3 (Sem–6/CBCS) CHE HC 1

2024

CHEMISTRY

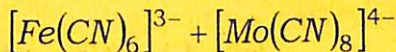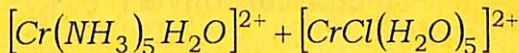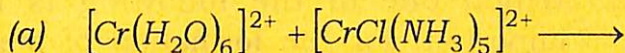(Honours Core)

Paper : CHE-HC-6016

(Inorganic Chemistry–IV)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Choose the correct answer $1 \times 7 = 7$

    (a) $\left[Cr(H_2O)_6\right]^{2+} + \left[CrCl(NH_3)_5\right]^{2+} \longrightarrow$

    $\left[Cr(NH_3)_5 H_2O\right]^{2+} + \left[CrCl(H_2O)_5\right]^{2+}$

    $\left[Fe(CN)_6\right]^{4-} + \left[Mo(CN)_8\right]^{3-} \longrightarrow$

    $\left[Fe(CN)_6\right]^{3-} + \left[Mo(CN)_8\right]^{4-}$

    Which one of the following is correct statement ?

    (i) Both involve inner sphere mechanism

(ii) Both involve outer sphere mechanism

(iii) Reaction I follows inner sphere mechanism and reaction II follows outer sphere mechanism

(iv) Reaction I follows outer sphere mechanism and reaction II follows inner sphere mechanism

(b) Wilkinson's catalyst is

(i) $[RhCl_3(PPh_3)_3]$

(ii) $[RhCl_3(PPh_3)]$

(iii) $[RhCl(PPh_3)_3]$

(iv) $[RhCl_2(PPh_3)_2]$

(c) Which one of the following is not important for the formation of stable metal carbonyls?

(i) Metals with low oxidation states

(ii) Metals with small size

(iii) Lowering of carbon-oxygen bond order

(iv) EAN is obeyed

(d) Which of the following is a wrong statement about industrially important catalytic processes?

(i) The proportion of H_2 gas in water-gas mixtures can be increased.

(ii) All metals in Fischer-Tropsch catalytic processes have ability to chemically absorb carbon monoxide.

(iii) Nickel is best surface for methanation in Fischer-Tropsch processes,

(iv) Water gas cannot be obtained from natural gas.

(e) Which of the following precipitates cannot be observed by use of group V reagents?

(i) $BaCO_3$

(ii) $SrCO_3$

(iii) $CuCO_3$

(iv) $CaCO_3$

(f) Which is true about $Mn(CO)_4NO$?

(i) The complex is paramagnetic and follows $18e^-$ rule

(ii) The complex is diamagnetic and follows $18e^-$ rule

(iii) The complex is paramagnetic and does not follow $18e^-$ rule

(iv) The complex is diamagnetic and does not follow $18e^-$ rule

(g) The n in symbol for hapticity (η^n) represents :

(i) number of ligands attached to the metal

(ii) number of atoms of the ligand within a bonding distance to the metal

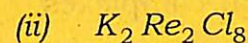(iii) charge on the ligand

(iv) co-ordination number of the metal

2. Answer the following : 2×4=8

(a) Draw the structure of $Fe_2(CO)_9$ and $CO_2(CO)_8$

(b) Common ion effect plays an important role in qualitative analysis. Explain.

(c) Define ground state trans-effect with an example.

(d) What is the number of metal-metal bond in the following compounds?

(i) $Mn_2(CO)_{10}$

(ii) $K_2 Re_2 Cl_8$

3. Answer **any three** of the following : 5×3=15

(a) Explain the mechanism of nucleophilic substitution reaction in square planar complexes.

(b) Explain EAN rule. Which of the following obey this rule :

$$Cr(CO)_6 ; Fe(\eta - C_5H_5)_2$$

Draw the structure of

$$\eta^5 - C_5H_5 - Re(CO)_2C_5H_5$$

(c) Discuss the methods of removal of oxalate and phosphate ions during the qualitative analysis of salt mixture.

(d) Draw the catalytic cycle of the hydroformylation of alkene. Discuss the reactions involved in various steps.
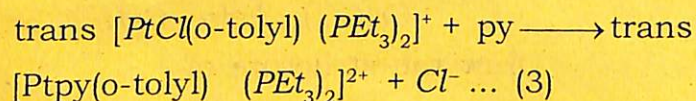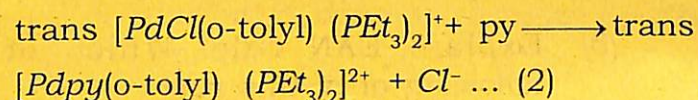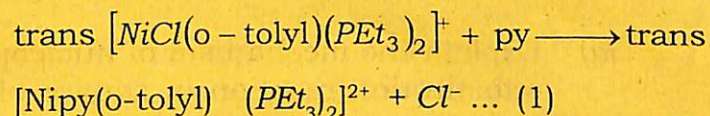
(e) Explain the mechanism of outer sphere redox reaction of co-ordination compounds. 2+2+1=5

4. Answer *any three* of the following :

    $10 \times 3 = 30$

(a) (i) Discuss Eigen-Wilkins mechanism of ligand substitution reactions in octahedral complexes. 4

(ii) For the following substitution reactions :

trans $\left[NiCl(o-tolyl)(PEt_3)_2\right]^+ + py \longrightarrow$ trans

$[Nipy(o\text{-}tolyl) \ (PEt_3)_2]^{2+} + Cl^-$ ... (1)

trans $[PdCl(o\text{-}tolyl) \ (PEt_3)_2]^+ + py \longrightarrow$ trans

$[Pdpy(o\text{-}tolyl) \ (PEt_3)_2]^{2+} + Cl^-$ ... (2)

trans $[PtCl(o\text{-}tolyl) \ (PEt_3)_2]^+ + py \longrightarrow$ trans

$[Ptpy(o\text{-}tolyl) \ (PEt_3)_2]^{2+} + Cl^-$ ... (3)

The observed rates of reaction (1) is 50 times faster than reaction (2) which, in turn, is about 100,000 times faster than reaction (3). Explain. 2

(iii) Define kinetically labile and inert complexes. The high spin complex ion $\left[Cr(H_2O)_6\right]^{2+}$ is labile but the low spin complex ion $[Cr(CN)]^{4-}$ is inert. Explain. $2+2=4$

(b) Discuss synthesis, chemical properties of $(\eta - C_5H_5)_2 Fe$ and give a description of bonding in this important organometallic compound. $2+2+6=10$

(c) Discuss the role of organometallic compounds in catalysis with special reference to

(i) Synthesis gas by metal carbonyl complexes

(ii) Alkene hydrogenation by Wilkinson's catalyst. $5+5=10$

(d) Explain the preparation, structure and bonding of Zeise's salt. The IR stretching frequency of $C = C$ bond in metal ethylene complex is found to be 1576 cm^{-1} whereas the corresponding the corresponding frequency for free C_2H_4 is 1625 cm^{-1}. Explain.
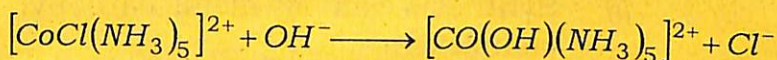
$1+2+5+2=10$

(e) (i) What is Zeigler-Natta catalyst? How is it prepared ? Explain its major application. $2+2+1=5$

(ii) What is Wacker process? Give one example. Mention the main three catalytic reaction sequence involved in it.

$1+1+3=5$

Contd.

(f) *(i)* Explain with suitable example how steric crowding at the reaction center influence the rate of substitution reactions in square planar and octahedral complexes. 3+3=6

(ii) Discuss the mechanism of the following substitution reaction :

$$[CoCl(NH_3)_5]^{2+} + OH^- \longrightarrow [CO(OH)(NH_3)_5]^{2+} + Cl^-$$

4

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2024

CHEMISTRY

(Honours Core)

Paper : CHE–HC–6026

(Organic Chemistry–V)

Full Marks : 60

Time : Three hours

**The figures in the margin indicate
full marks for the questions.**

1. Answer the following questions : 1×7=7

    (a) Give an example of triphenylmethane dye.

    (b) Write the name of the five-membered cyclic hemeacetal form of D-ribose.

    (c) Draw the structure of the product obtained from sodium borohydride reduction of D-glucose.

    (d) In which region NMR spectra are observed ?

(e) Which of the following statements is false about glucose ?

    (i) It is a reducing sugar.

    (ii) It is a disaccharide.

    (iii) It has a pyranose structure.

    (iv) It is a polyalcohol.

(f) Fill up the blank :

Two monosaccharides are joined through a ____ bond to form a disaccharide.

(g) Mention the configuration of natural rubber.

2. Give answer of the following : $2 \times 4 = 8$

(a) Draw the Fisher projection diagram of the tetroses.

(b) Name the monomer units of Buna-S-rubber.

(c) (i) Between nitrobenzene and nitrophenol which one is more intensely coloured ?

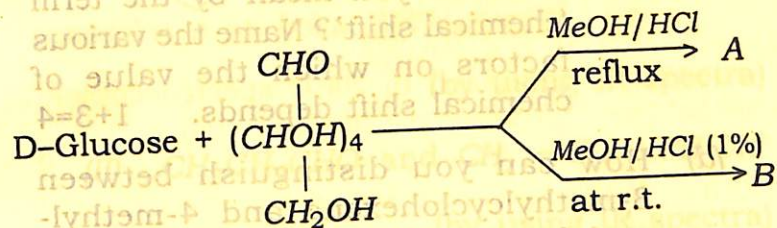   (ii) What are the commonly encountered transitions in UV spectroscopy ?

(d) Fill up the blanks :

Starch contains about 20% of a water-soluble fraction called ____ and 80% of water-insoluble fraction called ____.

3. Answer *any three* of the following : $5 \times 3 = 15$

(a) (i) Find out A and B in the following reaction :   2

$$D\text{–Glucose} + (CHOH)_4 \quad \begin{array}{c} \xrightarrow[\text{reflux}]{MeOH/HCl} A \\ \xrightarrow[\text{at r.t.}]{MeOH/HCl\ (1\%)} B \end{array}$$

with structure:
$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

(ii) Write the synthesis of methyl orange.   3

(b) Write true or false for the following statements : $1 \times 5 = 5$

    (i) Fructose exists as both pyranose and furanose structures.

    (ii) The simplest carbohydrate is glyceraldehyde.

(iii) Galactose is not a disaccharide.

(iv) Hydrolysis of starch with dil. H_2SO_4 at 393K under pressure gives _____ glucose.

(v) Glucose is also known as dextrose.

(c) *(i)* Fill up the blank : 1

No two compounds except the _____ can have similar IR-spectra.

(ii) What do you mean by the term 'chemical shift'? Name the various factors on which the value of chemical shift depends. 1+3=4

(d) How can you distinguish between 3-methylcyclohexene and 4-methylcyclohexene on the basis of mass spectroscopy?

(e) Write short notes on : *(any two)*

2½×2=5

(i) Zeigler-Natta polymerisation
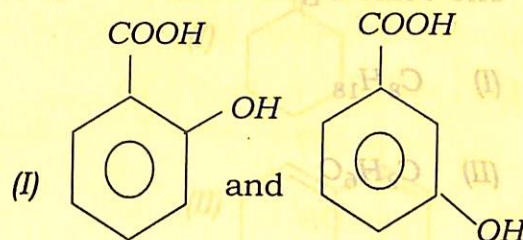
(ii) Amylose

(iii) Volcanization of rubber

(iv) Degree of polymerisation

4. Answer *any three* of the following : 10×3=30

(a) *(i)* Define absorbance. 1

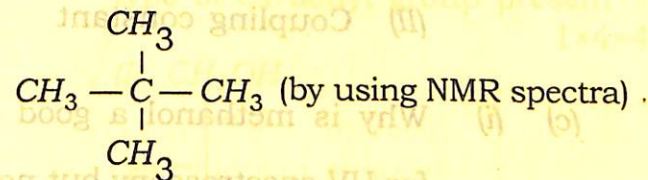*(ii)* How will you differentiate between the following pairs of compounds?

3×3=9

(I)   and

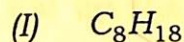*(II)* CH_3CH_2CHO and $CH_2=CH-CH_2OH$

(by using IR spectra)

(III) $CH_3-CH_2-CH_2-CH_3$ and

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$ (by using NMR spectra).

(b) (i) Predict the structural formula for the compounds with the following molecular formulas showing only one PMR signal each : 2×2=4

(I) C_8H_{18}

(II) C_2H_6O

(ii) Why is TMS used as a reference standard in NMR spectroscopy ? 3
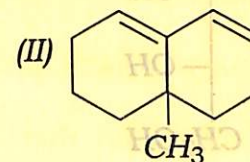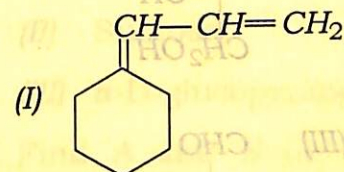
(iii) Define : 1½×2=3
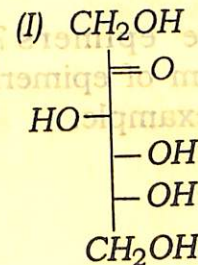
(I) Spin-spin splitting

(II) Coupling constant

(c) (i) Why is methanol a good solvent for UV spectroscopy but not for IR spectroscopy ? 2

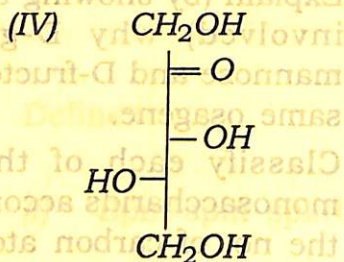(ii) By using the Woodward-Fieser rules, calculate the absorption maximum for the following compounds : 2×2=4

(I)
$$CH—CH=CH_2$$

(II)
CH_3

(iii) Explain (by showing the reactions involved) why D-glucose, D-mannose and D-fructose form the same osagene. 4

(d) (i) Classify each of the following monosaccharids according to both the no. of carbon atoms and the type of carbonyl group present : 1×4=4

(I) CH_2OH
$=O$
$HO—$
$—OH$
$—OH$
CH_2OH

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(II)

$$\begin{array}{c} CHO \\ HO- \\ HO- \\ -OH \\ -OH \\ HO- \\ CH_2OH \end{array}$$

(I)

(III)

$$\begin{array}{c} CHO \\ -OH \\ -OH \\ CH_2OH \end{array}$$

(II)

(IV)

$$\begin{array}{c} CH_2OH \\ =O \\ -OH \\ HO- \\ CH_2OH \end{array}$$

(iii) Explain (by showing the reactions involving why D-glucose, D-mannose and D-fructose form the same osazone.

(b) (i) Classify each of the following monosaccharides according to both the number of carbon atoms and the type of carbonyl group present : 1×4=4

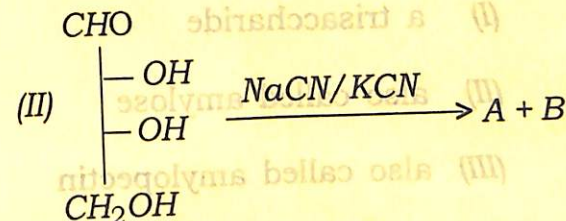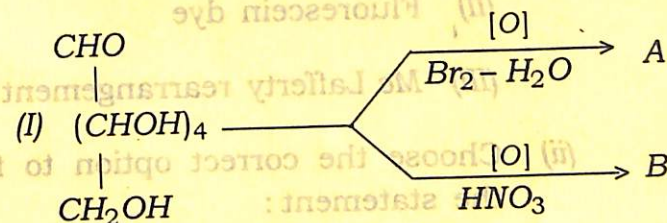(ii) What are epimers ? Give the mechanism of epimerisation with suitable example. 1+5=6

(e) (i) Give the Haworth projection diagram of : *(any two)* 1½×2=3

(I) Lactose

(II) Sucrose

(III) α-D-glucopyranose

(ii) Find A and B in the following reactions : *(any two)* 2+2=4

(I)
$$\begin{array}{c} CHO \\ (CHOH)_4 \\ CH_2OH \end{array} \quad \begin{array}{c} \xrightarrow{\;[O]\;\; Br_2-H_2O\;} A \\ \xrightarrow{\;[O]\;\; HNO_3\;} B \end{array}$$

(II)
$$\begin{array}{c} CHO \\ -OH \\ -OH \\ CH_2OH \end{array} \xrightarrow{\;NaCN/KCN\;} A + B$$

(iii) Draw the most stable conformer of—

    (I)   α-D-glucose, and

    (II)   β-D-mannose.

       (in polar solvent)   1½×2=3

(f) *(i)* Explain with suitable example : **(any two)**   2×2=4

    (I)   Chain-growth polymerisation

    (II)   Fluorescein dye

    (III) *Mc* Lafferty rearrangement

(ii) Choose the correct option to fill the statement :   1

    "Starch is____."

    (I)   a trisaccharide

    (II)   also called amylose

    (III)   also called amylopectin

    (IV)   mixture of amylose and amylopectin

(iii) Give *one* example of each of the following :   1×2=2

    (I)   Carbohydrate that acts as a biofuel.

    (II)   Write two uses of congo red.

(iv) Illustrate the process of Killiani-Fisher synthesis of an aldotetrose from an aldotriose.   3

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