6 SEM TDC CHMH (CBCS) C 13

2024

(May)

CHEMISTRY

(Core)

Paper : C–13

[Inorganic Chemistry
(Organometallic Chemistry)]

Full Marks : 53
Pass Marks : 21

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer from the following : 1×7=7

(a) The PO_4^{3-} group should be removed before proceeding to analysis is

(i) group IV

(ii) group V

(iii) group III

(iv) group II

(b) Which of the following combinations of basic radicals belongs to group V ?

(i) Zn, Co, Mg

(ii) Ba, Ca, Sr

(iii) Ca, Mg, Zn

(iv) Sr, Ca, Co

(c) Considering $(C_5H_5)Fe(CO)_2Cl$ is obeying the 18-electron rule, what is the hapticity of C_5H_5 group?

(i) 3

(ii) 1

(iii) 5

(iv) 2

(d) Which of the following complexes has the lowest value of stretching frequency in the IR spectrum?

(i) $[Ti(CO)_6]^{2-}$

(ii) $[V(CO)_6]^-$

(iii) $[Mn(CO)_6]^+$

(iv) $[Cr(CO)_6]$

(e) Which of the following complexes does not obey 18 e^- rule?

(i) $Fe(\eta^5-C_5H_5)_2$

(ii) $Cr(\eta^3-C_5H_5)_2$

(iii) $Fe(CO)_5$

(iv) $[V(CO)_6]^-$

(f) Which of the following has the minimum *trans*-effect?

(i) C_2H_4

(ii) NO_2^-

(iii) NH_3

(iv) Br^-

(g) Which of the following is used in hydroformylation of unsaturated hydrocarbons?

(i) $RhCl(PPh_3)_3$

(ii) $Ir(CO)Cl(PPh_3)_2$

(iii) $HCO(CO)_4$

(iv) $Zr(CH_3)ClPh_2$

UNIT—I

2. *(a)* What is common-ion effect? Discuss the role of NH_4Cl in the precipitation of group III basic radicals. 1+2=3

Or

(b) What is interfering radical? How do they interfere in the precipitation of basic radicals in a particular group? Establish with suitable example. 1+2=3

3. *(a)* What is soda extract? Discuss the chemistry of soda extract with suitable example. 1+3=4

(b) Write down the basic radicals present in group IV and its group reagent. 1

UNIT—II

4. Answer any *three* of the following : 2×3=6

(a) Assuming 18 e^- rule is being obeyed, calculate the number of metal-metal bonds in the following two complexes :

(i) $Fe_3(CO)_{12}$

(ii) $Os_4(CO)_{14}$

(Continued)

(b) Write down the structures of the following :

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

(ii) $Co_2(CO)_8$

(c) Mention the conditions necessary for isolobality of two molecular fragments.

(d) Compare the reactivity of ferrocene with that of benzene.

5. Answer any *three* of the following : 3×3=9

(a) Write down any two methods of preparation of binuclear carbonyls with suitable examples. 1½+1½=3

(b) Explain π-acceptor behaviour of CO in the light of MO diagram. 3

(c) What is Zeise's salt? Discuss its structure. 1+2=3

(d) Ferrocene shows *(i)* metalation reaction and *(ii)* Mannich condensation. Establish with suitable examples. 1½+1½=3

(Turn Over)

6. Write a short note on any *one* of the following : 2

(a) Ziegler-Natta catalyst

(b) Schlenk equilibrium

UNIT—III

7. Answer any *four* of the following : 3×4=12

(a) Discuss the associative mechanism of substitution in octahedral complex and show its reaction profile. 2+1=3

(b) How does thermodynamic stability of complex differ from its kinetic stability? Explain. 3

(c) Explain *trans*-effect in square planar complexes with suitable examples. 3

(d) Discuss the effect of the following factors on the rate of aquation of a hexacoordinated complex : 1½+1½=3

(i) Charge on the complex

(ii) Chelation

(e) Discuss the base hydrolysis reaction of a cobalt complex. 3

(Continued)

UNIT—IV

8. Discuss the mechanism of the following processes (any *three*) : 3×3=9

(a) Alkene hydrogenation by Wilkinson's catalyst

(b) Hydroformylation by cocatalyst

(c) Wacker process

(d) Fischer-Tropsch reaction

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1. Choose the correct answer from the following : 1×5=5

(a) The pair of isomers which cannot be distinguished by infrared spectroscopy is

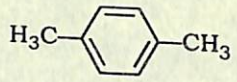
(i) *cis*- and *trans*-isomers

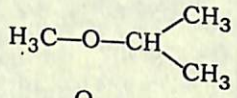
(ii) tautomers

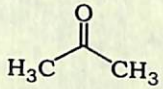
(iii) enantiomers

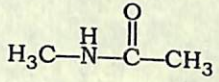
(iv) diastereoisomers

(b) Which of the following compounds shows two PMR signals?

(i) 

(ii) 

(iii) 

(iv) 

(c) Which of the following pairs gives the same osazone?

(i) Sucrose and fructose

(ii) Mannose and fructose

(iii) Glucose and galactose

(iv) Maltose and lactose

(d) Which of the following is not an example of thermoplastic plastic?

(i) Teflon

(ii) Dacron

(iii) Epoxy resin

(iv) Nylon

(Continued)

(e) Azo dye is produced by the interaction of an aromatic diazonium chloride with

(i) aliphatic primary amine

(ii) nitrous acid

(iii) phenol

(iv) aromatic aldehyde

UNIT—I

2. Answer the following questions (any *five*) : 2×5=10

(a) Why does $nb \rightarrow \pi^*$ transition for carbonyl group shift to lower wavelength on increasing the polarity of solvent?

(b) How could you distinguish among 1°, 2° and 3° amines by infrared spectroscopy?

(c) The mass spectra of two different isomeric cycloalkanes show molecular ion peak at $m/z = 98$. One of them shows a base peak at $m/z = 69$ and the other at $m/z = 83$. Identify the cycloalkanes.

(d) What is Larmor frequency? How is it related to the external magnetic field strength?

(Turn Over)

(e) How can you distinguish between *cis*- and *trans*-stilbene with the help of UV-visible spectroscopy?

(f) CH_3OH is good solvent for UV-visible spectroscopy but bad solvent for infrared spectroscopy. Explain briefly.

3. Conjugated diene has high λ_{max} than isolated diene. Explain with suitable example. 3

Or

The mass spectra of a hydrocarbon show an abundant molecular ion peak at *m/e* 120. UV-visible spectrum indicates aromatic character. NMR spectrum indicates signal at 1·2δ (*d*, 6*H*), 2·8δ (*m*, 1*H*) and 7·2δ (s, 5*H*). Determine the structure of the hydrocarbon and explain the spectral data.

4. Answer the following questions (any *two*) : 4×2=8

(a) The PMR signal for vinylic proton is observed at high δ-value compared to acetylenic proton. Explain.

(Continued)

(b) An organic compound having molecular formula C_4H_8O gives characteristic band at 275 nm (ε_{max}17) in its UV spectrum. In infrared spectrum, two peaks at 2940–2855 cm^{-1} and 1715 cm^{-1} are observed. In the mass spectrum, peak at *m/e* 29 and 15 is observed. PMR spectrum of the compound is as follows :

δ2·5 (*q*, 2*H*), δ2·12 (s, 3*H*) and δ1·07 (*t*, 3*H*)

Identify the compound and explain the band/peak.

(c) What is base peak? With the help of IR spectroscopy, how can you study H-bonding in *ortho*- and *para*-nitrophenol?

UNIT—II

5. Answer the following questions (any *three*) : 2×3=6

(a) Glucose, mannose and fructose give same osazone. Explain.

(b) How will you convert D-glucose to D-mannose?

(Turn Over)

(c) Draw the conformers of α-D and β-D glucose. Which conformer is more stable?

(d) Why does anomeric —OH group undergo methylation with CH_3OH and HCl under reflux but others do not?

6. Explain mutarotation with probable mechanism. 3

UNIT—III

7. Answer the following questions : 2×3=6

(a) What do you mean by the terms 'chromogen', 'bathochrome', 'auxochrome' and 'hypsochrome'?

(b) β-carotene is orange red in colour. Account for the origin of its colour.

(c) Discuss briefly the quinonoid theory for colour and constitution.

8. Write one synthesis each of the following : 1½×2=3

(a) Bismark brown

(b) Malachite green

(Continued)

Or

Account for the colour change when phenolphthalein is used as indicator in acid-base titration. 3

UNIT—IV

9. Discuss the mechanism of free-radical addition polymerization having AIBN as free-radical generator. 3

Or

Write short notes on isotactic, syndiotactic and atactic polymers.

10. Answer the following questions : 2×3=6

(a) What is natural rubber? How does it differ from gutta-percha?

(b) Write a short note on plasticizer.

(c) Write down at least two uses of Bakelite and PVC.

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