

Chemistry 210
“Organic Chemistry I”
Winter Semester 1999
Dr. Rainer Glaser

Examination #1

“Structure, Bonding and Properties of Organic Molecules.
Structure, Stereochemistry and Properties of Alkanes.”

Friday, February 12, 1999, 9:00 - 9:50

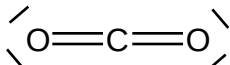
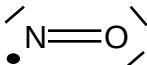
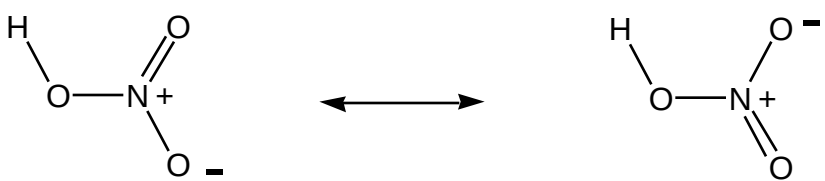
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Answer Key

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Question 1. Lewis-Kekule Structures & Hybridization. (14 points)

The article “U.S. FLOATS NEW 'BUBBLE' PROPOSAL” (*Asahi News Service*, December 11, 1997) brought up some timely issues in atmospheric chemistry. Carbondioxide, nitrogenoxide, and nitric acid were among the molecules responsible for the greenhouse effect. For each of these molecules, provide the Lewis-Kekule structure. For HNO_3 , several resonance forms are needed and you should provide all the major resonance forms. In all cases, clearly indicate formal charges (if any).

CO_2 	NO 
Radical? Yes - No (Circle correct)	Radical? Yes - No (Circle correct)
HNO_3 	
Radical? Yes - No (Circle correct)	

The hybridization of the C-atom in carbondioxide:

The hybridization of the N atom in HNO_3 :

The overall bond order of the CO bond in carbondioxide:

The π -bond order of the CO bond in carbondioxide:

sp

sp^2

2

1

Question 2. Organic Structures and Properties. (16 points)

PE1-Q2 What kinds of node surfaces are there in the 3s atomic orbital?

- a. No node surfaces
- b. One node plane
- c. One spherical node
- d. One node plane and one spherical node
- e. Two spherical nodes**

PE1-Q4 What is the ground state electron configuration of lithium?

- a. $1s^2 2s^2 2p^6 3s^1$
- b. $1s^2 2s^2 2p^6 3s^2$
- c. $1s^2 2s^1$**
- d. $1s^2 2s^2$
- e. $1s^1$

PE1-Q11 What are the pi-bond orders of the CC bonds in allyl cation, $[H_2CCHCH_2]^+$ and in allyl anion, $[H_2CCHCH_2]^-$?

- a. Cation and anion 0
- b. Cation 0 and anion 1/2
- c. Cation and anion 1/2**
- d. Cation 1/2 and anion 1
- e. Cation and anion 1

PE1-Q15 Consider methylguanidine. (Guanidine is like urea but contains an =NH group instead of the =O. Methylguanidine contains one methylamino group.) Which one of the three N-atoms is most likely to be protonated?

- a. The imine N-atom (=NH)**
- b. The amino N-atom ($-NH_2$)
- c. The methylamino N-atom ($-NHMe$)

Question 3. Intermolecular Interactions. (10 points)

The article “TANKER BLEEDS OIL IN TOKYO BAY. WORST SPILL IN JAPAN'S HISTORY” (*AP and Reuters*, July 3, 1997) talked about oil spills and modern ways of oil spill remediation. Oil spill remediation is based on the optimal use of knowledge about **intermolecular bonding**.

Crude oil consists of a mixture of hydrocarbons. Most of the hydrocarbons in crude oil are aliphatic and saturated. Let's review the intermolecular forces that act (a) between water molecules in pure water, (b) between alkane molecules in oil (consider “octane” as a typical alkane in oil). Then explain why water and octane do not mix. Your explanation should include a clear statement that describes the interaction between a water molecule and octane and how that compares to the interactions in pure water and pure octane, respectively. Be brief and concise.

Intermolecular forces in **pure water**:

Hydrogen bonding. Show a few water molecules and indicate H-bonds between partially positively charged H-atoms and partially negatively charged O-atoms

Intermolecular forces in **pure octane**:

Molecules without dipole and without any bond dipole moments.
London dispersion forces only: temporary dipole - induced dipole

Why do **water & octane** not mix?

Octane-octane interactions are weak and easy to break.
Octane prefers to interact with water (dipole-induced dipole) than with octane (temp. dipole (temp. dipole - induced dipole)
Water is just not interested in giving up its H-bondings!

Question 4. Molecular Orbitals and Hybridization.. (16 points)

- PE1-Q1 Which statement about the Linear Combination of Atomic Orbitals (LCAO) is NOT true?
- a. Comb. of atomic orbitals (AOs) on different atoms produces molecular orbitals (MOs).
 - b. Comb. of atomic orbitals (AOs) on the same atom produces hybrid atomic orbitals (HAOs).
 - c. Comb. of hybrid atomic orbitals (HAOs) on different atoms gives molecular orbitals (MOs).
 - d. Comb. of atomic orbitals (AOs) on one and the same atom produces molecular orbitals (MOs).**
 - e. Comb. of molecular orbitals on different molecules produces new molecular orbitals.

- PE1-Q3 Where is the node plane of the π -molecular orbital of ethene?
- a. The molecular plane**
 - b. The plane perpendicular to the molecular plane containing both C-atoms
 - c. The plane perpendicular to planes in (a) and (b)
 - d. The π -MO is bonding and has no node
 - e. The π -MO only has a spherical node but no node plane

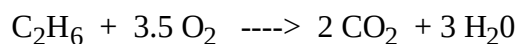
- PE1-Q9 Ammonia is a pyramidal molecule with formula NH_3 . Which orbital is the highest-lying occupied molecular orbital (HOMO)?
- a. The HOMO is an sp^3 AO, the non-bonding lone pair.**
 - b. The HOMO is an $\text{sp}^3\text{-sp}^3$ N-H bond
 - c. The HOMO is an s-sp^3 N-H bond
 - d. The HOMO is the 3s N-AO
 - e. The HOMO is the 3p N-AO

- PE1-Q11 Which equation defines the electrical dipole moment?
- a. dipole moment = plus charge x minus charge x distance
 - b. dipole moment = |charge| x distance**
 - c. dipole moment = |plus charge| x |minus charge| x distance
 - d. dipole moment = $\text{charge}^2 \times \text{volume}$
 - e. dipole moment = charge x volume

Question 5. “Combustion” Reactions. (14 points)

The article “ALTERNATIVES TO INTERNAL COMBUSTION” (New York Times, May 24, 1997) talked about better ways to generate power from fuels. Humans always burned “fuels”, early one wood and animal fats, and more recently fossil fuels, natural gas, coal, methanol, ethanol, hydrogen gas, There have been discussions as to what fuel would be most efficient and would have the least detrimental effects on the environment. But nobody thought the problem lies less with the choice of fuel but with the very notion of “burning”. Until the people from Ballard came around. The genius lies with the realization that the energy comes from oxidizing the fuels “in some way” and it does not have to involve “burning”. Write down the stoichiometric equation for the “complete” combustion of ethane leading to carbondioxide and water. Then state what products are formed during combustion of ethane if the combustion is incomplete.

Stoichiometric Equation for the Complete Combustion of Ethane:



Products of Incomplete Combustion of Ethane:

CO and C, water

Explain the difference in the **heats of combustion** of **cyclopropane** and **cyclohexane**. State whether the heat of combustion of cyclopropane is larger or smaller than the heat of combustion of cyclohexane. Compare the heats of combustion on a per CH_2 group basis (**qualitative** comparison suffices.). Briefly explain why; a key word or a short phrase is all that is needed.

Cyclopropane has the larger heat of combustion. More energy is released
Cyclopropane is strained. The geometric bond angles are much smaller than
The hybridization angle.
Cyclopropane forms banana bonds with less overlap than linear bonds.

Question 6. Alkanes. (16 points)

Ex-Q6 Identify the correct name of $\text{CH}_3\text{-C}(\text{CH}_3)_2\text{-CH}_2\text{-CH}_3$.

- a. **2,2-dimethylbutane**
- b. methylneopentane
- c. 2-methyl-2-ethylpropane
- d. 2,2-dimethylpentane
- e. 3,3-dimethylbutane

Ex-Q8 How many C-atoms are there in one molecule of 3-(1,2-dimethylpropyl)-5-propyldecane?

- a. 16
- b. **18**
- c. 20
- d. 22
- e. 24

Ex-Q10 What types of C-atoms are present in tertiary butane, $\text{HC}(\text{CH}_3)_3$?

- a. **One tertiary and three primary C-atoms.**
- b. One tertiary and three secondary C-atoms.
- c. Three tertiary and one primary C-atoms.
- d. Three primary and one secondary C-atoms.
- e. One quaternary and three primary C-atoms.

Ex-Q16 What is the technical name of the process by which long-chain alkanes are thermally broken down, in the absence of hydrogen gas, to shorter chain hydrocarbons?

- a. Reforming
- b. **Cracking**
- c. Hydrocracking
- d. Distillation
- e. Refining

Question 7. Rotational Energy Profile of Butane. (14 points)

Draw the rotational energy diagram for butane. Of course, we will consider the rotation about the central bond of butane. Begin the diagram on the left with the eclipsed structure that has the two methyl groups in a *cis* arrangement (dihedral angle 0). Draw the curve for the rotational energy profile into the pre-drawn graph area. Draw the Newman projections of the two minima and of the two transition state structures in the boxes on top. Use arrows to indicate which structures goes with which one of the minima or transition state structure. Provide the relative energy between the minima in kcal/mol.

Draw the Newman Projections in these spaces.

