2018

M.Sc. 4th Semester Examination

CHEMISTRY

PAPER—CEM-401

Subject Code—24

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

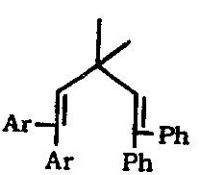
(Organic Special)

Group—A

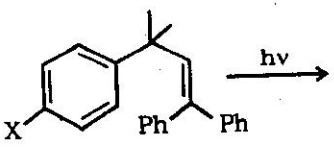
Answer any *four* questions. 2×4

Group—A (1)

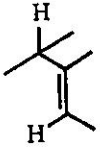
Predict the products for the following photochemical reactions and justify you answer : 2+2+2+2

1. 

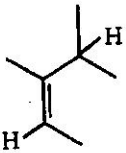
A, when Ar = p-MeO-C_6H_4 and
B, when Ar = p-NC-C_6H_4

2. 

C, explain the rate of reaction when X = H, OMe and CN

3. 

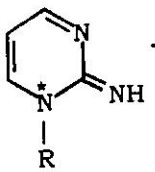
$\xrightarrow[\text{Eosin, } O_7]{h\nu}$ D + E (1:1)

4. 

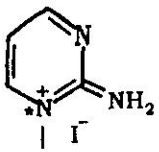
$\xrightarrow[\text{Rose bengal, } O_2]{h\nu}$ F + G (4:1)

Group—A (2)

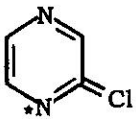
Write down the product for each transformation and establish the mechanism, [*] is ^{15}N labeled :

5. 

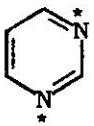
$\xrightarrow{H_2O}$ A

6. 

Aq. NaOH, warm → B

7. 

KNH2, Liq. NH3 → C

8. 

Aq. N_2H_4, 130°C → D (Not ^{15}N labeled)

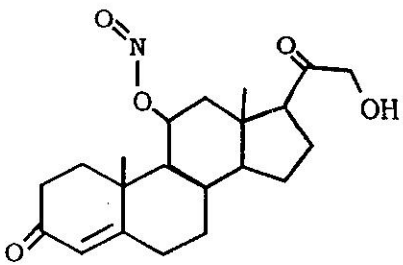
Group—B

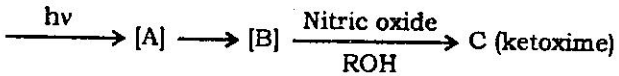
Answer any *four* questions. 4×4

Group—B (1)

9. Define Barton reaction. What are the criterions for Barton reaction ? What do you mean by remote substitution ? Explain the difference between Barton reaction and Hofmann-Loeffler-Freytag reaction with a scheme.

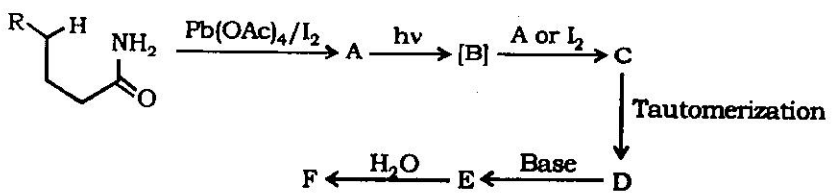
10. Write down the structure of the products with proper mechanism for the following reaction scheme :



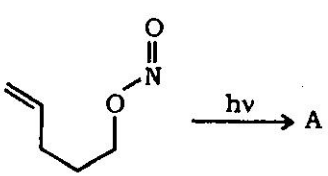


Group—B (2)

11. Predict the product for the following transformation explaining properly each step :



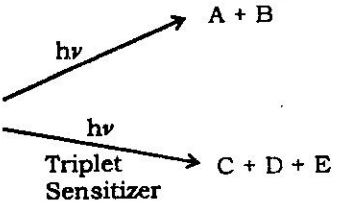
12.



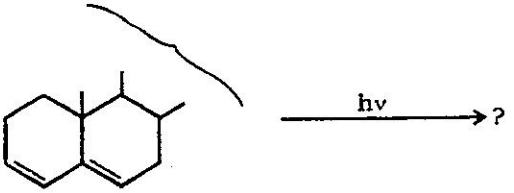
Group—B (3)

Write down the products in solution mentioning the major product for the following photochemical reactions with proper explanation and mechanism :

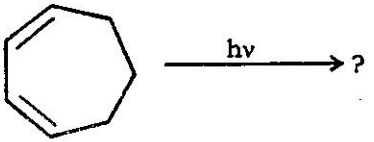
13. 1, 3 butadiene



14. (a)



(b)



Group—B (4)

15. Write the structures of the following coenzymes

(i) NAD and (ii) FAD.

What are the active parts present in the molecules and participate in the metabolic process of biological system.

16. How thiamine pyrophosphate decarbodylates the pyruvic acid and maintains its original state of reactivity ?

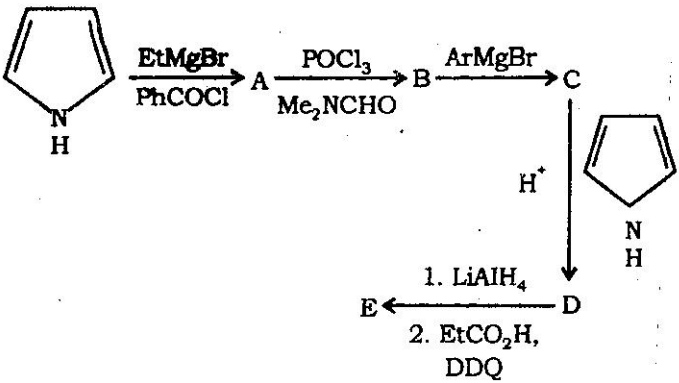
Group—C

Answer any *two* questions. 8×2

17. Explain with proper reason, at room temperature imidazole is solid however 1-methylimidazole is not solid. Establish the role of histidine in some hydrolytic enzymes. Explain the 'Proton Shuttle' mechanism in protein via imidazole.

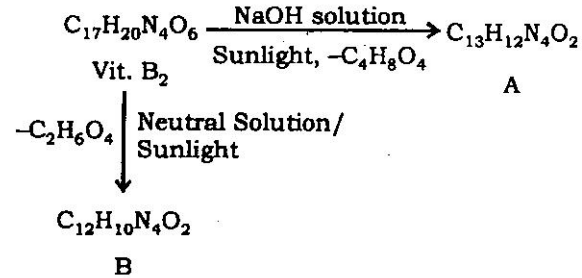
1+4+3

18. What is CDI ? Explain the role of CDI in peptide synthesis chemistry with proper reaction scheme to make an amide. Write down the products for the following transformation :



$\frac{1}{2}+2\frac{1}{2}+5$

19. The compound riboflavin (Vitamin B2) gives the following product on successive treatments as follows :



Deduce the structures of (A) and (B) and establish which one is stable and also indicate the point of attachment of the elimination part. 4+4

20. A monosaccharide (Vit. C) with molecular formula ($C_6H_8O_6$) decolorizes $KMnO_4$ solution, forms hydrazone, precipitate silver on treating with Tollen's reagent and soluble in alkaline (NaOH) solution. It also exhibits violet coloration with $FeCl_3$ solution. Vitamin C on treating with I_2 solution produces a compound, molecular formula $C_6H_6O_6$ [A], which on further treatment with (I_2/cold NaOH solution) yields oxalix acid (COOH-COOH) and $C_4H_8O_4$ [B]. Assign the structure of 'B' and indicate the structure of 'A' as well as Vitamin 'C'.

4+3+1

(*Inorganic Special*)

Group—A(a)

1. Answer any *two* questions : 2×2

(a) Schematically present all the possible binding modes of CO as ligand.

(b) Draw the qualitative MO diagram indicating relative energies of orbitals involved in metal-metal multiple bonding.

(c) Is it possible to replace all the 'CO' molecules from $Cr(CO)_6$ complex ? Explain.

(d) What do you mean by quintuple bond ?

Group—A(b)

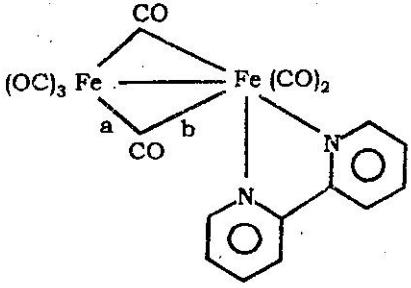
Answer any *two* questions. 4×2

2. What happens when $Fe(CO)_5$ is treated with

(i) BH_4^- and (ii) OH^- ?

Cite the intermediates for both the reactions.

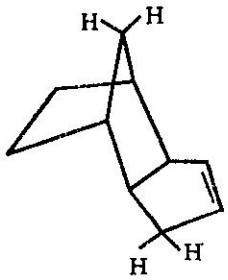
3. Explain the Carbonyl bonding pattern in the following complex :



a = 1.89 Å
b = 2.37 Å

4. Predict the final product for the following reaction :

(a) $Fe(CO)_5 + C_p \longrightarrow$

(b) $Mo(CO)_6 +$ 

$\xrightarrow[\text{diglyme, 1h}]{\text{750w}}$

(c) $\left[Cr(CO)_5\right]^{2-} + MeOH \longrightarrow$

(d) $Mn_2(CO)_{10} + H_2 \xrightarrow{200\ bar}$

5. (a) Justify closed trigonal bipyramidal structure of the $[Os_5(CO)_{16}]$ cluster.

(b) Predict the structure of the metal framework of $Co_3(CO)_9(\mu_3 - CCl)$ cluster by TVE Count.

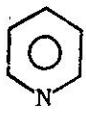
Group—A(c)

Answer any *one* question.

6. (a) Predict the metal core structure of the $[Os_8(CO)_{22}]^{2-}$ cluster. Draw the structure.

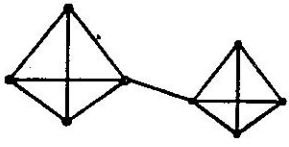
(b) $Os_5(CO)_{18}$ offers 'raft-cluster'. Is this consistent with the number of valence electrons available ?

(c) Predict the product of the following reactions :

(i) $Mn_2(CO)_{16} +$  $\xrightarrow{120^\circ C}$

(ii) $\left[Mn(CO)_5\right]^- \xrightarrow{Fe(CO)_5}$ 3+3+2

7. (a) How will you synthesize $[Fe_3(CO)_{11}]^{2-}$ starting from $Fe_3(CO)_{12}$? Write down the structure of $[Fe_3(CO)_{11}]^{2-}$.

(b) $[Ir_8(CO)_{22}]^{2-}$ offers  structure. Propose an appropriate electron counting scheme for this cluster.

(c) For $HRu_6(CO)_{17}B$ cluster, confirm that the total valence electron count is consistent with its the octahedral framework structure.

Group—B(a)

8. Answer any *two* questions : 2×2

(a) Materials having no permanent magnetic dipoles are called antifermagnetic. Is this statement true ? Explain.

(b) Explain the term "susceptibility" in magnetism.

(c) What is Lande interval rule ?

(d) Write short note on "Direct metal-metal interaction".

Group—B(b)

Answer any *two* questions. 2×4

9. Distinguish between ferromagnetic and antiferromagnetic materials. Give examples for each class.

10. Explain the diamagnetic nature of bis (diazoaminobenzenato) copper (II) complex.

11. Which one of the following two complexes will have more superexchange interaction and why ?

(i) $\left[(NH_3)_5Cr-O-Cr(NH_3)_5\right]Br_4$

(ii) $\left[(NH_3)_5Cr-OH-Cr(NH_3)_5\right]Br_5$

12. Explain the following magnetic moment data (at 27°C)

$[Sm(acac)_3]$: 1.4 B.M.
$[Eu(acac)_3]$: 3.5 B.M.

Group—B(c)

Answer any *one* question. 1×8

13. Derive an expression for magnetic moment for a substance whose multiplet width is large as compared to kT. 8

14. Derive Curie equation for paramagnetic compound. 8

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(*Physical Special*)

Group—A

Answer any *four* questions of the following. 2×4

1. The spatial part of the wavefunction of an atom in its ground state is 1s(1)1s(2). Write down its spin wave function.

2. Find the term symbol for the lowest energy state of nitrogen atom.

3. State and explain the parity selection rule for magnetic dipole transition.

4. State Koopman's theorem.

5. Electronic configuration of excited H_2 molecule is $1\sigma_g^1 1\sigma_u^1$. Write down the spin wavefunction of the triplet state with $m_s = 0$.

6. Hartree-Fock equation is called Intrego-differential equation — Explain.

7. State the rules for energy ordering of terms of many electron atom.

8. Find the molecular term symbol for N_2^+.

Group—B

Answer any *four* questions of the following. 4×4

9. $|j, m\rangle$ are the simultaneous eigen kets of operator J^2 and J_z. Obtain the matrix representation of J_z when $j = \frac{5}{2}$.

10. Find the eigen value and eigen vectors of the following matrix :

$$\begin{pmatrix} 1 & -2 \\ 1 & 4 \end{pmatrix}.$$

11. Obtain the eigen values of S_z and S^2 operator for atom with four no. of electrons (N = 4) in closed shell configuration.

12. Give a schematic diagram with appropriate term symbols for 1s → 2p transition in H-atom (i) in the absence and (ii) in the presence of an external magnetic field.

13. Write down the spin-orbit interaction Hamiltonian for L-S coupling scheme. Obtain the expression of spin-orbit interaction energy (E_{so}).

14. Use j-j coupling scheme to obtain the atomic terms for p^2 configuration.

15. Raising operator for total angular momentum operator, J_+ *follows the following* equation,

$$J_+|J, m\rangle = C_+(J,m)\,|J, m+1\rangle.$$

Find the value of C_+ (J, m)

16. Use L-S coupling scheme to obtain the possible terms for d^2 configuration and hence obtain the ground state term.

Group—C

Answer any *two* questions of the following. 2×8

17. The Hamiltonian, H and another observable, A of a certain three level system is represented by the following matrices,

$$H = \hbar\omega \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

$$A = \lambda \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

where 'ω' and 'λ' are positive real numbers. Find the eigen values and eigen vectors of 'H' and 'A'. 4+4

18. Write down the possible wave functions in the form of Slater determinant for a two electron atom (Assume pure spin state). Obtain the energy expectation value of each state and hence show that the energy of the triplet state is lower than the singlet state. 2+6

19. Deduce the expression of $\hat{p}_x$ and $\hat{H}$ of linear Harmonic Oscillator in terms of raising and lowering operators. Hence obtain the matrix representation of p_x and H. 4+4

20. Deduce Hartree-Fock equation for many electron atom. How do you obtain HF orbitals using self consistant field (SCF) method. 5+3
