(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 :

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

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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 1×7=7

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

$[Cr(NH_3)_5H_2O]^{2+} + [CrCl(H_2O)_5]^{2+}$

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

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

Which one of the following is correct statement ?

(i) Both involve inner sphere mechanism

Contd.

(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 : 10×3=30

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

(ii) For the following substitution reactions :

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

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

trans $[PtCl(\text{o-tolyl})\ (PEt_3)_2]^+ + \text{py} \longrightarrow$ trans $[\text{Ptpy(o-tolyl)}\ (PEt_3)_2]^{2+} + Cl^-$ ... (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 $[Cr(H_2O)_6]^{2+}$ is labile but the low spin complex ion $[Cr(CN)]^{4-}$ is inert. Explain. 2+2=4

(b) Discuss synthesis, chemical properties of $(\eta - C_5H_5)_2Fe$ 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