

# COMPETITIVE REACTIONS

## Equilibria and Rates in Carbonyl Reactions

**THE PROBLEM TO BE INVESTIGATED:** The competitive reactions in the preparation of semicarbazone derivatives of an aldehyde and a ketone will be examined.

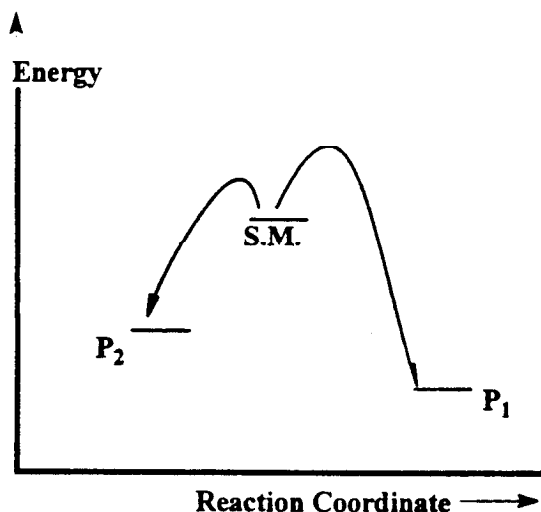


Fig. The thermodynamically more stable product ( $P_1$ ) has a higher energy barrier than the kinetic product ( $P_2$ ).

**BACKGROUND INFORMATION:** In typical laboratory experiments, most organic reactions are performed *under conditions that do not achieve equilibrium* between the products and the starting materials. This means that the sole or major product is due to *kinetic control*. Under conditions that favor an approach to equilibrium between products and starting material, the principal final product may be different from that resulting from kinetic control [ cf. McMurry: 14.6 ]. The reaction of aldehydes and ketones with semicarbazide illustrates the effect of these factors.

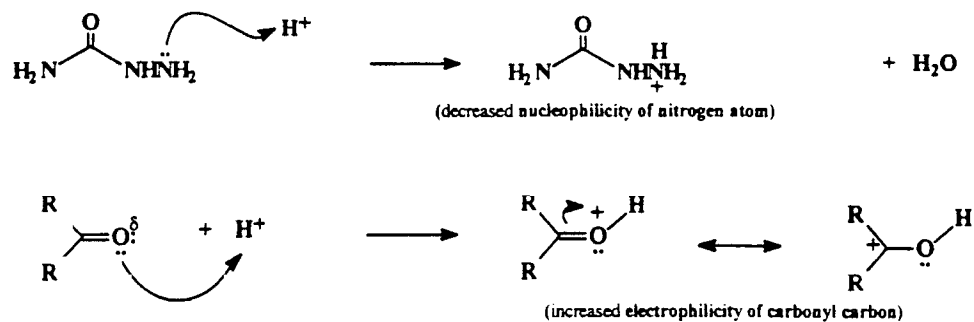
Eq. 1



Electrophile                  Nucleophile

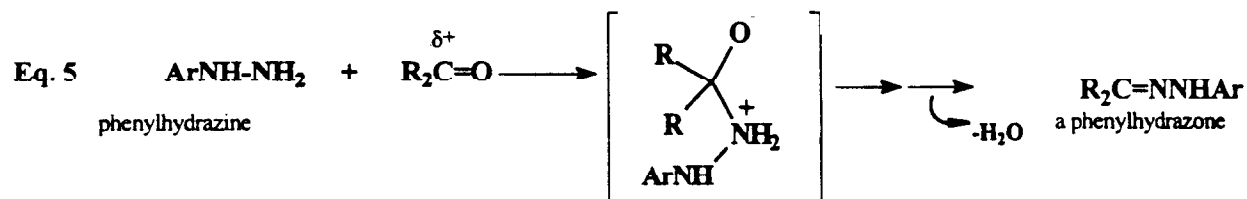
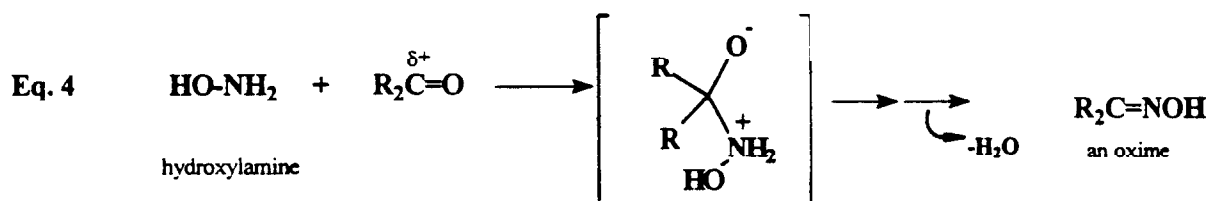
Note: Y represents a residual group such as hydroxyl, benzene, or etc.

**THE NATURE OF THIS INVESTIGATION:** In reactions of the type shown in Eq. 1, *acid catalysis* is involved. Increased acidity beyond about pH 4.9 decreases the amount of free semicarbazide through salt formation ( Eq. 2 ), and this reduces the rate because of *diminished nucleophilic* activity of the cation. But the carbonyl compound is subject to acid catalysis: addition of a proton to the carbonyl group *enhances its electrophilic* character (and, hence, rate of reaction:



The optimum conditions for interaction of **aldehydes** and **ketones** with reagents to form derivatives such as semicarbazones ( Eq. 1 ), oximes ( Eq. 4 ), and **arylhydrazones** ( Eq. 5 ) involve buffered solutions. Sodium acetate, phosphate or bicarbonate may be used for buffering. Note that *the products from these reactions are often used as derivatives of aldehydes and ketones.*

Among the **arylhydrazones**, the 2,4-dinitrophenylhydrazones ( Ar = 2,4-dinitrophenyl- ) and



phenylhydrazones ( Ar =  $\phi$ - ), are derivatives frequently prepared from the corresponding **arylhydrazines**. [Recall the cyclohexanone experiment utilizing the 2,4-DNP reagent in the laboratory CHM 2210L ]. Products from equations 4 and 5 result from addition and elimination reactions (nucleophilic acyl addition/elimination).

## PROCEDURE

For those experiments requiring boiling water, the baths should be set up and the water should be boiling BEFORE the Erlenmeyer flasks containing the reaction mixtures are placed in the bath!

The cyclohexanone and furfural are being dispensed from burets. Take the mixtures of the

other reactants and into these, place separately the required volumes of the two liquids.

Parts I and II should be run during the first session and part III during session 2. For a more efficient use of the available time in session 1, the experiments should be run in the following order: IA, IIB, IIA and IB. Note also that as the mixture in part IA is standing for 15 min it is advisable to start part IIB and have it heating for 1.5 hr as you work on the other parts. Good record keeping is essential as is labeling of the various reaction mixtures at all stages. It is suggested that you use a separate page for each part.

You have to look up the reported melting points of the two semicarbazones prepared in part I in the tables of derivatives provided. Drying of these derivatives can be hastened by placing in an oven at ca 100°C for about one-half hour. All products should be turned in properly labeled.

## PART I. SEMICARBAZONE FORMATION

**(I.A)** Dissolve 5.3 g of **sodium bicarbonate** in 65 mL of water in a 250 mL beaker and slowly add 3.0 g (.0269 mole) of **semicarbazide hydrochloride**, and when the effervescence ceases add 2.7 mL (0.0261 mole) of **cyclohexanone** from the buret provided. Swirl or stir the mixture for several minutes then let it sit for 15 min at **room temperature** with occasional stirring. Collect the product by suction filtration (Buchner funnel) and rinse with some water. Recrystallize it in the **usual** manner from a minimum amount of **water** (chill before collecting and use cold water to rinse). Allow to dry until the following session and determine the melting point. Turn in the unused portion from part IIIA in a vial labeled **cyclohexanone-semicarbazone (IA)** and other pertinent information.

**(I.B)** Dissolve 5.3 g of **sodium bicarbonate** in 65 mL of water in a 125 mL Erlenmeyer flask and slowly add 3.0 g of **semicarbazide hydrochloride**, and when effervescence ceases add 2.1 mL (0.253 mole) of distilled furfural (a.k.a. furaldehyde) from the buret provided. Swirl to mix well, add a boiling chip and heat in a bath of boiling water for 20 minutes. Allow the mixture to cool to room temperature, collect the solid by suction filtration and rinse with some water. Recrystallize in the **usual** manner from **methanol** (about 18-20 mL of solvent per gram of product). Use chilled methanol to rinse the collected product. Allow to dry until the following session and determine the melting point. Turn in the portion not used in part IIIB in a vial labeled **furfural-semicarbazone (IB)** and other pertinent information.

## PART II. COMPETITIVE REACTIONS

**(II.A)** Dissolve 2.0 g of **sodium bicarbonate** in 25 mL of water in a 100 mL beaker and slowly add 1.0 g of **semicarbazide hydrochloride**, and when the effervescence ceases add the following from the burets provided: 0.8 mL of **furfural** and 1.0 mL of **cyclohexanone**. Stir for 5 minutes at **room temperature** (do NOT heat) and collect the product in a Buchner funnel (suction filtration and rinse with some water. Recrystallize in the **usual** manner from **methanol** (ca. 7-8 mL solvent per gram of product). Use chilled methanol to rinse the recrystallized precipitate. Allow to dry until the next session and determine the melting point. Identify the product by melting point and mixture melting point with that of the authentic samples of the semicarbazones prepared in Part I. (Turn in product.)

**(II.B)** To a 50 mL Erlenmeyer flask add the same quantities of the materials given in part II.A

in the same order (watch out for frothing!). Add a boiling chip and place the flask in a bath of boiling water and keep it there for 1.5 hr. Add small portions of water to the flask from time to time to keep the level about the same throughout the reaction. Cool the mixture to room temperature, collect the solid by suction filtration (Buchner funnel) and wash with some water. Do the recrystallization and characterization as described in IIA. (Turn in product.)

### PART III. INTERCONVERSION ATTEMPTS

(III.A) Place the following in a 50 mL Erlenmeyer flask: 0.5 g of **cyclohexanone semicarbazone**, 10 mL of water and 0.4 mL of **furfural** and mix well. Add a boiling chip and heat the mixture in a bath of boiling water for 20 min. Allow the mixture to cool to room temperature and collect the solid (suction filtration, Buchner funnel) and wash with water. Recrystallize in the **usual** manner from the minimum amount of methanol (ca. 8 mL/1 g product) and rinse the product with chilled methanol. Dry and determine the melting point to identify as noted in IIA. (Turn in product.)

(III.B) Repeat the **entire** sequence described in experiment IIIA but **INSTEAD** use a mixture of 0.5 g of **furfural semicarbazone**, 10 mL of water and 0.4 mL **cyclohexanone**. Dry the purified product and determine the melting point to identify as noted in IIA. (Turn in product.)

**THE LABORATORY REPORT:** In your report, your discussion - with the appropriate spectra - will be important. Tabulate your results and use equations where appropriate. The identities of products from **II.A**, **II.B**, **III.A**, and **III.B** should be revealed. Be sure to indicate which are the kinetic and thermodynamic products. Are your results consistent with the data? Label and turn in your samples with the proper codes.

#### **Helpful Hints - Competitive Reactions**

- Crystals obtained after suction filtration are still "wet" with solvent (especially when water is the solvent). When a melting point is to be determined immediately, a small sample may be "squeezed dried" by placing it (ca. 0.5g) between several folded filter papers. Using a beaker or Erlenmeyer flask, press the paper sliding the glassware over it. Open the filter paper and using the spatula, scrape the pressed crystals to a dry region, refold the filter paper, and repeat the process. Note that any *trace* of water will depress the melting point.
- If you prefer, the infrared spectra of the semicarbazones may be prepared in a KBr dispersion.