

Chemistry 125 Third Examination  
November 13, 2000

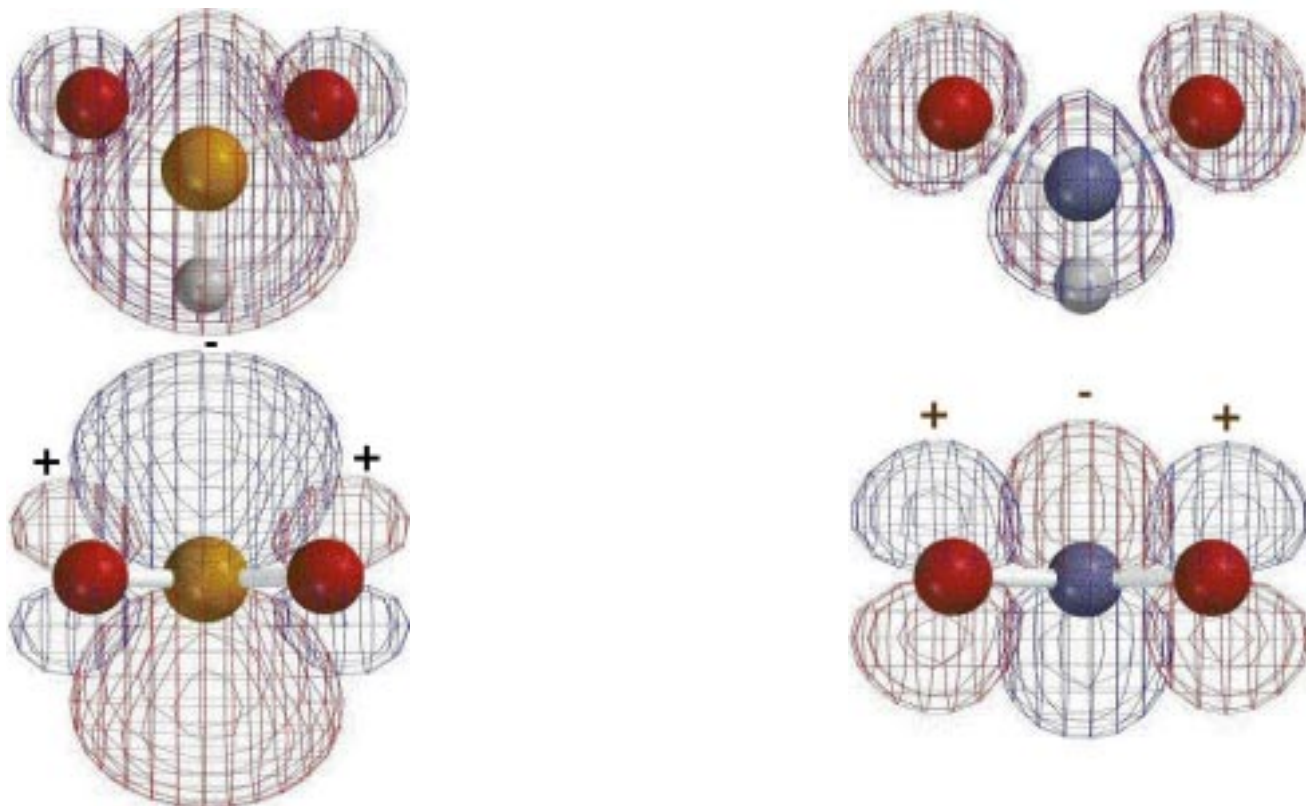
Name \_\_\_\_\_

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided.  
**Read each question carefully to see what it asks for, and be sure to answer all of its parts.**

1. One of the key reactions in organic chemistry is the attack of an amine ( $R_3N:$ ) on a carbonyl group ( $R_2C=O$ ).
- (a) (7 min) Describe **EXPERIMENTAL** evidence that defines the structural changes that occur during this reaction.  
[It would be helpful to draw a **graph**.]

(b) (5 min) Rationalize the structural changes shown in Part (a) in terms of changes in molecular orbitals.

2. (6 min) The figure below compares analogous orbitals of two "Y"-shaped molecules. The substituents on the central "X" atom are two oxygen atoms and one hydrogen. Each orbital is shown in two views. The top view looks down on the "Y", and the lower view sights along the X-H bond. In one case the "X" atom is nitrogen; in the other case it is boron. On the basis of **orbital shapes**, **EXPLAIN** which picture shows  $\text{HNO}_2$  and which shows  $\text{HBO}_2$ .

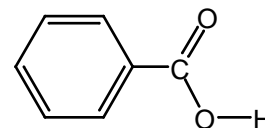


### Carboxylic Acids

3. (6 min) A reaction of **acetic acid** played a key role in the break between the German/Swedish and the French schools of organic chemistry around 1840.
- What was the experimental result?
  - In what ways did it seem inconsistent with the theories of one school?
  - What sort of new theory did it suggest to the other school?

4. **Benzoic Acid** appears over and over in the story of the development of theory for organic chemistry.

(a) (9 min) Explain the role benzoic acid played in the experiment and/or theory of each of the following individuals:  
Lavoisier (1789)



Liebig & Wöhler (1832)

Körner (1869)

(b) (4 min) In 1865, when he **first** published a "structural" formula for benzene, Kekulé said that he considered his formulae superior to those of Crum Brown, although he ultimately adopted the latter type of notation. Draw a formula for **benzoic acid** using Kekulé's notation and one using Crum Brown's notation. Be faithful to their individual styles.

**Kekulé**

**Crum Brown**

(c) (4 min) What did Kekulé and Crum Brown wish to show with their formulae? On what basis, other than ease of drawing, did chemists ultimately decide in favor of one type of notation over the other?

**5. HOMO-LUMO Theory for FORMIC ACID (HCOOH)**

(a) (4 min) **From the naïve view of localized** (non-interacting) bonds and lone-pairs, what orbitals would you consider reasonable candidates for the HOMO and LUMO of formic acid. **Suggest at least two candidates for each category.** Say a little about what factors might differentiate the energies of the localized orbitals in each category.

HOMO candidates:

LUMO candidates:

(b) (4 min) Explain how a more sophisticated viewpoint involving **mixing** among localized orbitals might affect the HOMO/LUMO energies discussed above. Draw the resonance structures corresponding to this mixing, and use curved arrows to show "electron shifts".

(c) (1 min) Say where you would expect a proton to add to formic acid and draw the structure of the product, with appropriate resonance structures, if necessary.