Experiment 8
Photoassisted Reduction of Metal Complexes

Reference Chapters: 6, 8, 10

Objectives

After performing this experiment, the student shall be able to:

- Understand what a metal chelate is and prepare one in the laboratory.
- Explain the effect of light on the rupture of a metal-complex bond.
- Produce and identify a metal ion from the photolysis of a metal chelate.

Introduction

Ligands are present in the environment due to a plethora of natural and anthropogenic events. They affect metal adsorption onto natural oxides, the dissolution of natural oxides and of metal scales, metal ion removal and uptake by biological systems, metal-solubilization in soils, and the like. Thus, an understanding of the environmental reactions and fate of ligands and metal complexes is of keen importance.

As discussed in Chapters 2 and 6, natural light induces many processes of environmental significance either directly (when light is absorbed by the species of interest) or indirectly (when light excites or produces an intermediate species called *mediator* that then reacts with the species of interest). For example, the photolysis of metal complexes is important because it obviously affects their concentration and fate (see Section 6.3). A typical example is the photolysis of iron—carboxylato complexes (i.e., complexes with oxalate, aminopolycarboxylates, citrate and humic and fulvic acids) that can occur with high quantum yields. For this reason, in the present experiment an FeEDTA complex is formed and photolyzed, and its metal ion product made evident by a color-producing reaction. EDTA was selected because it is a strong complexing agent for many metal ions and a persistent pollutant due to its high stability (it is even resistant to decomposition by ionizing radiation and heat) and low biodegradability.

Photodegradation of [Fe(III)EDTA]

As discussed in Section 6.3 some EDTA complexes are light-sensitive; for instance, [Fe(III)EDTA] can undergo total photolysis in a sunny day within several hours. Others are only slightly affected (e.g., [Mn(II)EDTA], [Co(III)EDTA]), while others are not affected by light at all. The ability of [Fe(III)EDTA] to undergo a photoredox reaction is very fortunate because—as stated above—EDTA is a refractory compound and thus the natural photolytic pathway provides a means for its destruction.

A simplified photoreduction reaction using a carboxylic anion as the ligand (e.g., oxalate) is the following:

$$[Fe(III)(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe(II) + 2C_2O_4^{2-} + CO_2^{-\cdot} + CO_2 \quad (1)$$

Note that in the $C_2O_4^{2-}$ ligand, C has an oxidation state of 3+ whereas in CO_2 it is 4+. Then, C underwent oxidation in order to reduce Fe(III) to Fe(II), which is then released from the complex.

In the following qualitative experiment, an [Fe(III)EDTA] complex will be exposed to light (either natural or artificial) and decomposed to produce Fe(II), which then reacts with iron hexacyanate (III) yielding a highly colored solution of another complex (see Ibanez, 2000).

Experimental Procedure

Estimated time to complete the experiment: 1 h

Materials	Reagents
3 10-mL volumetric flasks	$FeCl_3 \cdot 6H_2O$
1 1-mL graduated pipet	$K_3[Fe(CN)_6]$
3 Beral pipets	Na_2H_2EDTA
5 test tubes, 5 cm-long	6 M NaOH
1 Slide projector	D. I. water
Aluminum foil	

Prepare 10 mL of an Fe(III) solution by adding 0.8 g of $FeCl_3 \cdot 6H_2O$ to 8 mL of H_2O in a volumetric flask. Stir and dilute to the 10-mL mark. In another 10-mL flask dissolve 1 g of $K_3[Fe(CN)_6]$ and dilute to the mark. Lastly, add 1 g of Na_2EDTA to 5–6 mL of H_2O in a third 10-mL flask, and add approximately 1 mL of 6 M NaOH to facilitate dissolution of the EDTA species; then, dilute to the mark. These procedures yield three solutions (approximately 0.3 M each) that should be enough for a large class because only one drop of each is needed. **Caution: K_3 $(Fe(CN)_6)$ is harmful by inhalation, ingestion and through skin contact.**

Now, place approximately 1 mL of distilled water, one drop of the $FeCl_3$ solution, and one drop of the $K_3[Fe(CN)_6]$ solution in a 5-cm long test tube. Do this in duplicate (the second one is the *blank* test tube). Add one drop of the Na_2 EDTA solution to each tube and shake. Wrap the blank test tube with aluminum foil so as to keep it away from light. Expose the other test tube to sunlight or to the light of an overhead projector (or of a slide projector). In a few minutes, a dramatic color change is observed. The blank test tube is then unwrapped, and the difference between both is annotated.

Name________________________Section________________________Date________________________

Instructor____Partner________________________________

PRELABORATORY REPORT SHEET—EXPERIMENT 8

Objectives

Flow sheet of procedure

Waste containment and recycling procedure

PRELABORATORY QUESTIONS AND PROBLEMS

*1. The pH is a key parameter in the present experiment. Calculate and plot the distribution diagram of EDTA as a function of pH. Predict what would happen if a pH of 2 were used? A pH of 4? Why is a high pH recommended for the present experiment?

2. Find in the literature at least three direct photolytic processes used for the destruction of wastes.

3. When should an indirect method be considered for the photodestruction of a waste?

Additional Related Projects

- Study the photolysis kinetics in this experiment by taking the absorbance of the complex obtained as a function of time.
- Analyze the effect of pH in the present experiment by using different values.
- Design an experiment to demonstrate the production of CO_2 during the photolysis of the FeEDTA used in this experiment. (See Lockhart and Blakeley, 1975).
- Design and perform experiments with other ligands (e.g., citrate, oxalate, some non-carboxylated organics, etc.) and other iron (II/III) indicators (e.g., *o*-phenanthroline, $K_4[Fe(CN)_6]$, SCN^-).
- Try to photolyze a Mn(II)EDTA or Co(III)EDTA complex in the same manner as it is done with Fe(II)EDTA in the present experiment. Perform qualitative tests for the presence of the metal ions after photolysis.

* Answer in this book's webpage at www.springer.com

Name____________________ Section____________________ Date____________________

Instructor______________________________ Partner______________________________

LABORATORY REPORT SHEET—EXPERIMENT 8

Observations

1. Color of the initial reaction mixture ________________

2. Color of the reaction mixture after irradiation ________________

3. Color of the blank after irradiation ________________

4. Time allowed for the reaction ________________ min

POSTLABORATORY PROBLEMS AND QUESTIONS

*1. Discuss the reason for the color change in one tube and not in the other.

*2. If Fe(III) were photo produced instead of Fe(II), what indicator would you use?

*3. The $C_2O_4^{-\cdot}$ radical is a precursor for the $CO_2^{-\cdot}$ product from reaction 1, and can react with ambient dioxygen to yield the radical anion X (that contains only O). In acidic media, the diatomic X reaches an equilibrium with a triatomic neutral radical, Y (that contains H and O). X and Y disproportionate in acid to give dioxygen and a neutral species, Z that is capable of transforming Fe(II) back to Fe(III). Z contains H and O, possesses an O-O bond, and can undergo disproportionation (dismutation) to yield dioxygen plus water. What are the chemical formulas of X, Y, and Z?

* Answer in this book's webpage at www.springer.com

Student Comments and Suggestions

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