RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SIXTH SEMESTER EXAMINATION, MAY 2016

THIRD YEAR [BATCH 2013-16]

Date : 03/05/2016
CHEMISTRY (Honours)

Time : 11 am – 1 pm
Paper : VIII
Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

[*Attempt* ***one question*** *from each Unit*]

Unit – I

1. a) Explain whether true or false (Attempt **any two**) : [2×2]
   i) A molecule with zero dipole-moment cannot change its rotational state.
   ii) A given Raman-spectrum line of NO molecule shows $\Delta J = 0$ spectral line.
   iii) HBr molecule considered as an harmonic oscillator, has the maximum intense line for $v \neq 0$.

   b) Calculate the ratio of molecules in rotational level J = 2 relative to J = 0 for a molecule with rotational constant $1{\cdot}2\ \text{cm}^{-1}$ at 300 K. [2]

   c) Discuss the semi-classical theory of the Raman effect. [3]

   d) Explain why De and ke for $D^{35}Cl$ are essentially the same as De and ke for $H^{35}Cl$ but D_0 for these two species differs. [3]

2. a) Some band origins of $^1H^{35}Cl$ IR bands are

$$\begin{array}{ccc} 0 \rightarrow 1 & 0 \rightarrow 2 & 0 \rightarrow 3 \\ 2886\,\text{cm}^{-1} & 5668\,\text{cm}^{-1} & 8346\cdot 8\,\text{cm}^{-1} \end{array}$$

   Calculate $\tilde{\nu}_e$ and $\tilde{\nu}_e x_e$ for $^1H^{35}Cl$. [3]

   b) Derive a relation for the highest populated rotational level (J_{max}) in terms of rotational constant (B) and temperature. (Assume rigid rotor model for this derivation). [3]

   c) Qualitatively describe the pure vibrational active and vibrational Raman active modes of CO_2 molecule. Also show that 'mutual exclusion principle' is valid here. [4]

   d) Using concept of virtual state, explain Raman Scattering is a 2 photon process. [2]

Unit – II

3. a) State Franck-Condon principle. Comment of the probable intensities of lines obtained in vibrational-electronic spectra of a diatomic molecule, using this principle. [3]

   b) Draw a labelled Jablonski diagram with brief explanation of first order radiative proceses. [4]

   c) What do you mean by the term 'transmittance'? Find out the condition of I_a (absorbed intensity) to change linearly with concentration. [3]

   d) An uranyl oxalate actinometer is irradiated for 15 minutes with radiation of 435 nm. At the end of this time it is found that oxalic acid equivalent to 12ml of 0·001 molar $KMnO_4$ solution has been decomposed. Quantum efficiency of the actinometer is 0·58 with this wavelength of light. Find out the average intensity of light used in joule/s unit. [3]

4. a) Justify or criticize :
   i) "Quantum yield of primary photochemical reaction may or may not be unity"
   ii) "Phosphorescence spectra is more red-shifted than fluorescence spectra." [2×2]

   b) A molecule absorbs a quantum of light and undergoes transition to the first excited state. It then returns to the ground state through fluorescence. Assume that a quencher (Q) is present in the system which partially quenches fluorescence. Write down these events as steps of a mechanism and comment on the order of individual step. Find out the expression of fluorescence intensity and draw the suitable Stern-Volmer plot. What information can be obtained from this plot? [4]

c) A likely mechanism of photolysis of acetaldehyde is—

$$CH_3CHO + h\nu \rightarrow CH_3 + CHO$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$$

$$CH_3CO \rightarrow CO + CH_3$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$

Derive the expression for the rate of formation of CO and the quantum yield for CO. [3]

d) A certain photochemical reaction takes place when the reaction mixture is irradiated either by red light $(\lambda = 800\,\text{nm})$ or by violet light $(\lambda = 400\,\text{nm})$. Find out in which case there will be more reaction if 100 J of energy is absorbed. [2]

Group - B

[***Attempt one question from each Unit***]

Unit – III

5. a) Compare the rates of bromine water oxidation of α–(D)–Glucose and β–(D)–Glucose. [3]

b) Outline the pathways to convert :

i) D–Arabinose to D–Mannose

ii) D–Glucose to D–fructose [3]

c) When D-Arabinose is subjected to cyanohydrin synthesis, glucononitrile and mannononitrile are formed as major product, respectively, under two different reaction conditions. Explain. [3]

d) What is Merrifield resin? Show the steps in the synthesis of the tripeptide Ala.phe.gly in the solid phase with the help of the resin. State the advantages of the solid phase peptide synthesis. [4]

e) Write the names and structures of any one pruine and one pyrimidine base related to nucleic acids. [2]

6. a) Discuss the mechanism of osazone formation by an aldohexose. Why osazone formation does not proceed beyond the first two carbon atoms? [3]

b) Mutarotation of glucose is catalysed by phenol-pyridine mixture and more effectively by 2-hydroxypyridine. Explain with mechanism. [3]

c) How N-terminal of an aminoacid in a peptide is determined by Edman's method? Why it is more advantageous than Sanger's method? [3]

d) Draw the structures of the following nucleotides. [2]

i) guanosine triphosphate (GTP)

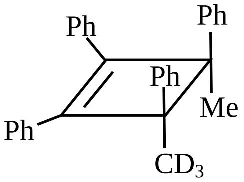
ii) deoxycytidine monophosphate (dCMP)

e) What is the sequence of amino acids in a heptapeptide Gly, Ser, HiS_2, Ala_2, Asp that is hydrolysed to tripeptides Gly.Ser.Asp, His.Ala.Gly and Asp.His.Ala. [2]

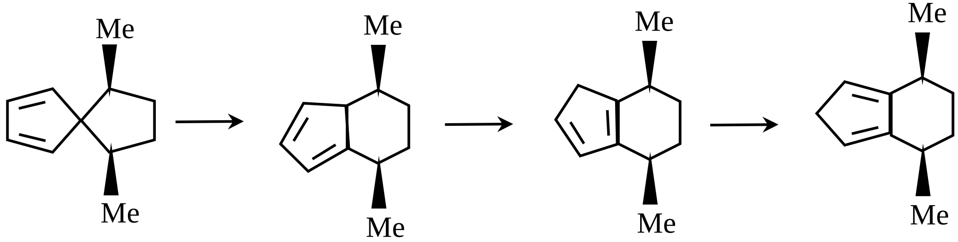
f) Oxidation of citronellal with chromic acid gives 3-methyladipic acid and acetone. Suggest the structure of the citronellal. [2]

Unit – IV

7. a) How would you employ pericyclic reactions in the synthesis of the following: [3]

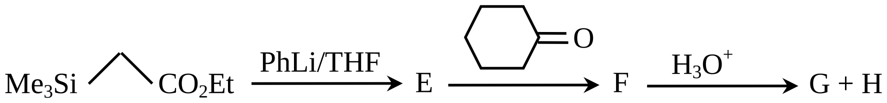


b) Indicate the type of sigmatropic shift in the following reaction sequence. [3]



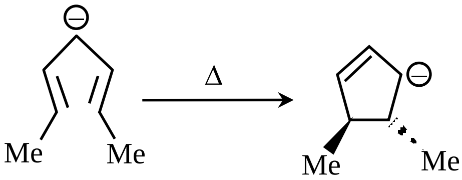
c) Using Me_3SiCN as one of the reagents covert p–benzoquinone into methylquinol. [2]

d) Identify 'E' to 'H' in the following reaction sequences. [2]

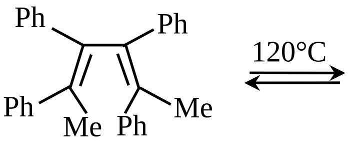


8. a) [1,3] sigmatropic shift is difficult to achieve thermally. Explain the phenomenon using F.M.O approach. [2]

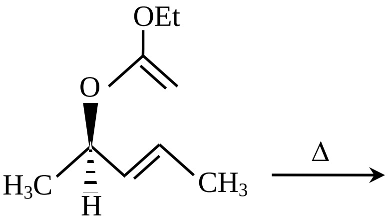
b) Use orbital drawings to determine whether this reaction is allowed or forbidden : [2]



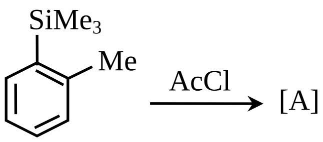
c) Predict the product of the following reaction from FMO consideration. [2]



d) Predict the product(s) in each of the following reaction showing the sterochemistry and indicate the reaction pathways : [3]



e) Write down the structure of [A]. [1]



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