

Experiment 1

Title: The preparation, analysis, and reactions of an ethanedioate complex of iron

Date: 5-2-2007 and 12-2-2007

Objective:

- To prepare oxalate complex of iron from the reaction with ammonium iron (II) sulphate
- To deduce the oxidation states of iron in the complex
- To determine the amount of iron and oxalate in the oxalate complex of iron by titration.
- To investigate the molecular formula of the complex formed by preparation, analysis and the reaction of an ethanedioate (oxalate) complex of iron
- To deduce the chemical properties of the complex of iron from the reactions with dilute sodium hydroxide, ammonium thiocyanate solution, and ammonium thiocyanate solution in the presence of dilute sulphuric acid respectively, compared to the reaction of iron(III) chloride and the reagents above.

Introduction

Iron is nearly always determined by reduction to the dipositive state followed by titration with manganate(VII) or dichromate(VI). However oxalate would interfere and must be determined first by titration with permanganate. After titration, any iron present will be Fe(III) then reduced by tin(II) chloride and hydrochloric acid, and the Fe(II) determined with dichromate.

Materials and Methods

Procedure for preparation

10.53g of ammonium iron(II) sulphate, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, was weighed using a rough balance and put into a 400cm^3 beaker, followed by the addition of few drops of dilute sulphuric acid and 30cm^3 of water, and heated until a clear solution was obtained. Then a solution of 5.08g oxalic acid dihydrate in 30cm^3 of water was added. The mixture was heated cautiously, with continuous stirring to boil. Then the yellow precipitate of hydrated iron(II) oxalate was allow to settle. The supernatant liquid was poured off and the precipitate was washed once with hot water by decantation. A hot solution of 7.49g of potassium oxalate monohydrate in 20cm^3 of water was added and the mixture was cooled to 40°C . 20cm^3 of 6% hydrogen peroxide solution was added a few drops at a time with continuous stirring. The temperature must be kept below 50°C . Then the mixture was heat to the boiling point and 2.503g of oxalic acid dihydrate was added. After stirring for 2-3 minutes, a clear green solution was obtained. Then, it was filtered using a filter paper and a

long-stemmed funnel. 10cm³ of 95% ethanol was added to the clear solution to redissolve any precipitated crystals by warming on a steam bath. The solution bottle was then covered by aluminum foil and was set-aside in a dark cupboard for crystallization to occur. The crystals were separated by filtration using a sintered-glass funnel. Then it was washed twice with a mixture of equal volumes of ethanol and water, and followed by twice with acetone. The solid was allowed to air dry by suction. The weight of the dry solid was weighed and the yield was calculated.

Procedure for Analysis

(a) Oxidation with permanganate

Two portions of 0.38g of the sample complexes were added into two conical flasks separately. Each sample was dissolved in 10cm³ of water and 15cm³ of dilute sulphuric acid. When the solution was heated to 70°C, the thermometer was removed and washed down, and was titrated with the standard, approximately 0.02M solution of permanganate. A pink color was persisting for 30 seconds at the end-point. The resulting solution was kept for the determination of iron in (b).

(b) Percentage of iron

15cm³ of concentrated hydrochloric acid was added to the solution obtained in (a). When the solution was heated to the boiling point, tin(II) chloride was added a few drops at a time until the yellow colour of the complex was discharged. Then few more drops of tin(II) chloride were added. Once the solution was cooled to room temperature, one portion 10cm³ of mercury(II) chloride solution was added quickly. 10cm³ of 40% phosphoric acid and 10 drops of barium diphenylamine sulphonate indicator solution were added to the reduced solution. The solution was then titrated with the standard (approx. 0.01M) dichromate solution. Just before the end-point, the color of the solution was changed from colorless to grey-green; at this point the dichromate solution was added dropwise until the violet color persisted throughout the solution and this was taken as the end-point.

Procedure for the reactions of the complex Oxalate

Three test tubes with our product and three with iron(III) chloride were prepared and marked correspondingly. Dilute sodium hydroxide, ammonium thiocyanate, and ammonium thiocyanate with dilute sulphuric acid were added separately into each of the three test tubes containing our product and the three containing iron(III) chloride. The interaction of aqueous solution of iron(III) chloride and the complex with the

above added reagents was compared.

Results:

Mass of ammonium iron(II) sulphate used= 10.53g

Mass of diluted sulphuric acid used=5.08g

Mass of potassium oxalate monohydrate used = 7.49g

Mass of oxalic acid dihydrate used= 2.503g

Mass of our product obtained= 5.925g

Titration with permanganate titration

Mass of complex (g)	0.38	0.38
Initial reading (cm ³)	1 st 0.8, 2 nd 2.6	1 st 5.7, 2 nd 18.3
Final reading (cm ³)	1 st 48.9, 2 nd 5.7	1 st 48.2, 2 nd 18.8
Volume of 0.02M permanganate used (cm ³)	48.1+3.1=51.2	42.5+0.5=43

The average of the weight of complex = $(0.38+0.38)/2 = 0.38\text{g}$

The average volume of permanganate used = $(51.2 + 43)/2 = 47.1 \text{ cm}^3$

Titration with dichromate

Weight if complex (g)	0.38	0.38
Final reading (cm ³)	23.2	35.5
Volume of 0.01M dichromate used (cm ³)	11.2	12.3

The average of the weight of complex = $(0.38+0.38)/2 = 0.38\text{g}$

The average volume of dichromate used = $(11.2+12.3)/2 = 11.75\text{cm}^3$

Observation of the reactions of the complex oxalate

	Iron(III) chloride	Complex
Dilute sodium hydroxide solution	The solution changed from yellow to pale yellow solution with reddish brown precipitate.	The solution changed from pale green to pale yellow solution with reddish brown precipitate.

Ammonium thiocyanate solution	The solution changed from yellow to clear dark red solution.	No observable change
Ammonium thiocyanate solution + dilute	The solution changed form yellow to dark red	The solution change form pale green to red solution.

sulphuric acid	solution.	
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Discussion

Question

1) Deduction for the qualitative test

In the qualitative test, both the complex and iron (III) chloride were reacted with dilute sodium hydroxide solution respectively and brown precipitates were formed that indicated the presence of $\text{Fe}(\text{OH})_3(\text{s})$:



For the reaction between iron (III) chloride reacted and ammonium thiocyanate, it showed a similar reaction:

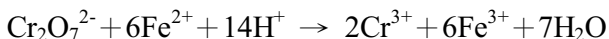


The dark red solution formed indicated the formation of $\text{Fe}(\text{SCN})^{2+}$. However, as Fe^{3+} form stable complex with the oxalate, the Fe^{3+} ions cannot react with CNS^- ions to form red complex. While in the presence of dilute sulphuric acid, more Fe^{3+} ions can be released to form red complex with CNS^- ions. Thus, the resulting solution is dark red.

As the complex prepared had similar reactivity as FeCl_3 , we can assume that the oxidation state of iron in the complex is also +3.

2) Calculations

a) From the dichromate titration,



Volume of dichromate used = 11.75cm^3

Molarity of dichromate = 0.01M

$$\begin{aligned} \text{no. Of moles of dichromate ions} &= 0.01 \times 11.75 \times 10^{-3} \\ &= 1.175 \times 10^{-4} \text{mol} \end{aligned}$$

Mole ratio of $\text{Cr}_2\text{O}_7^{2-}$: Fe^{3+} = 1 : 6

$$\begin{aligned} \text{No. of moles of iron(III) ions} &= (1.175 \times 10^{-4}) \times 6 \\ &= 7.05 \times 10^{-4} \text{mol} \end{aligned}$$

$$\begin{aligned} \text{The mass of complex containing 1 mole of iron} &= 0.38 / 7.05 \times 10^{-4} \text{mol} \\ &= 539.01 \text{g} \end{aligned}$$

b) From the permanganate titration,



Volume of permanganate used = 47.1cm^3

Molarity of permanganate used = 0.02M

no. of moles of permanganate ions

$$= 0.02 \times 47.1 \times 10^{-3}$$

$$= 9.42 \times 10^{-4} \text{ mol}$$

Mole ratio of MnO_4^{4-} : $\text{C}_2\text{O}_4^{2-} = 2:5$

no. of moles of oxalate ions = $(9.42 \times 10^{-4} \times 5)/2$

$$= 2.355 \times 10^{-3} \text{ mol}$$

Mole ratio of $\text{C}_2\text{O}_4^{2-}$: $\text{Fe}^{3+} = 2.355 \times 10^{-3} : 7.05 \times 10^{-4}$

$$= 3.34:1$$

$$\sim 3:1$$

As the sample complex contain iron(III) ions, oxalate ions, potassium ions and water molecules, the formula of the complex is $\text{K}_x\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot y\text{H}_2\text{O}$

Since the complex is electrically neutral, so the no. of moles of potassium:

$$[(+1)(x)] + (+3) + (-2)(3) = 0$$

$$x = 3$$

\therefore the formula of the complex is $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot y\text{H}_2\text{O}$

$$3 \times 39.10 + 55.85 + 3 \times (2 \times 12.01 + 4 \times 16.00) + y(1.01 \times 2 + 16.00) = 539.01 \text{ g}$$

$$437.21 + 18.02y = 539.01 \text{ g}$$

$$18.02y = 101.8 \text{ g}$$

$$y = 5.649$$

$$y \sim 6$$

\therefore the formula of the hydrated complex is $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 6\text{H}_2\text{O}$

c) no. of moles of ammonium iron(II) sulphate

$$= 10.53 \text{ g} / [2(14.01) + 2(32.07) + 14(16.00) + 20(1.01) + 55.85]$$

$$= 0.0268 \text{ mol}$$

no. of moles of complex = $5.925 / 539.01$

$$= 0.011 \text{ mol}$$

Percentage yield of the complex = $\frac{\text{no. of mole of iron in the complex}}{\text{no. of mole of iron in ammonium iron(III) sulphate}}$

$$= 0.011 / 0.0268 \times 100\%$$

$$= 41.04\%$$

3) The structure for the complex anion present in the product:

The complex anion lacks a centre and a plane of symmetry so optical isomers exist so the compound could in principle exhibit optical isomerism.

Source of errors and improvement

The percentage yield of the complex was only 41.04%, it might be due to the loss of product and the presence of impurities. For instance, too much acetone was used to wash the crystals as a result some of the crystals are dissolved and lost. Moreover, there was loss of sample during the transfer process as some solid might adhere on the flasks or Buchner funnel. For improvement, proper amount of acetone should be used to wash the crystals to minimize the loss of product. Slowly pour off the supernatant liquid and try to avoid the loss of solids. More sets of titration can be done in order to improve the accuracy. When adding hydrogen peroxide solution into the mixture during the preparation of the oxalate, the process should be taken slow enough to ensure that the temperature does not rise above 50°C. Otherwise, side products may come out which affect the yield of our final product. Also, the oxalate should be equally placed in the sintered-glass funnel to ensure best filtration.

According to our calculation, the formula of the hydrated complex is $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 6\text{H}_2\text{O}$. However, the formula of the hydrated complex should have 3 water molecules theoretically. This may be due to the inaccurate mass of the complex due to the experimental error such as the presence of extra water or impurities which increases the final mass of the complex.

Some important notes and safety precaution

Aluminium foil should be used to wrap the conical flask containing the product before putting it in a dark place as the product is photosensitive.

Sintered-glass was used instead of filter paper as filter paper is easier to retain the product causing loss in yield. After the suction filtration, remove the rubber tube first instead of the sintered-glass funnel to prevent sucking back of the filtrate.

As concentrated hydrochloric acid was highly corrosive, it can attack the respiratory system and skins, the adding process should be preceded in the fume cupboard and should take more care when pouring it. Moreover, most of the reactants used in this experiment are highly toxic, we should avoid handling all these solid and avoid spillage of solutions. When handling highly flammable ethanol, no naked flames in the vicinity should exist.

Conclusion:

In this experiment, the mass of the complex prepared was 5.925 g and the percentage yield is 41.04%. The oxidation state of the iron in the complex is +3 and the mass of complex containing 1 mole of iron is 539.01 g. The formula of the hydrated complex is $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ and the complex is optically active according to its structure.