Chem 91/131 2007 Problem Set 1 (25 pts)
(Topic: Intro to Catalysis)

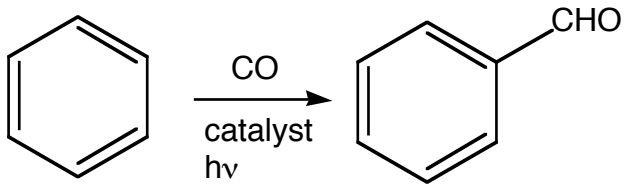
1. (4 pts, 1 each) XYZ Industries wants to develop the following processes, all intended to run at 80 °C with no input of electrical energy or radiation. Which would be easy, which would be worth trying, and which are unreasonable? Explain your answers in terms of the thermodynamics of the processes.

(a) Splitting water into H_2 and O_2.
(b) Decomposing CO_2 to C and O_2.
(c) Making NH_3 from N_2 and H_2.
(d) Hydrogenating double bonds in vegetable oil.

2. (3 pts, 1 each) True or False? Explain your answers.

(a) A catalyst introduces a new reaction pathway with a lower activation energy.
(b) Since the Gibbs energy (ΔG) is more favorable for a catalytic reaction (in comparison to an uncatalyzed one), yields of the product are increased by catalysis.
(c) Highly favorable Gibbs energies (ΔG) for the attachment of reactants and products to the catalyst are the key to catalytic activity.

3. (10 pts, 2 each) Consider the *photochemical* reaction of benzene and CO to give benzaldehyde.



This transformation is catalyzed under low CO pressure at room temperature by several Ir and Rh complexes, such as $IrH(CO)_2(dppe)$, $IrH_3(CO)(dppe)$, $IrBr(CO)(dppe)$, or $MCl(CO)(PPh_3)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$, M = Rh or Ir).

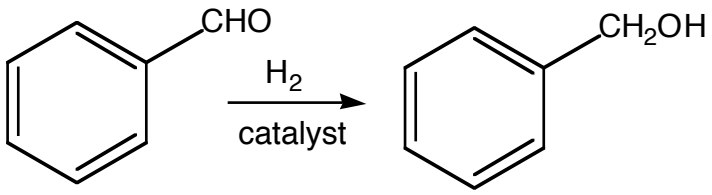
(a) Suggest a **mechanism** for the reaction. *[Note: UV irradiation (photochemistry) of metal carbonyls or dihydrides often yields CO, or H_2, and generates a vacant coordination site.]*

(b) No matter which catalyst is used, the amount of benzaldehyde formed is small. According to thermodynamic values, ΔG° for the reaction at 298 K is +1.7 kcal/mol. Find the **equilibrium constant** for the reaction and **the relative percentages of benzene and benzaldehyde at equilibrium**.

(c) Qualitatively plot of benzaldehyde concentration vs time for this system, and explain your reasoning.

(d) A benzene-d_6 solution of $Rh(Cl)(CO)(PPh_3)_2$ containing 5 equiv of PhCHO was placed under 1.2 atm of labeled ^{13}CO and irradiated at 22 °C. Monitoring the reaction by ^1H NMR showed that
1. ^{13}CO was incorporated into the benzaldehyde
2. the benzaldehyde concentration decreased over time, and benzene formed
Explain these observations.

(e) The reaction of benzaldehyde with hydrogen to give benzyl alcohol has ΔG° at 298K = –3.1 kcal/mol.



In a research proposal, a student suggests catalyzing the reaction of benzene, H_2 and CO to make benzyl alcohol, by using a combination of one of the catalysts above and another catalyst to reduce the benzaldehyde formed to benzyl alcohol ("tandem catalysis").
1. Are high yields of benzyl alcohol possible in this proposed sequence?
2. What potential problems might slow down the proposed process using the mixture benzene/CO/H_2/catalyst-1/catalyst-2?

4. (8 pts, 0.4 each) For each of the following complexes, give the metal oxidation state, the number of d-electrons, and the total electron count at the metal center. Circle any 18-electron complexes.

(a) $Rh(PPh_3)_3Cl$

(b) Cp_2ZrCl_2

(c) $[Rh(CO)_2I_2]^-$

(d) $[Pd(dppp)(Me)(MeCN)]^+[OTf]^-$

(e) $Ni[P(OMe)_3]_4$

(f) $Rh(PPh_3)_3(CO)(H)$

(g) $Rh(dppe)(\eta^6\text{-}BPh_4)$

(h) $H_2[PtCl_6]$

(i) $[Co(CO)_4]^-$

(j) $[RhI_3(CO)_2Me]^-$

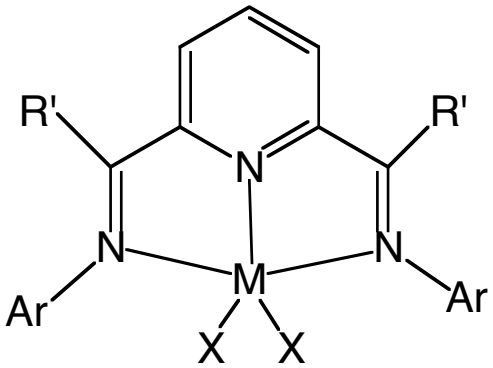
(k) $CpTiCl_3$

(l) $Ni(PPh_3)(Ph_2PCH_2CO_2)(H)$

(m) $Ti(\eta^5\text{-}C_5Me_4SiMe_2N(t\text{-}Bu))Me_2$

(n) $[Cp_2ZrMe]^+[B(C_6F_5)_4]^-$

(o) M = Fe or Co; X = Cl (see structure)



(p) $RuCl_2(PCy_3)_2(CHPh)$

(q) $Mo[OCMe(CF_3)_2]_2(NAr)(CHCMe_2Ph)$

(r) $Ru(H)(Cl)(PPh_3)_3$

(s) OsO_4