Chemistry 210
"Organic Chemistry I"
Winter Semester 2004
Dr. Rainer Glaser

Examination #1
"Alkanes: Combust, Oxidize, Dehydrogenate, and Halogenate."

Posted: Saturday, February 14, 2004.

Collect: Wednesday, February 18, 2004, after lecture.

Name:
Answer Key

Question 1. Combustion: Old & New.	35	
Question 2. Autoxidation of Ether.	10	
Question 3. Autoxidation of Methane.	15	
Question 4. Radical Chain Halogenation.	24	
Question 5. Radical Inhibitor.	16	
Total	100	

Question 1. Combustion. (35 points)

University reactor shows promise for `hydrogen economy'

Associated Press, Published February 12, 2004.

Researchers at the University of Minnesota say they have built a prototype reactor that produces hydrogen from ethanol so efficiently that it could one day power conventional fuel cells for homes.

The technology is cheaper and more efficient than the current commercial method of capturing hydrogen from fuel, which is done with fossil fuels in large refineries, the scientists said. They said the reactor they built is much smaller and simpler and requires less energy.

Their technology could be coupled with a fuel cell to generate nearly enough energy to power an average-sized home, according to the scientists, who will publish their findings in the Feb. 13 issue of the magazine *Science*.

“This points to a way to make renewable hydrogen that may be economical and available,” said Lanny Schmidt, a chemical engineer who led the study. Gregg Deluga and graduate student James Salge also worked on the project. All three are in the department of chemical engineering and materials science.

The men built the reactor, a 2-foot-high apparatus of tubes, valves and wires, in a laboratory on the university's East Bank. The hydrogen-driven fuel cell they envision might be a little larger than a coffee cup.

Right now, hydrogen can be made cheaply only in large refineries that use fuels such as natural gas.

The new technology holds promise for a “hydrogen economy” that would use hydrogen to fuel cars and make electricity. It also holds economic potential for Midwest farmers, who are leaders in the production of corn-based ethanol. A bushel of corn, the researchers said, yields three times as much power if its energy is channeled into hydrogen fuel cells rather than burned with gasoline.

Hydrogen, a clean energy source, emits no pollution or greenhouse gases. President Bush supports funding for the development of hydrogen-powered fuel cells that are commercially viable.

George Sverdrup, a technology manager at the National Renewable Energy Laboratory, said he was encouraged by the research.

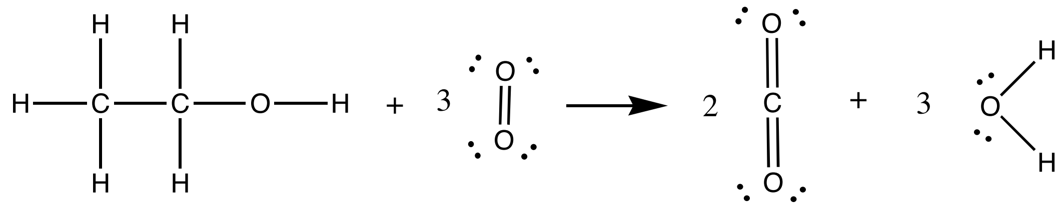
“When hydrogen takes a foothold and penetrates the marketplace, it will probably come from a variety of sources and be produced by a variety of techniques,” he said. “So this particular advance and technology that Minnesota is reporting on would be one component in a big system.”

While ethanol could be an important part of a hydrogen economy, Sverdrup said it's unlikely corn itself would be enough to support the entire system.

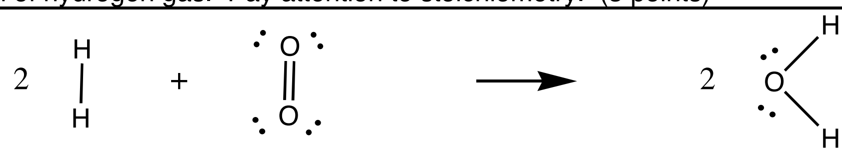
The University of Minnesota researchers initially envision people buying ethanol to power the small fuel cell in homes in remote areas where installing power lines isn't feasible. The cell could produce 1 kilowatt of power, nearly enough for an average home.

According to their estimate, a gallon of ethanol costing $1 could be used to produce energy for about 4 cents per kilowatt hour. That would be in the ballpark with national figures for the cost of raw energy, said a spokesman for the Edison Electric Institute, a national energy association.

(a) Using complete structural formulas (e.g. show all atoms, bonds and lone pairs), write down the reaction for the complete combustion of ethanol. Pay attention to stoichiometry. (6 points)



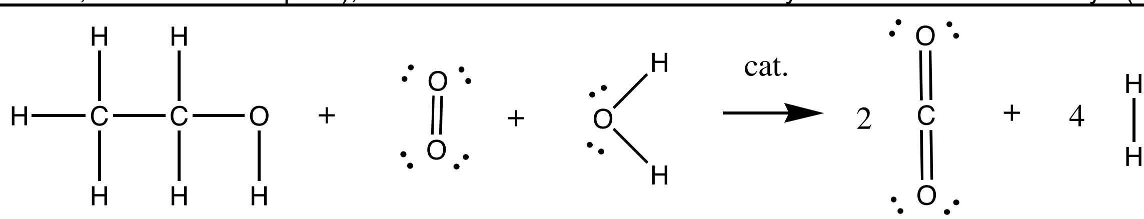
(b) Using complete structural formulas (e.g. show all atoms, bonds and lone pairs), write down the reaction for the complete combustion of hydrogen gas. Pay attention to stoichiometry. (3 points)



(c) Considering your answers to (a) and (b), why would we want to have a "hydrogen economy"? (2 points)

Hydrogen oxidation yields only water, no carbon dioxide.

(d) Find the article in *Science* magazine (online at http://www.sciencemag.org) and read it. What is the overall reaction for the dehydrogenation of ethanol (e.g. what else is produced). Using complete structural formulas (e.g. show all atoms, bonds and lone pairs), write down this overall reaction. Pay attention to stoichiometry. (4 points)



(e) The hydrogen source ethanol is said to be renewable. Where is the ethanol coming from? Is the technology in place to produce large quantities of ethanol in this way? (4 points)

From biomass, grains.

Yes, ethanol made in this way is used as part of gasoline (up to 15%).

(f) Hydrogen gas can be used as fuel for a combustion engine and also as fuel for a fuel cell. The overall reaction is the complete oxidation of hydrogen. How does "combustion" differ from "fuel cell oxidation"? Name at least one advantage and one disadvantage for the two modes of energy production. (8 points)

Combustion: How it works. Oxidation of hydrogen to water. Ignition and Flame. Energy produced: Heat, mechanical energy.	Fuel Cell: How it works. Oxidation of hydrogen to water. Catalyst. Energy produced: Electricity.
Advantage of Combustion: Easy. Just ignite.	Advantage of FC Oxidation: No wasted heat.
Disadvantage of Combustion: Much heat is wasted.	Disadvantage of FC Oxidation: Catalyst expensive.

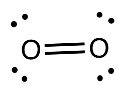
(g) In the context of our discussion of "Alternatives to Internal Combustion", you read an article on a fuel cell pact between the United States and Europe. Everybody seems to agree that the future most likely is based on hydrogen as the main fuel and there also seems to be agreement that not all of the fuel will come from biomass. There is a clear difference, however, as to how the Americans and the Europeans plan to make their hydrogen. Briefly explain how the Americans and the Europeans want to make their hydrogen. Name at least one advantage and one disadvantage for both of the approaches. (8 points)

American Hydrogen Production Plan. Burn coal to make heat. Use the heat to make electricity. Use electricity to make hydrogen from water. (Or Coal + water –(cat.)→ COx + hydrogen)	European Hydrogen Production Plan. Use natural gas. Use catalytic process to get the hydrogen. Burn some natural gas to make heat required.
Advantage: Coal is cheap. Lots of it.	Advantage: Gas is cheap. Lots of it.
Disadvantage: Coal burning causes NOx and SOx.	Disadvantage: Natural gas transport. More expensive plants needed for catalytic process.

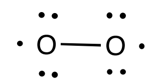
Question 2. Autoxidation of Ether. (10 points)

Consider the autoxidation of diethyl ether, H_3C-CH_2-O-CH_2-CH_3. There is a preference for the autoxidation to occur at the position right next to the ether oxygen (e.g. at the CH_2 group). Draw the Lewis structure of O_2 in the way that satisfies the classical rules for the drawing of Lewis structures. Draw the Lewis structure of O_2 again in a way that reflects that fact that oxygen is a diradical. Using complete structural formulas (e.g. show all atoms, bonds, lone pairs and unpaired electrons), write down the three reaction steps in the correct boxes: H-abstraction by O_2, H-abstraction by the alkylperoxy radical, and O_2 addition to alkyl radical. Circle the radical that "carries" the chain (e.g. is consumed in the first chain reaction step and is formed in the second chain reaction step).

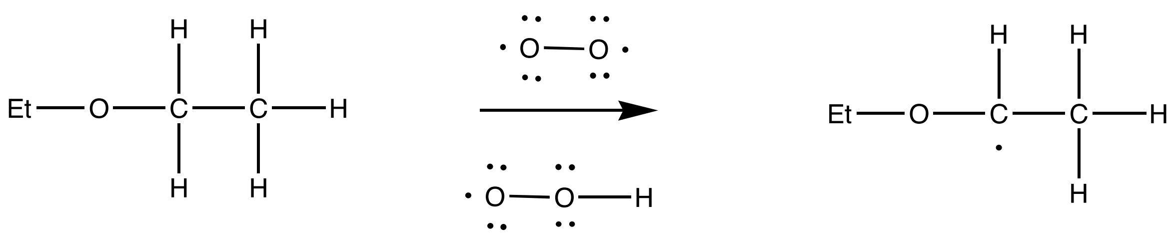
Classical Lewis Structure for Dioxygen (1 point)



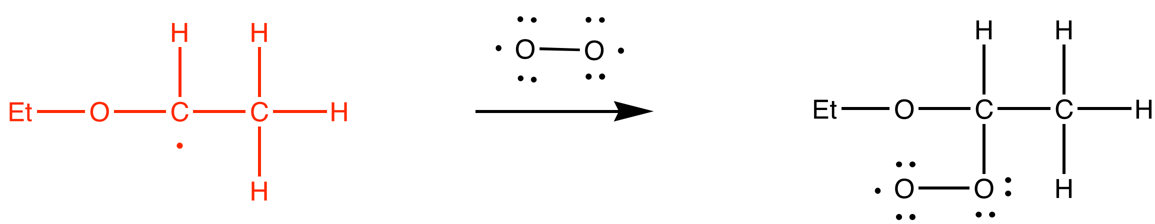
Diradical Lewis Structure for Dioxygen (1 points)



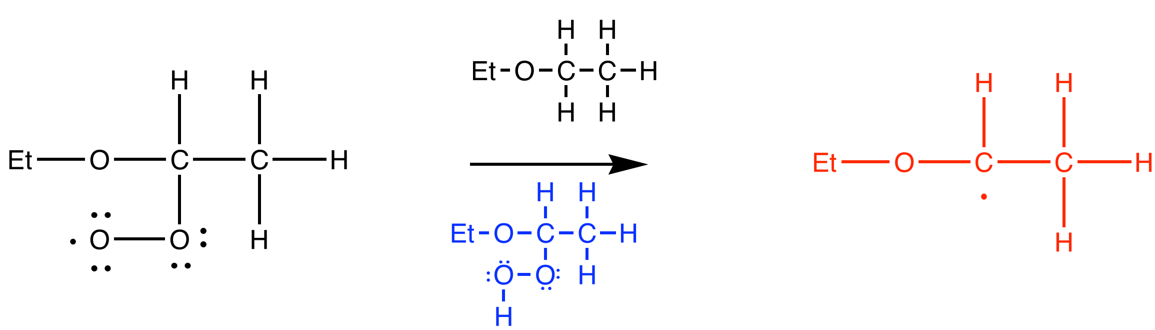
Initiation Reaction (2 points):



First Step of Radical Chain Reaction (3 points):



Second Step of Radical Chain Reaction (3 points): Product is blue, chain carrying radical in red.



Question 3. Autoxidation of Methane. (15 points)

Oxidative Coupling of Methane in the Gas Phase: Simulation and Reaction Mechanism, Sekine, Y.; Nishimura, T.; Fujimoto, K. *Energy & Fuels* **1998**, *12*, 828-829.

The autoxidation of methane, CH_4, was discussed in the above paper (no need to read the paper) and Figure 4 is taken directly from that paper. The authors use sum formulas to abbreviate the discussion. Let's make sure we understand exactly what is going on. Redraw the diagram with complete structural formulas (show all atoms, all bonds, all lone pairs, all unpaired electrons).

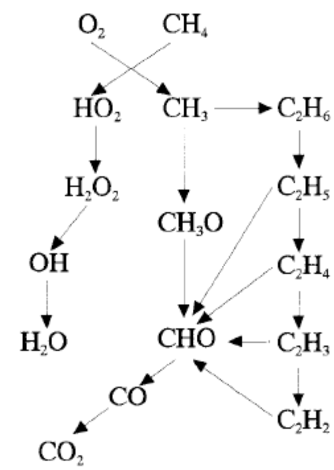
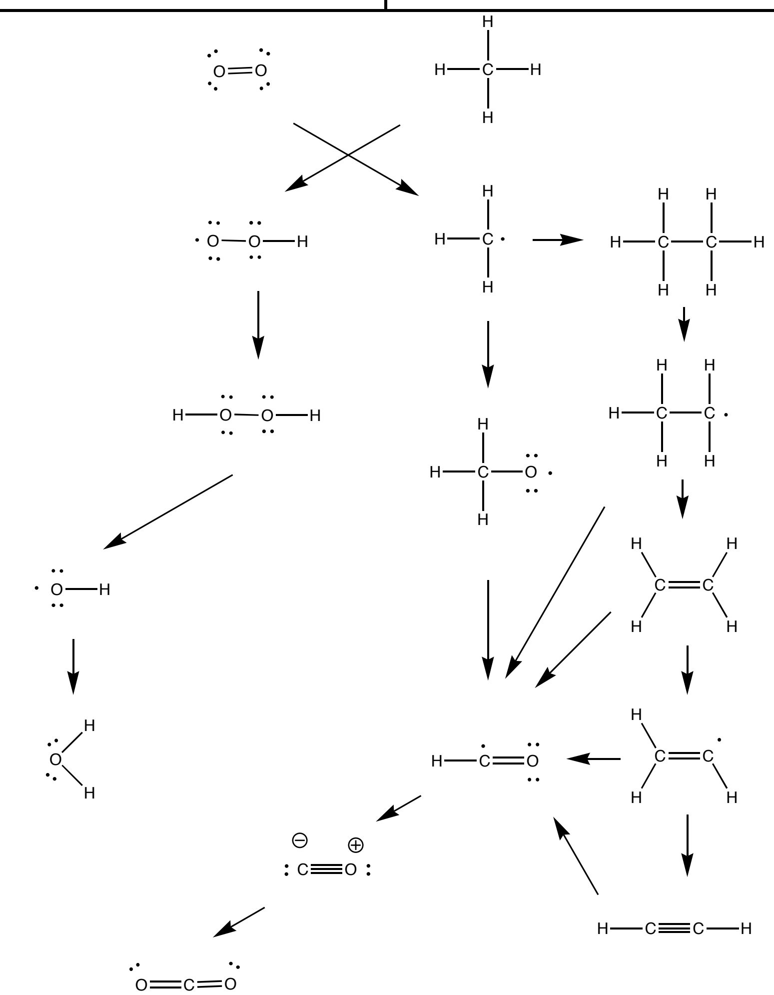
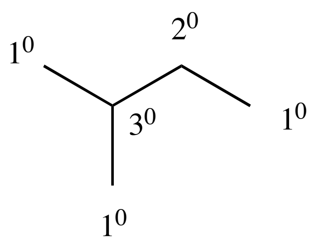


Figure 4. Estimated reaction network on oxidative coupling of methane.

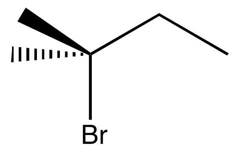


Question 4. Radical Chain Halogenation. (24 points)

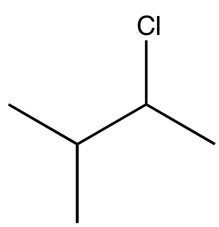
Draw the structure of isopentane and identify each carbon atom as primary (1°), secondary (2°) or tertiary (3°):



Major product of the monobromination of <u>iso</u>pentane:

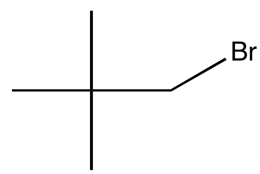


Major product of the monochlorination of <u>iso</u>pentane:



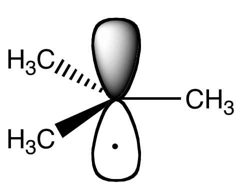
Statistics and selectivity! (hard)

Major product of the monobromination of <u>neo</u>pentane:



(Tricky!)

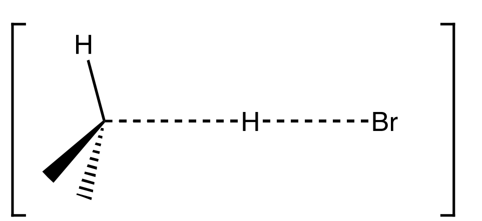
Perspective drawing of tertiary butyl radical. Make sure that the drawing reflects the correct geometry at every C-atom and indicate the C-hybridization.



radical center is sp^2

methyls are sp^3

Perspective drawing of the transition state structure for the monobromination of propane. Draw the bond lengths such that their relative lengths make sense! Make sure the TS structure reflects that the TS is ______ (early, **late**).

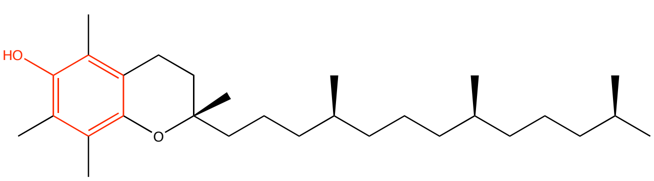


Question 5. Radical Inhibitor. (16 points)

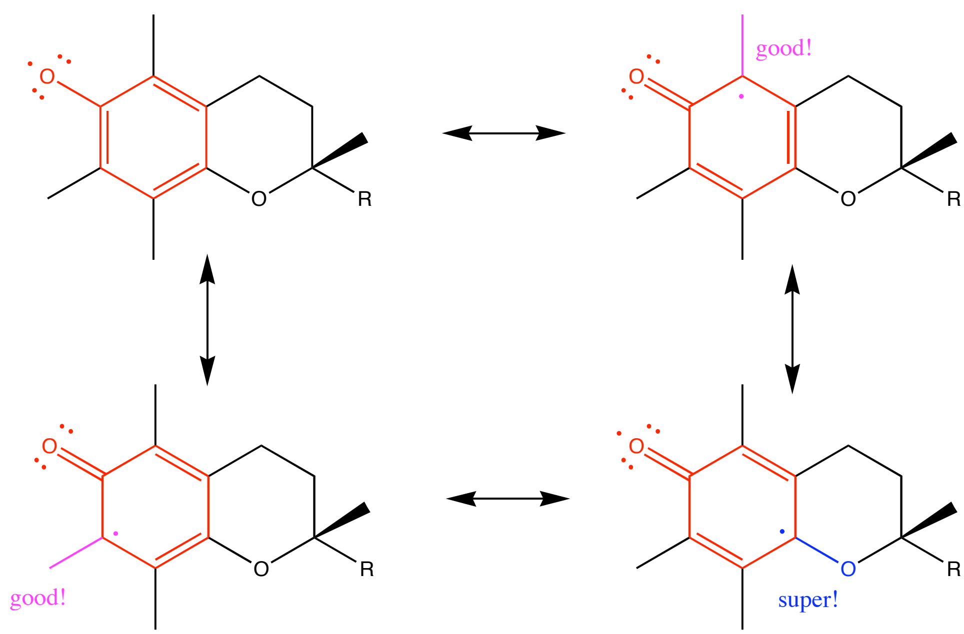
The following text appears on a web site by Michael W. Davidson, Florida State University: "Vitamin E was the fifth vitamin discovered when researchers found that a dietary deficiency in laboratory rats produced fetal death in pregnant females. The name "tocopherol" was derived from the Greek words for childbirth (***tos***), to bring forth (***phero***), and the chemical designation for an alcohol (***ol***). Vitamin E acts as a co-enzyme in cellular membranes and serves as a scavenger for free radicals that are destructive to the membrane and internal cellular components. Natural sources of vitamin E are vegetable oils, sunflower seeds, almonds, and peanuts."

Find the structure of Vitamin E in your textbook or elsewhere and draw its complete structural formula. Indicate which H atom is abstracted by a reactive radical. Draw the structure of the radical formed by H abstraction, draw as many resonance forms of the radical as needed, and explain why this new radical is less reactive (a "coach potato radical").

Vitamin E Structure:



Radical of Vitamin E:



Resonance stabilization! Less reactive radical.