RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SIXTH SEMESTER EXAMINATION, MAY 2017
THIRD YEAR [BATCH 2014-17]
CHEMISTRY (Honours)
Paper : VIII [Gr.A&B]

Date : 02/05/2017
Time : 11 am – 1 pm
Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

[*Attempt one question from each Unit*]

Unit – I

1. a) True or False, explain. (**any two**) : [2×2]
   i) A molecule with zero dipolemoment cannot change its rotational state.
   ii) Raman spectrum involves a 2 photon process.
   iii) The difference between the vibrational levels (successive) is independent to the corresponding quantum number, always.

   b) Rotational absorption lines from $^{1}H^{35}Cl$ gas were found at the following wavenumbers : 145·37, 165·89, 186·23, 206·60 cm^{-1}.
   i) Calculate the moment of inertia and the bond length of molecule. [3]
   ii) Can you predict the position of the $^{2}H^{35}Cl$ corresponding lines? Explain with assumption involved. [2]

   c) Give examples of three model systems where the energy gap between 2 successive levels (i) remains the same (ii) decreases (iii) increases with increasing energy level. Also give the expression for the energy gap for each system. [3]

2. a) For vibrational Raman spectroscopy Stokes' radiation is much more intense than anti-Stokes' radiation but for rotational Raman spectroscopy they are of equal intensity —justify. [3]

   b) A microware spectrometer capable of operating between 60cm^{-1} and 90cm^{-1}, was used to observe the rotational spectra of HI and DI. Absorptions were measured as follows for three successive line,

HI (cm^{-1})	DI (cm^{-1})
64·275	65·070
77·130	71·577
89·985	78·094

   Determine the J value between which the transition has occurred for the first line in each case.
   For these above data check whether the bond length remains constant for the isotopic substitution. [At. wt. of I = 130] [4]

   c) A particular molecule undergoes spectroscopic transitions between ground state and an excited state of life time 10S. Calculate the width of the spectral line in hertz considering collisional broadening or Doppler broadening to be absent. [2]

   d) An AB_2, type of molecule can be either linear or non-linear. From the 'Exclusion Rule' one can have the qualitative idea about the structure. Explain with the rule. [3]

Unit – II

3. a) Consider a transition where the ground singlet state is less polar than the excited singlet. Explain how the fluorescence wavelength corresponding to such a transition would change if an electrolyte (one that does not interact with the fluorophore) is added to the solvent (water). [3]

b) i) Consider a molecular system with two electrons occupying two different spatial orbitals. Taking into account both spin and spatial states, write down all the possible electronic states of the system that are permitted by the Pauli's exclusion principle. [3]

ii) Mention the M_s and S values of all the states and classify the states as singlet and triplet states. [2]

c) A 0·01 molar solution of a compound transmits 20% of the sodium D line when the absorbing path is 1·50 cm. What is the molar absorption coefficient of the substance? The solvent is assumed to be completely transparent. [3]

d) What is the physical basis of Born-Oppenheimer approximation? [2]

4. a) Intensity of phosphorescence increases in presence of heavy atoms —justify. [2]

b) Write down the Frank-Condon principle. What is Frank Condon factor? [3]

c) In the photochemical decomposition of $C_2H_4I_2$,

$$C_2H_4I_2 + h\nu \rightarrow C_2H_4 + I_2$$

with radiation of 424 nm, the I_2 formed after 20 minutes required 41·14cc of 0·0025(M) solution of $Na_2S_2O_3$. The intensity of the light source was $9{\cdot}15\times10^{-4}\,J.S^{-1}$. Calculate the quantum yield of the process. [3]

d) Consider the following mechanism

$$M + h\nu_i \xrightarrow{k_a} M^*$$

$$M^* + Q \xrightarrow{k_q} M + Q \text{ (quenching)}$$

$$M^* \xrightarrow{k_f} M + h\nu_f \text{ (fluorescence)}$$

'I_f' and 'I_a' being the fluorescence intensity and the intensity of the absorbed light respectively, show that $\frac{1}{I_f} = \frac{1}{I_a}\left(1 + \frac{k_q}{k_f}[Q]\right)$ [3]

e) Why generally the fluorescence intensity increases as temperature is lowered? [2]

Group – B

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

Unit – III

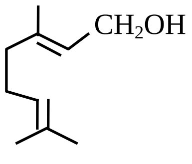
5. a) Methyl D-glucoside upon periodic acid oxidation was found to consume two moles of the acid per mole of the substrate molecule and produced 1 mole of formic acid besides giving 1 mole of a dialdehyde. Use these findings in predicting the ring size of the glucoside. [3]

b) E,F,G are three aldohexoses. E and F yield D-sorbital when they are catalytically hydrogenated. E and F yield different osazones when treated with excess phenyl hydrazine. F and G give the same osazone but different alditols. Give the structure of E, F and G assuming F and G are D-aldohexoses. [3]

c) Identify the products of the following reactions and explain their formation with mechanism.

$$-\text{NHCHR}^1\text{CONH}\underset{\substack{|\\ \text{CH}_2\text{CH}_2\text{SMe}}}{\text{C}}\text{HCONHCHR}^2\text{CO}- \xrightarrow[\text{aq. HCO}_2\text{H}]{\text{BrCN}} ?$$ [4]

d) What is special isoprene rule? Show whether the following compound obeys the said rule. [3]

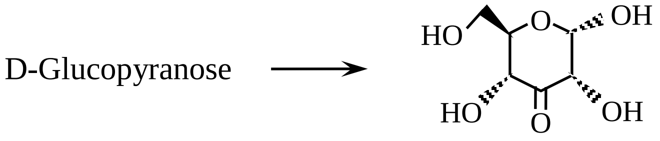


e) Write the structures and names of nucleosides and nucleotides corresponding to base guanine. [2]

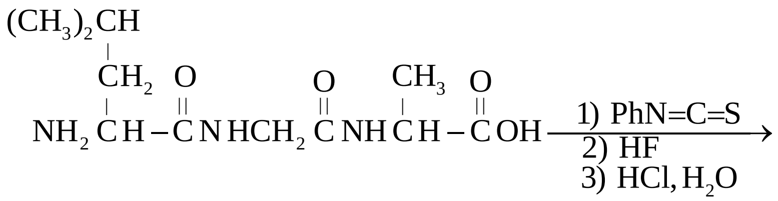
6. a) Show the mechanism of oxidation of aldoses with bromine water and explain which anomer will undergo oxidation at faster rate. [2]

b) Explain whether it is possible to distinguish between glucose and fructose by Fehling's test. [2]

c) Carry out the following conversion : [3]



d) Give the products of the following reactions : [2]



$$\mathrm{NH_2\overset{\overset{(CH_3)_2CH}{|}}{\overset{CH_2}{\overset{|}{C}}}H-\overset{O}{\overset{||}{C}}NHCH_2\overset{O}{\overset{||}{C}}NH\overset{CH_3}{\overset{|}{C}}H-\overset{O}{\overset{||}{C}}OH\xrightarrow[\text{2) HF} \;\; \text{3) HCl}, H_2O]{\text{1) PhN=C=S}}}$$

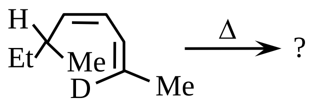
e) Use FDNB to distinguish between Lys. Gly and Gly.Lys. [2]
[Lysine : $H_2N(CH_2)_4CH(NH_2)COOH$]

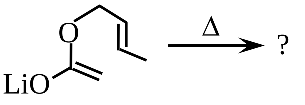
f) Draw the H-bonded complementary base pairing structure in DNA. [2]

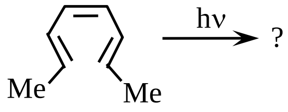
g) With a suitable chemical reaction establish that geraniol incorporates a geminal dimethyl group located on an sp^2-carbon. [2]

Unit – IV

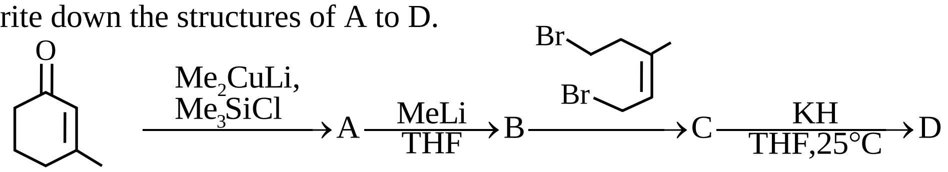
7. a) Predict the products and designate the pericyclic steps involved in the following reactions. [2×3]

i) 

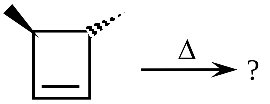
ii) 

iii) 

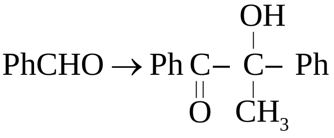
b) Write down the structures of A to D. [4]



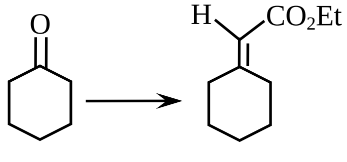
8. a) Predict the products and explain the following reactions by FMO theory. [3]



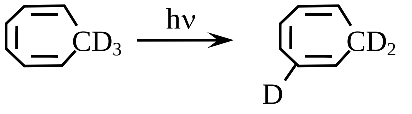
b) Carryout the following conversion using organosilicon reagent. [2+2]

i) 

$$\mathrm{PhCHO \rightarrow Ph\underset{\underset{O}{||}}{C}-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-\ Ph}$$

ii) 

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



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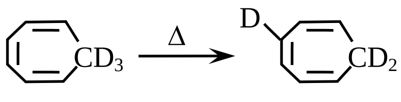

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