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Please print your name

CHM4155

FINAL EXAM (50%)

Dr. J.C. Scaiano

April 27, 2007

Family name: _____

First name: _____

Student #: _____

Time allowed: 180 minutes

NO BOOKS OR NOTES ALLOWED

NO MOLECULAR MODELS ALLOWED

CALCULATORS ALLOWED

Question	1	2	3	4	5	6	7	8	Total
Value	30	15	15	10	10	10	10	10	100
Mark									
Notes									

IMPORTANT: You must answer questions # 1, 2 and 3

You must answer 4 questions only from questions 4 to 8. Please indicate below which question you do NOT want marked. If you make no selection, question 8 will not be marked.

Please do NOT mark question: _____ ←

1. (30 MARKS – stars show marks) Short Answer: no part marks.

a) ****For the hypothetical reaction A + B → C + D, the activation energy is 26 kcal/mol. For the reverse reaction, the activation energy is 16 kcal/mol. What is the enthalpy change for the forward reaction ($\Delta H_{reaction}$)? _____**

b) ***If you plot the inverse of concentration (1/c) in function of time for a given chemical reaction and obtain a straight line, the reaction occurs through a**

FIRST ORDER UNIMOLECULAR SECOND ORDER process.

c) ***The rate constant for a diffusion-controlled reaction will**

INCREASE DECREASE STAY CONSTANT

with decreasing solvent viscosity.

d) ****Catalytic reforming of benzene to yield cyclohexane requires a(n) ACID METAL catalyst and requires HIGH LOW NO hydrogen pressure.**

e) ***The blue luminescence of cool flames is due to emission from the excited state of**

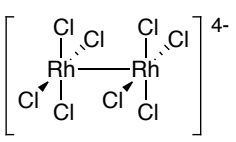
FORMALDEHYDE PEROXIDES SOOT

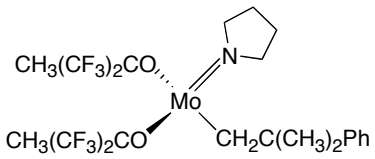
f) ***One way to prevent a combustion reaction from leading to an explosion is**

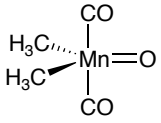
_____.

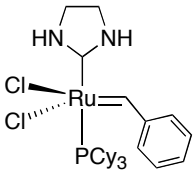
g) ***In the box, write one possible industrial synthesis of acrylonitrile.**

h) ***Which of these structures is a possible olefin metathesis catalyst?**









i) *In the Monsanto catalytic process, methanol is converted into _____.

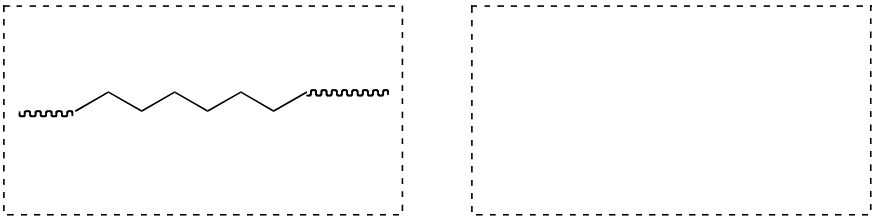
j) *Surfactants with branched hydrophobic tails clean better than surfactants with linear hydrophobic chains. Why are linear surfactants used in practice? (choose <u>one</u>)

- ❑ **BRANCHED SURFACTANTS DO NOT DISSOLVE EASILY**
- ❑ **LINEAR SURFACTANTS ARE CHEAPER**
- ❑ **BRANCHED SURFACTANTS ARE NOT BIODEGRADABLE**
- ❑ **LINEAR SURFACTANTS DO NOT CAUSE RASHES ON SKIN**

k) *Sodium dodecyl sulfate (SDS) is added in water at different concentrations. Associate the concentration of SDS in water with the resulting self-assembled structure.

VERY LOW [SDS]	**MONOLAYER**
LOW [SDS]	**SPHERICAL MICELLE**
HIGH [SDS]	**ROD-LIKE MICELLE**

l) *Draw the chemical structure of the monomer used to make the polymer below:



m) *A vinyl monomer is polymerized using free radical vinyl polymerization. It was observed that using cyclohexane as the solvent reduces the molecular weight of the polymer, where using benzene does not. Why?

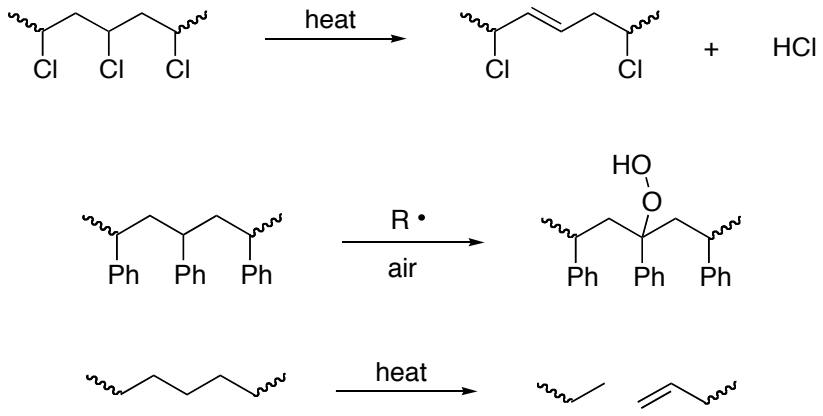
_____

_____

n) *Polyethylene can be made using many different synthetic methods. Associate each synthetic method with the resulting polymer. (Hint: LLDPE stands for linear low density polyethylene)

FREE RADICAL POLYMERIZATION	**HDPE**
ZIEGLER-NATTA POLYMERIZATION	**LLDPE**
CO-POLYMERIZED WITH A BRANCHED ALKENE	**LDPE**

o) *Which of the following reactions would induce the <u>largest loss</u> in mechanical strength of the plastic? (choose one)



p) *Below, draw a representative stress-strain curve for an elastomeric polymer (be precise, and include axis labels).

q) *Draw the possible monomer(s) used to make Nylon 2,4 by step growth polymerization.

r) *Polyacrylonitrile can be made via anionic polymerization. Which of the following should be rigorously removed from the reaction vessel?

Li^+ Na^+ WATER AIR MAGNETIC FIELDS

s) *What will be the average chain length of the resulting polymer if 1 mole of acrylonitrile is initiated by 0.001 mole of an anionic initiator?

_____

t) *Which of these additives would be the *most* efficient at preventing light-induced damage in a polymer?

PLACTICIZER SUNSCREEN RADICAL SCAVENGER WATER

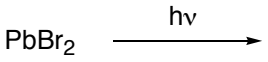
u) *When a new car is introduced on the market, it is available in only a few colours. Explain why the industry shift from paints to resins for cars has limited the number of available colours for new cars.

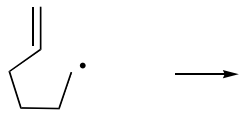
_____

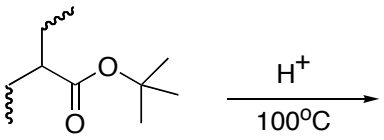
_____

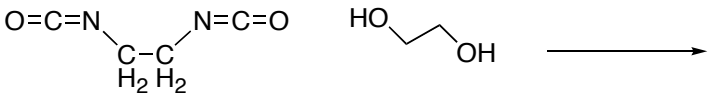
v) *The above polymerization is occurring at a rate of 0.05 mol/hr. If the concentration of the initiator is doubled, then the chain length will INCREASE DECREASE by a factor of $\frac{1}{4}$ $\frac{1}{2}$ $\frac{1}{\sqrt{2}}$

w) ****Give the product of the following reactions









x) *When you are looking outside through your window, you are exposed to:

UVA UVB UVC X-RAYS

y) *In microlithography, a photoresist film that becomes less soluble after exposure to light will give an image that is

POSITIVE NEUTRAL NEGATIVE REVERSE

<u>BONUS QUESTIONS</u>

***Synthetic rubber has a higher T_g than natural rubber. Try to rationalize this observation.**

_____

_____

***In a class demonstration, we showed that polystyrene packing chips (Styrofoam) "dissolves" very easily in acetone. One packing chip, however, did not. Name the polymer that was used to make that particular packing chip and explain why it did not dissolve.**

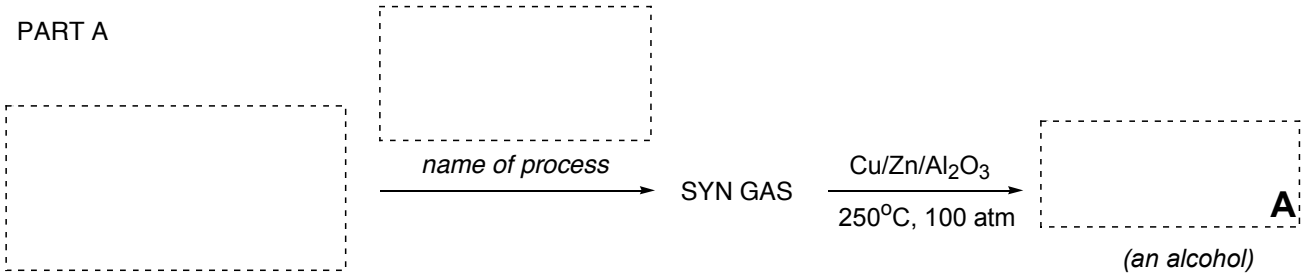
_____

_____

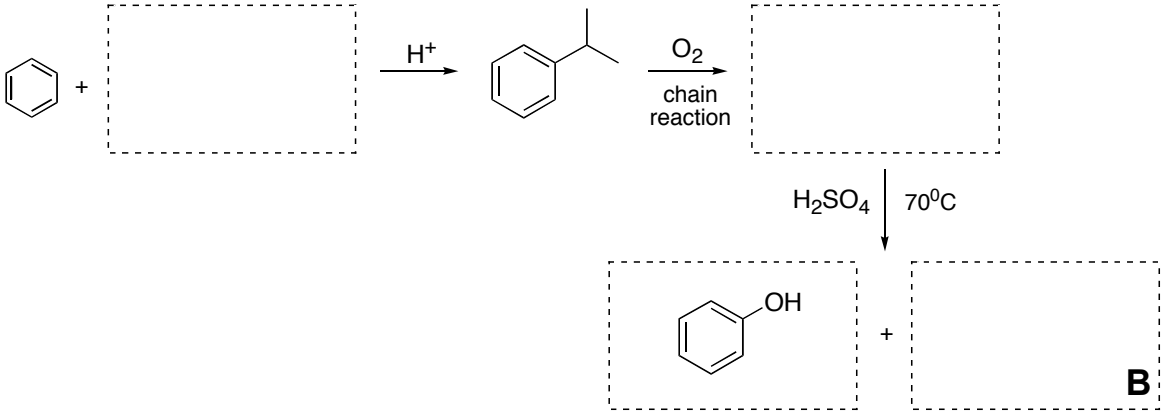
2. (15 MARKS) INDUSTRIAL ORGANIC CHEMISTRY

Complete the following reactions, showing the synthesis of a valuable product.

PART A

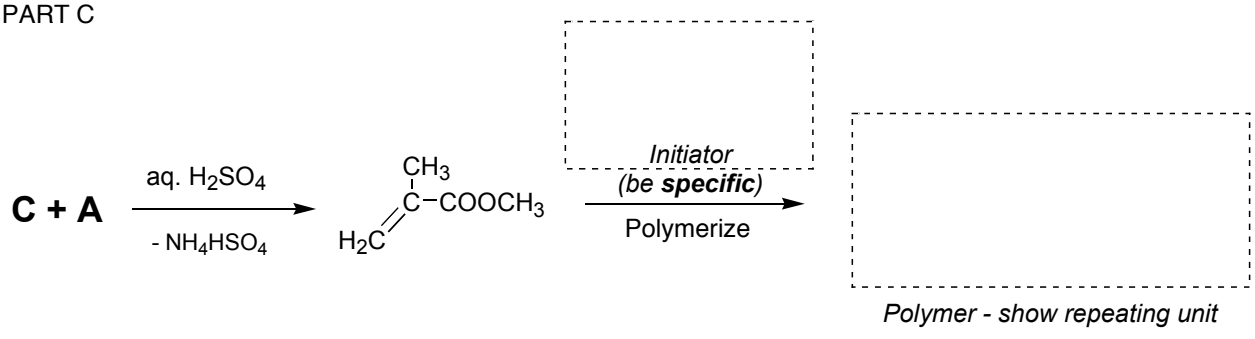


PART B



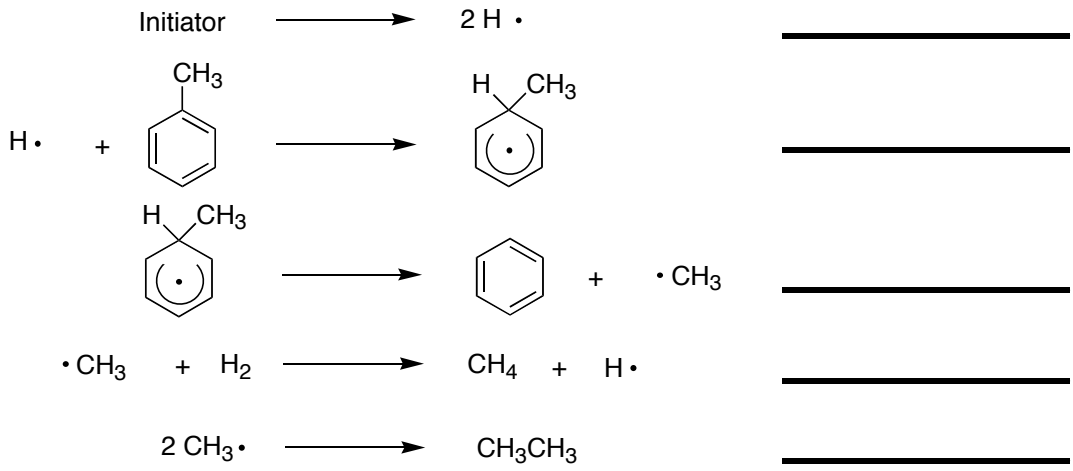
FOR THIS REACTION, INCLUDE ELECTRON-PUSHING ARROWS:

PART C



The *full name* of this polymer is:

3. (15 MARKS) FREE RADICAL REACTIONS
The following mechanism shows the hydrodealkylation of toluene at 700°C.



(a) Directly on the reaction scheme, identify all the steps in the mechanism.

(b) Write the overall reaction.

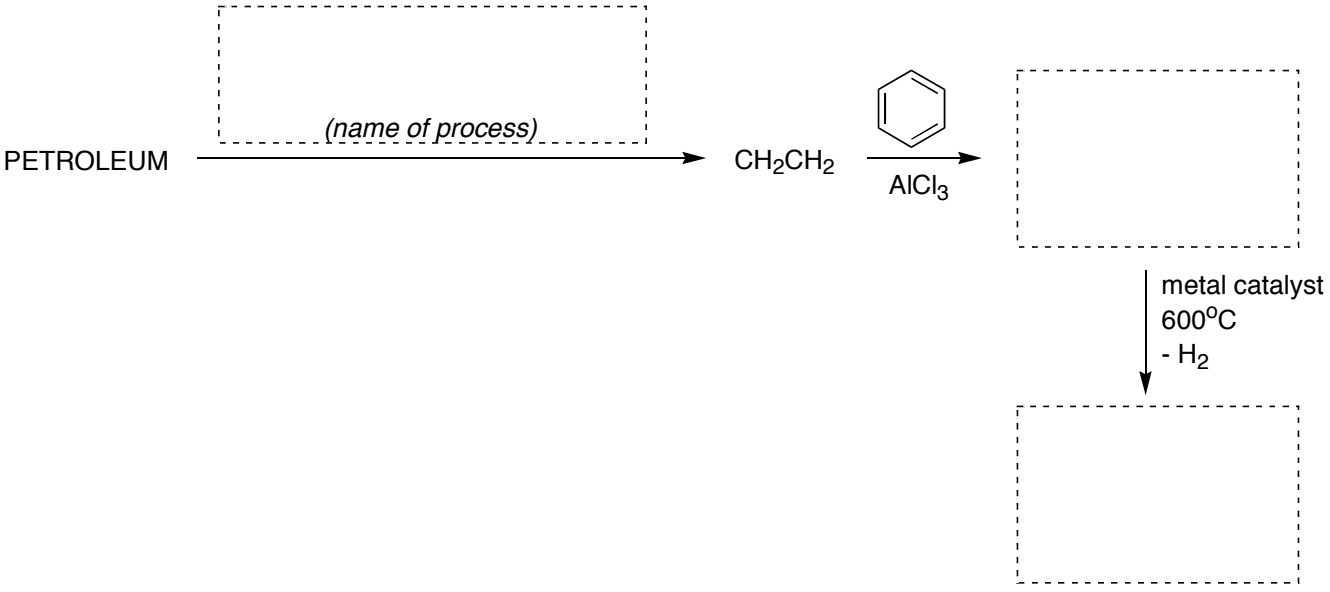
(c) Label the scheme with the appropriate rate constants and derive the rate expression for the chain reaction.

--- QUESTION CONTINUED ON NEXT PAGE ---

3. CONTINUED…

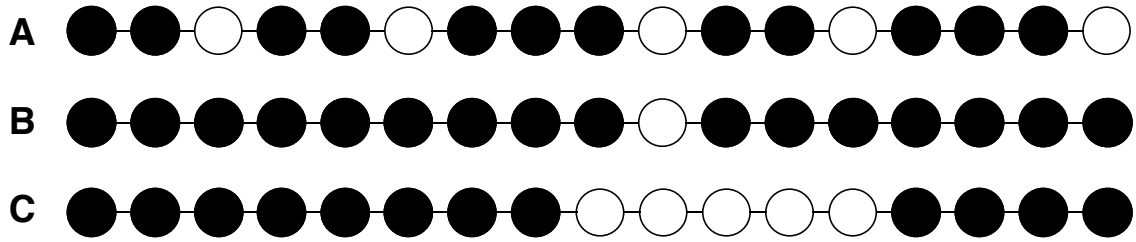
(d) Explain, using reactions, why the hydrogen atom (H•) adds to the aromatic ring in toluene instead of abstraction from the labile bonds in the CH_3 group.

(e) Fill in the blanks below.



4. (10 MARKS) POLYMER CHEMISTRY

In a copolymerization reaction, the parameters r_1 and r_2 describe the tendency of a polymer with a radical centre derived from one of the monomers to react with another monomer molecule of the same type, or with a different one. Polymers A, B, and C below have been prepared by free radical polymerization of monomers X (r_1) and Y (r_2). Identify which polymer corresponds to each case and explain your answer for polymers B and C.



Case 1	Case 2	Case 3
$r_1 = 7$	$r_1 = 2.5$	$r_1 = 12$
$r_2 = 5$	$r_2 = 0.001$	$r_2 = 0.001$

(a) (3 marks) The polymers are: _____ _____ _____
(insert letter A, B or C in each space)

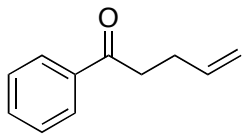
(b) (3 marks) I have selected polymer A as case _____ for the following reasons:

(c) (3 marks) I have selected polymer C as case _____ for the following reasons:

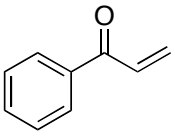
(d) (1 mark) In polymer A, the black monomer units correspond to X or Y?

5. (10 MARKS) POLYMER DEGRADATION AND THIN FILMS

(a) (3 marks) Consider polymers made from the two monomers shown below. Which would decrease in mechanical strength faster upon exposure to UV light? Explain, using chemical reactions.



A



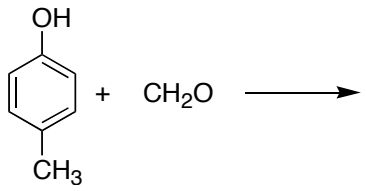
B

(b) (2 marks) The degradation of the above polymers by UV light can be reduced by adding *ortho*-hydroxybenzophenone to the polymer. Explain how this additive reduces UV-induced degradation.

---QUESTION CONTINUED ON NEXT PAGE---

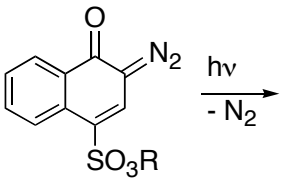
5. CONTINUED…

(c) (2 marks) Draw the structure of the polymer that would result from these two monomers.



What happens to the polymer upon the addition of methoxylated melamine and acid?

(d) (3 marks) The necessary acid can be generated using diazanaphthoquinones as photoacid generators. Show the intermediates and final product in the reaction of DNQ with light.



DNQ

6. (10 MARKS) POLYMER AND SURFACTANT APPLICATIONS

(a) (6 marks) Choose one of the following common polymers discussed in class (circle your selection):

PETE **NYLON-6,6**

HDPE **POLYTETRAFLUOROETHYLENE**

Fill in the spaces below with details about the polymer you've chosen.

Monomer Formula: **Polymer Formula:**

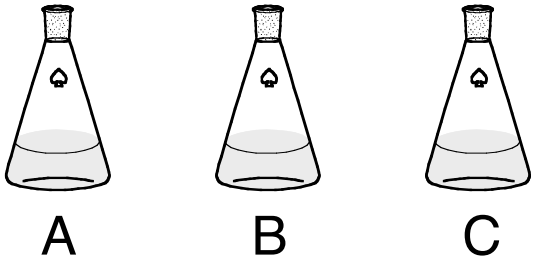
Method of synthesis:

Polymer Properties:

---QUESTION CONTINUED ON NEXT PAGE---

6. CONTINUED…

(b) (4 marks) In three Erlenmeyer flasks, you are given three unknown samples of dishwasher detergent, shampoo, and laundry detergent. Use the observations below to determine which sample is which, and briefly explain your decision.



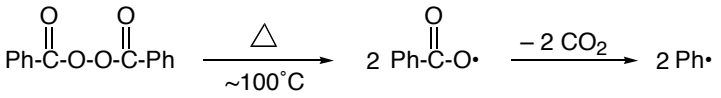
A : makes foam, slightly acidic

B : makes foam, slightly basic

C : no foam, strongly basic

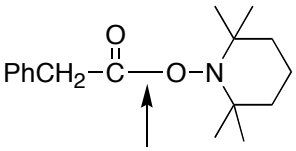
7. (10 MARKS) POLYMERIZATION METHODS

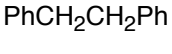
(a) (3 marks) Polystyrene can be made *via* free radical vinyl polymerization. Show the mechanism for the polymerization, using benzoyl peroxide as the initiator.



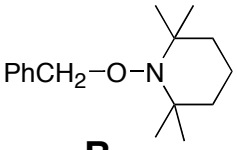
Initiation

(b) (4 marks) When irradiated with UV light, the molecule below cleaves homolytically at the position indicated by an arrow.





A

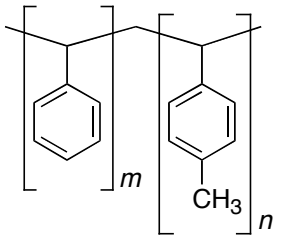


B

During the irradiation, it was observed that in the first few seconds of the reaction, product A is the major product. However, at the end of the reaction, B was the overall dominant product (>90%). Why is A the product favoured early in the reaction but B is the overall major product?

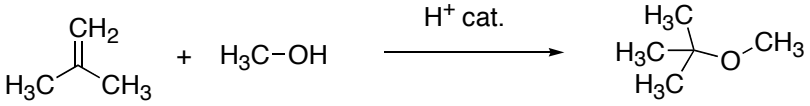
---QUESTION CONTINUED ON NEXT PAGE---

(c) (3 marks) Briefly explain how the block copolymer shown below can be made using the molecule from part (b) as the initiator.



8. (10 MARKS) ASSORTED QUESTIONS

(a) (3 marks) Using group additivity values, estimate the ΔH^o of the following reaction.



Answer: _____

Group	Value	Group	Value	Group	Value
C-$(H)_3$ (C)	-10.20	C-$(C_d)(C)(H)_2$	-4.76	O-(C)(H)	-37.9
C-$(H)_2(C)_2$	-4.93	C-$(C_t)(C)(H)_2$	-4.73	O-(C_d)(H)	-37.9
C-(H)$(C)_3$	-1.90	C-(C_d) $(C)_2$ (H)	-1.48	O-(C_t)(H)	-37.9
C- $(C)_4$	0.50	C-$(C_d)(H)_3$	-1.72	O-(O)(H)	-16.3
C_d-$(H)_2$	6.26	C-$(H)_3$(O)	-10.1	O-(CO)(H)	-58.1
C_d-(H)(C)	8.59	C-$(H)_2$(C)(O)	-8.1	O-$(C)_2$	-23.2
C_d-$(C)_2$	10.34	C-$(H)_2(O)_2$	-16.1	O-(C_d)(C)	-30.5
C_t-(H)	26.93	C-(O)(H)$(C)_2$	-7.2	O-(C)(O)	-4.5
C_t-(C)	27.55	C-$(C)_3$(O)	-6.6	O-(CO)(C)	-43.1

---QUESTION CONTINUED ON NEXT PAGE---

8. CONTINUED…

(b) (2 marks) What are the structural differences between a bio-hard and a bio-soft detergent? What do those terms mean?

(c) (2 marks) Phosphorescent states are generally longer lived than fluorescent ones, and phosphorescence occurs at longer wavelengths than fluorescence. Explain, using diagrams to support your answer.

(d) (3 marks) For the majority of Canadian natural gas reserves, the gas is *sour.*

What compound is responsible for this?

How is it removed? (show a reaction)

Why is it removed?