Experiment 5
Synthesis and Analysis of a Complex Iron Compound

Part 1: Synthesis

CH 204 Spring 2006

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Last Week

Acid/Base titration

Standardizing a solution

moles H^+ = moles OH^-

Calculating moles by $\frac{\text{grams}}{\text{MW}}$ and Molarity x Volume

Three-week experimental adventure quest!

This week: Synthesis of potassium oxalatoferrate salt.

Next two weeks: Qualitative identification of the compound we have made through quantitative analysis of oxalate and iron. The iron analysis lab (Experiment 7) has an unknown summary sheet.

Synthesis — Makin' stuff

Putting together chemical pieces to create a desired molecule. This often requires several steps, with waste products and loss of material along the way.

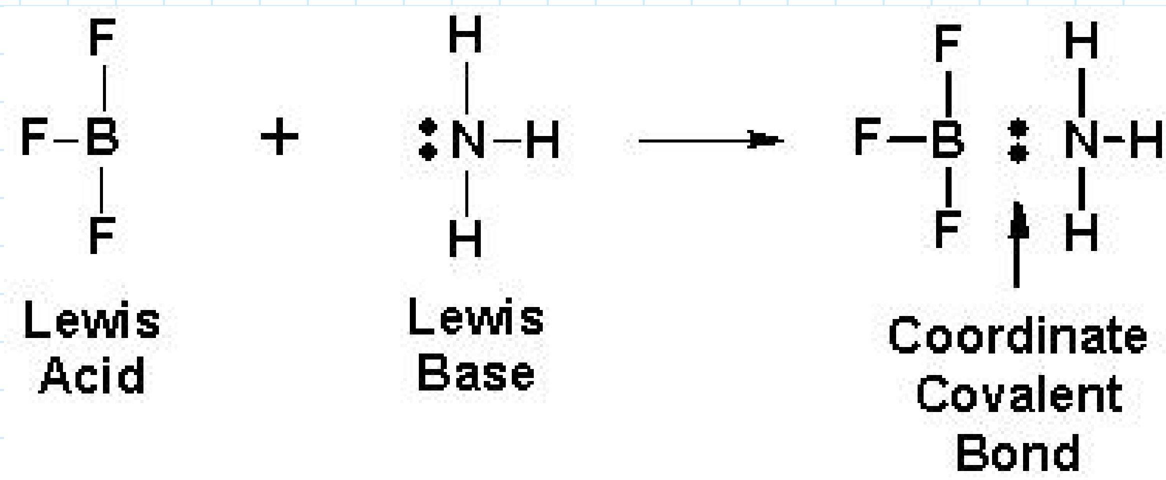
$$\text{Starting material} \longrightarrow \overset{\text{Series of reactions}}{\longrightarrow} \underset{\text{"Precursors"}}{\longrightarrow} \longrightarrow \text{Product}$$

We will synthesize potassium oxalatoferrate.

Lewis Acids and Bases

Lewis Acid An electron-deficient species, i.e, an electron pair acceptor.

Lewis Base An electron-rich species, i.e., an electron pair donor.



Coordinate covalent bond: two shared electrons in a bond, but both electrons come from the same atom.

Metal complex ions

- Coordination compounds formed by Lewis bases coordinating around a central metal ion

- The coordinating bases are known as ligands

- Oxalate is a bidentate ligand — it forms <u>two</u> coordinate bonds with the central metal

What is potassium oxalatoferrate?

Oxa-who?

An ionic crystal.

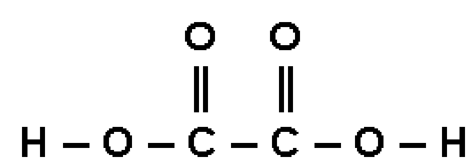
$$K_x[Fe_y(C_2O_4)_x]\bullet zH_2O$$

Cation: K^+

Anion: $Fe_y(C_2O_4)_x^{x-}$

Waters of hydration

Atkins and Jones page 624:
How to name d-metal complexes
and coordination compounds



Oxalic Acid, $H_2C_2O_4$

Waters of hydration?

- Many common ionic crystals have no waters of hydration, and are comprised only of cations and dogions (NaCl).

- Other ionic crystals have large empty spaces within the crystal structure, and the the crystal is more stable if these holes are filled with locked-in H_2O molecules. $CuSO_4 \bullet 5H_2O$ is a common example. BTW, that's a LOT of water!

- Some solids are hydroscopic (aka hygroscopic) and absorb moisture from the air (NaOH). This absorbed water is **NOT** present in a specific ratio to the ions and is **NOT** part of the crystal structure. It's just glommed on to the outside of the crystal in variable amounts.

A quick look at our starting material

$Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$

This is not a coordination compound.

It's a crystal made up of two different cations (Fe^{2+} and NH_4^+) balanced by SO_4^{2-}. If dissolved in water, all the pieces go their separate ways just like any other ionic salt.

Another look at our little green darling

$K_x[Fe_y(C_2O_4)_x]\cdot zH_2O$ is comprised of

- K^+ potassium
- Fe^{2+} or Fe^{3+} ferrous or ferric ion
- $C_2O_4^{2-}$ oxalate ion
- H_2O water

What are the values of *x, y, and z?*

Procedure Overview

- Take an Fe^{2+} salt and precipitate the iron as Iron (II) Oxalate solid.
- Oxidize the iron to Fe^{3+} in the presence of excess oxalate. The precipitate will dissolve as the complex ion forms in solution.
- Precipitate the iron complex ion as the potassium salt.

Oxidation reduction ("redox") reactions

- Oxidation: loss of electrons
- Reduction: gain of electrons
- Redox: exchange of electrons

In a redox reaction, one species loses electrons and another species gains them. We look at these reactions one half at a time.

Oxidation half-reaction

- Oxidation of Fe^{2+} to Fe^{3+}

$$Fe^{2+} \rightarrow Fe^{3+} + e-$$

- Our Fe^{2+} exists in the form of a precipitate.

$$FeC_2O_4 + 2C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-} + e^-$$

This is called the oxidation *half-reaction,* because the reduction half of the reaction (in which something else gains the electrons that Fe^{2+} has lost) is not shown.

Reduction half reaction

The oxidizing agent — the chemical that gets reduced (gains electrons) is hydrogen peroxide:

$$H_2O_2 + e^- \rightarrow \ldots?$$

Hydroxide ions?

Water and oxygen?

H_2 and O_2?

How many electrons do we need?

I'm so confused!

More than one way to skin a cation

The traditional way to balance redox half-reactions makes actual use of chemical knowledge and demonstrates an understanding of the chemistry that's going on.

The easy way is something that even a third-grader can do without the least knowledge of chemistry.

Look at the oxidation states in H_2O_2

- H^+ could gain an electron and be reduced to H^0 (H_2 gas), but H^+ is pretty stable in solution.
- Oxygen is nearly always O^{2-}, except in its elemental form (O_2, when it is O^0), or in peroxides, when it is O^-.
- So reduce each of the O^- to O^{2-} ($O^=$)

$$H^+_2O^-_2 + 2e^- \rightarrow H^+_2O^= + O^=$$

Hmmmmm...

Get rid of that free-floating O^{2-}

$$H^{+}{}_{2}O^{-}{}_{2} + 2e^{-} + 2H^{+} \rightarrow H^{+}{}_{2}O^{=} + H^{+}{}_{2}O^{=}$$

$$H_2O_2 + 2e^{-} + 2H^{+} \rightarrow 2H_2O$$

This is our reduction half-reaction.

The easy way

The oxidizing agent — the chemical that gets reduced (gains electrons) — is hydrogen peroxide:

$$H_2O_2 + e^- \rightarrow \ldots?$$

Balance O by adding H_2O for every O

Balance H by adding H^+ for every H

Balance charge by adding e-

The easy way

$H_2O_2 + e^- \rightarrow ...?$ Add 2 H_2O to the right

$H_2O_2 + e^- \rightarrow 2H_2O$ Add 2 H^+ to the left

$H_2O_2 + 2H^+ + e^- \rightarrow 2H_2O$

Need 2 e- on the left.

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ Done!

Add the two half-reactions

$FeC_2O_4 + 2C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-} + e^-$

$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$

Balance the electrons before you add the equations:

$2FeC_2O_4 + 4C_2O_4^{2-} \rightarrow 2Fe(C_2O_4)_3^{3-} + 2e^-$

$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$

$2FeC_2O_4 + 4C_2O_4^{2-}\ H_2O_2 + 2H^+ \rightarrow 2Fe(C_2O_4)_3^{3-}$

$+ 2H_2O$

Grading this lab

- No real data to speak of, so not the usual lab report
- Discussion questions count for more
- Record your observations during the experiment — precipitation, color changes, evolution of gases, dissolving of precipitates.

WARNING!

Follow lab directions carefully or there will be no beautiful green crystalline delight for you!

Do **NOT** overheat solutions in the lab today!

If crystals don't form in the end, add another 10 ml of ice-cold ethanol.