Fig. 4-1

Frederich Wöhler (1800 - 1882).
Synthesized urea from inorganic chemicals (1828)
http://www.homepages.hetnet.nl/~b1beukema/wohler.html

Experiment 4

WÖHLER'S SYNTHESIS OF UREA

Text Topics and New Techniques

Wöhler's synthesis of urea, vitalism, isomerism.

Discussion

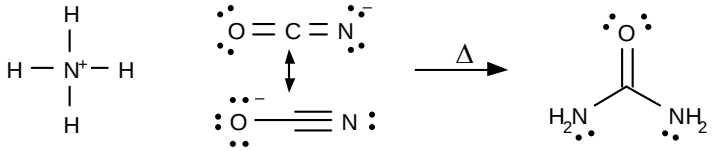
In the second experiment, vanillin and an unknown were recrystallized. In the third experiment, the success of the recrystallizations and the identity of an unknown was determined using melting ranges. Today, an attempt will be made to synthesize urea, purify the urea using recrystallization and identify the product (hopefully urea) using a melting range determination. Thus, this experiment utilizes three of the primary procedures of organic chemistry: synthesis, purification and identification.

One of the primary goals of organic chemistry is the synthesis of compounds that have desirable properties or that help unravel the mysteries of organic chemistry. Almost two centuries ago, a synthesis very similar to the one you will perform today helped organic chemistry take a giant step forward. By performing the synthesis and following it with recrystallization and melting range determinations, you should be able to confirm or refute the almost 200 year old discoveries of one of the pioneers of organic chemistry, Frederich Wöhler.

Lets journey back in time to the 1820's. Organic chemistry was defined differently than it is today. Instead of the current definition, **the chemistry of compounds that contain carbon**, organic chemistry was considered to be the study of compounds derived from living species. It was believed that compounds derived from plants and animals had a special quality called "vitalism" and it was thought that vitalism would not be present in compounds synthesized from "inorganic" substances. Frederich Wöhler's serendipitously prepared urea from compounds (silver cyanate and ammonium chloride) obtained from sources regarded as non-living. Wöhler demonstrated that the urea he prepared and urea obtained from animals have the same properties and are therefore identical. This was the first reported demonstration that the concept of vitalism was not valid. Even so, it took about 50 years after Wöhler's experiment and additional supporting evidence for vitalism to disappear from science literature and for today's definition of organic chemistry to be accepted. Although the scientific community discarded vitalism over a century ago, there are many people today who demonstrate their belief in vitalism by purchasing the higher priced natural Vitamin C rather than the lower priced but identical synthetic Vitamin C.

Besides invalidating the vitalism concept, Wöhler's synthesis of urea from ammonium cyanate was one of the first demonstrations of another extremely important concept in organic chemistry. Ammonium cyanate and urea have the same molecular formula [CH_4N_2O] but distinctly different properties. For an interesting quotation by Wöhler, see the ***Preface***.

$NH_4OCN(aq) \quad -\Delta-> \quad CO(NH_2)_2(aq)$



For example, ammonium cyanate is ionic and therefore a strong electrolyte. Urea has only covalent bonds and although it is very soluble in water, urea is a non-electrolyte. Compounds with the same formula but different properties are called isomers. As you progress through this course you will study two major classes of isomers called structural (or constitutional) and stereoisomers. There are many subdivisions to both of the major classes of isomers.

In today's experiment, you will perform a modified version of Wöhler's synthesis and use melting points to decide if the product you obtain from inorganic starting materials is the same as urea that is commercially available.

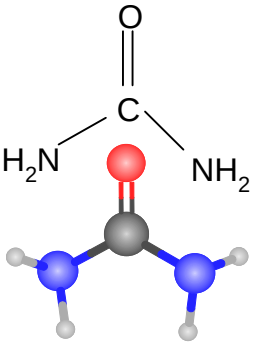
Technique

EVAPORATION. In many procedures, the desired product ends up dissolved in a solvent. The next step involves evaporation of the solvent. In this experiment, the solvents will be evaporated using water vapor as a source of heat. Evaporation is usually carried out in a hood or at reduced pressure (under vacuum) so that the vapors do not contaminate the laboratory air. For today's experiment, the water can be evaporated on the desk top but the 2-propanol should be evaporated in a hood.

Procedure

AN ATTEMPT TO PERFORM A MODIFIED WÖHLER SYNTHESIS OF UREA. The double replacement reaction of potassium cyanate with ammonium sulfate, if it goes, would be expected to yield ammonium cyanate and potassium sulfate.

$$2\ KOCN(aq) + (NH_4)_2SO_4(aq) = 2\ NH_4OCN(aq) + K_2SO_4(aq)$$



However, since both products are ionic, soluble solids, the mixing of solutions of potassium cyanate and ammonium sulfate would not be expected to produce any obvious observations. When Wöhler heated a mixture of silver cyanate and ammonium chloride, he found that he could recover the covalently bonded urea from the reaction mixture. Thus via one or more steps, the reaction below apparently took place in Wöhler's system after a double replacement similar to the one above.

$$NH_4OCN(aq) \quad -\Delta-> \quad CO(NH_2)_2(aq)$$

The overall reaction expected for the reaction of potassium cyanate and ammonium sulfate with heat is:

$$2\ KOCN(aq) + (NH_4)_2SO_4(aq) = 2\ CO(NH_2)_2(aq) + K_2SO_4(aq)$$

One of your responsibilities today will be to run the reaction above and determine if urea is produced. As this is the first synthesis of your course, the procedure is spelled out below in detailed steps. In future experiments, as you gain experience with the techniques and an understanding of the reasons for various steps, the amount of detail in the instructions will be reduced.


Figure 4-2

1. To an evaporating dish, add 2.0 g of potassium cyanate, 2.0 g of ammonium sulfate and 15 mL of water.
2. Carefully place the dish on top of a 400 mL beaker that is about $\frac{2}{3}$ full of water on top of a hot plate. Turn on the hot plate until the water in the beaker boils at a reasonable rate. Stir the contents of the evaporating dish with a glass rod until all of the solid has dissolved. Continue boiling the water until all of the water in the evaporating dish has evaporated (about 30 minutes). *Explain in your notebook the reason for the heating.*
3. Carefully add 10 mL of 2-propanol to the evaporating dish with the water in the beaker still boiling. Loosen and pulverize the solid in the dish while it is being heated. *Include the purpose of the 2-propanol in your report.*
4. When the 2-propanol is at or near its boiling point, use tongs to carefully remove the evaporating dish and allow it to cool for a few minutes.
5. Decant the liquid into a Büchner funnel that is connected via a trap to an aspirator with the water running full. See *Figure 2-2*. It is ok if a small amount of solid transfers to the funnel. Just leave the solid in the funnel on the paper. Replace the evaporating dish in the beaker of boiling water, add 10 mL more of 2-propanol, heat till it boils, remove the dish, allow it to cool and transfer the liquid to the Büchner funnel. This time transfer as much of the solid as possible to the funnel as well. Add another 10 mL of 2-propanol to the dish, stir the contents without heating this time and add the 10 mL to the funnel. *Include the reason for the use of the 2nd and 3rd ten mL portions of 2-propanol in your notebook.*
6. Remove the hose and the Büchner funnel from the filter flask. Weigh a clean, dry evaporating dish and add the liquid from the filter flask to the dish. If the product crystallizes in the filter flask, heat the flask until the solid dissolves before transferring the liquid to the dish. Rinse the filter flask with a few mL of 2-propanol and add this to the evaporating dish. *Why is the evaporating dish weighed?*
7. Place the dish on the beaker of boiling water again and evaporate the contents to dryness in the hood. *Generally, the second evaporation proceeds faster than the first one. Explain why.*
8. Weigh the dish and calculate the experimental and percent yields of product.
9. Determine the melting point of the product and of an intimate mixture of product and urea. The alcohol washing procedure above is probably better described as a separation technique rather than a purification technique. Therefore, don't be surprised if the product is impure and gives you a low and broad melting range.
10. As indicated above, the urea may still be impure. At the instructor's discretion, recrystallize according to these instructions. Urea has moderate solubility in 2-propanol and low solubility in ethyl acetate and a mixture of the two should work as a mixed solvent for the recrystallization of urea. Weigh out about half of your synthesis product and add about 10 mL of ethyl acetate. Add a boiling stick and heat to the boiling point on a hot plate. While maintaining boiling, add 2-propanol using a Beral pipet as required to dissolve all the solid. This will probably take about double the volume of ethyl acetate used. Remove from the ice bath, cool, ice cool, induce crystallization and vacuum filter. Use cold ethyl acetate to wash the flask and the crystals (why ethyl acetate rather than 2-propanol?). Allow the crystals to dry, weigh, determine the percent recovery and the melting range of the product.

REFERENCES

Kauffman, G. B.; Chooljian, S. H. *J. Chem Educ.*, **1997**, *74*, 1493.
Cohen, P.S.; Cohen, S. M. *J. Chem Educ.*, **1996**, *73*, 883.
Tanski, S.; Petro, J.; Ball, D. W. *J. Chem Educ.*, **1992**, *69*, A128.
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Prelaboratory Preparation - *Experiment 4*

Before entering the laboratory for this experiment, you should study the *Safety* and *Chemistry Resources* sections of this book. Next, at the beginning of your report in your notebook, you should list the goals of this experiment. Also, you should prepare a table that includes the literature melting range of urea. Be sure to include references for all sources of information. In addition, you should include in the urea table, the masses and moles of the reactants and the experimental and theoretical yields in grams of the urea. See the example below. Make sure you familiarize yourself with the meaning of the words serendipitous and isomer. X indicates either not available or unnecessary.

cmpd.	formula	formula mass (g/mol)	exptl. mass (g)	exptl. moles	theoretical moles	literature melting point (°C)	source	exptl. melting point (°C)
potassium cyanate			2.0		X	X	X	X
ammonium sulfate			2.0		X	X	X	X
urea								
recryst. urea (if done)								
potassium sulfate			X	X		X	X	X

Generally, it is not necessary to repeat the procedure given but the source of the procedure should be cited. However, if the procedure is modified in any way, complete documentation of the nature of the changes and the reasons for the changes is required.

Observations

Report all observations including evidence that a reaction occurred, masses and melting ranges.

Conclusions

This section should include the following:

1. In the ***Prelaboratory Preparation*** section, you were asked to list the goals of this experiment. Were the goals achieved? Explain your answer.
2. Was the modified Wöhler synthesis successful? Give reasons for your answer.
3. If the synthesis of urea was successful, suggest reasons for percent yields less than 100%.
4. How could the procedure for the synthesis be improved?
5. If you recrystallized the urea, did the recrystallization improve the purity of the urea?
6. Early in this experiment, it was indicated that the Wöhler synthesis was notable not only because it refuted the vitalism concept but also because it was one of the first demonstrations of isomerism. The claim that both Wöhler and you (in today's experiment) have demonstrated the existence of isomers can be disputed because ammonium cyanate was not isolated in either case. Does this argument have any merit? Explain your answer.