REV-01
MSC/41/14/17

2022/12

SET B

M.Sc. CHEMISTRY
THIRD SEMESTER
INORGANIC CHEMISTRY III
MSC – 301

[USE OMR FOR OBJECTIVE PART]

Duration : 3 hrs. **Full Marks : 70**

(PART-A: Objective)

Time: 30 min. **Marks: 20**

Choose the correct answer from the following: ***1X20=20***

1. The mechanism of the reaction between $[Fe(CN)_6]^{4-}$ and $[Fe(bpy)_3]^{3+}$ (bpy=2,2′-bipyridine) is
   a. Outer-sphere electron transfer
   b. Inner-sphere electron transfer
   c. Self exchange reaction
   d. Ligand exchange followed by electron transfer
2. Consider the reaction
   A. $[Cr(H_2O)_6]^{2+} + [CoCl(NH_3)_5]^{2+} \longrightarrow [Co(NH_3)_5(H_2O)]^{2+} + [CrCl(H_2O)_5]^{2+}$
   B. $[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$
   Which one of the following is the correct statement
   a. Both involve in inner-sphere mechanism
   b. Both involve in outer sphere mechanism
   c. Reaction A follows inner sphere and reaction B follows outer sphere mechanism
   d. Reaction B follows inner sphere and reaction A follows outer sphere mechanism
3. The reaction of $Ni(CO)_4$ with the ligand L (L= PMe_3 or $P(OMe)_3$ yields $Ni(CO)_3L$. The reaction is
   a. Associative
   b. Dissociative
   c. Interchange(Ia)
   d. Interchange(Id)
4. Syngas is mixture of
   a. CO and H_2O
   b. CO and H_2
   c. CO_2 and H_2
   d. CO_2 and H_2O
5. The first step of hydroformylation reaction is inhibited by
   a. Low pressure of CO
   b. High pressure of CO
   c. Not affected by CO pressure
   d. None of the above
6. Oxidation state of the metal of the catalyst involved in Monsanto Acetic Acid process
   a. +1 b. +2 c. +3 d. None of the above
7. The co-catalyst for Wacker process is
   a. Cu_2Cl_2
   b. $CuCl_2$
   c. Both of the above
   d. None of the above
8. A true statement about base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$
   a. It is a first order reaction
   b. The rate determining step involves the dissociation of chloride in $[Co(NH_3)_4(NH_2)Cl]^{+}$
   c. The rate is independent of the concentration of the base
   d. The rate determining step involves the abstraction of a proton from $[Co(NH_3)_5Cl]^{2+}$

9. The major product formed by hydroformylation of 1-butene
a. 2-methyl butanal
b. Pentanol
c. Pentanal
d. None of the above

10. 1,2 insertion reaction -
a. Takes place with change in oxidation state of the metal.
b. Is reverse of beta-hydride elimination.
c. Is migratory elimination.
d. None of the above.

11. The Magic number for the species $[Ni_2Cp_3]^+$ is-
a. 30
b. 34
c. 42
d. 36

12. The number of unpaired electron in the compound $Mn(C_5H_5)_2$ is -
a. 1
b. 3
c. 2
d. 5

13. The stronger M-C bond
a. Increases the tendency of CO to leave the metal ion.
b. Neither increases nor decreases the tendency of CO to leave the metal ion.
c. Decreases the tendency of CO to leave the metal ion.
d. None of the above.

14. The reactivity of ferrocene ring is similar to that of
a. Benzene
b. Naphathalene
c. thiophene and phenol
d. None of the above

15. Identify the first –row transition metal for the 18-electron species $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$, where M is-
a. Fe
b. Co
c. Cr
d. Mn

16. Base hydrolysis of $[CoCl(NH_3)_5]^{2+}$ is an overall second order whereas that of $[Co(CN)_6]^{3-}$ is of first order. The rates depend in both cases solely on the concentration of the cobalt complex. This may be due to
a. Absence of ionizable proton in $[CoCl(NH_3)_5]^{2+}$ & $[Co(CN)_6]^{3-}$
b. S_N1CB mechanism in the case of $[CoCl(NH_3)_5]^{2+}$ only
c. S_N1CB mechanism in the case of $[Co(CN)_6]^{3-}$ only
d. S_N1CB mechanism in both the complexes

17. The reactions of benzene are mainly electrophilic substitution, but as a coordinated ligand it undergoes -
a. Free radical reaction
b. Nucleophilic substitution
c. Redox reactions
d. None of the above.

18. The associatively activated substitution even in 18 electron complexes with NO ligand is feasible because -
a. Linear NO ligand switches to angular NO.
b. Angular NO ligand switches to linear NO.
c. It becomes 20-electron system.
d. None of the above.

19. In which of the following compounds the total electron count is not 60.
a. $Co_4(CO)_{12}$
b. $Rh_4(CO)_{12}$
c. $Ir_4(CO)_{12}$
d. $H_4Re_4(CO)_{12}$

20. The species $\{Cp_2\ TiCl_2\}$ can behave as-
a. Lewis base
b. Lewis Acid
c. Bronsted acid
d. Bronsted base

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PART-B : Descriptive

Time : 2 hrs. 30 mins. Marks : 50

[Answer question no.1 & any four (4) from the rest]

1. a. What are the three strategies adopted for the synthesis of Transition Metal Alkyls? 3

   b. What is Tolman Cone Angle? How does it influence the dissociative mechanism? 3

   c. Explain the effect of charge on the substrate during the aquation of octahedral complexes. 2

   d. Write the name and formula of the organometallic catalyst used widely for polymerization reaction. What is asymmetric oxidation? 2

2. a. Describe one synthesis of Fisher and Schrock type of Metal carbene and describe the bonding in each of the Metal-carbene complex. 5

   b. Describe the characterization of the compound $(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Fe(CO)_2$ with the help of ^{1}HNMR spectra. 5

3. a. Describe the Bonding in Metal-Olefin complex. Draw the structure of $Fe(CO)_4(C_2H_4)$. 5

   b. Arrange the following compounds in decreasing order of relative rate of hydrogenation using wilkinson's catalyst and explain.
   cyclohexene, cis-2-butene, trans-2-butene, 2,3-dimethyl-2-butene. 5

4. a. Give an account of the carbonylate anion as the nucleophile. 3

   b. What is alkene metathesis? Outline the key steps in this reaction. 3

   c. What is Grubbs Catalyst? Mention its role. 4

5. a. What is oxidative addition? How does it differ from reductive elimination? 4

   b. Give a brief account of the beta-hydride elimination. 3

   c. Discuss the conditions under which benzene undergoes nucleophilic substitution? 3

6. **a.** Why the rate of aquation of trans $[Co(en)_2Cl(OH)]^+$ is faster than that of $[Co(en)_2NH_3Cl]^{2+}$? Explain. 5

b. Explain the two mechanisms to explain base hydrolysis of octahedral ammine complexes. 5

7. **a.** Define annation reaction. Write the mechanism by considering steady state principle. 5

b. What are the conditions of inner sphere mechanism? Explain the mechanism using one chemical reaction. 5

8. **a.** Describe Monsanto acetic acid catalytic cycle mentioning all the steps and showing oxidation states of metal center of all of the species involved in the cycle. 5

b. Write three reactions and their names for C-C bond formation using metal catalyst. Show the general catalytic cycle for these reactions. 5

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