

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. SIXTH SEMESTER EXAMINATION, MAY 2015

THIRD YEAR

CHEMISTRY (Honours)

Paper : VIII

Date : 05/05/2015

Time : 11 am – 1 pm

Full Marks : 50

[Use a separate Answer book for each group]

Group - A

Unit – I

[Answer any one question]

1. a) State Franck-Condon principle. Using it explain the formation of electronic spectra for a diatomic molecule having internuclear distances equal in ground and excited states. [2]
b) The dissociation energy of H_2 is 431.809 KJ/mole. If hydrogen is illuminated with radiation of wavelength 253.7 nm and if we assume that absorption of light quanta occurs followed by dissociation of H_2 molecules, how much of the original energy per mol quanta absorbed will appear as kinetic energy of the atoms? [4]
c) Draw the potential energy curve for ground electronic state of a diatomic molecule schematically showing the dissociation energy in this state. What do you understand by this potential energy? [2+1]
d) Hydrogen iodide decomposes to hydrogen and iodine when it is irradiated with radiation of frequency 1.45×10^{15} Hz. when 2.31J of energy is absorbed by HI(g), 0.153 mg of HI(g) is decomposed. Calculate the quantum yield for this reaction. [4]
2. a) i) What is meant by a photostationary state?
ii) When a solution of anthracene is irradiated with UV light, dimerization of anthracene is favored with increase of dimer concentration. Find out an expression for the concentration of the dimer at high monomer concentration at the photostationary state. [3]
b) In the photochemical combination of $H_2(g)$ and $Cl_2(g)$ a quantum efficiency of about 10^6 is obtained with a wavelength of 480 nm in terms of Cl_2 . How many moles of HCl (g) would be produced under these conditions per Joule of radiant energy absorbed? [3]
c) Define IC and ISC. Comment on their relative ease with proper justification. [3]
d) i) Give a schematic diagram of absorption and fluorescence spectrum against wave-length of radiation.
ii) Differentiate fluorescence from phosphorescence with respect to change in spin multiplicity and time scale citing reasons in brief. [1+3]

Unit – II

[Answer any one question]

3. a) i) The general forms of the anharmonic eigenfunctions can more easily be appreciated by adopting the Morse potential function. Show that the oscillator shows harmonic behaviour near r_e with force constant k given by $k = 2D_e\beta^2$ (terms having their usual meanings) [2]
ii) Find out the wave numbers for the anharmonic oscillator, at which fundamental and 1st hot band appear. [2]
b) State the form of energy for a diatomic rigid rotor. Herefrom arrive at the statement that the lines in a rotational spectrum are equispaced. [1+2]
c) Comment on the intensity distribution of rotational lines within a vibrational state. [3]
d) 'Stokes lines are more intense than anti-stokes lines.' Justify or criticize the statement. [2]
4. a) Consider a hypothetical molecule of empirical formula AB_2 . From the IR and Raman spectra, how does one conclude about the geometry of the molecule? [3]
b) Homonuclear diatomics are rotationally inactive but rotational Raman active. Justify or criticize. [3]

- c) The 1st three stokes lines in the rotational Raman spectrum of $^{16}\text{O}_2$ are separated by 14.4 cm^{-1} , 25.8 cm^{-1} and 37.4 cm^{-1} from the exciting radiation. Using the rigid rotor approximation obtain a value for r_0 . [3]
- d) "The anharmonic oscillator approximation leads to increased crowding of vibrational levels at higher vibrational quantum number." Comment on the statement with suitable energy function. [3]

Group - B

Unit – III

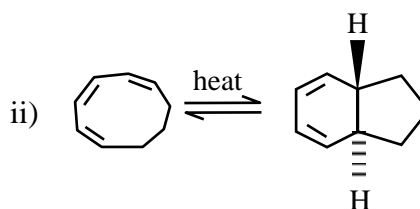
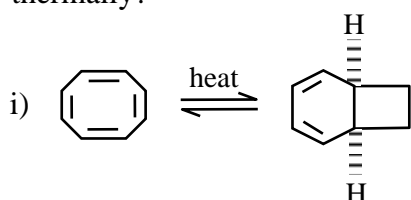
[Answer any one question]

5. a) Draw the chair conformations for α - and β -D-(+)-glucopyranose. Why most naturally occurring glucopyranosides are β -anomers? [1+1]
- b) An aldohexose (I) is oxidized by HNO_3 to a *meso*-glycaric acid (II). Ruff degradation of (I) yields (III), which is oxidized to an optically active dicarboxylic acid (IV). Ruff degradation of (III) yields (V), which is oxidized to L-(+)-tartaric acid (VI). Represent compounds (I) through (VI). [4]
- c) What is the sequence of amino acids in a tripeptide that is partially hydrolysed to the dipeptides Gly.Leu and Asp.Gly with reason? [2]
- d) How can Edmann method be used for the determination of primary structure of protein — explain. [3]
- e) Why is RNA hydrolyzed in alkali but DNA is stable in alkali? [2]
- f) With a suitable chemical reaction establish that geraniol incorporates a geminal dimethyl group located on an sp^2 carbon. [2]
6. a) In anhydrous MeOH, the equilibrium mixture of D-glucose contains 50% of the α -form, whereas in water it is 38%. Account for the observation. [3]
- b) Compare the rate of oxidation of β -D glucopyranose and its α -isomer by bromine water with plausible explanation. [2]
- c) How would you explain the non-reducing property of sucrose? [2]
- d) Aspartame (NutraSweet) is a remarkably sweet-tasting dipeptide ester. Complete hydrolysis of aspartame gives phenylalanine, aspartic acid, and methanol. Mild incubation with carboxypeptidase has no effect on aspartame. Treatment of aspartame with phenyl isothiocyanate, followed by mild hydrolysis, gives the phenylthiohydantoin of aspartic acid. Propose a structure for aspartame. [2]
- e) i) Does Chargaff's rule imply that equal amounts of guanine and adenine are present in DNA? That is, does $G = A$?
- ii) Does Chargaff's rule imply that the sum of the purine residues equals the sum of the pyrimidine residues? That is, does $A+G = C+T$?
- iii) Does Chargaff's rule apply only to double-stranded DNA, or would it also apply to each individual strand if the double helical strand were separated into its two complementary strands? [3]
- f) Synthesise citral from 6-methyl-hept-5-en-2-one. [3]

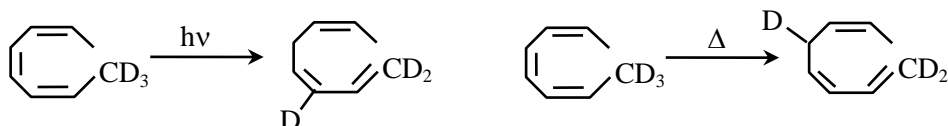
Unit – IV

[Answer any one question]

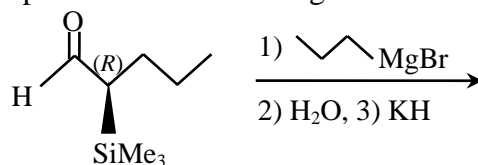
7. a) Which of the following electrocyclic reactions should occur readily by a concerted mechanism thermally? [3]



- b) Account for the difference in the products obtained under photochemical and thermal conditions. [3]

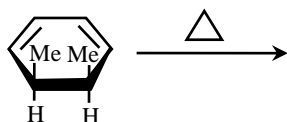


- c) What products would you expect from the following reactions. Give mechanism for the reaction. [2]

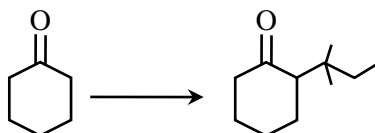


- d) "Aryl silanes undergoes *ipso* substitution with electrophiles"—explain with suitable example. [2]

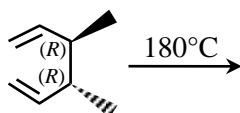
8. a) Give the products of the following thermal electrocyclic ring opening reaction. Explain the stereochemistry of the product with the help of FMO approach. [3]



- b) Carry out the following conversion using Me_3SiCl as one of the reagents. [2]



- c) Write down the product and suggest a mechanism : [2]



- d) What are the limitations of acyloin condensation in the preparation of small ring (4–7) compounds? How are these difficulties overcome? [3]

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