

Chemistry 125 Third Examination November 13, 2000 Answers

	Exam 3	Sum of 3 Hour Exams
Average	75.6	225.5
1/3 of scores greater than	81	238
2/3 of scores greater than	72	216

Average score by question:

1 (11.7/14); 1b (8.1/10); 2 (7.9/12); 3 (9.7/12); 4a (14.3/18); 4b (6.0/8); 4c (6.1/8); 5a (6.6/8); 5bc (5.2/10)

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**.]

The experimental evidence is the x-ray crystal structure data compiled by Bürgi and Dunitz for numerous compounds containing both the amine nitrogen group and the ketone group. It is described on the following web page, some version of the diagram on which was the graph expected for the answer:

<http://www.chem.yale.edu/~chem125/125/quantum/end/burgidunitz.htm>

[Note that the answer for Part (a) was to involve **experimental** evidence, not a discussion of theory.]

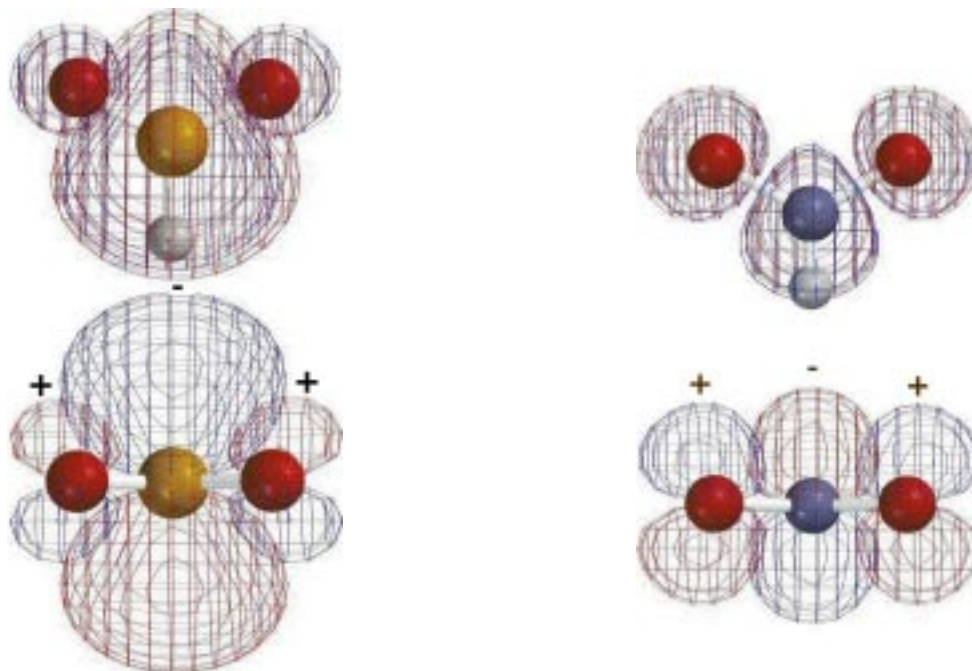
(b) (5 min) Rationalize the structural changes shown in Part (a) in terms of changes in molecular orbitals.

The HOMO (unshared pair on Nitrogen) approaches the LUMO (π^* of $C=O$) at the large Carbon end and at an angle (110°) that keeps it away from the lobe on the oxygen atom with the opposite sign.

As the Nitrogen pulls closer to the carbon, its electrons begin to partially occupy the π^* of $C=O$, weakening the C-O attraction and lengthening the C-O bond.

As the Nitrogen forms a bond to the carbon, the carbon hybridization changes to achieve better overlap with the nitrogen. This pulls s-character from the bonds of C to the other substituents, and the C-R bonds bend back from the approaching N.

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 HNO₂ and which shows HBO₂.



The location of nodes and the relative signs of lobes in these MOs show that they are the highest-energy (most antibonding) combination of the three p-orbitals. Thus the largest orbital will be on the atom with the lowest nuclear charge (least electronegative), because the more favorable AOs were mostly used in the lower-energy MOs. The orbital on the left is the larger on the central atoms, thus this must be the Boron atom.

[It is true that the central atom tends to be emphasized in this MO in either molecule because this maximizes anti-bonding, but this fact is not necessary in discriminating between B and N.]

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.
- (a) What was the experimental result?

Reaction of acetic acid (C₂H₃O•OH) with chlorine (in the presence of light) resulted in trichloroacetic acid (C₂Cl₃O•OH), which was still had acidic properties, and HCl byproduct.

- (b) In what ways did it seem inconsistent with the theories of one school?

Radical theory assumed that chemical reactions could not alter the fundamental radical (here "acetyl" - C₂H₃O). Furthermore "dualism" was part and parcel of the radical theory, and in this reaction a "positive" element H, was replaced by a "negative" element Cl. Thus there must be more to the association between elements than the attraction of positive to negative.

[Curiously enough, electrostatics **IS** the only significant source of potential energy in chemistry, what else there would be is the crazy kinetic energy of quantum mechanics.]

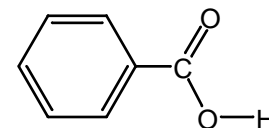
- (c) What sort of new theory did it suggest to the other school?

The "Type" or "Unitary" or "Substitution" theory of the French School. Elemental atoms were associated in a particular pattern (type), but substituent atoms (like H in the water type) could be replaced by other elements or radicals without fundamentally altering the characteristics of the substance. There was no longer an explanation for the force that held atoms in these molecular patterns, though their mutual attraction was analogized to gravity.

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)

The "radical of benzoic acid" ("radical benzoïque") was cited by Lavoisier as one of the "compound radicals" or bases that could be converted to acids by oxidation. [He may have analyzed the elemental composition of benzoic acid, but I do not know that he did experimental work with benzoic acid.]



Liebig & Wöhler (1832)

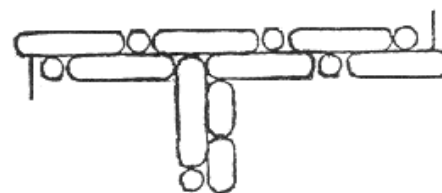
L & W converted "oil of bitter almonds" C_6H_6O , which we call benzaldehyde, into benzoic acid ($C_6H_6O_2$) by reaction with oxygen. This was one of many chemical conversions that resulted in products containing the constant C_6H_5O as a component, which they called the "benzoyl" radical. [This concept was quite different from Lavoisier's, in

Körner (1869)

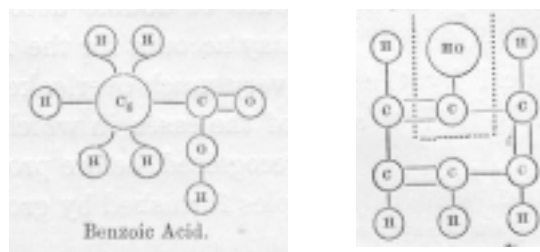
Benzoic acid was a key product in experiments Koerner used to establish the equivalence of the six positions in benzene (which is consistent with, but does not require, a symmetrical hexagonal structure in 3-D). The three known isomers of hydroxybenzoic acid could be related to the same benzoic acid and to the same phenol (hydroxybenzene). Thus these isomers did not differ in the absolute position of either of these groups, but only in their relative positions. At a minimum this meant to Koerner that at least three of the six positions in benzene were equivalent. [Subsequent experiments established that a fourth and a fifth position were equivalent to the members of this set, and in the fullness of time the sixth position was also shown to be a member.]

(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: Here is Kekulé's own "structure" of benzoic acid from the 1865 paper. Note the clean distinction between double and single carbon-carbon bonds, the vertical lines that denote the closure of the six-carbon "ring", the length of ellipses proportional to the element's valence, the fact that tangency only counts as a bond when it is perpendicular to the long axis of an ellipse (except that he makes a bond from the tip of a the "carboxyl" carbon.



Crum Brown: Here is Crum Brown's structure of benzoic acid. Note that the atoms are enclosed in circles and that single and double bonds are shown by lines. [His picture of phenol (hydroxybenzene, further right) shows the ring carbon atoms explicitly. The dotted lines are irrelevant to his structure.]



(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?

They wanted to show CONSTITUTION (the nature and sequence of bonds), not the arrangement of atoms in "physical" 3-D space. The problem with Kekulé's notation was that he used it to "explain" the existence of too many isomers [had he not used it himself for this purpose, he could always have argued that it should not be used in this way. As it was he had to adopt the Couper/Crum Brown style, without giving any credit to them.]

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:

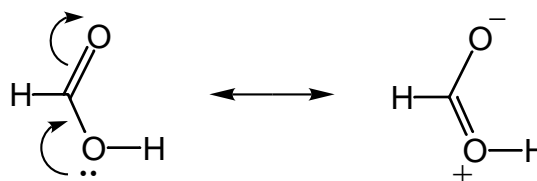
- (1) Unshared electron pair on an oxygen atom. High because it is not involved in a bond, even though it is on an electronegative oxygen atom.
- (2) Unshared electron pair on another oxygen atom, or a different unshared pair on the same oxygen. Note that hybridization could make a difference in different pairs on an oxygen.
- (3) π orbital of C=O. High because of relatively poor π overlap and because of poor energy match between C and O. Still it should be lower than an unmixed atomic orbital on oxygen. Thus the highest localized orbital would be a pair of electrons in a p-orbital of the OH oxygen atom.

LUMO candidates:

- (1) π^* orbital of C=O. Low because of relatively poor π overlap and because of poor energy match between C and O.
- (2) σ^* orbital of O-H (or of O-C). Low because of poor energy match between H (or C) and O. One would think that the π^* would be lower because of the additional factor of poor overlap.

(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 used curved arrows to show "electron shifts".

There would be overlap between the unshared p-electron HOMO orbital on the OH oxygen and the π^* LUMO. The new mixed HOMO would be lower than an unshared pair on O, and the new LUMO should be higher than the π^* of C=O.



(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.

The proton should add to the carbonyl oxygen, which, as shown in part (b) above, has a partial negative charge, and thus has a higher-energy unshared pair of electrons. The protonated acid has two equivalent resonance structures.

