

Five Year Integrated M.Sc. Examination 2022

Semester - V

Course: CH-3-5-1

(Chemistry)

Time: Four Hours

Full Marks: 80

Questions are of value as indicated in the margin

Group-A

1. Answer **any ten** questions: 10 × 2
= 20
- (a) Comment on the geometry of BF_3 molecule according to Bent's rule
 - (b) Show the geometry of I_3^- ion according to VSEPR theory with proper explanation.
 - (c) Compare the stability of H_{12} and H_8 molecules.
 - (d) What are the shapes of CH_2 and BH_2^+ molecules?
 - (e) Absorption spectra of $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ is broad. Explain.
 - (f) Establish the spinel type in Mn_3O_4 .
 - (g) Draw χ_M versus T plot for diamagnetic, paramagnetic, ferromagnetic and antiferromagnetic compounds.
 - (h) $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is green whereas $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is colorless. Explain.
 - (i) Benzyl chloride is more reactive than ethyl chloride both under $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ conditions. Explain.
 - (j) The rate of reaction of 1-bromobutane with azide ion increases 5×10^3 times on changing the solvent from methanol to acetonitrile. Explain.
 - (k) Nucleophiles are usually anions but some anions are not nucleophiles. One such example is BF_4^- . Explain the inertness of BF_4^- .
 - (l) Explain why a synthetic chemist will normally prepare aryl alkyl ether from a phenoxide plus a haloalkane rather than from an alkoxide plus an aryl halide.

Group-B

Answer **any four** questions

- 2. Draw the involved molecular orbitals of BeH_2 molecule by considering participation of H-group orbitals and show the qualitative molecular orbital diagram of the above said molecule. 3+2
- 3. Write the mathematical formulations for the MO formation after LCAO for BH_2 molecule. Draw the MO energy diagram of the same molecule. 3+2
- 4. Draw the Walsh diagram of NH_2 molecule and give reasons for variation of energy of molecular orbitals with the change of bond angle. 2+3
- 5. Draw the involved molecular orbitals considering symmetry adapted linear combination for H_3 species and show the involved MO diagram. 3+2

6. Show the electronic configuration of H_3^- , H_3^+ and H_3 . Comment on their stability order. What will be the geometry of H_3^+ and H_3 ? 1.5+1.5
+ 2

Group-C

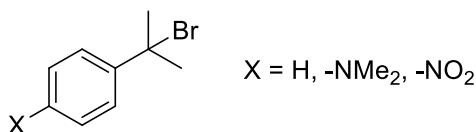
Answer *any four* questions

7. Construct the microstate table for p^2 electronic configuration. Deduce the various term states associated with it using the table. Hence establish which will be the ground state term and write the relative energies of the terms. 2+1.5
+1.5
8. (a) Thiocyanate reacts with Fe^{3+} to form a highly colored species and not with Fe^{2+} , but the opposite behavior is noticed in the case of 2,2'-bipyridyl reacting with Fe^{2+} and Fe^{3+} . – Explain. 2
(b) Draw the Orgel's diagram for d^3 electronic state and show the possible transitions. 3
9. (a) CN^- forms six-coordinated complexes with Cr(III) and Co(III), but with Ni(II) the most stable complex formed is four coordinate $\text{Ni}(\text{CN})_4^{2-}$. – Explain. 2
(b) What is paramagnetism? What is its essential criterion? 1
(c) Find out the spin-only magnetic moment of the metal ion in $[\text{MnCl}_4]^{2-}$. 2
10. (a) What are the important characteristics of a Tanabe-Sugano diagram? 2
(b) Explain the origin of the intense color in MnO_4^- . A similar type of species is ClO_4^- , but it is colorless, why? 2+1
11. (a) Explain the variation of enthalpy of hydration of bivalent metal halides from Ca^{2+} to Zn^{2+} . 2
(b) What is Curie-Weiss law and when it is applicable? Hence, explain Curie and Neel temperatures with appropriate illustration. 1+2

Group-D

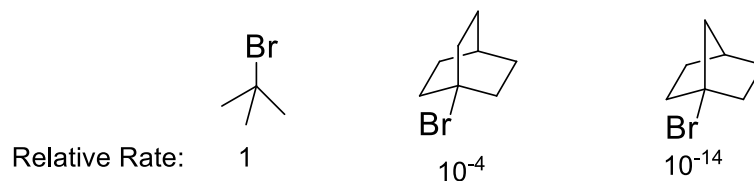
Answer *any four* questions

12. (a) The incorporation of radioactive iodide ($^*\text{I}$) into enantiopure 2-iodooctane in acetone as solvent leads to the following observation, $(k_a/k_\beta) = 2$, where k_a is the rate constant of racemization and k_β is the rate constant of radioactive iodine incorporation. Show the mechanism and explain how does these data support an $\text{S}_\text{N}2$ mechanism? 2.5
(b) Arrange the following substrates in order of increasing reactivity in solvolysis reaction. 2.5

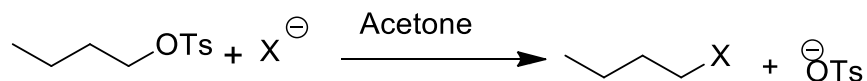


Justify your proposed order showing the mechanism of a typical solvolysis reaction.

13. (a) Explain the observed relative rates of solvolysis of the following compounds in 80% aq. EtOH: 2.5

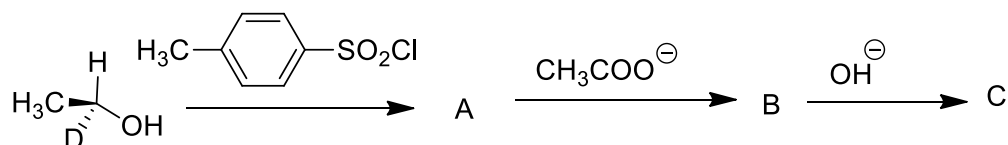


- (b) Account for the following observations. In the following reaction, 2.5

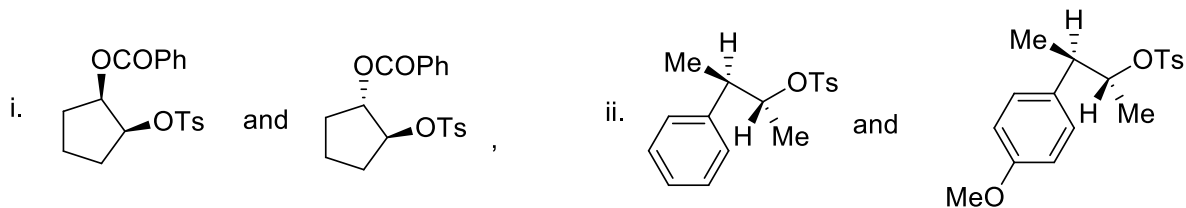


the order of nucleophilicity for the various halides is $\text{I}^- > \text{Br}^- > \text{Cl}^-$, when LiX is used, but the order is $\text{Cl}^- > \text{Br}^- > \text{I}^-$ when $\text{Bu}_4\text{N}^+\text{X}^-$ is used.

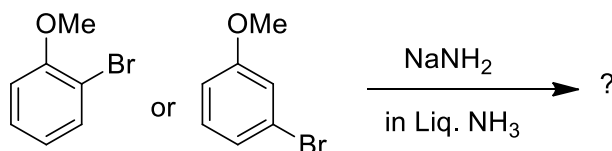
14. (a) Account for the stereochemical course involved in each step of the following reaction sequence and give three dimensional structures for A, B, and C. 2.0



- (b) Deduce, among each of the following pairs, for which member anchimeric assistance is of greater importance during solvolysis reactions. Justify. 2×1.5

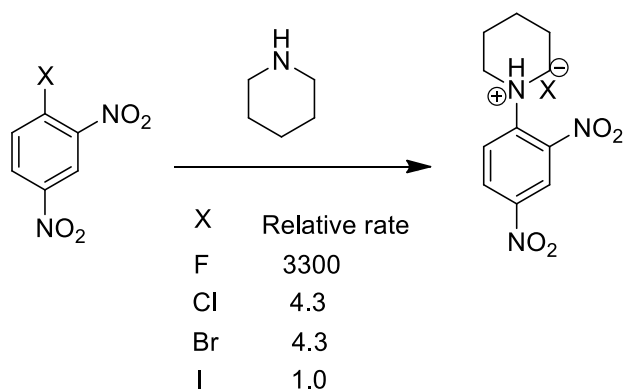


15. (a) Complete the following reactions and explain showing plausible mechanism. 2.5



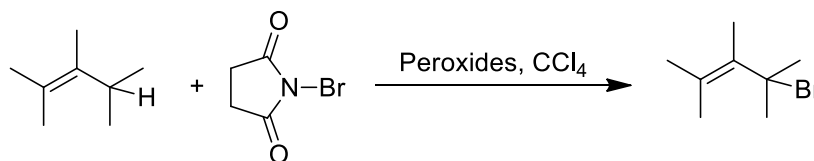
(b) Explain the following observation during the following aromatic nucleophilic substitution reaction.

2.5



16. (a) Provide mechanistic insight of the following allylic bromination reaction:

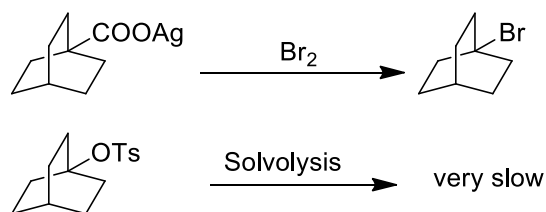
3.0



Predict the role of NBS in this reaction. In addition, provide evidences in support of the mechanism.

(b) Explain the following observation mechanistically.

2.0



What can be concluded from this observation?