

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, MAY 2018

FIRST YEAR [BATCH 2017-20]

INDUSTRIAL CHEMISTRY (Honours)

Date : 19/05/2018

Time : 11 am – 3 pm

Paper : II

Full Marks : 75

[Use a separate Answer Book for each group]

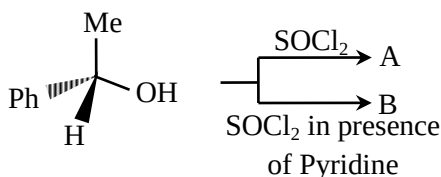
Group – A

[25 marks]

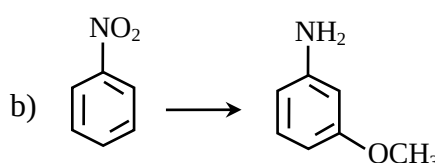
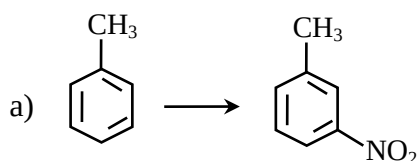
(Answer any five questions)

[5×5]

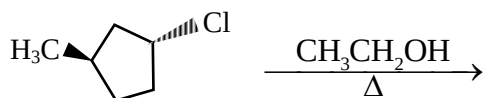
1. a) Identify A and B in the following reaction and explain their formation. [3]



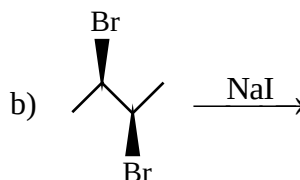
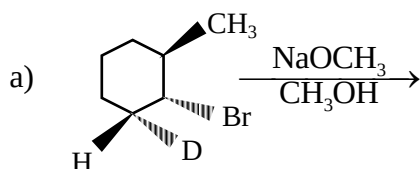
- b) Write the differences between nucleophilicity and basicity. [2]
2. Explain the following observation. [2·5×2]
- a) The hydrolysis of methyl chloride takes place in much faster rate in presence of sodium iodide.
- b) t-butyl chloride undergoes solvolysis in 70% water / 30% acetone at a slower rate than 80% water / 20% acetone.
3. Carry out the following conversions. [2·5×2]



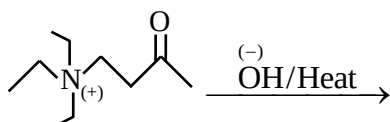
4. a) 2,4,6-Trimethylbenzoic acid does not undergo esterification under ordinary acid catalysis condition (A_{AC2} mode), whereas in concentrated sulphuric acid it undergoes quantitative esterification. Explain. [3]
- b) Provide the structure of the major organic products which results in the reaction below: [2]



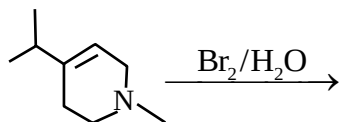
5. Predict the product of the following reactions with mechanism. [2·5×2]



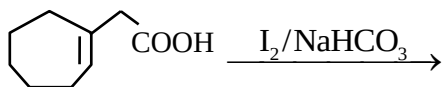
6. a) When (R)-2-bromopropanoate ion is treated with dilute sodium hydroxide, retention of configuration of the product is observed. Explain. [3]
- b) Write the major product of the following reaction with explanation. [2]



7. a) What will be the product of addition of bromine water to the alkene? [2]

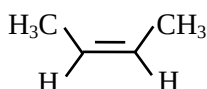


- b) Give the mechanism and the product (no stereochemistry is required) for the following reaction. [2]

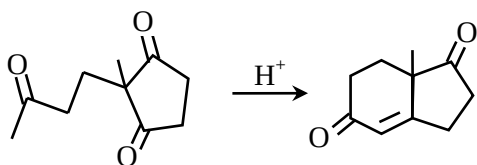


- c) What is peroxide effect? [1]

8. a) Starting with acetylene, how could the following compound be synthesized (write down the reagents only, no mechanism required)? [2]



- b) Comment on the selectivity shown in the following cyclization. [2]



- c) “Hemiacetal formation is catalysed by acid or base, but acetal formation is possible only with an acid catalyst” — Justify the statement. [1]

Group - B

[25 marks]

(Answer any five questions)

[5×5]

9. a) What do you mean by levelling effect and differentiating effect of solvent? Explain with example. [2]

- b) Which is a stronger base and why? Explain. [3]

- i) NH_3 , PH_3 ii) NH_3 , NF_3

10. a) Compute and explain the course of reaction by appropriate acid-base concept in the following (given below) : [3]

- i) $\text{CH}_3\text{I} + \text{Na}^+(\text{Mn}(\text{CO})_5)^- \rightarrow \text{NaI} + \text{CH}_3[\text{Mn}(\text{CO})_5]$.

- ii) $2\text{CF}_3\text{I} + \text{Na}^+[\text{Mn}(\text{CO})_5]^- \rightarrow \text{NaI} + \text{Mn}(\text{CO})_5\text{I} + \text{C}_2\text{F}_6$.

- b) Explain the acid strength of $(\text{HO})\text{ClO}_x$ with increasing the value of 'X' from zero to three. [2]

11. a) Would have any effect on the acidity or basicity of the solution. When Cs_2SO_3 is added to a solution of SOCl_2 in liquid SO_2 . Explain by an acid-base concept. [2·5]

- b) pK_1 of H_3AsO_3 is 9.2 whereas for K_1 of H_3PO_3 it is ~ 1.8 (approx). Explain these two observations properly. [2.5]

12. a) A rose red precipitate is formed when NiSO_4 solution is treated with dimethylglyoxime at mild basic medium. Write down the structural formula of the compound. What is the nature of the compound? Give the IUPAC name of it. [3]

- b) What do you mean by ambidentate ligand and flexidentate ligand? Explain their character with example of ligands. [2]
13. a) Draw the structures of the possible isomeric forms of the co-ordination complex of a formula $[MA_3B_3]^{n+}$ (where A and B are two separate monodentate ligands). [2·5]
- b) What is 'chelate effect'? Explain the term with a suitable example. [1·5]
- c) Which one of the following has lighter proton affinity value? F^- and Cl^- [1]
14. a) Oxidising properties of $KMnO_4$ depends on the pH of the aqueous solution of $KMnO_4$. Justify with the help of Nernst equation. [3]
- b) Why any acid-base indicator can be used when a strong acid is titrated by a strong base? Explain. [2]
15. a) Balance the reaction using ion-electron method. [2]
- $$Mn^{2+} + BiO_3^- + H_2O \rightarrow MnO_4^- + Bi^{3+} + H^+$$
- b) Calculate the red-ox potential values at the following three stages of titration of 0·1(N) Fe^{2+} with 0·1(N) $K_2Cr_2O_7$ in 1N H_2SO_4 medium
- i) 25 ml Fe^{2+} + 24·95 ml $K_2Cr_2O_7$
- ii) 25 ml Fe^{2+} + 25 ml $K_2Cr_2O_7$
- iii) 25 ml Fe^{2+} + 25·05 ml $K_2Cr_2O_7$
- (Given $E^\circ_{Fe^{3+}/Fe^{2+}} = +0·77V$; and $E^\circ_{Cr_2O_7^{2-}/2Cr^{3+}} = 1·33V$) [3]
16. a) Ferricyanide solution cannot oxidise the iodide to iodine but it can do so if trace amount of Zn^{2+} solution is added to a slightly acetic acid solution. Why? [2]
- [Given : E° for $[Fe(CN)_6]^{3-} / [Fe(CN)_6]^{4-} = 0·36V$; E° for $I_2 / 2I^- = 0·54V$.
- b) Fe^{2+} ion cannot be estimated quantitatively by the standard $KMnO_4$ solution in hydrochloric acid medium without use of the Zimmermann Reinhardt solution —Explain. [3]
- Given : E° of $MnO_4^- / Mn^{2+} = 1·51V$; E° of $Cl_2 / 2Cl^- = 1·36V$

Group - C

[25 marks]

(Answer any five questions)

[5×5]

17. a) Discuss with an example what is meant by photostationary state. [2]
- b) With a suitable mechanism, prove that the quantum yield of photochemical decomposition of HI is 2. [3]
18. a) Justify or criticize : "Quantum yield $\phi > 1$ of a photochemical reaction is in contradiction to the Einstein's law of photochemical equivalence." [2]
- b) A reaction responds to both red and violet light ($\lambda = 800nm$ and $400nm$ respectively) with an equal quantum yield. Will there be more photochemical reaction per 400J of light in the red than in the violet or vice versa? [3]

19. a) How do you account for the abnormal high value of the ionic mobilities of H^+ and OH^- ions in water? [2]
 b) In the photochemical combination of $\text{H}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ a quantum efficiency of 1×10^{-6} has been obtained with a wavelength of 480 nm. How many moles of HCl would be produced under these conditions per calorie of radiant energy absorbed? [3]
20. a) State the Stark-Einstein Law of Photo-chemical equivalence. Define Quantum yield. (ϕ) [2+1]
 b) Calculate the equilibrium constant of the reaction between Fe^{2+} and MnO_4^- in 1(M) acidic medium. Given $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ and $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}}$ are 0.77 volts and 1.51 volts respectively at 298K. [2]
21. a) A 5% solution of CaCl_2 with electrode area (A) of 2.54 cm^2 with distance between electrode (L) 0.65 cm has a specific conductance (W) of 0.178 ohm. What is the equivalent conductance of solution if density = 1.0 gm/cc? [3]
 b) Describe a calomel electrode with the cell reaction involved. [2]
22. a) Set up the galvanic cell for the following spontaneous reaction. [1]

$$2\text{Cr}(\text{s}) + 3\text{Hg}_2\text{Cl}_2(\text{s}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 6\text{Cl}^-(\text{aq}) + 6\text{Hg}(\text{l})$$

 b) How would you titrate a solution of AgNO_3 against KCl potentiometrically? And how would you determine solubility product K_{sp} of AgCl from there? [3]
 c) The absorbance value of a test solution is 0.30. What will be the percentage of transmission of incident light? [1]
23. a) The stoichiometry of a reaction indicates the order of the reaction. Justify or criticize. [1]
 b) Derive Michaelis-Menten equation in enzyme catalysis and show the result graphically illustrating the change in order of the kinetics involved. [4]
24. a) The rate constant of the reaction $\text{S}_2\text{O}_8^{2-} + \text{I}^- \rightarrow \text{product}$, Will be influenced by the addition of KCl in the reaction mixture at a given temperature. Justify [2]
 b) A first order reaction is 25% complete in 30 minutes at 227°C and in 10 minutes at 237°C . Calculate the energy of activation. [3]

_____ × _____