**Exam 1 Organic Chemistry 3514**

**Alfred State College 4 October 2013**

Your name:\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_answers\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ 1 pt \_\_\_\_\_\_/100 pts

* 1. **Lewis Model Bonding Part 1 ( 9 pts total/3 pts each)**

Sketch the most stable Lewis structures that **strictly** obey the octet rule for the compounds below:

***(include formal charges , lone pairs & indicate if symmetric resonances are present when necessary by writing `RES’)***









W 2

SO3 also ok (RES) CO2 COCl2

* 1. **Lewis Model Bonding Part 2 (9 pts total/ 3 pts each)**

1. Draw the best structure for SOF2 that strictly obeys the octet rule and indicate where the formal charges are likely to be. *(S is central atom. Structure may have a net charge. Include all formal charges , lone pairs*)





Best structure for

SOF2 that strictly obeys

Octet rule

Best (no formal charges) also okay

1. If we relax the octet rule but insist on minimizing formal charge, what is the best structure for SOF2?

*(Structure may or may not have a net charge. Include all formal charges , lone pairs*)



See above or:

1. With the help of appropriate Lewis models, explain why CO is over 200 times more likely to react with the iron in your blood than O2?

*(-):C*≡*O: (+) has formal charge such that the (-)C end is strongly attracted to the Fe3+ of the blood’s heme. In contrast, :O=O: has not formal charge and is much less effective at binding Fe3+*

\_\_\_\_/19 includes name

* 1. **Lewis Model Bonding Part 3 ( 15 pts total)**

1. Consider the 4 compounds below:

.. .. .. .. .. .. .. .. .. ..

:O=C-S=O: :O-C=S=O: H-O-C≡S-O: :O-C-S-O:

| .. | .. .. .. .. | .. ..

H H H

**A B C D**

Which compound(s) (if any) contains a neutral S ? \_\_\_\_\_\_D\_\_\_\_

2 pts/line

Which compound(s) (if any) contains O with a formal charge of -1 ? \_\_\_B,C,D\_\_\_\_\_\_\_\_\_\_

Which compounds(s) (if any) contains S with a formal charge of +2 ? \_\_\_\_\_\_B,C\_\_\_\_\_\_\_\_

Which compound(s) (if any) have an overall net charge of +1 ? \_\_\_\_\_\_\_\_A,B,C\_\_\_\_\_\_\_\_\_\_

Which compound(s) (if any) are anions (possess net negative charges) ? \_\_\_\_\_D\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Which compound: **A B C D** has the minimum formal charge of the group ? (circle your answer)

1. For each pair below, circle the compound that is most stable using the rough Lewis model reactivity rules : (1 pt each/3 pts total)
2. **CH4**  vs. CH3Cl ii) NO vs. **NO2-** iii) CO vs. **CO2**
3. Draw a structure using the molecular formula: C2H4O that satisfies the octet rule and results in zero formal charge on all the atoms. (2 pts)



* 1. **Pauling’s Localized Hybrid Bonding Model (6 pts total/1 pt each)**

1. Identify the hybridization on the **bolded** elements in the compounds below:

**..** .. .. ..

**:S**=C=O: H3C- **N**-H HO-**C**≡C-H O=**N**-H

|

H

\_\_sp2\_ \_sp3\_\_\_ \_sp\_\_\_ \_sp2\_\_

1. Name two advantages the Pauling hybrid model has over the Lewis model.
2. \_\_\_\_\_\_explains reactivity order of ethane < ethylene <acetylene\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
3. \_\_\_\_\_\_explains how multiple bonds can arrange themselves between atoms\_\_\_\_\_\_\_\_\_\_\_

Others possible (rearrangement of AO🡪MO; reactivity of ethylene on Pt; pi electron character)

\_\_\_/17

* 1. **MO Theory (4 pts)**

1. Fill in the MO Fill in the MO diagram below for the hypothetical diatomic: **OF** . (2 pts) (O has 8 electrons, F has 9 electrons)
2. \_\_\_\_\_

\_\_\_\_ \_\_\_\_ 1.5 anti-bonds

\_\_\_\_ \_\_\_\_

3 bonds \_\_\_\_

\_\_\_\_

\_\_\_\_

net non-bonding

\_\_\_\_

\_\_\_\_

b) How many net bonds exist for **OF** according to MO theory ? \_3-1.5=1.5\_\_\_

c) Will **OF** be paramagnetic ? **YES** NO

* 1. **Nomenclature of Alkanes (16 pts total)**

1. Using just IUPAC rules, name the compounds below: (2 pts each)









CH3CH(CH3)C(CH3)2(CH2)2CH3

1-(2,2-dimethylcyclopentyl)hexane old school 3-ethyl-2,2-dimethylnonane

4-(1-methylethyl)-2,5-dimethylheptane or 1-hexyl-2,2-dimethylcyclopentane

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_



Hexylcyclohexane 2,3,3-trimethylhexane 3-chloro-4-(methylethyl)-3,6-dimethyloctane

1. Provide common names for the compounds below: (4 pts total/1 pt each)









\_tertbutyl chloride neopentyl chloride\_ isobutyl bromide sec-butyl bromide

\_\_\_\_/20

* 1. **Functional groups (6 pts)**

Supply the name or chemical equivalent for the functional group designations below:

R-CHO= \_\_\_\_aldehyde\_\_\_\_\_\_\_\_\_\_\_\_\_ R-O-R’ = \_\_\_ether\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Carboxylic acids \_\_RCOOH\_\_\_\_\_\_\_\_\_\_\_ ketones =\_\_\_\_\_RR’C=O\_\_\_\_\_\_\_\_

CH3 -CH=CH2 is an example of a(n) \_\_alkene\_\_\_\_\_ example of an alcohol=\_\_\_\_\_\_\_any R-OH\_\_\_\_

* 1. **Ring and Rotational Isomer Language (10 pts total)** 

**A B C D**

1. Which structure(s) aboveis/ are gauche \_B\_\_ b)Which structure(s) aboveis/are eclipsed ? \_C,D\_
2. Which structure(s) above is/are anti ?\_\_A\_\_\_\_\_\_ d)What is the most stable rotamer above \_A\_\_

Consider the dichloro ring compound shown on the right:



1. Provide the most complete name for it : (2 pts)

**Trans (ax,ax)-1,2-dichlorocyclohexane**

1

1. If the above compound is `ring’ flipped, draw the positions

The two chlorines would take on on the `flipped’ ring below:

**trans ( eq,eq)**



**Cl 2**

**1**

1. Sketch (eq, eq) 1,3-dichlorocyclohexane below and indicate Cl

Whether it is cis or trans:



Cl

Cl

**1 3**

(eq, eq) 1,3-dichlorocyclohexane is:

**cis trans (circle your choice)**

1. What ring conformation is drawn below ? **I am a(n) \_\_\_\_boat\_\_\_\_\_\_\_\_\_\_\_\_\_ ring conformer**

**\_\_\_/16**

* 1. **Free Radical Chemistry of Alkanes (23 pts total)**

1. **Key Facts for Methane ( 1 point each/5 points total)**

Write down 5 facts that characterize the reaction behavior of methane under free radical halogenations.

1. Reaction occurs only at >250oC or with input of correct uv light
2. λ of excitation causing reaction is the dissociation wavelength of the reacting halogen, X2
3. Photo yield can be in the thousands

iv) Reactivity order follows trend F2>Cl2> Br2> I2

1. Can temporarily quench reaction with input of O2
2. **Mechanism of Free Radical Methane Bromination (6 pts)**

Write down the mechanism forwarded to explain the overall reaction:

hυ

*xs*  Cl2 + CH4 CH4-mCl + m HCl, m =1,2,3,4

***step # elementary reaction commentary***

***hv***

1  **Cl2 ------> 2X\*** chain-initiation (rather like making a cancer cell)

2 **Cl\* + CH4 -------> HCl + CH3\*** chain propagation....

3 **Cl2 + CH3\* -------> CH3Cl + Cl\*** (one begets another... ! Note that radicals

**...... etc. etc.** are implicated in aging and cancer)

Multiple substitutions of X can occur on originally generated CH3X by same mechanism, e.g.:

2’ **Cl\* +CH3Cl -------> CH2Cl\* + HCl (if you didn’t show this part, that was ok)**

3’ **CH2Cl\* + Cl2 -------> CH2Cl2 + Cl\***

The process is terminated by radical-radical recombination or quenching by O2.

4a **Cl\* + Cl\*---> Cl2**

4b**CH3\* + CH3\* --->CH3CH3**chain termination

4c **CH3\* + Cl\*---> CH3Cl**

4d **CH3**\* **+ O2-----> CH3OO\*** (final `peroxyl’ radical is rather stable => it sucks peroxyl radical energy from CH3\*)

1. Sketch the equivalent ***Activated Complex’ = Energy Diagram Picture (=Eyring-Polanyi diagram)***

for the mechanism above. Indicate in particular where the following are located on the diagram:

EA = activation energy , M= metastable state, P = product state, position of activated complex; where step 2 and step 3 (from above mechanism) start and end. (5 pts)

**See below**

**activated, 5-coordinate X-->CH3----H complex**

**at top of first hill**

**M**= metastable state

**P** = product state

**Potential**

**Energy** **M**

*activation*

**CH3\* +HX**

*barrier*

*Heat (Enthalpy) of Reaction*

**P**

**CH3X + X\***

Up the big hill and down to M Up the little hill and down to P

**CH4  + X\*🡪**

**X2 + CH3\*🡪**

**step 2 step 3** .....etc

**Progress of Reaction**

\_\_\_/14

* 1. Chemistry of Alkanes (continued)

1. Sketch the activated complex for methane with fluorine and with iodine in the two boxes provided below: (6 pts/3 pts each)

Fluorine activated complex Iodine activated complex



 flat sp2 tetrahedral sp3

1. What two new facts are associated with the radical halogenation of higher alkanes like propane, butane etc. ?
2. \_\_\_\_3o > 2o>1o site reactivity\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
3. \_\_\_\_I2 > Br2 >Cl2 site selectivity\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
4. Which reacts faster: **F2 with CH4**or **Br2 with CH4** circle choice
   1. **Miscellaneous This and That (7 pts)**
5. Steam distillation relies on the two components being separating having a large

difference in water\_\_\_\_\_\_solubility\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

1. Re-crystallization assumes that the soluble impurities are low\_\_\_in concentration compared to the target species.
2. Linus Pauling’s valence bond model is good at calculating energies of molecules T **F**
3. A pure substance’s melting point is the maximum value obtainable and has a narrow(small)\_melting point range.
4. You use a Claisen head in which technique ? (CIRCLE CHOICE)

fractional recrystallization Solvent separation simple distillation **steam distillation**

1. MO theory explains why O2 is paramagnetic : **T** F
2. Any day doing Organic Chemistry is a \_\_good\_\_\_\_\_\_\_\_\_\_day. ☺ free point

\_\_\_/16