CHEMISTRY 342   FINAL

Dr. Aquino   April   19, 2011

Answer all Questions in your exam booklets. A periodic table is provided. You have 3 hours.

[15] Question 1

a) What is the difference between chemisorption and physisorption?   When might one be favoured
   over the other? (3 marks)

b) Explain why the Haber process (in which Fe acts as a heterogeneous catalyst) must be carried out at both high temperature **and** high pressure. (2 marks)

c) In hydroformylation catalysis the yield of the straight-chain product can be increased by adding a bulky phosphine, such as (n-Bu)$_3$P, to the reaction mixture. Explain. (3 marks)

d) The hydroformylation of pent-2-ene using $Co_2(CO)_8$ as the catalyst was found to give rise to two aldehyde products in a ratio of about 2:1. Draw the two aldehydes that were formed and suggest which was formed in most and which in the least amount. (4 marks)

c) Contrast briefly the similarities and differences between so-called man-made catalytic processes and naturally occurring ones. (3 marks)

[12] Question 2

Draw and give the valence electron count for the metal of the following species. **(Show your work!)**

a) $Re_2Cp_2(\mu_2\text{-}CO)(CO)_4$ (Contains a Re-Re bond).

b) $Rh(C_2H_4)(PEt_3)_2Cl$

c) $[(\eta^7\text{-}C_7H_7)_2Cr]^{2+}$

d) Which of the above complexes would you expect to be *most* reactive? Give **two** reasons why?

[12] Question 2

Rh^I reacts with 2 moles of CO and 2 moles of I$^-$ to give a 4-coordinate *cis* product (**A**) (v_{CO} = 1960 cm^{-1}) which undergoes subsequent oxidative addition upon adding CH$_3$I to yield (**B**) (v_{CO} = 1985 cm^{-1}). (**B**) undergoes carbonyl insertion (or methyl migration) to yield (**C**) which has v_{CO} = 1750 and 1980 cm^{-1}. (**C**) adds CO to reform a 6-coordinate complex (**D**) (v_{CO} = 1765 and 1985 cm^{-1}). (**D**) then undergoes reductive elimination to regenerate (**A**) and yield (**E**). (**E**) undergoes hydrolyses to give (**F**) and HI. Draw the structures of compounds (**A**) through (**F**). (2 marks each)

[10] Question 4

a) Starting with the alkene complex shown in (a) in the Figure of the Wacker process below with *trans*-DHC=CHD in place of C$_2$H$_4$, assume dissolved OH$^-$ attacks from the side opposite the metal. Give a stereochemical drawing of the resulting compound of the type shown in (b) of the below Figure. (4 marks)

b) Assume attack on the coordinated *trans*-DHC=CHD by an OH$^-$ ligand coordinated to Pd, and draw the stereochemistry of the resulting compound. (4 marks)

c) Does the stereochemistry differentiate these proposed steps in the Wacker cycle? Why? (2 marks)

[13] Question 5

a) Is the redox reaction $[Co(NH_3)_6]^{3+}$ + $[Cr(H_2O)_6]^{2+}$ $\longrightarrow$ likely to proceed by an inner-sphere or outer sphere mechanism? Explain your answer thoroughly. (3 marks)

b) Why do square-planar substitution reactions often have two-term rate laws? Discuss the nature

and the origin of this rate law (4 marks).

c) When the two isomers (*cis* and *trans*) of $Pt(NH_3)_2Cl_2$ react with an *excess* of thiourea (tu = $S=C(NH_2)_2$), one product is $[Pt(tu)_4]^{2+}$ and the other is $[Pt(NH_3)_2(tu)_2]$. Identify which of these products (identify the isomer in the latter case) come from which initial isomers. Explain your answer. (Note: *trans*-effect series is: $NH_3 < Cl^- < tu$). (4 marks)

d) The vanadium-carbon distance in $V(CO)_6$ is 2.00 Å, but only 1.93 Å in $[V(CO)_6]^-$. Explain. (2 marks).

[9] Question 6

Draw out fully the product of each of the following reactions (2 marks each):

a) $(CO)_5W=C(Ph)(OH)$ + CH_2N_2 $\longrightarrow$
   (Ph and OH attached to C)

b) $[Pt(CO)Br_3]^-$ + NH_3 $\longrightarrow$

c) $(\eta^6\text{-bromobenzene})Mo(CO)_3$ + $NaOH$ $\longrightarrow$

d) $Mn(CO)_5^-$ + $CH_2=CHCH_2Cl$ $\xrightarrow{\Delta}$ **A** $\longrightarrow$ **B** (1 mark for **A**, 2 marks for **B**)

[4] Question 7

a) Why are there two separate water-exchange rates found for $[Cu(H_2O)_6]^{2+}$ in aqueous solutions? (2 marks)

b) Why does $[Co(CO)_3(PPh_3)_2]^+$ only have a single carbonyl stretching frequency? (2 marks)