

CHEMISTRY 342 FINAL

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Answer all Questions in your exam booklets. A periodic table is provided. You have 3.0 hours.

[13] Question 1

- a) Derive the rate law for octahedral ligand substitution proceeding via a D mechanism (5 marks).
- b) Give the equation and discuss the origin of the “two term” rate law for square planar substitution (4 marks).
- c) Explain the two major criteria that would lead two metal complexes to undergo an inner-sphere electron transfer mechanism (4 marks).

[14] Question 2

The precursor catalyst $\text{Rh}(\text{H})(\text{CO})_2(\text{PPh}_3)_2$ can be used in the catalytic synthesis of 1-pentanal from 1-butene in the presence of modest pressures of CO and H_2 (hydroformylation). Outline the catalytic steps for this process, giving an appropriate designation (eg. oxidative addition) for each type of reaction step and identifying each potential intermediate. (**Hint:** the 1st step is loss of a CO from the precursor to give the active $\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_2$ species and there are 7 steps in total).

[14] Question 3

- a) Determine the electron count around the metal (show your work). (2 marks each)
 - i) $[\text{Rh}(\eta^2\text{-}2,2'\text{-bipy})_2\text{Cl}]^+$
 - ii) $\text{Re}(\text{PPh}_3)_2\text{Cl}_2\text{N}$ (N is triple bonded to Re)
- b) On the basis of the $18e^-$ rule, identify the 1st row transition metal for each of the following. (2 marks each)
 - i) $\text{M}(\text{CO})_7^+$
 - ii) $\text{H}_3\text{CM}(\text{CO})_5$
 - iii) $[(\eta^3\text{-C}_3\text{H}_3)(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})]^-$
- c) On the basis of the $18e^-$ rule, determine the value of x. (2 marks each)
 - i) $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_x]_2$ (has Mn = Mn bond)
 - ii) $[\text{Co}(\text{CO})_3]^x$

[10] Question 4

Outline the catalytic steps involved in the manufacture of acetic acid from methanol (Monsanto).

[over]

[10] Question 5

- What is the difference between homogeneous and heterogeneous catalysis? (2 marks)
- List and describe three (3) desirable properties of a good catalyst. (Do not include “lowering of the activation barrier of a reaction” since a catalyst does this by definition). (6 marks)
- What is the difference between a uniform and multiphasic catalyst? (2 marks)

[14] Question 6

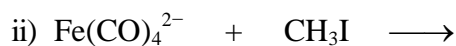
- Which of the following has the lowest C-O stretching frequency: $\text{Ni}(\text{CO})_4$, $[\text{Co}(\text{CO})_4]^-$ or $[\text{Fe}(\text{CO})_4]^{2-}$? Explain (3 marks)
- On forming $[\text{IrBr}(\text{CO})(\eta^2\text{-C}_2(\text{CN})_4)(\text{PPh}_3)_2]$, the C-C bond in $\text{C}_2(\text{CN})_4$ lengthens from 1.35 Å to 1.51 Å. Explain. (3 marks)
- On going from $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ absorptions in the IR spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1} . Explain thoroughly. (4 marks)
- Complexes of formula $\text{Rh}(\text{CO})(\text{phosphine})_2\text{Cl}$ have the C-O stretching bands shown below. Match the infrared bands with the appropriate phosphine and explain the trend. (4 marks)

Phosphines: $\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$, $\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$, $\text{P}(t\text{-butyl})_3$, $\text{P}(\text{C}_6\text{F}_5)_3$

$\nu(\text{CO}), \text{cm}^{-1}$: 1923, 1965, 1984, 2004

[10] Question 7

- The reaction of $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ (**A**) with C_6Me_6 in the presence of AgBF_4 gives $[(\text{C}_6\text{Me}_6)_2\text{Ru}][\text{BF}_4]_2$ containing cation (**B**). Treatment of this compound with Na yields a neutral Ru(0) compound (**C**). Draw structures of (**A**), (**B**) and (**C**). (2 marks each).
- Draw the product of each of the following reactions (2 marks each):



[85]

THE END