

Five Year Integrated M.Sc. Examination, 2019

Semester - VIII

Paper: CH-4-8-2A

Time: Three Hours

Full Marks: 40

Questions are of value as indicated in the margin.

Group-A

1. Answer **any five** questions: 5×2
- What is linear free energy relationship (LFER)?
 - What is ligand field activation energy (LFAE) and what are the important conclusions that can be drawn from its value?
 - What do you mean by photosensitiser?
 - Draw an orbital picture of the HOMO of 1,3,5-hexatriene.
 - What do you mean by Inter System Crossing (ISC) in photochemistry?
 - What could be the spins (I) of the nucleuses $^{13}\text{C}_6$ and $^2\text{D}_1$?
 - The Landé splitting factor (g_N) is the characteristic of each nucleus. Explain.

Group-B

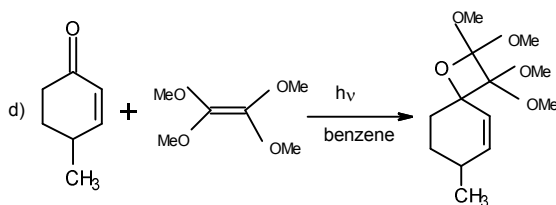
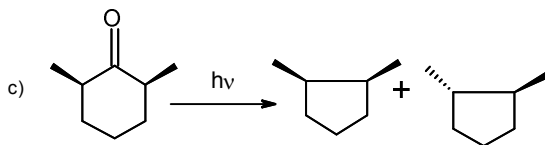
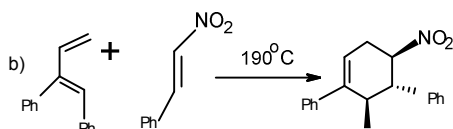
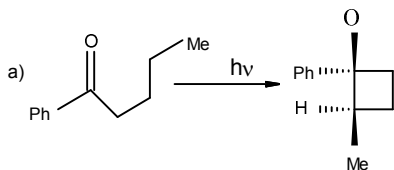
Answer **any one** question

2. a) Discuss about three different parameters that control k_{ex} values in water exchange reaction. 3
b) Thermodynamic and kinetic stability are not necessarily correlated. - Explain with appropriate examples. 3
c) Derive the rate law for a dissociative mechanism and find the value of k_{obs} when the leaving group is the solvent itself. Hence construct the double reciprocal plot. 3+1
3. a) What is the effect of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ on rate of a reaction? Hence explain what isokinetic trend is. 1+2
b) Using valence bond theory, explain associative path for the d^3 system. 2
c) Define stoichiometric and intimate mechanism. Draw the reaction profiles for different stoichiometric mechanisms with suitable reaction schemes. 2+3

Group-C

Answer **any one** question

4. a) Lewis acids catalyze some Diels-Alder reactions effecting a remarkable acceleration in the reaction-rate—Explain the fact. 3
b) What do you mean by reverse electron demand in Diels Alder Reaction? Explain with suitable example. 3
c) With the help of FMO method and suitable example, show that [2+2] cycloaddition reaction is photochemically allowed reaction. 4
5. Give the possible mechanism of the following reactions: 4×2.5



P.T.O.

Group-D

Answer *any one* question

6. a) What is the essential condition for a molecule to be ESR active? The coupling between electron and proton in H-atom is 50 mT, whereas it is only 2.3 mT in $\cdot\text{CH}_3$ radical. Explain why? Based on this data, calculate the percentage of time the electron spends over C-nucleus. 1+1+2
- b) What is exchange phenomenon? How can you use this technique to simplify the NMR spectra? 1+1
- c) What are “germinal” and “vicinal” nucleuses? Draw the NMR spectra of the $^{13}\text{CH}_3$ protons in $^{13}\text{CH}_3\text{CH}_3$ molecule. 1+3
7. a) What is recoil velocity? Why is it so important in Mossbauer spectroscopy? 1+1
- b) What is isomer shift or chemical shift in Mossbauer spectroscopy? Discuss about the parameter of a nucleus that controls the sign of the isomer shift? 1+2
- c) What is quadruple moment of a nucleus? Why such moment arises in a nucleus? The species, FeO_4^{2-} , gives a single line in Mossbauer spectrum at room temperature, whereas it shows six symmetrically spaced lines below 3.5 K. Explain with proper diagram. 1+1+3
