

## EXAM OF SCIENTIFIC CULTURE

### MAJOR CHEMISTRY

#### CO<sub>2</sub> hydrogenation

One possibility to limit CO<sub>2</sub> imprint on the global warming is to reduce CO<sub>2</sub> to more usable forms such as hydrocarbons. These can serve as base material for performing chemistry or simply as source of energy. The reduction of CO<sub>2</sub> is in the latter case a possible route for energy storage. Here we will discuss one such possibility: the hydrogenation of CO<sub>2</sub> in formic acid, which can be viewed as a way to store H<sub>2</sub> efficiently in condensed phase. Recently, new Iridium and Cobalt catalysts for the hydrogenation of CO<sub>2</sub> have been proposed that can be used in aqueous solutions.

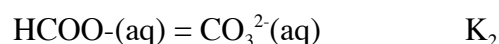
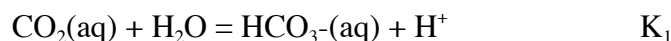
In the whole problem, standard conditions consist in gas pressures equal to  $P_0 = 1$  atm, aqueous concentrations equal to  $c^0 = 1$  mol/L and temperature  $T = 25^\circ\text{C}$ . We recall the gas constant  $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and the Faraday constant  $F = 96500 \text{ C}\cdot\text{mol}^{-1}$ . In the whole problem, all calculation will be done assuming that the solutions and gas are ideal.

- **Electronic structure of CO<sub>2</sub>**

1. Give the Lewis structure of CO<sub>2</sub>. What is its geometry?
2. The oxygen 2s level has an energy (-32.4 eV) much lower than the carbon 2s (-19.4 eV), oxygen 2p (-15.9 eV) and carbon 2p (-10.7 eV) levels, which have similar energies. Construct qualitatively the Molecular Orbital diagram of CO<sub>2</sub>. What is the resulting bond order? Is it compatible with the Lewis structure?
3. Is the carbon of CO<sub>2</sub> an electrophile or a nucleophile?
4. The first reduced form of CO<sub>2</sub> is the radical anion CO<sub>2</sub><sup>•-</sup>. Propose two Lewis structure of this anion assuming that the unpaired electron is localized on C or localized on O.
5. In aqueous solution, the observed angle is between 130° and 140°. Can you determine which is the most probable Lewis structure? Why is it stabilized in water?
6. The radical cation can then dimerize to form the oxalate C<sub>2</sub>O<sub>4</sub><sup>2-</sup>. Predict from the above consideration the Lewis structure of oxalate.

- **CO<sub>2</sub> in aqueous solution**

CO<sub>2(aq)</sub> has two acidities:



with the dissociation constants:  $\text{p}K_1=6.37$  and  $\text{p}K_2=10.32$  at  $25^\circ\text{C}$ .

Furthermore, Henry's constant for  $\text{CO}_2$  at  $25^\circ\text{C}$  is  $k_{\text{H}} = 29.8 \text{ atm}/(\text{mol}\cdot\text{L}^{-1})$  ( $k_{\text{H}}$  is the equilibrium constant of the reaction  $\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})$ ).

7. What are the two bases associated to  $\text{CO}_2(\text{aq})$ . Write the corresponding dissociation reactions.

8. Currently, the partial pressure of  $\text{CO}_2(\text{g})$  in the atmosphere is around  $355 \times 10^{-6}$  bar. Determine the pH of water in equilibrium with  $\text{CO}_2$  from the atmosphere.

9. A solution is prepared with  $\text{NaHCO}_3$  at  $1.0 \text{ mol}\cdot\text{L}^{-1}$ . What is the resulting pH? What are the concentrations of  $\text{CO}_2(\text{aq})$  and  $\text{CO}_3^{2-}(\text{aq})$ ?

10. In fact, there is an equilibrium between  $\text{CO}_2(\text{aq})$  and the species  $\text{H}_2\text{CO}_3(\text{aq})$ . The equilibrium constant of the reaction  $\text{CO}_2(\text{aq}) = \text{H}_2\text{CO}_3(\text{aq})$  is  $1.7 \times 10^{-3}$ . What is the  $\text{pK}_a$  of  $\text{H}_2\text{CO}_3(\text{aq})$ ?

- **Oxydo-reduction reactions**

11. Write the global reaction of hydrogenation of  $\text{CO}_2$  in formic acid  $\text{HCOOH}$

12. Write the Lewis structure of  $\text{HCOOH}$

13. What is the oxidation number of carbon in  $\text{CO}_2$ ? in  $\text{HCOOH}$ ?

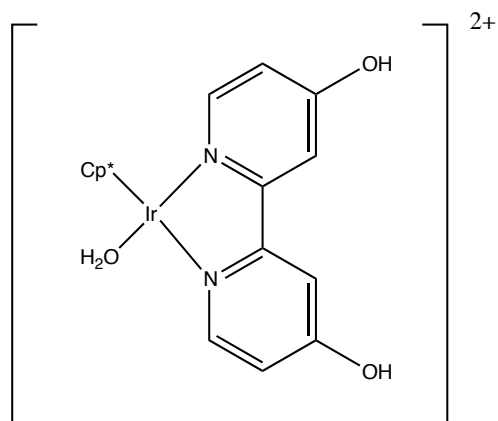
14. Write the half reaction of  $\text{CO}_2$  to  $\text{HCOOH}$  in acid conditions. How many electrons are exchanged between  $\text{CO}_2$  and  $\text{H}_2$ ?

15. Similarly, write the half reaction of reduction of  $\text{CO}_2$  to methane, the half reaction of reduction of  $\text{CO}_2$  to methanol.

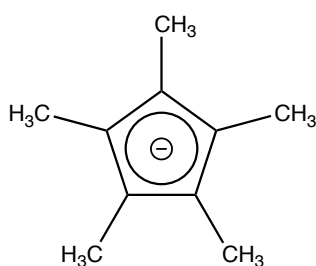
16. The standard reduction potential of the couple  $\text{CO}_2/\text{HCOOH}$  is  $E_0 = -0.114 \text{ V}$ . This corresponds to  $\text{pH} = 0$ . Determine the apparent reduction potential  $E'_0$  at  $\text{pH} = 7$ .

The standard reduction potential of the one-electron reduction of  $\text{CO}_2$  to  $\text{CO}_2^{\bullet-}$  is  $-1.9 \text{ V}$  versus the Standard Hydrogen Electrode (SHE) and is thus highly unfavorable. Standard reduction potentials for multi-electrons reduction of  $\text{CO}_2$  are substantially lower, as seen above, but a catalyst is needed.

In the following we will study Ir complexes as catalysts. These complexes were proposed in a recent publication [Hull et al. Nature Chemistry 4 (5): 383-88] opening a new route for  $\text{CO}_2$  hydrogenation in aqueous solutions. One of such complex is shown below, where  $\text{Cp}^*$  is a pentamethylcyclopentadienide anion.



1



Cp\*

- **Pentamethylcyclopentadienide anion**

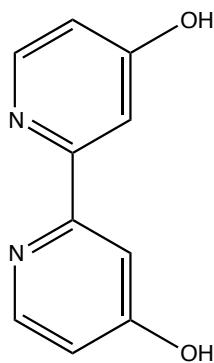
17. Give the mesomeric forms of the pentamethylcyclopentadienide anion, Cp\*.

18. What is the symmetry group of the pentamethylcyclopentadienide anion?

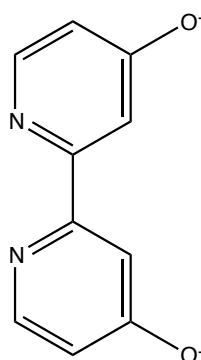
19. Is this compound aromatic? Justify

20. When a metal binds to Cp\* what is according to you the preferred metal position: in the cyclopentadiene plane or on the  $C_5$  symmetry axis of Cp\*. How many electrons participate to the binding to the metal?

- **4,4'-Dihydroxy-2,2'-bipyridine ligand**



2



2-2H<sup>+</sup>

**21.** The two hydroxy groups of compound **2** can donate a proton to give a double base, with  $pK_a = 5.3$ . Write the mesomeric structures of the doubly deprotonated compound **2**, denoted **2-2H<sup>+</sup>**

**22.** What is the hybridization state of the nitrogen atoms? For the protonated **2** and deprotonated **2-2H<sup>+</sup>** forms, are the lone pairs on the nitrogen atoms in a  $\sigma$  orbital or a  $\pi$  orbital?

- **Iridium complex**

**23.** The atomic number of Ir is  $Z = 77$ . The most abundant stable isotope of Ir is  $^{192}\text{Zn}$ . What is the composition in protons, neutrons and electrons of  $^{192}\text{Zn}$  ?

**24.** What is the electronic configuration of Ir ? What is the number of valence electrons ?

**25.** What is the oxydation state of Ir in the complex **1**?

**26.** Does the complex fulfill the 18 electrons rule. Justify.

**27.** Is the metal environment tetrahedral or octahedral? Propose a structure for the complex.

**28.** The deprotonation of **2** into **2-2H<sup>+</sup>** stabilizes the complex. Propose an explanation.

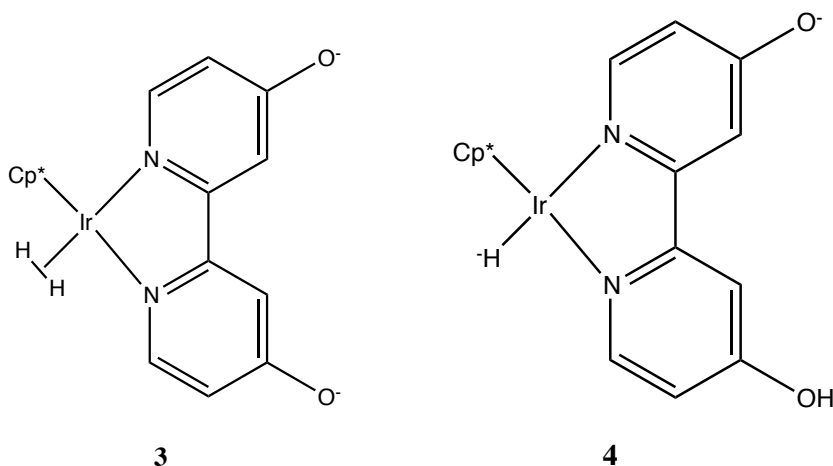
- **Hydrogenation mechanism**

Hydrogenation of  $\text{CO}_2$  occurs at high pH, larger than  $\text{pH} = 6$ , and is thus catalysed by the doubly deprotonated complex **1**, denoted **1-2H<sup>+</sup>**. The first step of hydrogenation of  $\text{CO}_2$  is the binding of  $\text{H}_2$  to Ir in place of the water ligand, complex **3**, and the second step is the dissociation of  $\text{H}_2$ .

**29.** The ligand remaining on the metal is a hydride H- forming complex **4**. Propose an explanation.

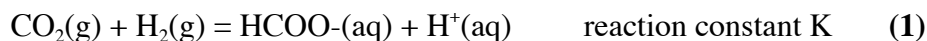
**30.** The net result of  $\text{H}_2$  dissociation is then a proton transfer to a deprotonated hydroxy group of **1-2H<sup>+</sup>**. The distance from  $\text{H}_2$  to the hydroxy groups is too large for a direct proton transfer. The proton transfer occurs through a proton relay mechanism mediated by a water molecule. Write schematically this proton relay mechanism, identifying the electron pair displacements.

**31.** The next step is  $\text{CO}_2$  binding to the hydride H-. Propose a structure for the resulting intermediate complex.



• **Thermodynamics and kinetics of CO<sub>2</sub> hydrogenation.**

We give here some thermodynamical quantities for the reaction



$$\Delta_r G^\circ = 43.27 \text{ kJ}\cdot\text{mol}^{-1} \text{ at } T = 25^\circ\text{C}$$

$$\Delta_r H^\circ = -32.35 \text{ kJ}\cdot\text{mol}^{-1} \text{ at } T = 25^\circ\text{C}$$

pKa of HCOOH(aq): pKa(25°C) = 3.7 at 25°C and pKa(80°C) = 3.85 at 80°C.

pKa of CO<sub>2</sub>(aq): pK<sub>1</sub>(25°C) = 6.37 at 25°C and pK<sub>1</sub>(80°C) = 6.0 at 80°C.

pKa of HCO<sub>3</sub><sup>-</sup>(aq): pK<sub>1</sub>(25°C) = 10.32 at 25°C and pK<sub>1</sub>(80°C) = 10.0 at 80°C.

**32.** Is the data for reaction (1) compatible with the standard reduction potential of the CO<sub>2</sub>(g)/HCOOH(aq) couple reported above, E<sub>0</sub> = -0.114 V?

**33.** Is reaction (1) exothermic or endothermic? How does the reaction constant K evolves when the temperature? Is it thermodynamically favorable to increase the temperature?

**34.** Compute the reactions constants for reaction (1) K(25°C) at 25°C and K(80°C) at 80°C, assuming that the reaction enthalpy Δ<sub>r</sub>H° is independent of the temperature in this temperature range.

**35.** Calculate the effective reaction constant K<sub>a</sub>' for the hydrogenation of CO<sub>2</sub>(g) in HCOO<sup>-</sup>(aq) at 25°C at pH = 8.4.

**36.** Similarly, calculate the effective reaction constant K<sub>b</sub>' for the hydrogenation of CO<sub>2</sub>(g) in HCOO<sup>-</sup>(aq) at 80°C at pH = 6.9.

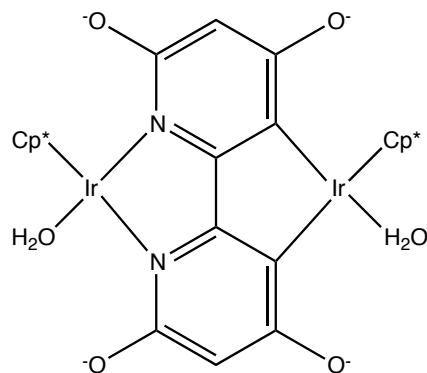
**37.** Is the hydrogenation of CO<sub>2</sub>(g) favorable at high pH or at low pH?

The authors of the study report tests of a very similar catalyst, complex **5**, at two different conditions:

Condition (a): Solution of  $250 \times 10^{-6} \text{ mol.L}^{-1}$  of **5** and  $1.0 \text{ mol.L}^{-1}$  of  $\text{NaHCO}_3$  in contact with a 1:1 gas of  $\text{H}_2$  and  $\text{CO}_2$  at 1 atm, at  $T = 25^\circ\text{C}$  for 216 hours.

Condition (b): Solution of  $2.0 \times 10^{-6} \text{ mol.L}^{-1}$  of **5** and  $2.0 \text{ mol.L}^{-1}$  of  $\text{KHCO}_3$  in contact with a 1:1 gas of  $\text{H}_2$  and  $\text{CO}_2$  at 50 atm, at  $T = 80^\circ\text{C}$  for 2 hours.

The final concentration of  $\text{HCOO}^-(\text{aq})$  was  $0.56 \text{ mol.L}^{-1}$  in condition (a) and  $0.16 \text{ mol.L}^{-1}$  in condition (b)



**5**

**38.** For a catalyst, we define the Turn Over Number (TON) as the average number of cycles performed per catalyst complex, and the Turn Over Frequency as the TON per unit time. Calculate the TON and TOF for complex **5** in the two conditions reported above. What is the interest of increasing temperature?

**39.** In condition (a) the pH of the solution is  $\text{pH} = 8.4$ . Is the system at equilibrium after 216 hours?

**40.** In condition (b), even though the concentration of  $\text{KHCO}_3$  is larger than the concentration of  $\text{NaHCO}_3$  in condition (a), the pH is significantly lower:  $\text{pH} = 6.9$ . Explain why it is so.

**41.** Is the system at equilibrium after 2 hours in condition (b)

- **Dehydrogenation of HCOOH**

One advantage reported by the author of the study is that complex **5** in its protonated form at  $\text{pH} < 5$  can catalyse the reverse reaction of dehydrogenation of  $\text{HCOOH}$  through the reaction



**42.** Calculate  $K_d$ . Is reaction (2) thermodynamically favorable?

**43.** At which pH would you perform dehydrogenation of  $\text{HCOOH}$ ? What acid would you choose for this purpose, starting from the final solution obtained in condition (a).

**45.** Assuming that the pressure of the 1:1  $\text{H}_2/\text{CO}_2$  gas is kept constant at 1 atm, what is the final concentration of  $\text{HCOOH}$  in the solution? Comment on the use of this system to store  $\text{H}_2$ .