(Objective questions)** carry ***three*** marks each and questions 31-44 **(Subjective questions)** carry ***fifteen*** marks each.

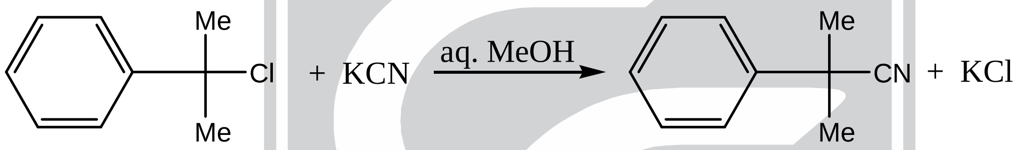
1. Arrange the following in the decreasing order of acidity of the hydrogen indicated in italic

(i) $\mathrm{CH_3CO\underline{CH_3}}$ (ii) $\mathrm{CH_3CO\underline{\mathit{CH}_2}COCH_3}$

(iii) $\mathrm{CH_3OOC\underline{\mathit{CH}_2}COOCH_3}$ (iv) $\mathrm{CH_3CO\underline{\mathit{CH}_2}NO_2}$

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

2. For the reaction shown below if the concentration of KCN is increased four times, the rate of the reaction will be



(a) doubled (b) increased four times
(c) unaffected (d) halved.

3. Benzyl chloride is reacted with different nucleophiles shown below. Arrange them in decreasing order of reactivity.

Nucleophilies: $\mathrm{HO^-, CH_3COO^-, PhO^-, CH_3O^-}$

(a) $\mathrm{CH_3O^- > HO^- > PhO^- > CH_3COO^-}$ (b) $\mathrm{HO^- > CH_3O^- > PhO^- > CH_3COO^-}$

(c) $\mathrm{HO^- > PhO^- > CH_3O^- > CH_3COO^-}$ (d) $\mathrm{CH_3COO^- > CH_3O^- > HO^- > PhO^-}$

4. The rate of nitration of the following aromatic compounds decreases in the order
(i) benzene (ii) pyridine (iii) thiophene (iv) toluene
(a) (iv) > (i) > (iii) > (ii) (b) (iii) > (iv) > (i) > (ii)
(c) (iii) > (ii) > (i) > (iv) (d) (ii) > (i) > (iv) > (iii)

5. The major product formed in the reaction of 1, 3-butadiene with bromine is

(a) $BrCH_2CH(Br)CH=CH_2$ (b) $CH_2=CH-CH_2CH_2Br$

(c) $CH_2=C(Br)-C(Br)=CH_2$ (d) $BrCH_2CH=CHCH_2Br$

6. The reaction of (+) 2-iodobutane and NaI* (I* is radioactive isotope of iodine) in acetate was studied by measuring the rate of racemization (k_r) and the rate of incorporation of I*(k_i).

$$\mathrm{(+)CH_3CH(I)CH_2CH_3 + NaI^* \longrightarrow CH_3CH(I^*)CH_2CH_3 + NaI}$$

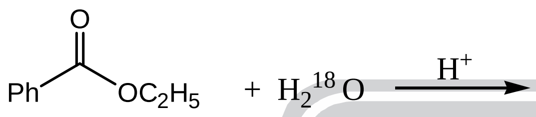
For this reaction, the relationship between k_r and k_i is:

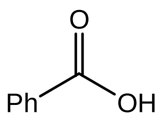
(a) $k_i = 2\times k_r$ (b) $k_i = (1/2)\times k_r$ (c) $k_i = k_r$ (d) $k_i = (1/3)\times k_r$

7. $$DNA \xrightarrow{Ba(OH)_2} (P)$$
$$DNA \xrightarrow{MgO/\Delta} PO_4^{3-} + (Q) \xrightarrow{HCl} (R) + (S) + \text{sugar}$$

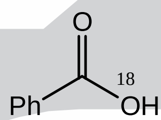
In the scheme shown above (P), (Q), (R) and (S) are
(a) (P) = purine bases, (Q) pyrimidine bases, (R) = nucleotides, (S) = nucleosides
(b) (P) = nucleosides,m (Q) = nucleotides, (R) = pyrimidine bases, (S) = purine bases.
(c) (P) = nucleosides, (Q) = nucleotides, (R) = (S) = purine bases.
(d) (P) = nucleotides, (Q) = nucleosides, (R) = pyrimidine base, (S) = purine base.

8. The products obtained from the following reaction are:

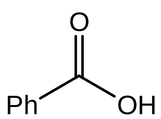


(a) 

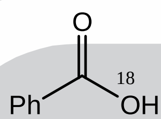
+ C_2H_5OH

(b) 

+ C_2H_5OH

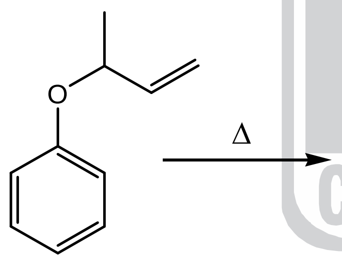
(c) 

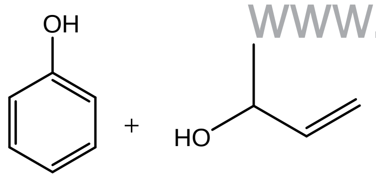
+ $C_2H_5{}^{18}OH$

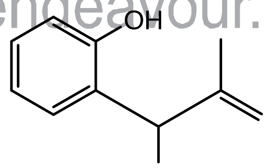
(d) 

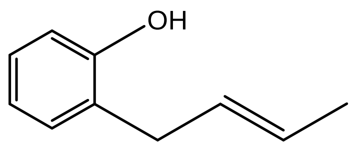
+ $C_2H_5{}^{18}OH$

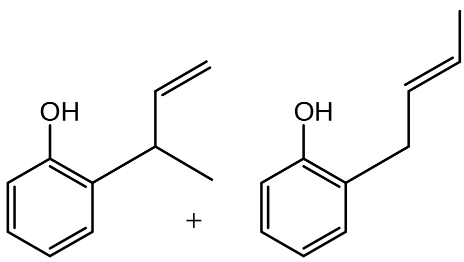
9. The product(s) obtained in the following reaction is (are)



(a) 

(b) 

(c) 

(d) 

10. Match the isoelectric point with the amino acids.

Amino acid	**Isoelectric point**
(X) H_2NCH_2COOH	(I) 9.5
(Y) $HOOCCH_2CH_2CH(NH_2)COOH$	(II) 6.0
(Z) $H_2N(CH_2)_4CH(NH_2)COOH$	(III) 3.1

(a) (X)-(II), (Y)-(III), (Z)-(I) (b) (X)-(III), (Y)-(I), (Z)-(II)
(c) (X)-(I), (Y)-(II), (Z)-(III) (d) (X)-(III), (Y)-(I), (Z)-(III)

11. The compound having the highest melting point is:
(a) LiCl (b) LiF (c) LiI (d) LiBr

12. The shape of SF_4 is:
(a) tetrahedral (b) trigonal bipyramidal
(c) square planer (d) octahedral.

13. The degree of hydration is expected to be maximum for
(a) Mg^{2+} (b) Na^+ (c) Ba^{2+} (d) K^+

14. The decreasing order of the first ionization energy of the following elements is:
(a) Xe > Be > As > Al (b) Xe > As > Al > Be
(c) Xe > As > Be > Al (d) Xe > Be > Al > As

15. The radioactive isotope used to locate brain tumors is:
(a) ${}^{2}_{1}D$ (b) ${}^{15}_{7}N$ (c) ${}^{131}_{53}I$ (d) ${}^{13}_{6}C$

16. The crystal field stabilization energy of high spin d^7 octahedral complex is:
(a) $-\frac{4}{5}\Delta_0+2P$ (b) $-\frac{4}{5}\Delta_0+3P$ (c) $-\frac{9}{5}\Delta_0+2P$ (d) $-\frac{9}{5}\Delta_0+3P$

17. The complex with the most colour among the following is:
(a) $[FeF_6]^{3-}$ (b) $[MnCl_4]^{2-}$ (c) $[CoCl_4]^{2-}$ (d) $[CoF_6]^{3-}$

18. On addition of a solution of $AgNO_3$ to a solution of $Na_2S_2O_3$, it turns black on standing due to the formation of :
(a) Ag (b) Ag_2S (c) $Ag_2S_2O_2$ (d) Ag_2SO_4.

19. Among the following complexes,
(i) $[Ru(\text{bipyridyl})_3]^+$ (ii) $[Cr(EDTA)]^-$
(iii) $trans-[CrCl_2(\text{oxalate})_2]^{3-}$ (iv) $cis-[CrCl_2(\text{oxalate})_2]^{3-}$
the ones that show chirality are
(a) (i), (ii), (iv) (b) (i), (ii), (iii) (c) (ii), (iii), (iv) (d) (i), (iii), (iv)

20. The electronic configurations that have orbital angular momentum contribution in octahedral environment are
(a) d^1 and high spin d^4 (b) d^1 and d^2
(c) d^2 and high spin d^6 (d) high spin d^4 and high spin d^6.

21. For an ideal solution formed by mixing of pure liquids A and B.
(a) $\Delta H_{mixing}=0$ (b) $\Delta H_{mixing}<0$ (c) $\Delta H_{mixing}>0$ (d) $\Delta S_{mixing}=0$

22. The relationship between the equilibrium constant K_1 for the reaction:

$$CO(g)+\frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$$

and the equilibrium constant K_2 for the reaction:

$$2CO(g)+O_2(g) \rightleftharpoons 2CO_2(g) \text{ is:}$$

(a) $2K_1 = K_2$ (b) $K_1 = K_2^2$ (c) $K_1 = K_2$ (d) $K_1^2 = K_2$

23. For H-like atoms, the ground state energy is proportional to

(a) $\frac{\mu}{Z^2}$ (b) $\frac{Z^2}{\mu}$ (c) μZ^2 (d) $\frac{1}{\mu Z^2}$

Where μ is the reduced mass and Z is the nuclear charge.

24. The value of integral $\int e^{-x}x^2dx$ is

(a) $x^2e^{-x}+2xe^{-x}+2e^{-x}$ (b) $\frac{-1}{2}\left(x^2e^{-x}+2xe^{-x}+2e^{-x}\right)$

(c) $\frac{1}{2}\left(x^2e^{-x}+2xe^{-x}+2e^{-x}\right)$ (d) $-x^2e^{-x}-2xe^{-x}-2e^{-x}$

25. For the reaction $aA \rightarrow$ products, the plot of $\frac{1}{[A]}$ versus time (t) gives a straight line. Order of the reaction is:

(a) 0 (b) 1 (c) 2 (d) 3

26. The pH of a solution prepared from 0.005 mole of $Ba(OH)_2$ in 100 cc water is:

(a) 10 (b) 12 (c) 11 (d) 13

27. For an electron whose x-positional uncertainity is 1×10^{10} m, the uncertainity in x-component of the velocity in ms^{-1} will be of the order of (Data: $m_e = 9\times10^{-31}\ kg, h = 6.6\times10^{34}\ Js$)

(a) 10^6 (b) 10^9 (c) 10^{12} (d) 10^{15}.

28. For the following system in equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s)+CO_2(g)$

the number of components, (C), phases (P) and degrees of freedom (F), respectively, are

(a) 2, 2, 2 (b) 1, 3, 0 (c) 3, 3, 2 (d) 2, 3, 1

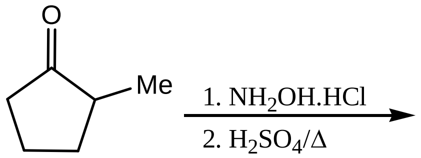
29. For the distribution of molecular velocities of gases, identify the correct order from following (where v_{mp}, v_{av}, v_{rms} are the most probable velocity, average velocity root mean square velocity, respectively):

(a) v_{rms}, v_{av}, v_{mp} (b) v_{mp}, v_{rms}, v_{av} (c) v_{av}, v_{rms}, v_{mp} (d) v_{mp}, v_{av}, v_{rms}

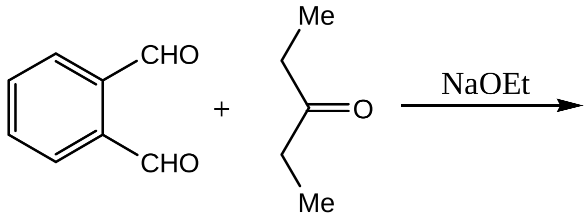
30. Given that $E^0_{Fe^{2+}/Fe} = -0.44V$ and $E^0_{Fe^{3+}/Fe^{2+}} = 0.77V$, the $E^0_{Fe^{3+}/Fe}$ is:

(a) 1.21 V (b) 0.33 V (c) –0.036 V (d) 0.036 V

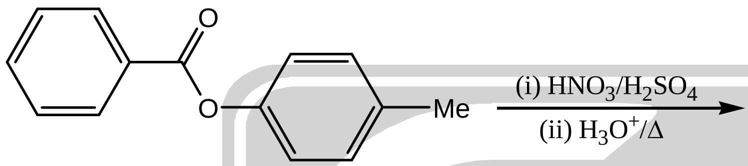
31. Identify the major product(s) formed in the following reactions. Intermediates and reaction mechanisms need not be discussed.

(a) 

[6]

(b) 

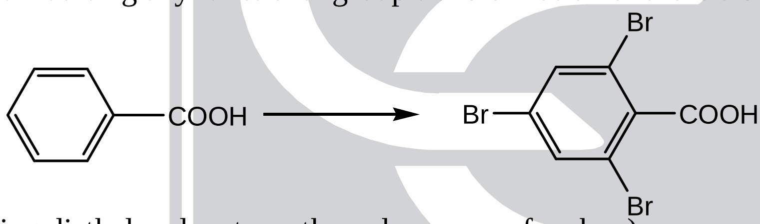
[6]

(c) 

[3]

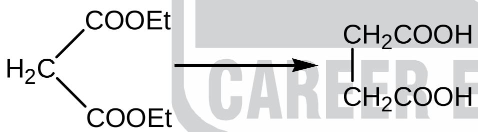
32. How may the following transformations be effected? Indicate the reagents/reaction conditions clearly in each step.

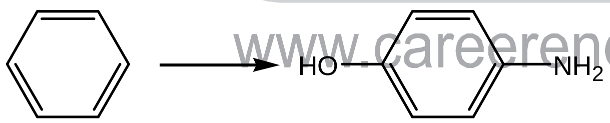
(a) (Not involving any functional group transformation of the COOH group in the starting material)



[6]

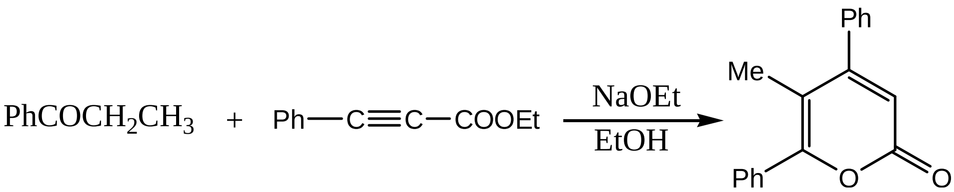
(b) (Using diethyl malonate as the only source of carbon) **[3]**



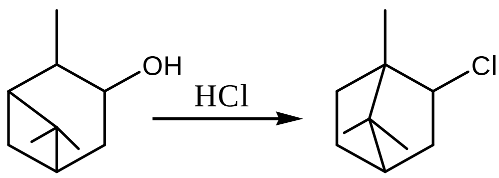
(c) 

[6]

33. Suggest a suitable mechanism for each of the following reactions.

(a) 

[6]

(b) 

[9]

34. Rationalize the following observations using suitable mechanism.

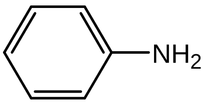
(a) Nitration of 4 t-butyltoluene gives 4-nitrotoluene as one of the products. **[3]**

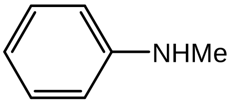
(b) cis-1-t-butylcyclohexyltrimethylammonium hydroxide undergoes Hoffmann elimination to yield 4-t-butylcyclohexene whereas the trans isomer does not (use conformations) explain.

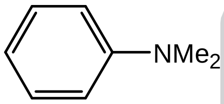
(c) $PhMgBr + 2PhCHO \xrightarrow[\text{2. acid workup}]{\text{1.dry ether}} PhCOPh + PhCH_2OH$ **[6]**

35. (a) Suggest a chemical method for the separation of a mixture contain p-N, N-dimethylaminophenol and p-aminobenzoic acid and give a confirmatory test for phenol. **[6]**

(b) Write the structures of X, Y and Z in the following **[9]**

(i)  $\xrightarrow[\text{2. }\beta\text{-naphthol/NaOH}]{\text{1. NaNO}_2\text{/dil. HCl, 0°C}}$ X

(ii)  $\xrightarrow{\text{NaNO}_2\text{/dil. HCl}}$ Y

(iii)  $\xrightarrow{\text{NaNO}_2\text{/dil. HCl}}$ Z

36. (a) Predict the hybridization and draw the structure of the following molecules based on VSEPR theory **[9]**

(i) I_3^- (ii) SO_3^{2-} (iii) $P(CH_3)_3F_2$

(b) Explain why PCl_5 exists and PH_5 does not. **[6]**

37. (a) Write balanced equations for the formation of **[6]**

(i) $P_2O_7^{-4}$ from PO_4^{-3} (ii) $\left[(H_2O)_4Fe(OH)_2Fe(OH_2)_4\right]^{4+}$ from $\left[Fe(OH_2)_6\right]^{+3}$

(b) Which one of the two solutions has lower pH? Justify your answer. **[9]**

(i) 0.1 M $Fe(ClO_4)_2$ or 0.1 M $Fe(ClO_4)_3$.

(ii) 0.1 M $Hg(NO_3)_2$ or 0.1 M $Zn(NO_3)_2$.

38. (a) Between $Co(H_2O)_6^{2+}$ and $Cu(H_2O)_6^{2+}$, which has more distorted structure and why? **[6]**

(b) Calculate CFSE (in unis of Δ_0) and spin only magnetic moment for the following complexes.

(i) $[CoF_6]^{3-}$ (ii) $[Fe(CN)_6]^{3-}$ (iii) $[NiCl_4]^{2-}$ **[9]**

39. (a) The radioactive element Ra (Z = 86) emits three alpha particles in succession. Deduce in which group the resulting element will be found? **[6]**

(b) A radioisotope sample has an initial activity of 23 dis/min. After 1/2 h, the activity is 11.5 dis/min. How many atoms of the radioactive nuclide were present originally? $\left[\alpha t_{1/2} = 0.69\right]$ **[9]**

40. (a) Write the products of the following reactions: **[9]**

(i) $CH_3I + HO^- \longrightarrow$ (ii) $CF_3I + HO^- \longrightarrow$ (iii) $2CF_3I + Na\left[Mn(CO)_5\right] \longrightarrow$

(b) Arrange BF_3, BCl_3 and BBr_3 in the increasing order of Lewis acidity and justify. **[6]**

41. Justify the following: **[15]**

(a) Considering CO_2 as an ideal gas, equipartition theorem products its total energy as 6.5 kT.

(b) ΔS for a process is the same whether the process takes place reversibly or irreversibly.

(c) The quantity ΔG equals the maximum non-expansion work done by a system in a constant temperature-pressure process.

(d) At constant temperature and pressure, $\Delta G = 0$ for a reversible phase change.

(e) Transition states cannot be isolated as independent chemical species.

42. The rate constant k for a second order reaction $P + Q \rightarrow \text{products}$ is expressed $\log_{10} k = 20 - \frac{3000}{T}$, where the concentration is in mol lit^{-1}, T is in absolute temperature and time is in minutes. The initial concentrations of both the reactants are 0.05 M. Calculate the activation energy and half life of the reaction at 27ºC. (R=2 cal K^{-1} mol^{-1}). **[15]**

43. The equilibrium constant for the reaction. **[15]**

$$Fe_3O_4(s) + CO(g) \rightleftharpoons 3FeO(s) + CO_2(g)$$

at 600ºC is 1.00. If a mixture intially consisting of 1 mole of Fe_3O_4, 2 moles of CO, 0.5 of FeO and 0.3 mole of CO_2 is heated to 600ºC at constant total pressure of 5 atmosphere, how many moles of each substance would be present at equilibrium?

44. (a) Use the time-independent Schrodinger equation to calculate the energy of a particle of mass ‘m’ with V = 0 in the state $\psi = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi z}{a}$ in a cubical box of length ‘a’. **[9]**

(b) At 20ºC, the vapour pressure of two pure liquids X and Y which form an ideal solution are 70 torr and 20 torr respectively. If the mole fraction of X in solution is 0.5, find the mole fraction of X and Y in the vapor phase in equilibrium with the solution. **[6]**