

Experiment 2

Acetylation of Ferrocene

The acetylation of ferrocene with acetic anhydride and phosphoric acid¹ is a simple, rapid reaction which gives a mixture of unchanged ferrocene (I) and acetylferrocene (II). Elution chromatography of the mixture in a regular chromatography column or a buret results in two highly colored bands. A yellow band, easily eluted from the column with petroleum ether, is unchanged ferrocene; and a reddish-orange band, eluted from the column with benzene or petroleum ether-ether, is acetylferrocene.

An appropriate scale synthesis involves three grams of ferrocene plus 10 ml acetic anhydride, to which two ml 85% phosphoric acid is added carefully with constant stirring. After about 10 minutes heating on a steam bath (protected by a CaCl_2 tube) the contents are poured onto about 40 g ice. When the ice is melted, the mixture is neutralized to pH 7 with solid NaHCO_3 . Approximately 1/2 hr of further chilling is needed to precipitate all the brown solid from the deep orange solution. The solid is collected on a suction filter and washed with water until the filtrate is pale orange. The solid should be air dried for 15 minutes.

A 0.3-g sample of the brown solid is dissolved in a minimum amount of benzene (1.5-2 ml) and introduced onto an alumina column with a long dropper. Solvent is run out until the level of deep orange-red solution has fallen to the level of the upper layer of sand. About 2 ml more benzene is added along the walls of the buret to ensure that all of the solution has entered the alumina column.

The column is filled with petroleum ether for the elution. The unchanged starting material, ferrocene (yellow), will travel through the column at a faster rate than the product, acetylferrocene (red-orange). The colors observed during the course of the chromatography provide an easy evaluation of separation. A deep brown color may be due to an intractable tar. When all the ferrocene has been separated from the acetylferrocene by elution with petroleum ether, **benzene** or petroleum ether-ether is used to remove the acetylferrocene from the column.

Experiment 3

Preparation of Copper (I) Chloride

INTRODUCTION

In most of its ionic compounds copper assumes a +2 oxidation state, having the valence configuration $3d^9$. In aqueous solution the Cu^{2+} ion typically shows a light blue color, although the presence of coordinating ligand species can result in complex ions with somewhat different colors. The color in all cases is a result of the incompletely filled $3d$ subshell. If, by contrast, copper assumes a +1 oxidation state, it has the completely filled subshell configuration $3d^{10}$. This pseudo-noble gas configuration, like the closed shell noble gas configurations of non-transition ions, excludes the $d-d$ transitions that give rise to the characteristic colors of most transition metal ions, such as Cu^{2+} , Cr^{3+} , Ni^{2+} , etc. Thus, Cu^+ is colorless in solution. Cu^+ forms an insoluble chloride, for which $K_{\text{sp}} = 1.72 \times 10^{-7}$. Cu^+ is unstable with respect to Cu^{2+} in aqueous solution. The relevant standard reduction potentials are:

Taken together, these show that in aqueous solution Cu^+ ions will spontaneously disproportionate to give Cu^{2+} ions and metallic copper:

Under nonstandard conditions, the reaction potential, E_{cell} , will be given by the Nernst equation. This suggests that any process that removes Cu^+ from solution will diminish the overall E_{cell} , thereby mitigating the disproportionation reaction. One way of achieving this is to produce the Cu^+ in the presence of excess chloride ion, resulting in production of a chloride complex of Cu(I) , followed by precipitation of CuCl . Both complex formation and precipitation result in removal of the Cu^+ from solution. The precipitate sequesters the Cu^+ ions in a form that is less susceptible to disproportionation. In the solid, the lattice energy stabilizes the +1 state, and disproportionation becomes nonspontaneous:

This is the synthetic strategy we will use in this experiment to obtain copper in the +1 state. Although CuCl stabilizes Cu^+ relative to disproportionation, this does not mean that the species is impervious to decomposition to the more stable Cu^{2+} ion. In contact with the preparative medium, where Cu^{2+} is being reduced to Cu^+ , CuCl will resist reconversion back to Cu^{2+} and Cl^- ions so long as the reducing agent (metallic copper) is present in excess. However, during collection of the product by filtration, CuCl becomes vulnerable to oxidation from O_2 , either from contact with the air or from significant amounts dissolved in wash liquids. Evidence of oxidation is the development of a pale green color due to formation of basic Cu(II) chloride, $\text{CuCl}_2 \cdot 3\text{Cu(OH)}_2$. *To prevent this, it is critically important to avoid allowing any of the several wash liquids to run through the filter completely, thereby sucking air through the moist product.*

As one wash liquid is nearly gone, add the next. The final washings with ether are meant to dry the product. Several ether washes (always avoiding air contact) are likely to be more effective than a single treatment. Any residual moisture should be driven off by immediate oven drying.

CHEMICAL REQUIRED:-

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Copper turnings, ethylene diamine, anhydrous ether, KCl , ethanol, Conc. HCl .

GLASSWARE REQUIRED: -

125ml Erlenmeyer flask with cork X (2), 50ml Erlenmeyer flask, 25ml beaker, 100ml measuring cylinder, 10ml measuring cylinder, petridish X (2), 100ml beaker, buchner funnel with filtration flask, glass rod, forceps.

PROCEDURE:-

1. In a 125-mL flask, bring about 100 mL of distilled water to a vigorous boil, turn off the heat, and allow the water to cool with the mouth of the flask loosely stoppered. This will remove much of the dissolved air from the water.
2. Add 60 mL of this water to another clean 125-mL flask, add 2 mL of ether, stopper tightly, and shake. This will help remove residual air. Keep the flask of deaerated water tightly stoppered until it is needed in the following procedure.
3. Dissolve 2 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 5 mL of water in a 50-mL Erlenmeyer flask, and then add 5 mL of conc. hydrochloric acid and 1.5 g of fine copper turnings. Heat on a hot plate, keeping air out of the mixture by inverting a small beaker over the mouth of the flask. Avoid vigorous boiling.
4. When no further color change occurs, carefully decant the warm solution into the 125 mL flask containing the 60 mL of deaerated water. Take care to prevent unreacted copper metal from being transferred with the solution. CuCl will precipitate in the 125-mL flask as a fine white powder.
5. Collect the solid by suction filtration on Büchner funnel and filter paper, taking care to keep the cake of precipitated CuCl covered with liquid at all times. As the level of liquid approaches the precipitate, add more solution.
6. After adding the last portion of solution and before all the liquid has been sucked through the filter, successively wash with two 4-mL portions of alcohol, and then four 4-mL portions of anhydrous ether.
7. With each wash liquid, *gently* stir up the precipitate, let the level fall to just above the cake, and then add the next wash liquid. After the final ether wash, allow the precipitate to be sucked to dryness.
8. Immediately transfer the product (still in the filter funnel) to a warm oven (110°C) or vacuum oven ($70 - 80^\circ\text{C}$), and allow to dry approximately one hour.
9. Transfer the dried product to a preweighed sample bottle and seal it tightly to prevent contact with moist air. Weigh the bottle and sample to determine the yield.

Reactions of CuCl

Prepare an aqueous solution (10-20 ml) of 0.1 g of KCl . To this solution, add a small amount of CuCl (about the amount that covers the tip of a micro-spatula). Note what happens and interpret your results. Now add a few drops of ethylenediamine, identify the precipitate, and comment.

REPORT:-

1. Submit your sample, clearly labeled with your name on it.
2. Balanced equations for the synthesis of CuCl , grams of product formed and percent yield.
3. Describe your observations and interpretations, including balanced chemical equations, for the reactions of CuCl and both aqueous KCl and ethylenediamine.
4. Suggest a different reducing agent that can be cleanly separated from the product and an alternative procedure for preparing CuCl . Give full citations used to develop the procedure.

