

Five Year Integrated M.Sc. Examination, 2017

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: 5x2
- Explain the role of $\Delta V^\ddagger$ in diagnosing the mechanistic pathway.
 - Comment on the lability/stability of d^2 and d^3 systems in the light of valence bond theory.
 - How you can convert cis-cyclooctene to trans-cyclooctene?
 - Which principle explains the intensity of vibronic transitions?
 - Why sigmatropic reaction needs higher activation energy than cycloaddition reaction?
 - How can you calculate the Landé splitting factor (g) of an electron?
 - What could be the spins (I) of the nuclei $^{17}\text{O}_8$ and $^{10}\text{B}_5$?
 - What is recoil velocity? Why is it so important in γ -rays spectroscopy?

Group-B

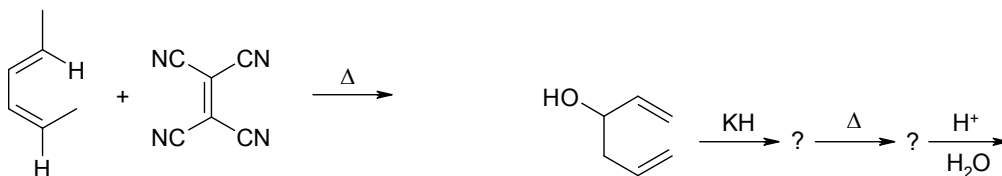
Answer **any one** question

2. a) Illustrate different types of ligand substitution reactions with examples (*at least 6*). 3
- b) Define stoichiometric and intimate mechanism. Draw the reaction profiles for different stoichiometric mechanisms with suitable reaction schemes. 2+3
- c) What is linear free-energy relationship? 2
3. a) 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
- b) Derive Eyring equation. 3
- c) Discuss about three different parameters that control k_{ex} values in water exchange reaction. 3

Group-C

Answer **any one** question

4. a) Draw the orbital correlation diagram for electrocyclic ring opening of cyclobutene. From this predict whether conrotatory or disrotatory mode will be allowed under thermal condition for this reaction. 4
- b) Give an example of $\pi^2s+\pi^2a$ cycloaddition showing the HOMO-LUMO interaction in the corresponding transition state. 4
- c) Write the structure of the products with stereochemistry in the following reactions. 1+1

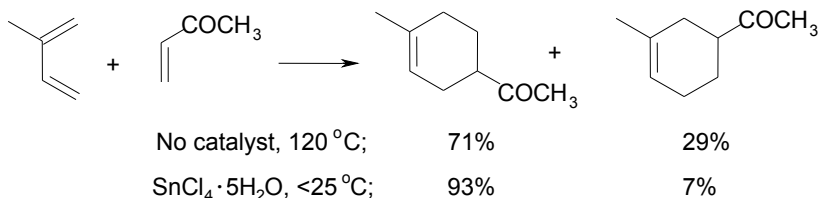


5. a) Why photosensitizer is used in photochemical reactions? 2
- b) Write the structure of the products with mechanism 2+2



P.T.O.

c) Explain the product ratio of the following reaction:



Group-D

Answer *any one* question

6. a) What is relaxation time? How many types of relaxation are observed in NMR spectra? How do they influence the NMR spectra? 1+2+1
- b) What is exchange phenomenon? How can you use this technique to simplify the NMR spectra? 1+2
- c) The chemical shift of the CH₃ protons in diethyl ether is $\delta = 1.16$ ppm and that of the CH₂ protons is 3.36 ppm. What is the difference in local magnetic field between two regions of the molecule when the applied field is 16.5 T? 3
7. a) What is the essential requirement for a molecule or ion to be ESR active? The ESR spectrum of a molecule or ion is expressed in term of its observed 'g' value. Why? The ground state of Fe³⁺ ion shows the 'g' value close to free electron having value 2.00. Explain. 1+2+2
- b) What is the advantage of using "Double Resonance" technique in ESR spectra? 2
- c) A radical containing two inequivalent protons with hyperfine constant 2.0 mT and 2.6 mT gives spectrum centred on 332.5 mT. At what fields do the hyperfine lines occur and what are their relative intensities? 3