1. *Oxidation-Reduction Reactions*

Introduction

We encounter oxidation-reduction reactions every day. Examples include the combustion of coal, natural gas, oil, and gasoline; the operation of an automobile's battery; the formation of an image on photographic film; and the removal of stains by a bleach.

Although oxidation-reduction reactions are diverse, when you compare a number of these reactions, you can find some common features. Each reaction consists of simultaneous oxidation and reduction. Moreover, the reactants must include an oxidizing agent and a reducing agent. Electrons are always lost by the reducing agent and gained by the oxidizing agent (Ebbing/Gammon, Section 4.5).

Purpose

You will begin by preparing aqueous solutions of three halogens: Cl_2, Br_2, and I_2. You will prepare these substances in solution from stoichiometric quantities of certain oxidizing and reducing agents. By observing the effect of these halogens on the corresponding halides (Cl^-, Br^-, and I^-), you will be able to rank the halogens according to their oxidizing strengths and the halides according to their reducing strengths. Your subsequent observations on the reactions of two halides, Br^- and I^-, with two common oxidizing agents will enable you to rank the latter according to their oxidizing strengths. You will also find that the products obtained from an oxidation-reduction reaction in an acidic solution can differ markedly from those obtained in a basic solution. Finally, and most important, you will write a balanced equation for each reaction that you have observed.

The halogens and the halides

You will deal with halogens and halides in each part of this experiment. A brief description of some of their properties will allow you to understand some of your observations more easily.

The halogens are found in Group VIIA of the periodic table. The members of this group are fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Because these elements belong to the same group, they have many similar properties. For example, their elemental form is diatomic (F_2, Cl_2, Br_2, I_2, and At_2), and each of them is an oxidizing agent. This experiment uses only Cl_2, Br_2, and I_2, however, because F_2 is such a strong oxidizing agent that special conditions are required for its study and because astatine is radioactive.

Aqueous solutions of Cl_2, Br_2, and I_2 can be prepared either by dissolving these elements in water or by generating them in solution as products of certain oxidation-reduction reactions. Aqueous solutions of these halogens are called chlorine water, bromine water, and iodine water, respectively. Each solution has its own characteristic color, depending on the concentration and thickness of the solution. Chlorine water is colorless to yellow; bromine water is yellow to red-brown; and iodine water is red-brown to brown.

These halogens are also soluble in cyclohexane (C_6H_{12}), a substance that is itself insoluble in water. When cyclohexane is added to an aqueous solution of a halogen, two layers are formed. The upper layer is cyclohexane, because it is insoluble and less dense than water. A portion of the halogen passes from the aqueous layer to the upper cyclohexane layer (a process called extraction). A characteristic color is then imparted to this layer. The color of a halogen in cyclohexane differs somewhat from its color in an aqueous solution, as you will discover during the experiment.

Reduction of a halogen (X_2) yields halide ions (X^-) accoarding to the half-reaction.

$$X_2 + 2e^- \rightarrow 2X^-$$

Because the halogens are oxidizing agents, the halide ions are reducing agents. Compounds of the halides are colorless if the positive ions belong to either Group IA or Group IIA, as in NaI or $CaCl_2$. Compounds of this type are ionic, so they are insoluble in cyclohexane.

Reduction of other common oxidizing agents

You will also encounter two other oxidizing agents in this experiment. These are $KMnO_4$ (potassium permanganate) and $FeCl_3$.

Reduction of purple MnO_4^- can give either green MnO_4^{2-} (manganate ion); brown-black MnO_2, which will be a solid; or Mn^{2+}, an ion that is pink but will be virtually colorless at the concentration found in this experiment. Reduction of Fe^{3+} will give Fe^{2+}, a pale green ion that will be virtually colorless at the concentration found in this experiment.

Concept of the experiment

You will mix aqueous solutions of potential oxidizing and reducing agents in each part of this experiment. However, do not expect a reaction to occur in every mixture that you prepare. If a reaction occurs, there will be certain telltale signals. For example, the formation or disappearance of the characteristic color of one of the halogens in a cyclohexane layer is usually a signal of a reaction in the aqueous layer.

Procedure

Getting started

1. Obtain 3 large test tubes with stoppers for the halogen solutions, 3 small test tubes, and one piece of fine filter paper.
2. Label the large test tubes so that you will know which halogen each one contains.
3. Obtain directions for discarding the solutions that you use during the experiment.

4. Remember the following safety precaution whenever you use cyclohexane during this experiment:

CAUTION: Cyclohexane is flammable. No open flames are allowed during this experiment.

Preparing aqueous solutions of the halogens

1. Prepare solutions of Cl_2, Br_2, and I_2 according to the directions that you provided in the Prelaboratory Assignment.
2. Use a balance to obtain the required mass of $Ca(OCl)_2$ on a piece of weighing paper.
3. Prepare each solution (under a hood, if possible) in a 125-mL Erlenmeyer flask, using a 10-mL graduated cylinder.
4. Add the reagents in the following order for chlorine water: (1) reducing agent, (2) acid (0.5 M H_2SO_4) if required, (3) water if required, and (4) oxidizing agent.
5. For bromine water, the reaction is slow. The rate depends on the concentrations of the reducing and oxidizing agents and of the acid. Therefore, add these substances and wait 15 min before adding the required amount of water; dilution will retard the rate of reaction.
6. Filter the iodine water using gravity filtration (see the Introduction to this manual) to remove insoluble CuI.
7. Store the halogen solutions in the large test tubes.
8. Place 15 drops of the chlorine water in one of the small test tubes, 15 drops of bromine water in the second, and 15 drops of iodine water in the third. Add about 1 mL of cyclohexane to each test tube and shake or swirl very gently. No stopper should be required. The color of the halogen should appear in the upper layer. View this layer against a white background. Record each color.

Attempting reactions of halogens with halides

1. Wash and dry the small test tubes.
2. Place 10 drops of 0.2 M NaCl in each of 2 test tubes.
3. Add 10 drops of bromine water to the first test tube and 10 drops of iodine water to the second one.
4. Add about 1 mL of cyclohexane to each of these test tubes, shake or swirl gently, and record your observations. If no reaction occurs, only the color of the halogen that you added will appear in the upper layer.
5. Wash and dry the test tubes.
6. In an identical fashion, test 10 drops of 0.2 M NaBr with chlorine water and iodine water. Record your observations.
7. Finally, after washing and drying the test tubes, test 5 drops of 0.4 M NaI with chlorine water and bromine water. Record your observations.

Attempting reactions with other common oxidizing agents

1. Wash and dry the small test tubes.
2. Place 15 drops of 0.2 M NaBr into each of the test tubes.
3. Add 1 drop of 0.1 M $KMnO_4$ to the first test tube and 5 drops of 0.1 M $FeCl_3$ to the second test tube.

4. Add 5 drops of 3 *M* H_2SO_4 to each test tube.
5. Add about 1 mL of cyclohexane to each test tube. Shake or swirl the test tubes very gently, and then record your observations for both layers.
6. Repeat Steps 1 through 5, using 8 drops of 0.4 *M* NaI instead of 15 drops of 0.2 *M* NaBr.
7. Wash and dry one of the test tubes.
8. Add 8 drops of 0.4 *M* NaI, 5 drops of 6 *M* NaOH, 1 drop of 0.1 *M* $KMnO_4$, and about 1 mL of cyclohexane to this test tube. Shake or swirl very gently and record your observations for both layers.
9. Dispose of the halogen solutions according to the directions provided by your laboratory instructor.

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Course:	....	Team members:	....
Section:	....		....
Instructor:	....		....

Prelaboratory assignment

1. Define the following terms:

   a. Oxidation

   b. Reduction

   c. Oxidizing agent

   d. Reducing agent

2. Give balanced equations that are in accord with the following reactions. You will use these reactions to prepare solutions of the halogens.

   a. The reaction of OCl^- (hypochlorite ion) and Cl^- in acidic solution gives Cl_2 as the only product containing the halogen.

b. The reaction of BrO_3^- (bromate ion) and Br^- in acidic solution gives Br_2 as the only product containing the halogen.

c. The reaction of Cu^{2+} with I^- in neutral solution gives I_2 and insoluble CuI. A neutral solution does not contain either an acid or a base.

3. Here and on the following pages, describe the preparation of 12 mL of a 0.050 *M* solution of each of the halogens, using the reactions in the preceding question. Available to you are solid $Ca(OCl)_2$; 0.20 *M* solutions of NaCl, NaBr, $NaBrO_3$, and $CuSO_4$; a 0.40 *M* solution of NaI; a 0.50 *M* solution of H_2SO_4; distilled water; and a 10-mL graduated cylinder (where volumes can be read to the nearest 0.1 mL). Calculate the required quantity of each reagent and the volume of water that must be added for dilution.

   a. Chlorine water

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b. Bromine water

c. Iodine water

4. What safety precaution must be observed during this experiment?

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Team members: ....
....
....

Results

Mass of $Ca(OCl_2)_2$ + paper (g): ....

Mass of paper (g): ....

Mass of $Ca(OCl)_2$ (g): ....

1. *Colors of the halogens in cyclohexane*

   Cl_2: ....

   Br_2: ....

   I_2: ....

2. *Reactions of the halogens with halides*

	Cl^-	**Br^-**	**I^-**
Cl_2	X	3.	5.
Br_2	1.	X	6.
I_2	2.	4.	X

3. *Reactions of other common oxidizing agents in acidic solution*

	Br^-	I^-
MnO_4^-	7.	9.
Fe^{3+}	8.	10.

4. *Reaction of* MnO_4^- *with* I^- *in basic solution*

	I^-
MnO_4^-	11.

Questions

1. You have made 11 observations. Each one has been numbered. This question asks you to consider the first 10. Indicate those cases in which no reaction occurred. If a reaction occurred, write a balanced equation that is in accord with your observation.

(1)

(2)

continued

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(3)

(4)

(5)

(6)

(7)

(8)

(9)

2. Consider the eleventh observation.

   a. The ultimate product that results from the oxidation of I^- in this reaction is IO_3^-. Although your observations will not prove that this colorless ion was formed, show that your results indicate that I_2 was not formed.

   b. The color of the aqueous layer will enable you to deduce the unambiguous product from the reduction of MnO_4^-. What is that product?

   c. Write a balanced equation for the reaction.

   d. How do the reactions in acidic and basic solutions differ?

3. a. Rank the oxidizing strengths of the halogens according to your results. Explain.

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b. Rank the reducing strengths of the halides. Explain.

c. Rank the oxidizing strengths of MnO_4^- and Fe^{3+}. Explain your ranking.