uOttawa

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CHM4155

MIDTERM 1 (25%)

11-Feb-2015

Family name: ___________________________

First name: ______________________________

Student #: ______________________________

Time allowed: 75 minutes

Question	1	2	3	4	5	6	Total
Value	16	10	8	8	8	8	50
Mark							
Notes							

IMPORTANT:

You must answer questions # 1 and # 2.

Answer 3 questions only from questions #3 to #6. Please indicate below which question you do NOT want marked. If you make no selection, question number 6 will not be marked.

Please do NOT mark question number: ________ ←

1. (16 POINTS) Short Answers – one or two points each.

a) C_6H_5-$CH_2\bullet$, a resonance-stabilized species, is known as the ________________________.

b) When he discovered mauveine, Perkins was supposed to be working on a synthesis of

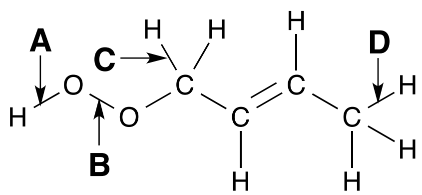
ASPIRIN CARBOLIC ACID INDIGO QUININE ACETYLENE

c) The equilibrium reaction between cyclohexane and n-hexene is accelerated by a

METAL ACID RADICAL OXIDE

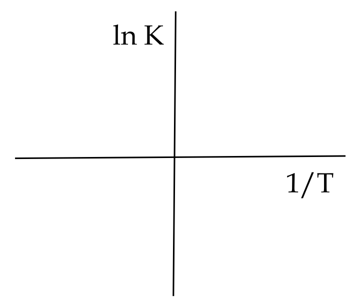
catalyst and requires HIGH LOW MEDIUM hydrogen pressures.

d) Classify the following indicated bonds (A to D) in order of *increasing* BDE:



_______ < _______ < _______ < _______

e) On the axes at right, sketch the expected van't Hoff plot for the following exothermic reaction: A(g) → B(g) + C(g)



f) Of the different types of coal found in nature, the variety with the lowest caloric value when burned is known as ____.

g) Zeolites are useful in catalytic cracking because they facilitate the formation of ____________________________________ intermediates. The main product of catalytic cracking of a long, linear alkane is ____.

h) In steam cracking, the purpose of the steam is: ____________________________________

____.

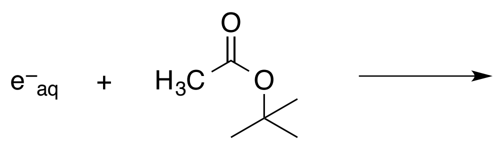
i) One reason why the Bergius hydrogenation process is currently unfavourable is

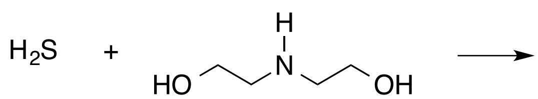
____

____.

j) All other factors being equal, as the flame speed of a fuel increases, the flame size ____.

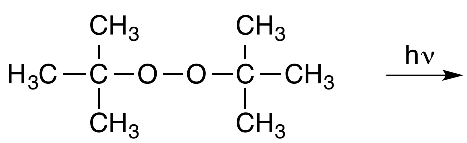
k) Complete the following reactions:





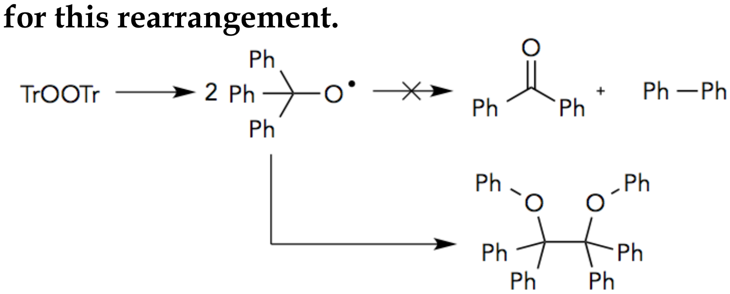
l) Premixed flames are generally hotter than diffusion flames because ________________ ____.

m) When di-*tert*-butyl peroxide (DTBP) is irradiated with a UV lamp, it photodecomposes to ethane and acetone. Give a possible mechanism for this reaction.



BONUS

When irradiated, di-trityl-peroxide (Ph_3OOPh_3) does not give benzophenone and biphenyl, but rather rearranges to the pinacol-coupling product shown below. Propose a mechanism for this rearrangement.



2. (10 POINTS) CUMULATIVE QUESTION

The following reaction is a possible thermal cracking termination reaction:

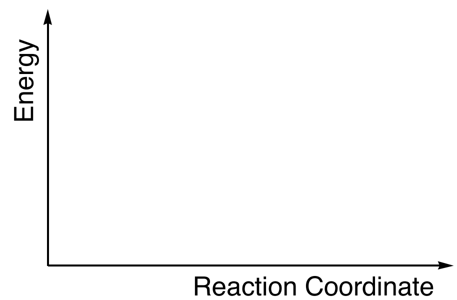
$$H\bullet \; + \; H\bullet \xrightarrow{\boxed{\quad\quad}} H_2$$

a) What is missing in the box above the reaction arrow? Why is it needed?

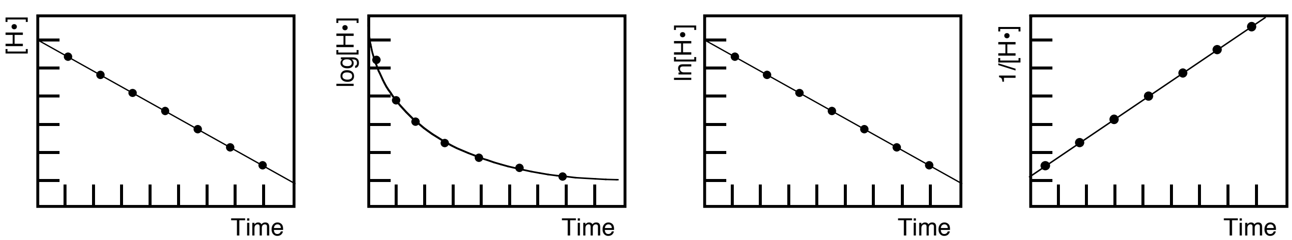
b) What would be the enthalpy of this reaction? (no specific value, just a qualitative answer please) What would be the expected rate constant for the reaction? (specific value please, with units!)

$\Delta H° =$ [ ] $k \sim$ [ ]

c) On the graph, draw the expected reaction profile for the termination, labeling the reactants and product.



d) Choose the correct kinetic profile that corresponds to the termination reaction.



A B C D

e) Explain (briefly) the following statement: "Under thermal cracking conditions, H• is the most stable free radical/odd-electron species".

3. (8 POINTS) FREE RADICALS

1-Chloropropane decomposes thermally according to the following mechanism:

$$CH_3CH_2CH_2Cl \longrightarrow CH_3CH_2CH_2\cdot + Cl\cdot$$

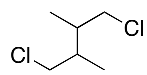
$$CH_3CH_2CH_2\cdot \longrightarrow C_2H_4 + CH_3\cdot$$

$$CH_3\cdot + CH_3CH_2CH_2Cl \longrightarrow CH_3\dot{C}HCH_2Cl$$

$$Cl\cdot + CH_3CH_2CH_2Cl \longrightarrow HCl \quad CH_3\dot{C}HCH_2Cl$$

$$CH_3\dot{C}HCH_2Cl \longrightarrow CH_3CH{=}CH_2 + Cl\cdot$$

$$2\ CH_3\dot{C}HCH_2Cl \longrightarrow$$



a) **(2 pts) On the right of the reaction scheme, identify all the steps in the mechanism.**

b) **(2 pts) Write the overall reaction:**

c) **(3 pts) Label the scheme with the appropriate rate constants and derive the rate expression for the chain reaction.**

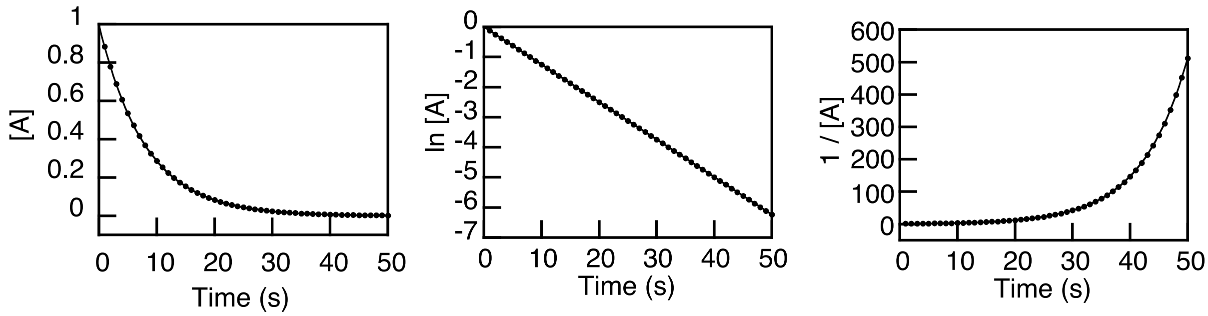
d) **(1 pt) What is one way to determine the chain length for this chain reaction?**

4. (8 POINTS) KINETICS

The progress of the reaction below is followed for 50 seconds.

$$A + B \rightarrow 2\,C$$

The following graphs are made using the experimental data:



a) (1 pt) According to the graphs, what is the order of the rate-determining step?

b) (3 pts) What is the value of the rate constant for the RDS?

c) (4 pts) What will [A] be after 30 seconds, if its initial concentration is 0.550 M?

5. (8 POINTS) FEEDSTOCKS

You are the CEO of a petrochemical company that needs to start producing major quantities of *p*-xylene (its price is rising, and you want to maximize profits!). Your company has access to raw petroleum, and all of the necessary reactors/catalysts etc. In the space below, outline how you would synthesize *p*-xylene. Include reaction conditions, where appropriate.

6. (8 POINTS) COMBUSTION

One mole of gaseous H_2 is burned in excess oxygen. The combustion is initiated with a match.

a) (1 pt) The process which produces 3 H• from each initial H• is called:

b) (4 pts) Complete the following series of propagation steps:

$$H\bullet + O_2 \longrightarrow$$

$$\bullet OH + H_2 \longrightarrow H\bullet + H_2O$$

$$O + H_2 \longrightarrow$$

$$\bullet OH + \quad \longrightarrow H\bullet +$$

$$H\bullet + \quad + \quad \longrightarrow 3\,H\bullet +$$

c) (3 pts) Mixtures of H_2 and O_2 are usually stable at room temperature and pressure. Why is a match needed to start the combustion? You may draw a reaction profile to help illustrate your answer.

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MIDTERM 2 (25%)

18-Mar-2015

Last name: ______________________

First name: ______________________

Student #: ______________________

Time allowed: 75 minutes

Question	1	2	3	4	5	6	Total
Value	18	8	8	8	8	8	50
Mark							
Notes							

IMPORTANT:

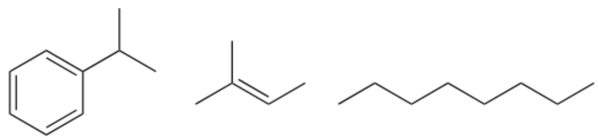
You must answer question # 1.

Answer 4 questions only from questions #2 to #6. Please indicate below which question you do NOT want marked. If you make no selection, question number 6 will not be marked.

Please do NOT mark question number: ________ 🡐

1. (18 POINTS) Short answers – one or two points each.

a) Place the following compounds in order of lowest to highest relative fuel quality:



A B C

__________ < __________ < __________

b) The equilibrium between CO and CO_2 produced from the combustion of a hydrocarbon is temperature *and* pressure dependent. Circle the preferred equilibrium direction at

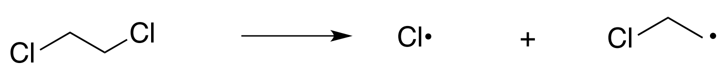
i.	**high temperature & low pressure:**	**CO favoured**	**CO_2 favoured**
ii.	**high pressure & low temperature:**	**CO favoured**	**CO_2 favoured**

c) Methanol is mostly produced from ______________________________________ using the ______________________________________ Process.

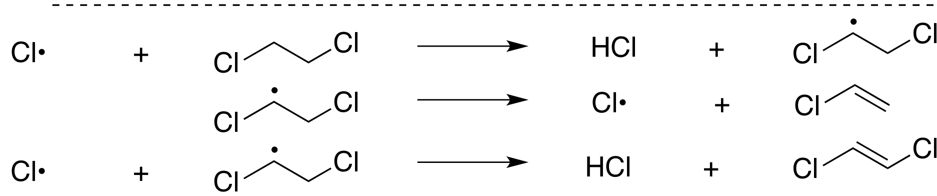
d) If a metal is coordinatively saturated, it must also be electronically saturated.

TRUE FALSE

e) The incomplete reaction mechanism for the cracking of 1,2-dichloroethane is shown below. Complete the mechanism by filling in the missing step (with electron-pushing arrows) and write the overall reaction in the box below.

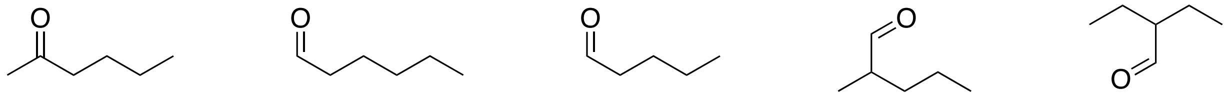


MISSING STEP



OVERALL REACTION

f) From the following molecules, indicate the *major* and *minor* product of the olefin hydroformylation of 1-pentene:



g) Circle the most appropriate reaction conditions for the conversion of syn gas to methanol.

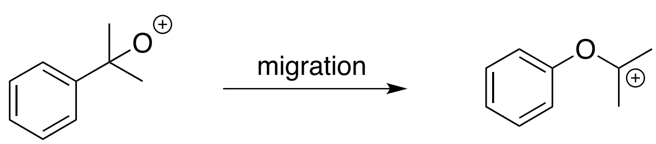
$$CO + 2H_2 \longrightarrow CH_3OH$$

CATALYST =	**ACID**	**BASE**	**METAL**
TEMPERATURE =	**250°C**	**25°C**	**1000°C**
PRESSURE =	**0.1 atm**	**2 atm**	**50 atm**

h) A dimerization reaction (A + A → A–A) is being carried out in SDS micelles. The micelle molarity is 0.010 M. In order to ensure an excellent reaction yield, the minimum concentration of A is ________________________________.

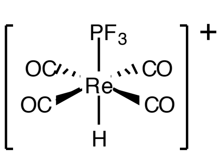
i) Natural surfactants are known as ________________________________ whereas synthetic surfactants are called ____________________________________.

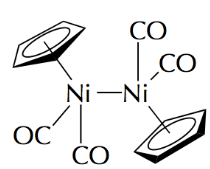
j) The following migration reaction is a key step in the Hock Process.



Add (a) electron pushing arrow(s) to the scheme above to show the mechanism for this step. The driving force for this migration is: ____.

k) Determine the oxidation state at the metal centre.





l) The surfactants which are most commonly involved in *cleaning* steps are:

ANIONIC CATIONIC NEUTRAL ZWITTERIONIC

m) In the boxes, draw surfactant examples of a bio-hard sulfonate and a bio-soft sulfate.

bio-hard sulfonate

bio-soft sulfate

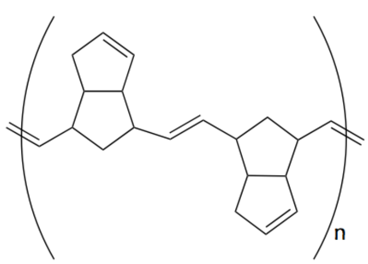
n) In an in-class demo, you found that one household cleaning product is slightly acidic (pH ~ 6.5). What was that product, and why is it acidic? ______________________________

____

____

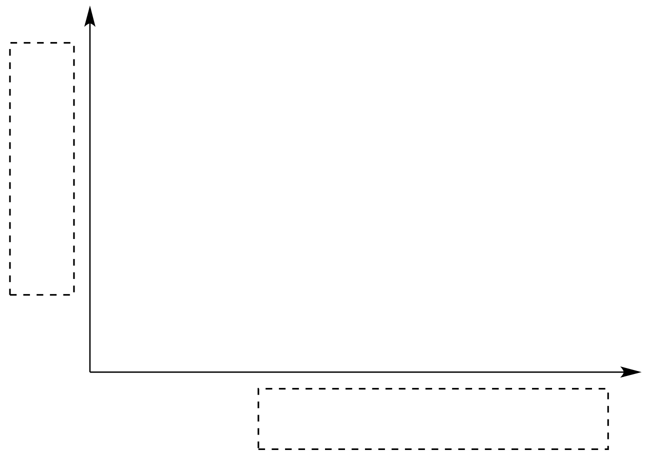
<u>BONUS</u>

The following polymer was generated by ROMP. Draw the structure of the original monomer that produced this polymer.



2. (8 POINTS) COMBUSTION

a) On the axes provided, draw a representative pressure-temperature curve for a typical internal-combustion engine gasoline.



b) Also on the axes, add a second curve representing a fuel destined for a higher-performance engine (a luxury car operating at a higher temperature, for example). Add a label to distinguish it from your first curve.

c) What is the quantifiable scale used to evaluate the quality of these two fuels? How would this value differ between part a and b?

d) Suggest two ways the fuel of part a could be transformed into the fuel of part b. Please be as specific as possible.

e) What key factor distinguishes an internal combustion engine from a diesel engine? Chemically speaking, how do the fuels differ?

3. (8 POINTS) ORGANIC SYNTHESIS

a) **Depict using an overall scheme (no mechanisms) the reaction steps that one would need in order to convert *toluene* to *cumene*. Include all reagents, relative reaction conditions, and important byproducts where applicable.**

b) **According to the *Sigma-Aldrich* catalog, cumene actually costs *less* ($34/L) than benzene ($64/L) even though the former is made from the latter. Give a possible reason for this.**

c) **Explain why, in the alkylation of benzene to make ethylbenzene, ethylene is always the limiting reagent.**

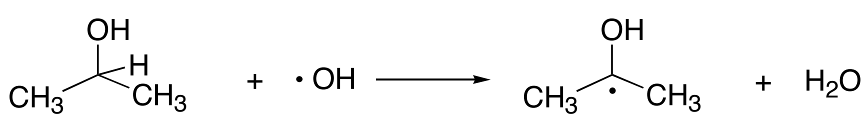
4. (8 POINTS) ORGANIC SYNTHESIS

One minor route to acetone is a liquid-phase oxidation developed by Shell and DuPont.

a) The first step in the synthesis is the hydrolysis of propylene to *iso*-propanol under acidic conditions. Show the mechanism for this reaction, with electron-pushing arrows.

b) The second step is the oxidation of *iso*-propanol to acetone by molecular oxygen in a free radical chain reaction, using hydrogen peroxide as the initiator. The initiation step and transfer step are shown below. Complete the remaining steps in the chain reaction.

$$H_2O_2 \longrightarrow 2\ \cdot OH$$



Propagation 1

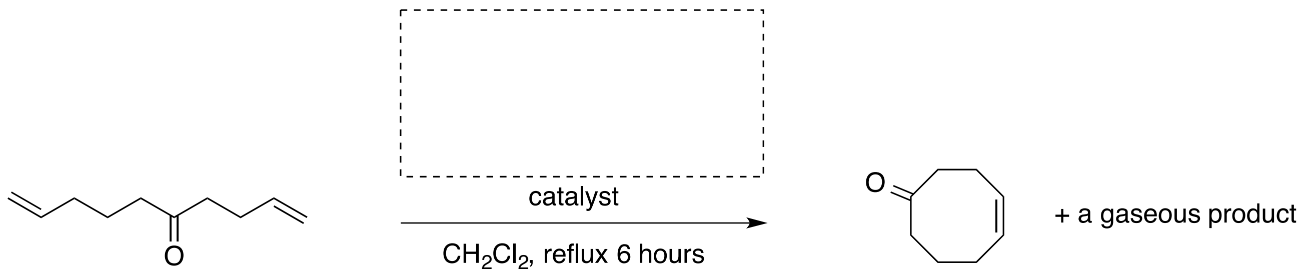
Propagation 2

Termination

c) What is the overall reaction for part (b)?

5. (8 POINTS) INDUSTRIAL CATALYTIC CYCLES

Rings larger than 6 or 7 carbons are usually difficult to prepare by conventional organic methods. However, cyclooctenone derivatives can be made using organometallic catalysis :



a) This type of transformation is called ____.

b) Propose a possible catalyst for the reaction shown above (draw it in the box).

c) This type of organometallic catalyst is called a/an ____________________________________.

d) Draw the mechanism for the ring-closing using your catalyst.

e) Though reactions in this category are usually reversible, complete consumption of the starting material is observed after 6 hours. What is the driving force of the above reaction?

6. (8 POINTS) SURFACTANT CHEMISTRY

The following figure illustrates three droplets of an oil-based liquid dirt on different surfaces immersed in a surfactant solution.

a) Estimate graphically the contact angles for these drops. What does the contact angle reflect in terms of interactions between different materials?

b) In which case is the surface *least* likely to be Teflon? **A** **B** **C**

c) If you had to choose a surfactant to remove this dirt, what type would you use? Can you give a specific example?

d) In the case of drop B, will the dirt be spontaneously released? If not, what else is required?

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CHM4155

FINAL EXAM (50%)

APRIL 2015

Last name: ____________________

First name: ____________________

Student #: ____________________

Seat Number: ____________________

Time allowed: 180 minutes

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.

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 POINTS) Short Answers – one or two points each.

a) One characteristic that distinguishes *basic research* from *applied research* is: ___________

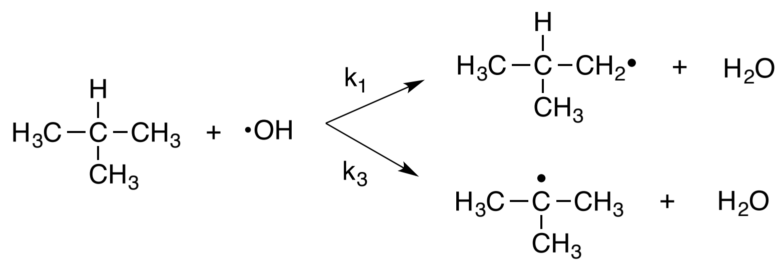
____

b) 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.

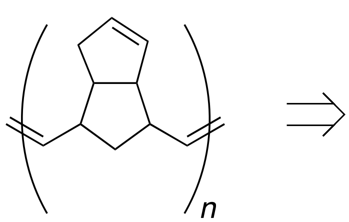
____

____

c) Under thermal cracking conditions, the value of the ratio of the rate constants for the two competing processes shown below would be k_1/k_3 = ________________.



d) The following polymer was generated by ROMP. Draw the structure of the original monomer that produced this polymer.



e) One advantage of suspension polymerization is: __________________________________

____

f) In FRVP, if the concentration of initiator is doubled, the expected molecular weight of the resulting polymer will also double. **TRUE** **FALSE**

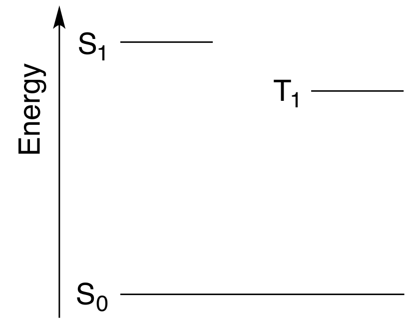
g) Three samples of polypropylene with different tacticities have exactly the same molecular weight distribution but they have different T_g's. Which PP has the highest T_g? ____

h) BTEX is obtained by catalytic reforming of naphtha. BTEX is an acronym for __________

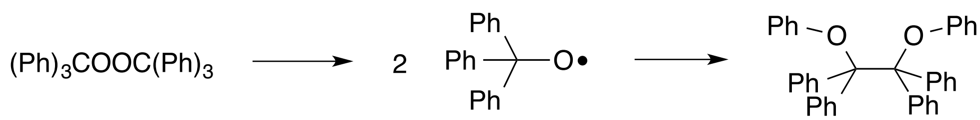
____

i) On the provided Jablonski diagram template, draw and label (i to iv) the appropriate arrows showing the following processes for a diamagnetic starting material:

- **i. absorption of a photon**
- **ii. fluorescence**
- **iii. spin flip to the triplet state**
- **iv. phosphorescence**



j) When irradiated, di-trityl-peroxide ($Ph_3COOCPh_3$) does not give benzophenone and biphenyl, but rather rearranges to the pinacol-coupling product shown below. Propose a mechanism for this rearrangement.



k) An example of a bio-hard sulfonate would have:

- ☐ **A BRANCHED HYDROPHOBIC TAIL WITH A $-OSO_3Na$ HEAD**
- ☐ **A BRANCHED HYDROPHOBIC TAIL WITH A $-SO_3Na$ HEAD**
- ☐ **A LINEAR HYDROPHOBIC TAIL WITH A $-OSO_3Na$ HEAD**
- ☐ **A LINEAR HYDROPHOBIC TAIL WITH A $-SO_3Na$ HEAD**

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

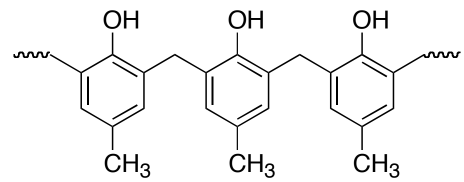
PLACTICIZER SUNSCREEN RADICAL SCAVENGER WATER

m) In synthesizing a dendrimer, if you begin building the molecule from the core outward, then you are using the ______________________________ approach.

n) **Novolac is a possible polymer made from phenol-formaldehyde polymerization. What is the purpose of the *para*-methyl group?** ________________________________

____

____

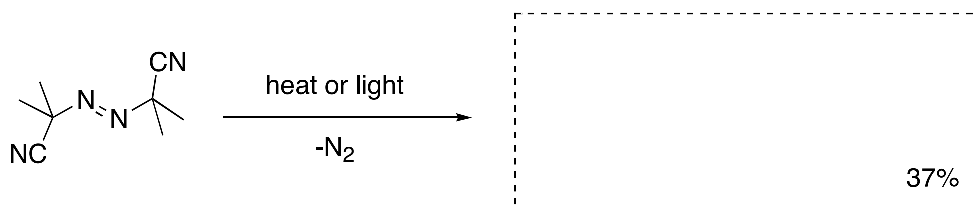


o) **According to the Arrhenius expression, if the activation energy for a reaction is zero (E_a=0) then the value of the rate constant for the reaction is equal to the parameter known as (specify name and symbol)**____.

p) **Polydimethylsiloxane (PDMS) is synthesized from a bifunctional silane, $(CH_3)_2SiCl_2$. What would be the effect on the polymer weight by adding small amounts of $(CH_3)_3SiCl$ to the polymerization reaction?**________________________________

____

q) **AIBN, a common initiator used in free radical polymerization, decomposes irreversibly by releasing N_2. It was found that only 63% of the radicals generated from AIBN initiate radical polymerization. What is the fate of the remaining radicals generated (draw the product)?**



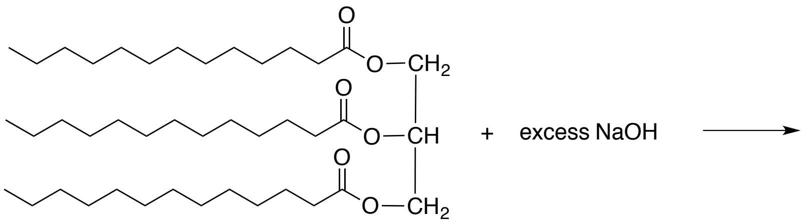
r) **Catalytic reforming of cyclohexane to yield benzene requires a(n) ACID BASE METAL catalyst and requires HIGH LOW MEDIUM hydrogen pressure.**

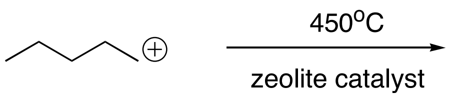
s) **For a molecule to act as an "excited state quencher" (and thus protect a polymer against photodegradation), one requirement is that the excited state energy for the quencher be less than or equal to the excited state energy of the polymer. The other requirement is:**

____

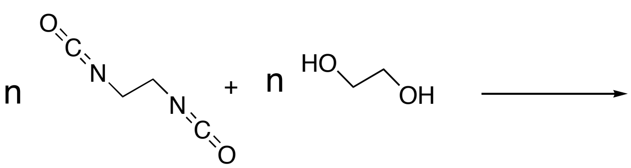
____

t) Give the <u>final</u> products of the following reactions (no mechanisms):





$$CaC_2 + H_2O \longrightarrow$$

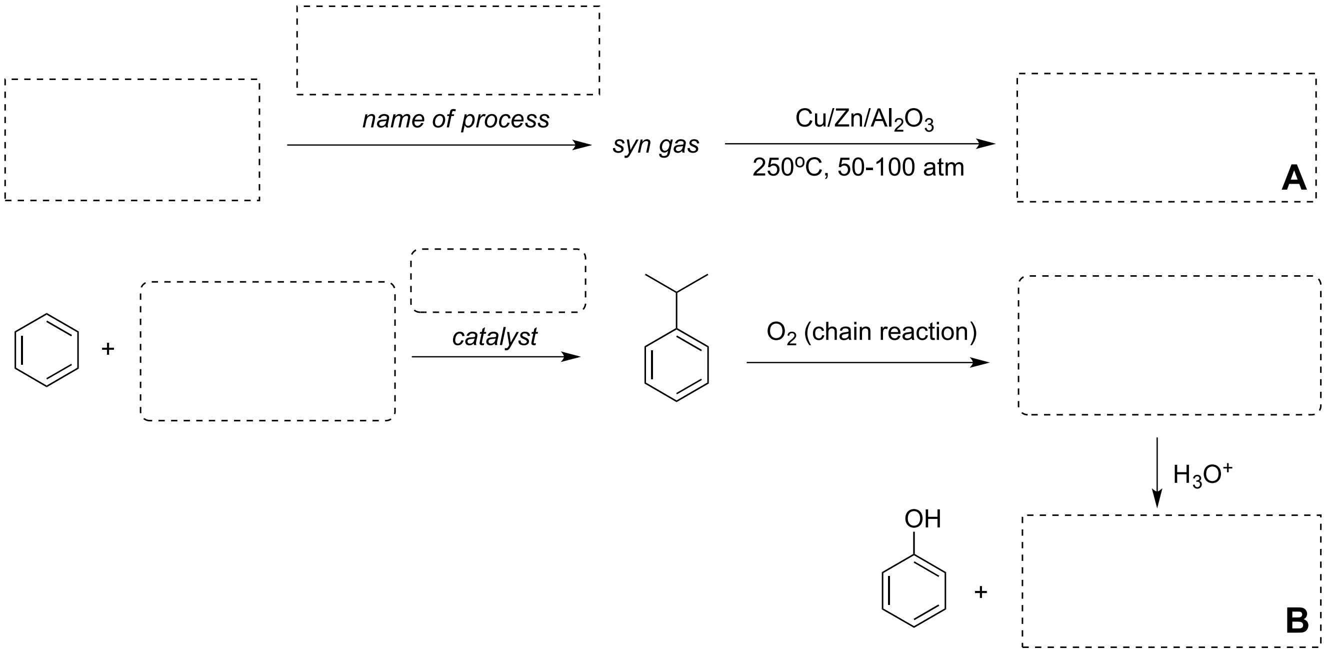


<u>BONUS</u>

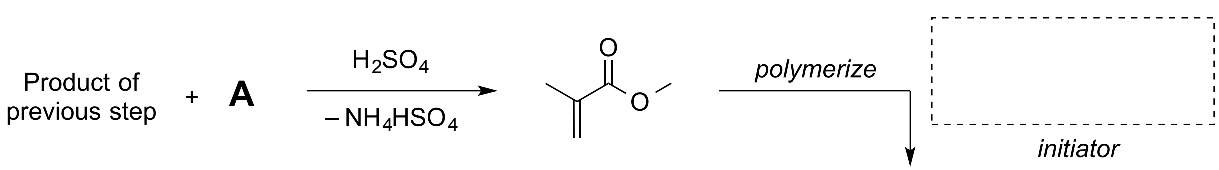
In a Youtube video, we watched a tennis ball being slowly compressed in a massive clamp (capable of exerting enormous pressure). Why do tennis balls compress and bounce so easily? When watched *via* a thermal camera, we saw that the temperature of the ball increased during the compression. Why?

2. (15 POINTS) INDUSTRIAL ORGANIC CHEMISTRY

Complete the following reactions, showing the formation of a common polymer.



In the space below, draw the mechanism for the reaction of **B** with $^{-}$CN (under basic conditions):

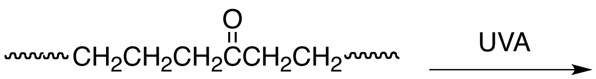


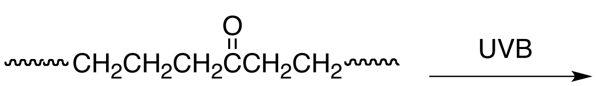
The full name and abbreviation of this polymer are:

Polymer - show repeating unit

3. (15 POINTS) POLYMER DEGRADATION

(a) Complete the mechanisms for the following reactions, showing the final MAJOR non-radical products:



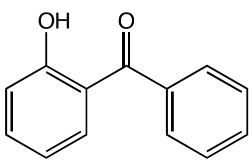


--QUESTION CONTINUED ON NEXT PAGE--

3. CONTINUED…

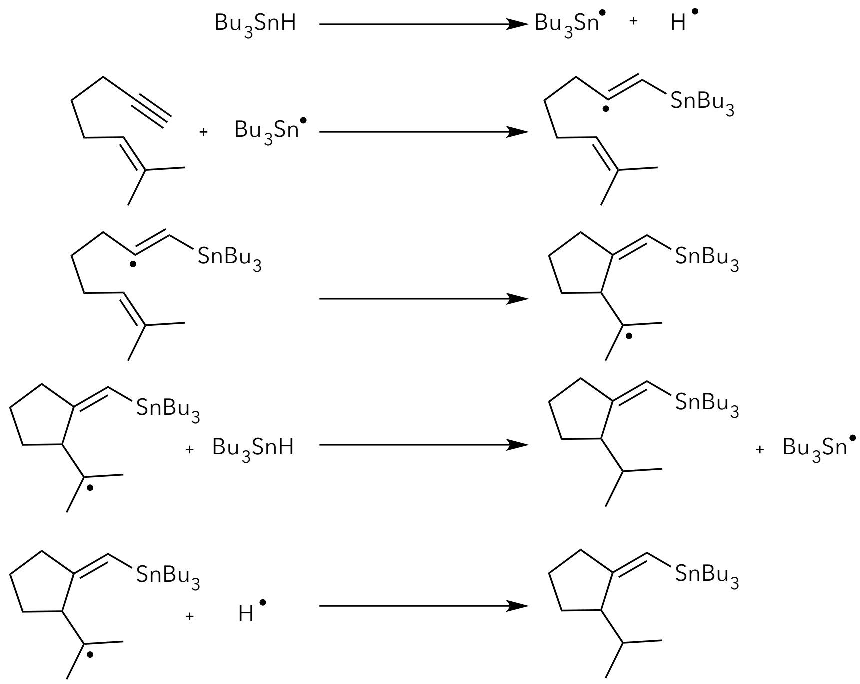
(b) In both cases, what is the principal effect on the polymer's mechanical properties?

(c) This photochemical degradation can be reduced by the addition of *ortho*-hydroxybenzophenone (shown below). Explain the <u>two roles</u> this additive plays in protecting against UV damage. You may use chemical equations to support your answer.



4. (10 POINTS) FREE RADICALS

Consider the following tin-mediated free radical chain reaction:



(a) (3 pts) Label each step of the chain reaction and indicate the RDS.

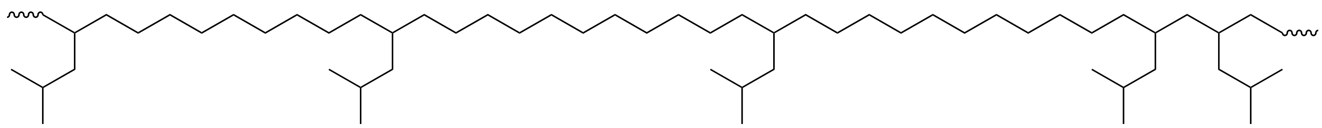
(b) (2 pts) What is the driving force of the third step?

(b) (2 pts) What is the overall reaction?

(c) (3 pts) The product of the reaction might be used as an additive for increasing the octane number of gasoline. Name three attributes of this compound that would be responsible for this behavior.

5. (10 POINTS) POLYMER CHEMISTRY

LLDPE is a copolymer made from the reaction of ethylene (monomer 1) with 2-methyl-1-pentene (monomer 2):



(a) (4 pts) Provide approximate values of r_1 and r_2, based on the representative polymer shown above, and thoroughly explain your reasoning.

(b) (3 pts) What does LLDPE stand for? How would its physical properties (e.g. T_g etc.) differ from LDPE? Explain, drawing structures if necessary.

(c) (3 pts) Draw and label representative stress-strain curves for the two plastics mentioned in part (b). Do not forget to label the axes. Which plastic might be more appropriate for use in grocery bags?

6. (10 POINTS) POLYMER AND SURFACTANT APPLICATIONS

(a) (5 pts) Choose one of the following common polymers discussed in class (circle your selection) and fill in the spaces below with details about the polymer you've chosen.

POLYBUTADIENE **POLYETHYLENETEREPHTHALATE**

POLYDIMETHYLSILOXANE **POLYTETRAFLUOROETHYLENE**

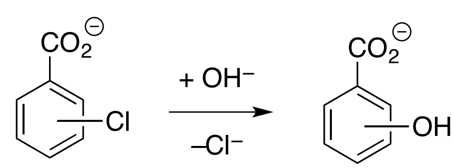
Monomer Formula: **Polymer Formula:**

Polymerization Method Used:

Polymer Properties (at least two):

(b) (5 pts) In the 1980's, Broxton studied the effects of cetyltrimethylammonium bromide (CTAB) micelles on the hydroxy-dehalogenation of benzoates (overall reaction shown). Provide an explanation for the trends in his experimental data, shown in the table.

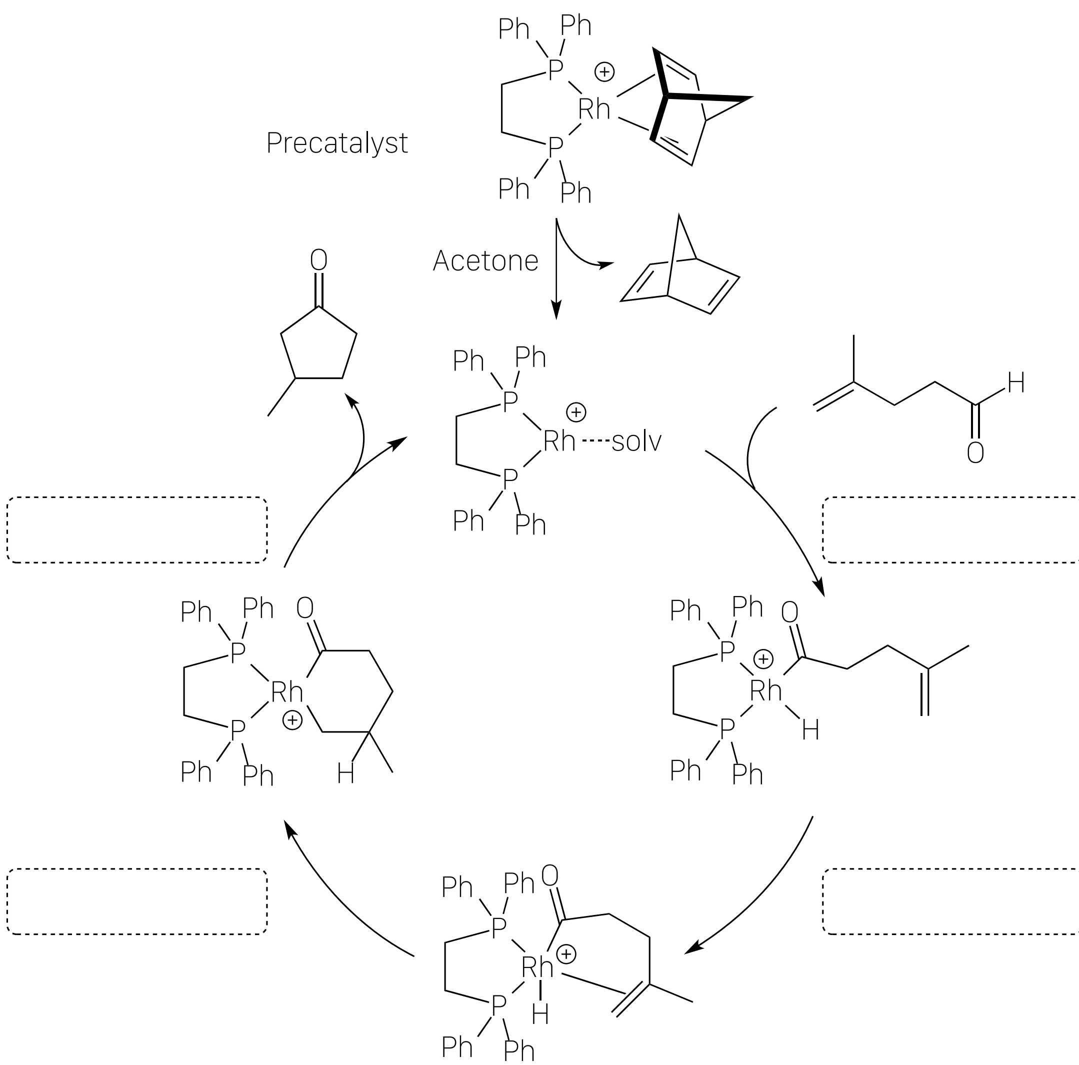
Substrate	Rate constant, in pure water (M^{-1} s^{-1})	Rate constant, in 40 mM CTAB (M^{-1} s^{-1})
p-chlorobenzoate	0.0635	1.505
o-chlorobenzoate	0.965	12.20



7. (10 POINTS) INDUSTRIAL CATALYTIC CYCLES

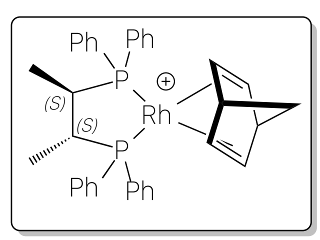
Shown below is the catalytic cycle for <u>intramolecular hydroacylation</u> using a modified Wilkinson's-type catalyst.

(a) (6 pts) In the boxes, write the name of each type of reaction step, and write the oxidation state of the rhodium centre below each intermediate.



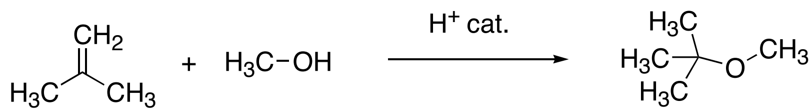
(b) (2 pts) What is the overall reaction?

(c) (2 pts) Suppose we changed the precatalyst to the one shown in the box at right. How might it affect the product of the reaction?



8. (10 POINTS) ASSORTED QUESTIONS

(a) (4 pts) Using group additivity values, estimate the ΔH° of the following reaction.



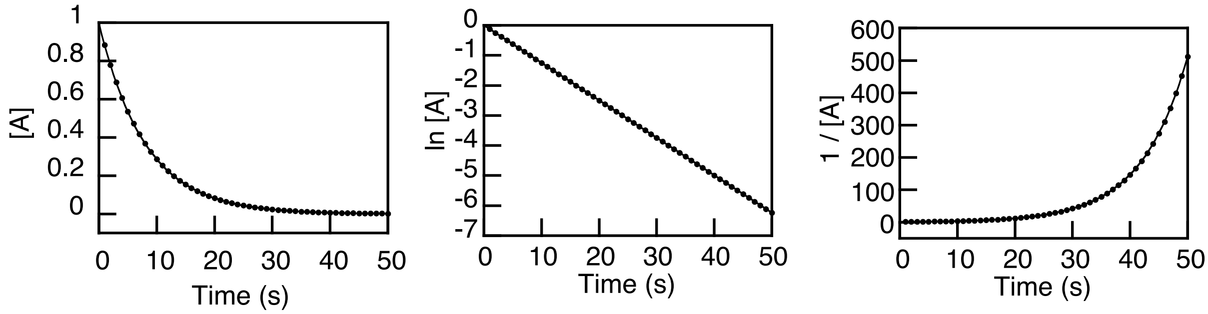
Answer: ______________________

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) (3 pts) The reaction A + B → 2 C is followed for 50 seconds and the following graphs are made using the experimental data. What would [A] be after 45 seconds, if its initial concentration is 0.780 M?



(c) (3 pts) Depict using an overall scheme (no mechanisms) the reaction steps that one would need in order to convert *toluene* to *cumene*. Include all reagents, relative reaction conditions, and important byproducts where applicable.

1. (16 POINTS) Short Answers – one or two points each.

a) C_6H_5-CH_2•, a resonance-stabilized species, is known as the benzyl (or benzylic) radical.

b) When he discovered mauveine, Perkins was supposed to be working on a synthesis of

ASPIRIN CARBOLIC ACID INDIGO (QUININE) ACETYLENE

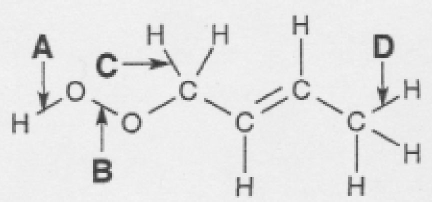
c) The equilibrium reaction between cyclohexane and n-hexene is accelerated by a

METAL (ACID) RADICAL OXIDE

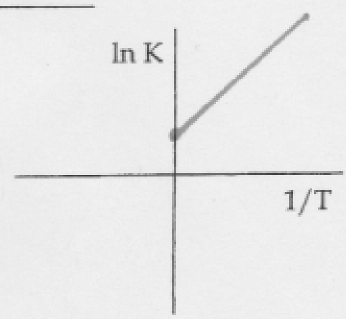
catalyst and requires HIGH LOW (MEDIUM) hydrogen pressures.

not a dehydrogenation or hydrogenation

d) Classify the following indicated bonds (A to D) in order of *increasing* BDE:



B < C < D < A



e) On the axes at right, sketch the expected van't Hoff plot for the following exothermic reaction: A(g) → B(g) + C(g)

ΔH ⊖
ΔS ⊕

$$\ln K_{eq} = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R}$$

f) Of the different types of coal found in nature, the variety with the lowest caloric value when burned is known as lignite.

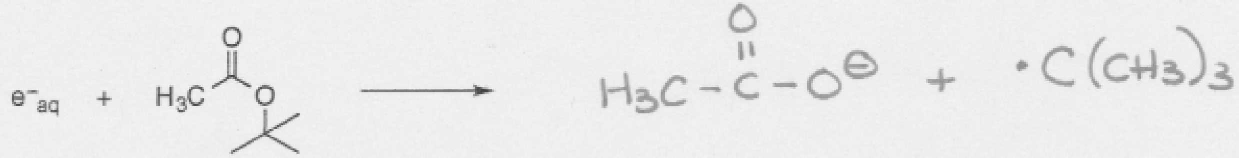
g) Zeolites are useful in catalytic cracking because they facilitate the formation of carbocation intermediates. The main product of catalytic cracking of a long, linear alkane is propylene.

h) In steam cracking, the purpose of the steam is: promote unimolecular/ intramolecular fragmentation (via dilution); prevent tar formation ($C + H_2O \rightarrow CO + H_2$)

i) One reason why the Bergius hydrogenation process is currently unfavourable is high H_2 pressures required; product mixture needs extensive separation/refining ⇒ $$$.

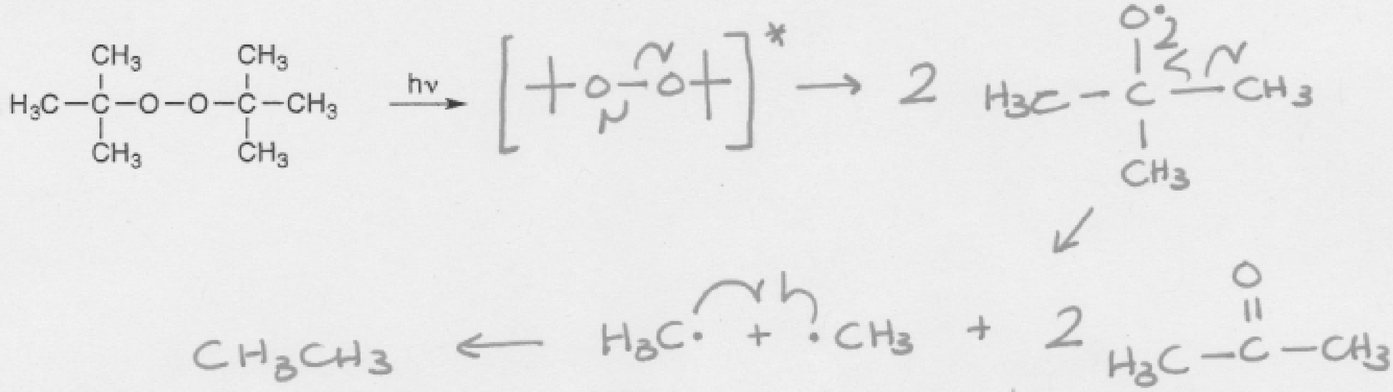
j) **All other factors being equal, as the flame speed of a fuel increases, the flame size** decreases.

k) **Complete the following reactions:**



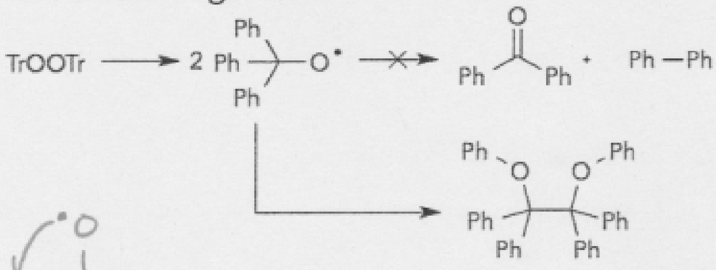
l) **Premixed flames are generally hotter than diffusion flames because** the oxidant (O_2) is already mixed with the gaseous fuel.
(no molecular diffusion needed) → more efficient comb'n

m) **When di-*tert*-butyl peroxide (DTBP) is irradiated with a UV lamp, it photodecomposes to ethane and acetone. Give a possible mechanism for this reaction.**

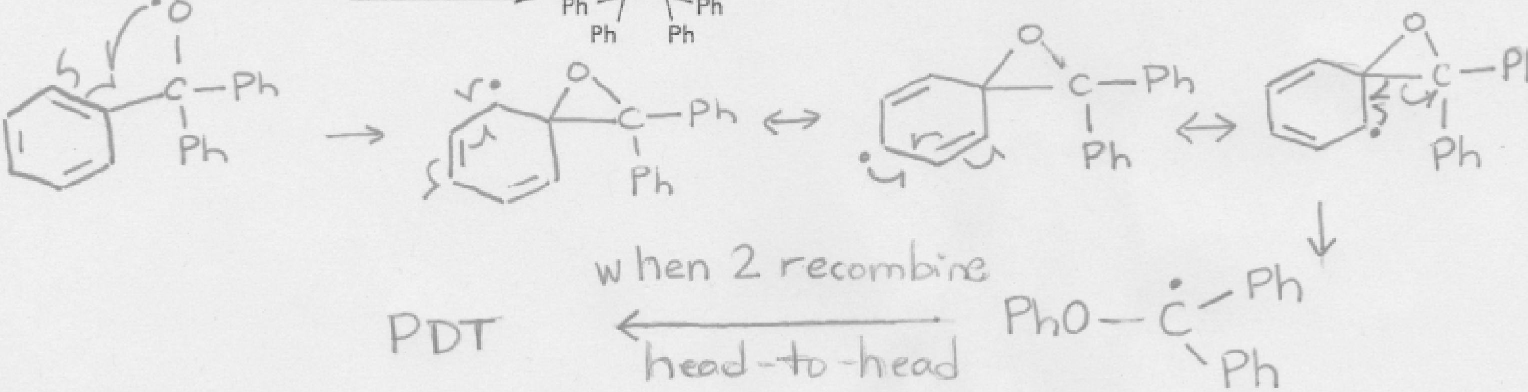


BONUS

When irradiated, di-trityl-peroxide (Ph_3OOPh_3) does not give benzophenone and biphenyl, but rather rearranges to the pinacol-coupling product shown below. Propose a mechanism for this rearrangement.



Wieland rearrangement (1,2-rearrangement) of the alkoxyl radical:



2. (10 POINTS) CUMULATIVE QUESTION

The following reaction is a possible thermal cracking termination reaction:

$$H\bullet + H\bullet \xrightarrow{\text{WALL}} H_2$$

a) **What is missing in the box above the reaction arrow? Why is it needed?**

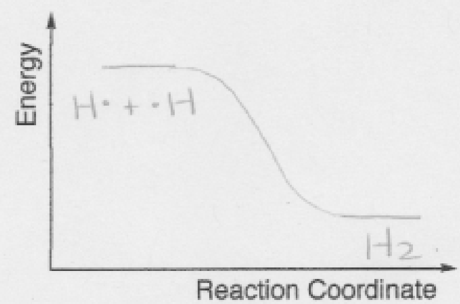
H_2 is born with excess energy EXACTLY equal to the H-H BDE, with no mechanism of dissipating that energy except to break the H-H bond. Thus, to be irreresible, it has to tranfer energy to a 3rd party

b) **What would be the enthalpy of this reaction? (no specific value, just a qualitative answer please) What would be the expected rate constant for the reaction? (specific value please, with units!)**

$\Delta H° =$ − BDE of H-H

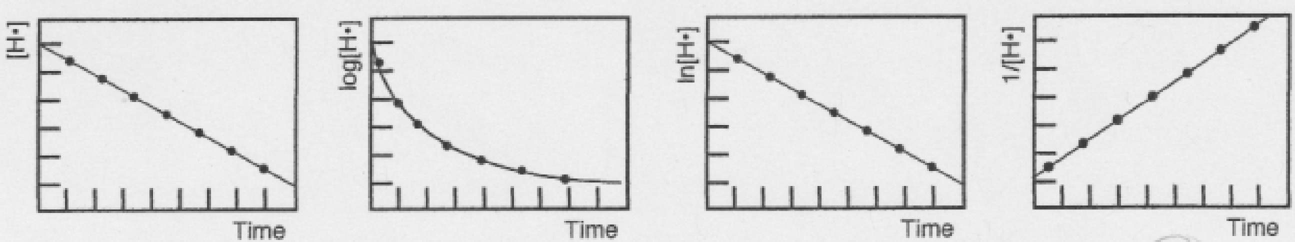
$k \sim 10^{10}\ M^{-1}s^{-1}$

c) **On the graph, draw the expected reaction profile for the termination, labeling the reactants and product.**



$E_a = 0$ kcal/mol

d) **Choose the correct kinetic profile that corresponds to the termination reaction.**



A B C (D) 2nd order

e) **Explain (briefly) the following statement: "Under thermal cracking conditions, H• is the most stable free radical/odd-electron species".**

High temperatures & gas phase: unimolecular reactions are favoured

∴ free radicals fragment to eventually give H•!

3. (8 POINTS) FREE RADICALS

1-Chloropropane decomposes thermally according to the following mechanism:

$CH_3CH_2CH_2Cl \xrightarrow{k_i} CH_3CH_2CH_2\cdot + Cl\cdot$ — initiation

$CH_3CH_2CH_2\cdot \longrightarrow C_2H_4 + CH_3\cdot$ — transfer

$CH_3\cdot + CH_3CH_2CH_2Cl \longrightarrow CH_3\dot{C}HCH_2Cl + CH_4$ — transfer

$Cl\cdot + CH_3CH_2CH_2Cl \longrightarrow HCl \quad CH_3\dot{C}HCH_2Cl$ — propagation ①

$CH_3\dot{C}HCH_2Cl \xrightarrow{k_p} CH_3CH{=}CH_2 + Cl\cdot$ — propagation ②

$2\ CH_3\dot{C}HCH_2Cl \xrightarrow{k_t}$  — termination

a) (2 pts) On the right of the reaction scheme, identify all the steps in the mechanism.

b) (2 pts) Write the overall reaction:

c) (3 pts) Label the scheme with the appropriate rate constants and derive the rate expression for the chain reaction.

$$\text{rate} = k_p[CH_3\dot{C}HCH_2Cl]$$

$$2k_i[CH_3CH_2CH_2Cl] = 2k_t[CH_3\dot{C}HCH_2Cl]^2$$

$$\therefore [CH_3\dot{C}HCH_2Cl] = \left(\frac{2k_i}{2k_t}\right)^{1/2}[CH_3CH_2CH_2Cl]^{1/2}$$

$$\therefore \text{rate} = k_p\left(\frac{k_i}{k_t}\right)^{1/2}[CH_3CH_2CH_2Cl]^{1/2}$$

d) (1 pt) What is one way to determine the chain length for this chain reaction?

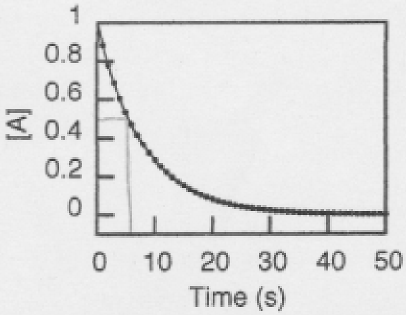
$$\lambda = \frac{\text{Yield of } HCl \text{ or } CH_3CHCH_2}{\text{Yield of } C_2H_4,\ CH_4,\ \text{or } CH_2ClCH(CH_3)CH(CH_3)CH_2C}$$

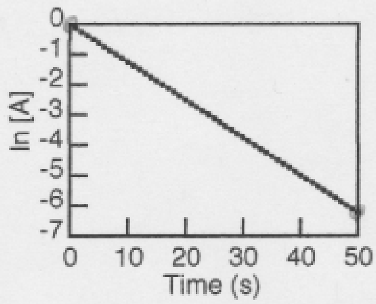
4. (8 POINTS) KINETICS

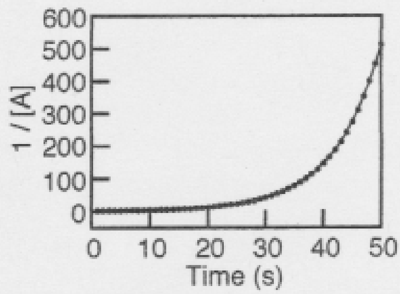
The progress of the reaction below is followed for 50 seconds.

$$A + B \rightarrow 2C$$

The following graphs are made using the experimental data:







a) **(1 pt) According to the graphs, what is the order of the rate-determining step?**

1st order

b) **(3 pts) What is the value of the rate constant for the RDS?**

Using [A] vs t graph: $t_{1/2} \approx 6$ sec $\therefore k = \frac{\ln 2}{t_{1/2}} = 0.17 s^{-1}$

Using ln[A] vs t graph: slope = −k $\therefore k = -\frac{-6.2 - 0}{50 - 0 s}$

$\approx 0.13 s^{-1}$

c) **(4 pts) What will [A] be after 30 seconds, if its initial concentration is 0.550 M?**

$\ln[A]_t = \ln[A]_0 - kt$

$= \ln(0.550) - (0.13 s^{-1})(30 s)$

$= -4.50$

$\therefore [A]_t = e^{-4.50} = 0.011$ mol/L

5. (8 POINTS) FEEDSTOCKS

You are the CEO of a petrochemical company that needs to start producing major quantities of *p*-xylene (its price is rising, and you want to maximize profits!). Your company has access to raw petroleum, and all of the necessary reactors/catalysts etc. In the space below, outline how you would synthesize *p*-xylene. Include reaction conditions, where appropriate.

Multiple answers, but the best (most $$) is:

PETROLEUM

↓ fractional distillation

NAPHTHA FRACTION (C_6-C_8)

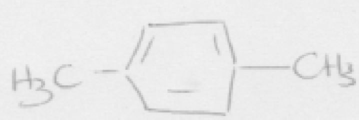
↓ catalytic reforming (isomerize + dehydrogenate)

BTEX FRACTION

↓ distill off benzene, toluene, and maybe o-xylene

C_8 AROMATICS (EtBz, M-X and P-X)

↓ separation with zeolites (narrow channels)



To maximize yields and $$: recoup leftover m-xylene & ethylbenzene and re-equilibrate to make more p-xylene.

6. (8 POINTS) COMBUSTION

One mole of gaseous H_2 is burned in excess oxygen. The combustion is initiated with a match.

a) (1 pt) The process which produces 3 H• from each initial H• is called:

branching

b) (4 pts) Complete the following series of propagation steps:

$$H\bullet + O_2 \longrightarrow \bullet OH + O$$

$$\bullet OH + H_2 \longrightarrow H\bullet + H_2O$$

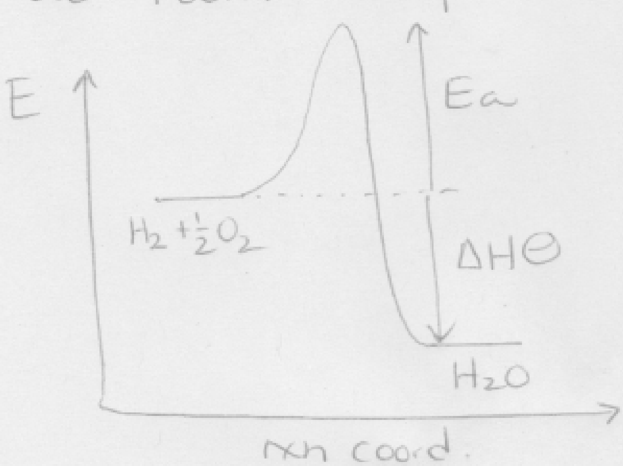
$$O + H_2 \longrightarrow H\bullet + \bullet OH$$

$$\bullet OH + H_2 \longrightarrow H\bullet + H_2O$$

$$H\bullet + O_2 + 3H_2 \longrightarrow 3\,H\bullet + 2\,H_2O$$

c) (3 pts) Mixtures of H_2 and O_2 are usually stable at room temperature and pressure. Why is a match needed to start the combustion? You may draw a reaction profile to help illustrate your answer.

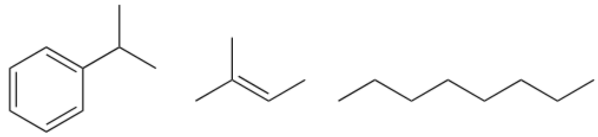
Yes, ΔG is negative (thermodynamically spontaneous) BUT Ea is LARGE. Therefore, the uncatalyzed reaction (without a spark) is VERY SLOW and does not occur appreciably at room temperature:



Ea is large
∴ k is small
∴ rate is SLOW.

1. (18 POINTS) Short answers – one or two points each.

a) Place the following compounds in order of lowest to highest relative fuel quality:



A B C

_____C_____ < _____B_____ < _____A_____

b) The equilibrium between CO and CO_2 produced from the combustion of a hydrocarbon is temperature *and* pressure dependent. Circle the preferred equilibrium direction at

i.	high temperature & low pressure:	CO favoured	CO_2 favoured
ii.	high pressure & low temperature:	CO favoured	CO_2 favoured

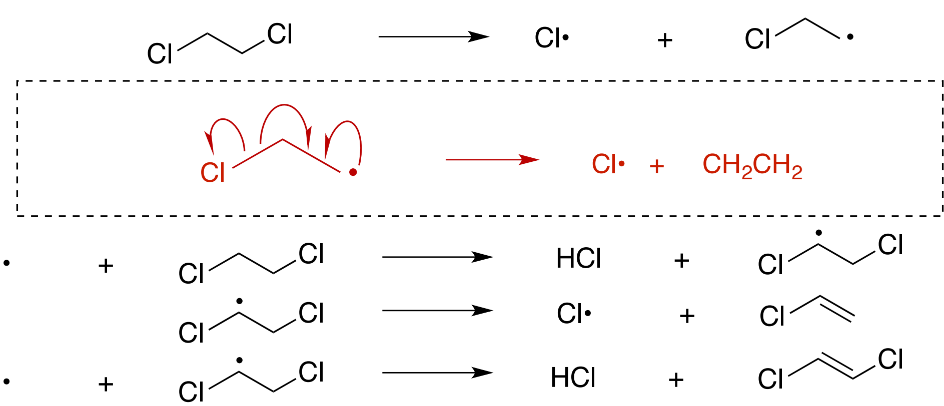
c) Methanol is mostly produced from __________syn gas______________ using the ___hydrogenation/syn gas/BASF_____ Process.

d) If a metal is coordinatively saturated, it must also be electronically saturated.

TRUE FALSE

e) The incomplete reaction mechanism for the cracking of 1,2-dichloroethane is shown below. Complete the mechanism by filling in the missing step (with electron-pushing arrows) and write the overall reaction in the box below.

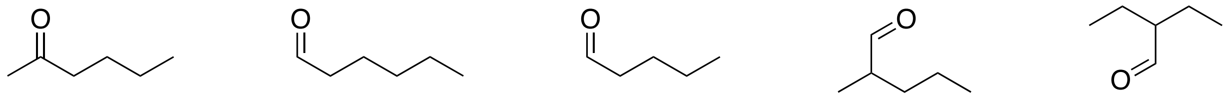
MISSING STEP



OVERALL REACTION

$ClCH_2CH_2Cl \longrightarrow HCl + CH_2CHCl$

f) From the following molecules, indicate the *major* and *minor* product of the olefin hydroformylation of 1-pentene:



MAJOR MINOR

g) Circle the most appropriate reaction conditions for the conversion of syn gas to methanol.

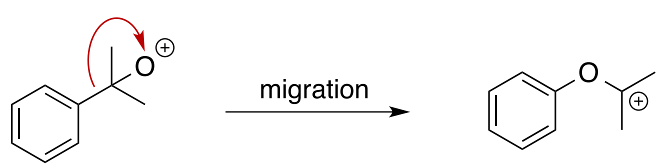
$$CO + 2\,H_2 \longrightarrow CH_3OH$$

CATALYST =	**ACID**	**BASE**	**METAL**
TEMPERATURE =	250°C	**25°C**	**1000°C**
PRESSURE =	**0.1 atm**	**2 atm**	50 atm

h) A dimerization reaction (A + A → A–A) is being carried out in SDS micelles. The micelle molarity is 0.010 M. In order to ensure an excellent reaction yield, the minimum concentration of A is ________0.020 M (occupancy = 2)____________.

i) Natural surfactants are known as _______soaps___________ **whereas synthetic surfactants are called** _____detergents___________________.

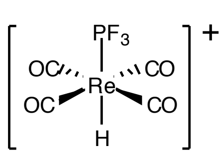
j) The following migration reaction is a key step in the Hock Process.



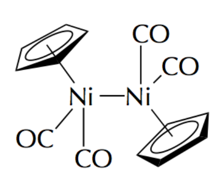
Add (a) electron pushing arrow(s) to the scheme above to show the mechanism for this step. The driving force for this migration is: ____

___conversion of a oxocation to a carbocation (C is less electronegative than O)___________.

k) Determine the oxidation state at the metal centre.



+2



+1

l) The surfactants which are most commonly involved in *cleaning* steps are:

ANIONIC CATIONIC NEUTRAL ZWITTERIONIC

m) In the boxes, draw surfactant examples of a bio-hard sulfonate and a bio-soft sulfate.

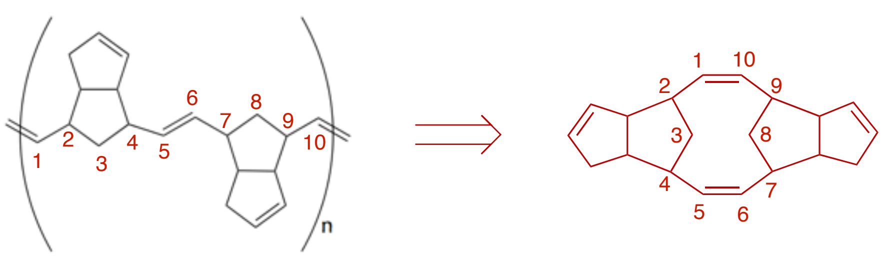
bio-hard sulfonate	bio-soft sulfate
Highly branched hydrophobic tail, polar head is a sulfonate group (R–SO_3^-)	linear hydrophobic tail, polar head is a sulfate group (R–OSO_3^-)

n) In an in-class demo, you found that one household cleaning product is slightly acidic (pH ~ 6.5). What was that product, and why is it acidic? ______

shampoo: slightly acidic pH leads to better overlapping scales of the hair shaft (hair appears shiny)

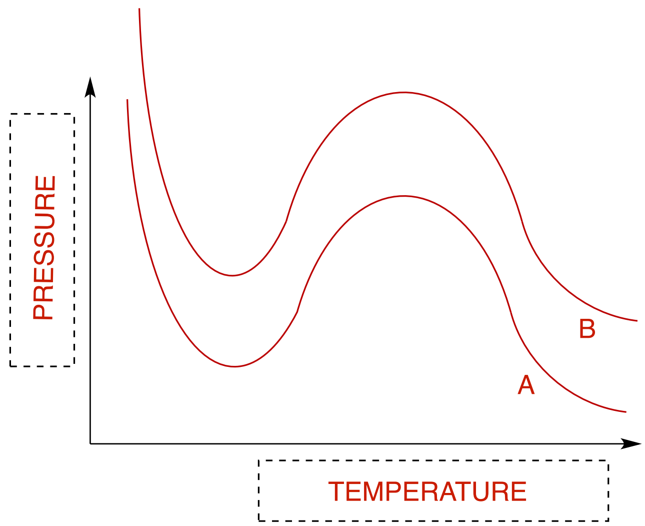
BONUS

The following polymer was generated by ROMP. Draw the structure of the original monomer that produced this polymer.



2. (8 POINTS) COMBUSTION

a) On the axes provided, draw a representative pressure-temperature curve for a typical internal-combustion engine gasoline.



b) Also on the axes, add a second curve representing a fuel destined for a higher-performance engine (a luxury car operating at a higher temperature, for example). Add a label to distinguish it from your first curve.

c) What is the quantifiable scale used to evaluate the quality of these two fuels? How would this value differ between part a and b?

OCTANE NUMBER: this value will be higher for the higher quality fuel (b).

d) Suggest two ways the fuel of part a could be transformed into the fuel of part b. Please be as specific as possible.

1. CATALYTIC REFORMING: transform some of the lower octane number compounds in the fuel (e.g. alkanes) into high octane number alkanes (e.g. aromatics) by isomerization and dehydrogenation reactions.
2. GASOLINE ADDITIVES: add octane boosters, such as oxygenates like ethanol or MTBE.

e) What key factor distinguishes an internal combustion engine from a diesel engine? Chemically speaking, how do the fuels differ?

IC ENGINE = detonation initiated by a spark plug
IC FUEL = smaller molecules (average 8 carbons), aromatics, alkenes, and branched compounds are best.

DIESEL ENGINE = detonation occurs spontaneously (at a specific T & P) *without a spark plug*
DIESEL FUEL = large (average 16 carbons) linear aliphatic compounds are best.

3. (8 POINTS) ORGANIC SYNTHESIS

a) **Depict using an overall scheme (no mechanisms) the reaction steps that one would need in order to convert *toluene* to *cumene*. Include all reagents, relative reaction conditions, and important byproducts where applicable.**

(can be shown as a flow chart or as a series of reaction instead):

1. HYDRODEALKYLATION OF TOLUENE TO BENZENE

- **thermally crack toluene at high temperatures in the presence of high pressure hydrogen to produce benzene and methane**

OR

- **catalytically crack toluene at medium temperature with a metal catalyst and high pressure hydrogen to produce benzene and methane**

2. ALKYLATION OF BENZENE TO CUMENE

- **treat excess cumene with propylene (from the catalytic cracking of petroleum) at medium pressure with an acid catalyst (can be Bronsted or Lewis) in a Friedal-Crafts reaction**

b) **According to the *Sigma-Aldrich* catalog, cumene actually costs *less* ($34/L) than benzene ($64/L) even though the former is made from the latter. Give a possible reason for this.**

Many possible answers here: as long as your answer is reasonable (e.g. economics of volume, benzene is more carcinogenic, etc. etc.) then it will be acceptable.

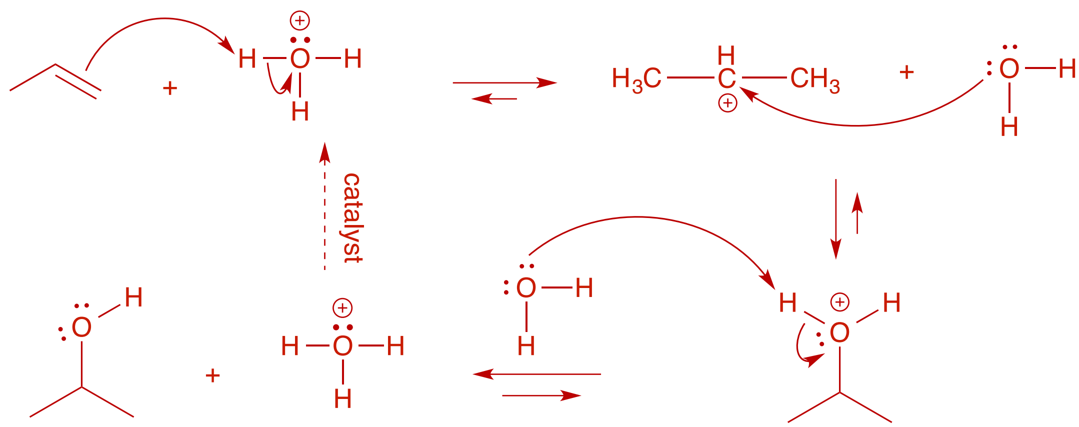
c) **Explain why, in the alkylation of benzene to make ethylbenzene, ethylene is always the limiting reagent.**

In the (similar to above) Friedal-Crafts reaction, if ethylene is added in excess amounts, it can lead to polyalkylation of benzene (e.g. produces diethylbenzene etc.). To reduce the yield of these unwanted side products, ethylene is the limiting reagent.

4. (8 POINTS) ORGANIC SYNTHESIS

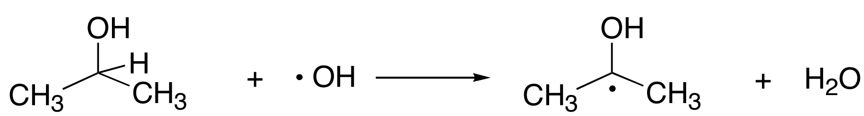
One minor route to acetone is a liquid-phase oxidation developed by Shell and DuPont.

a) The first step in the synthesis is the hydrolysis of propylene to *iso*-propanol under acidic conditions. Show the mechanism for this reaction, with electron-pushing arrows.



b) The second step is the oxidation of *iso*-propanol to acetone by molecular oxygen in a free radical chain reaction, using hydrogen peroxide as the initiator. The initiation step and transfer step are shown below. Complete the remaining steps in the chain reaction.

$$H_2O_2 \longrightarrow 2\ \bullet OH$$



$CH_3CH{\bullet}OHCH_3 + O_2 \rightarrow CH_3COCH_3 + HOO{\bullet}$ **Propagation 1**

$HOO{\bullet} + CH_3CHOHCH_3 \rightarrow H_2O_2 + CH_3CH{\bullet}OHCH_3$ **Propagation 2**

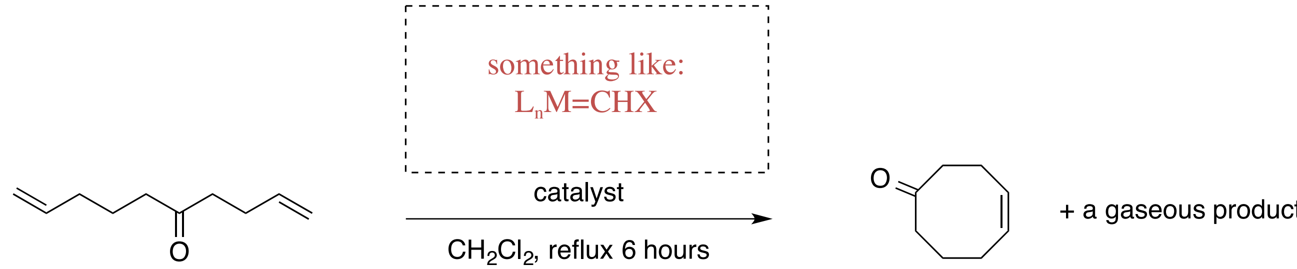
$2\ HOO{\bullet} \rightarrow H_2O_2 + O_2$ **Termination**

c) What is the overall reaction for part (b)?

ISOPROPANOL + O_2 → ACETONE + H_2O_2

5. (8 POINTS) INDUSTRIAL CATALYTIC CYCLES

Rings larger than 6 or 7 carbons are usually difficult to prepare by conventional organic methods. However, cyclooctenone derivatives can be made using organometallic catalysis :

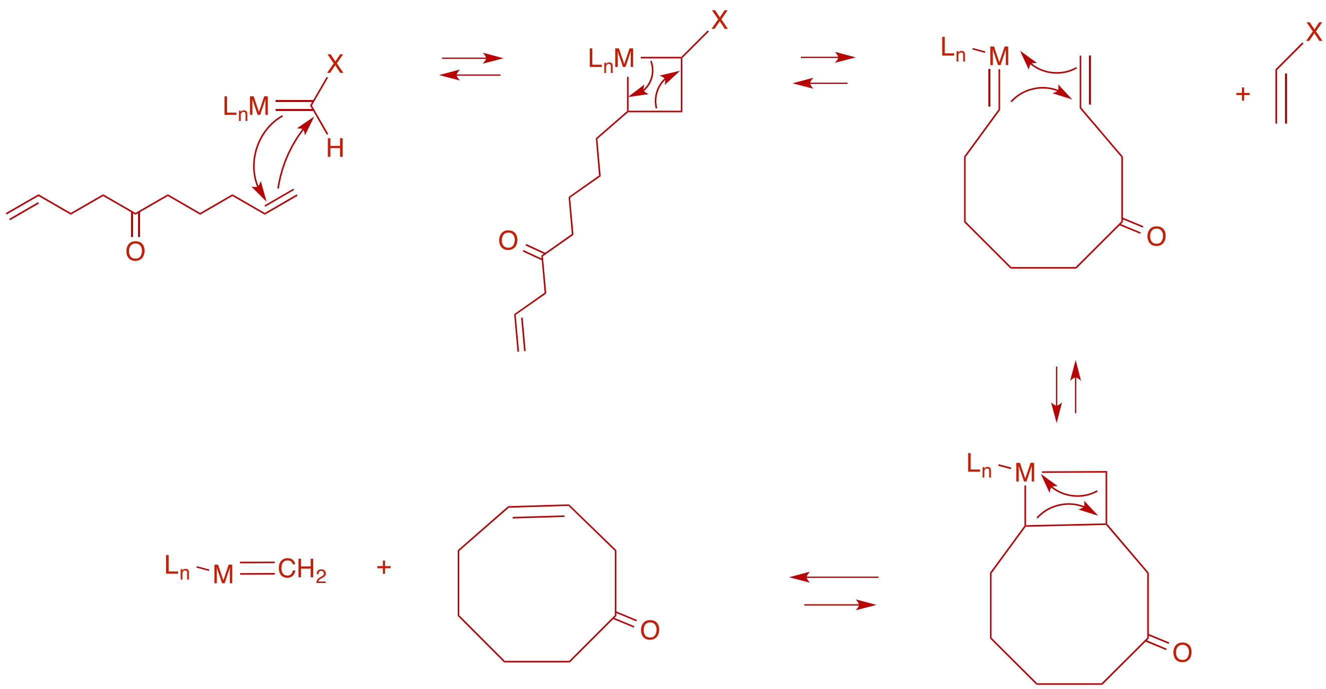


a) **This type of transformation is called ____ring-closing metathesis__________________.**

b) **Propose a possible catalyst for the reaction shown above (draw it in the box).**

c) **This type of organometallic catalyst is called a/an ____metal carbene________.**

d) **Draw the mechanism for the ring-closing using your catalyst.**



e) **Though reactions in this category are usually reversible, complete consumption of the starting material is observed after 6 hours. What is the driving force of the above reaction?**

The formation of ethylene, a gaseous product that bubbles away, pulling all the equilibria towards the final product.

6. (8 POINTS) SURFACTANT CHEMISTRY

The following figure illustrates three droplets of an oil-based liquid dirt on different surfaces immersed in a surfactant solution.

a) Estimate graphically the contact angles for these drops. What does the contact angle reflect in terms of interactions between different materials?

A = close to 180°
B = close to 90°
C = about 45°

The affinity between the drop and the surface increases from A to C. This implies a decreased interfacial tension between the two materials (stronger intermolecular forces).

b) In which case is the surface *least* likely to be Teflon? **A** **B** **C**

c) If you had to choose a surfactant to remove this dirt, what type would you use? Can you give a specific example?

An anionic surfactant. Any of the examples seen in clas are acceptable.

d) In the case of drop B, will the dirt be spontaneously released? If not, what else is required?

No; mechanical work (scrubbing etc.) is required to overcome the work of adhesion.

1. (30 POINTS) Short Answers – one or two points each.

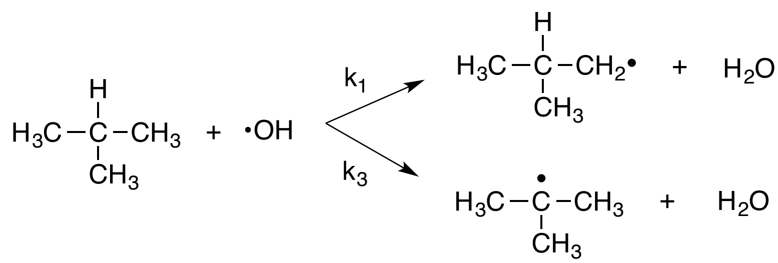
a) One characteristic that distinguishes *basic research* from *applied research* is: ___________

__basic = curiosity-driven research; applied = consumer-driven research______________

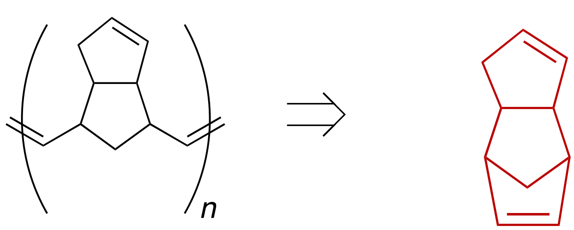
b) In a class demonstration, we showed that polystyrene packing chips (Styrofoam) "dissolves" very easily in acetone. One packing chip, however, did not. Name the polymer that was used to make that particular packing chip and explain why it did not dissolve.

__It was made of polyurethane, and did not dissolve because it is a network/thermoset polymer (cross-linked)____

c) Under thermal cracking conditions, the value of the ratio of the rate constants for the two competing processes shown below would be k_1/k_3 = _____9/1 = 9_________.



d) The following polymer was generated by ROMP. Draw the structure of the original monomer that produced this polymer.



e) One advantage of suspension polymerization is: ___Anything from the table of advantages/disadvantages in Chapter 10 is acceptable ______________________________

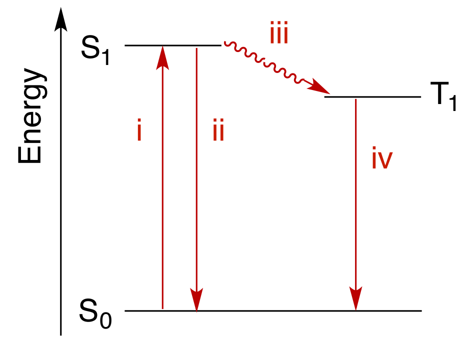
f) In FRVP, if the concentration of initiator is doubled, the expected molecular weight of the resulting polymer will also double.   TRUE   FALSE

g) Three samples of polypropylene with different tacticities have exactly the same molecular weight distribution but they have different T_g's. Which PP has the highest T_g? ___isotactic or syndiotactic PP are acceptable__________

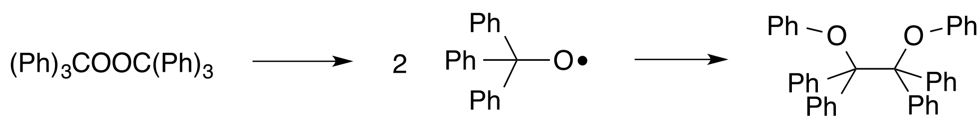
h) **BTEX is obtained by catalytic reforming of naphtha. BTEX is an acronym for ___________benzene/toluene/ethylbenzene/xylene ______________________________**

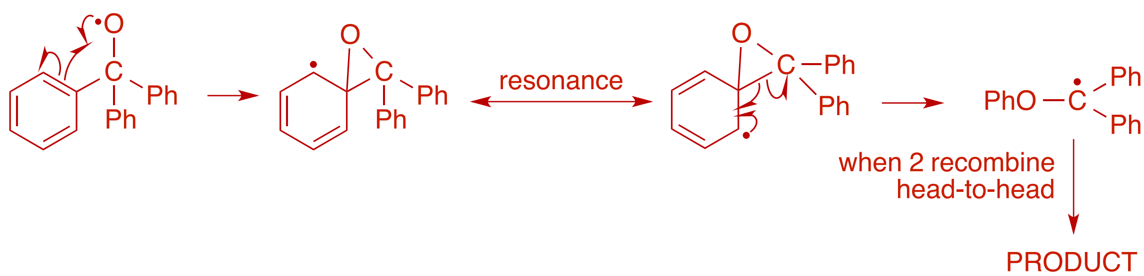
i) **On the provided Jablonski diagram template, draw and label (i to iv) the appropriate arrows showing the following processes for a diamagnetic starting material:**

- **i. absorption of a photon**
- **ii. fluorescence**
- **iii. spin flip to the triplet state**
- **iv. phosphorescence**



j) **When irradiated, di-trityl-peroxide ($Ph_3COOCPh_3$) does not give benzophenone and biphenyl, but rather rearranges to the pinacol-coupling product shown below. Propose a mechanism for this rearrangement.**





k) **An example of a bio-hard sulfonate would have:**

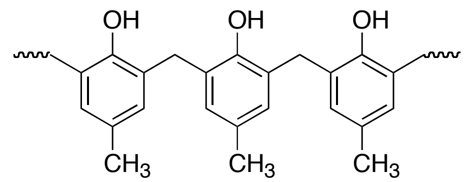
- ☐ **A BRANCHED HYDROPHOBIC TAIL WITH A $-OSO_3Na$ HEAD**
- ☐ **A BRANCHED HYDROPHOBIC TAIL WITH A $-SO_3Na$ HEAD**
- ☐ **A LINEAR HYDROPHOBIC TAIL WITH A $-OSO_3Na$ HEAD**
- ☐ **A LINEAR HYDROPHOBIC TAIL WITH A $-SO_3Na$ HEAD**

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

PLACTICIZER SUNSCREEN RADICAL SCAVENGER WATER

m) **In synthesizing a dendrimer, if you begin building the molecule from the core outward, then you are using the __divergent____ approach.**

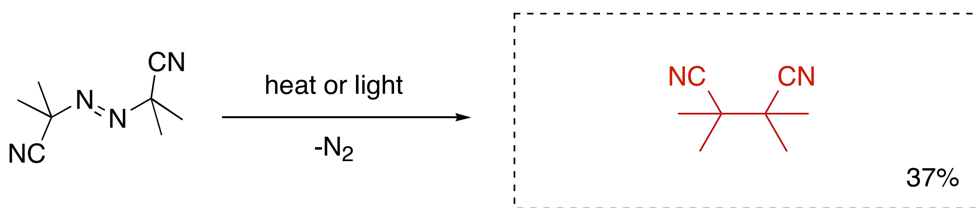
n) **Novolac is a possible polymer made from phenol-formaldehyde polymerization. What is the purpose of the *para*-methyl group?** ____Adding a methyl group blocks polymerization at the para position; the functionality drops from f = 3 to f = 2; a LINEAR polymer is formed instead of a NETWORK polymer.



o) **According to the Arrhenius expression, if the activation energy for a reaction is zero (E_a=0) then the value of the rate constant for the reaction is equal to the parameter known as (specify name and symbol)**___pre-exponential factor_________.

p) **Polydimethylsiloxane (PDMS) is synthesized from a bifunctional silane, $(CH_3)_2SiCl_2$. What would be the effect on the polymer weight by adding small amounts of $(CH_3)_3SiCl$ to the polymerization reaction?**_____It will decrease (the additive is monofunctional and would terminate polymer growth). ______________________________

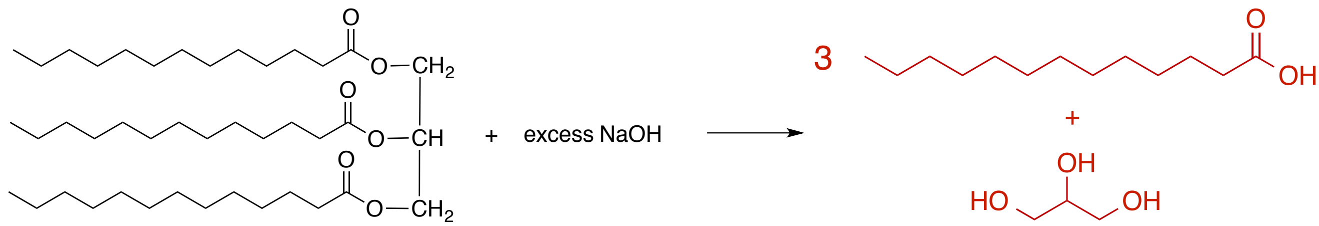
q) **AIBN, a common initiator used in free radical polymerization, decomposes irreversibly by releasing N_2. It was found that only 63% of the radicals generated from AIBN initiate radical polymerization. What is the fate of the remaining radicals generated (draw the product)?**

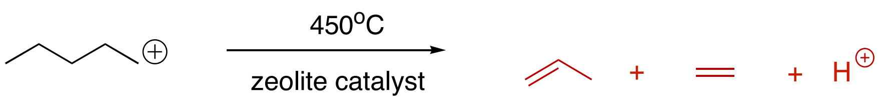


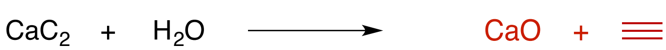
r) **Catalytic reforming of cyclohexane to yield benzene requires a(n) ACID BASE METAL catalyst and requires HIGH LOW MEDIUM hydrogen pressure.**

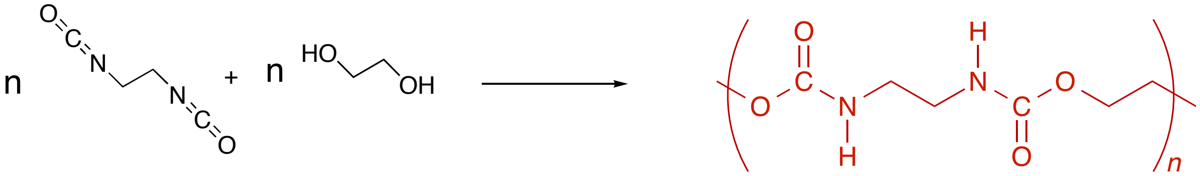
s) **For a molecule to act as an "excited state quencher" (and thus protect a polymer against photodegradation), one requirement is that the excited state energy for the quencher be less than or equal to the excited state energy of the polymer. The other requirement is:** ___The excited state quencher (Q*) must decay *via* a pathway that does NOT lead to the formation of free radicals. ______________________________

t) Give the <u>final</u> products of the following reactions (no mechanisms):









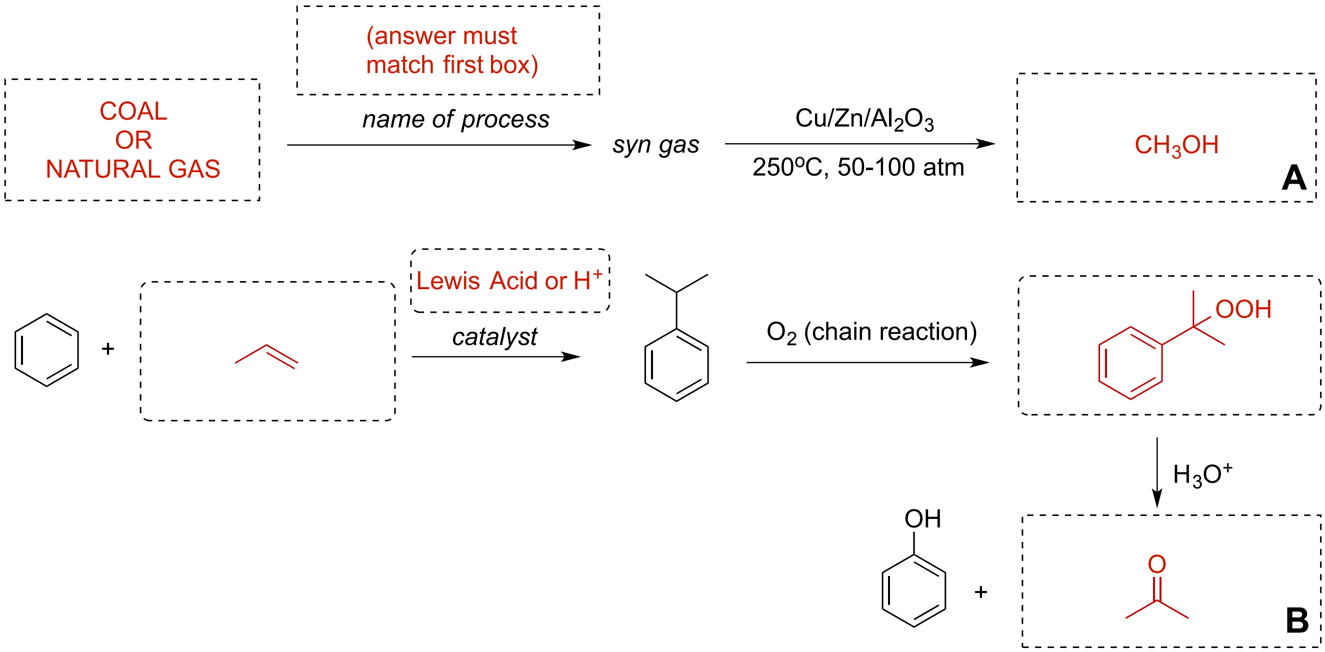
<u>BONUS</u>

In a Youtube video, we watched a tennis ball being slowly compressed in a massive clamp (capable of exerting enormous pressure). Why do tennis balls compress and bounce so easily? When watched *via* a thermal camera, we saw that the temperature of the ball increased during the compression. Why?

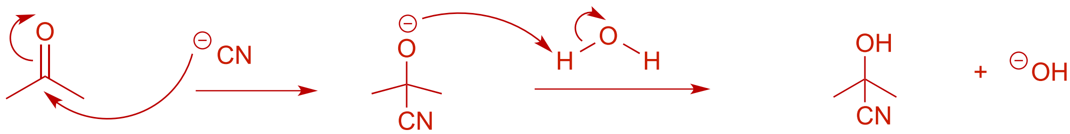
These are polymers with high COEFFICIENTS OF RESTITUTION – when compressed, the stored potential energy is easily converted back into kinetic energy, and the material is bouncy. The temperature is increasing because a portion of the potential energy is converted to THERMAL ENERGY (i.e. the coefficient of restitution is NOT exactly 100%!)

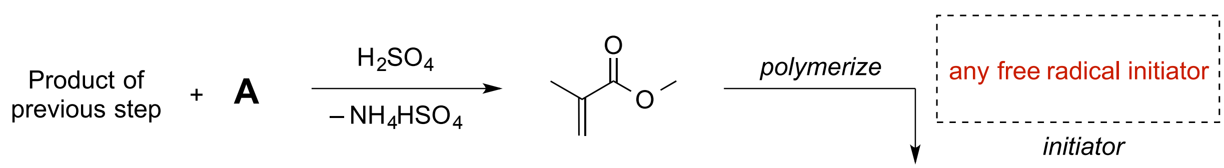
2. (15 POINTS) INDUSTRIAL ORGANIC CHEMISTRY

Complete the following reactions, showing the formation of a common polymer.



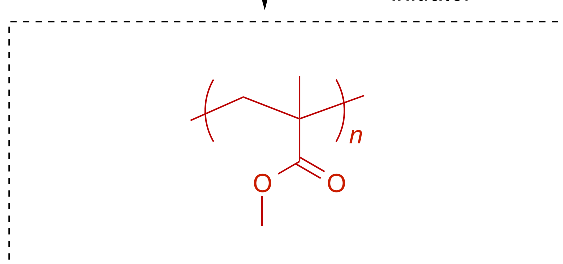
In the space below, draw the mechanism for the reaction of **B** with $^{-}$CN (under basic conditions):





The full name and abbreviation of this polymer are:

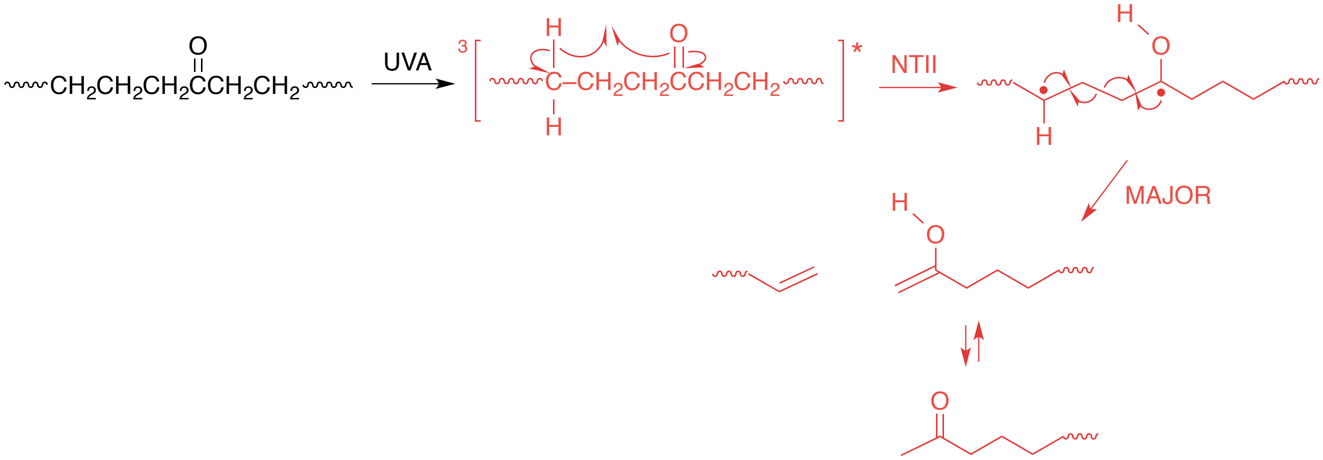
PMMA, polymethyl methacrylate

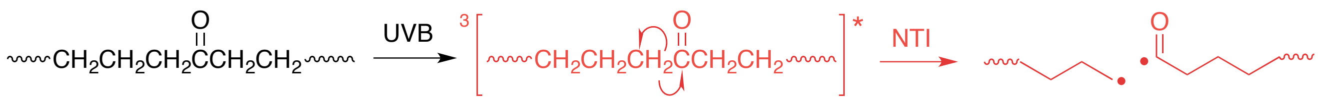


Polymer - show repeating unit

3. (15 POINTS) POLYMER DEGRADATION

(a) Complete the mechanisms for the following reactions, showing the final MAJOR non-radical products:

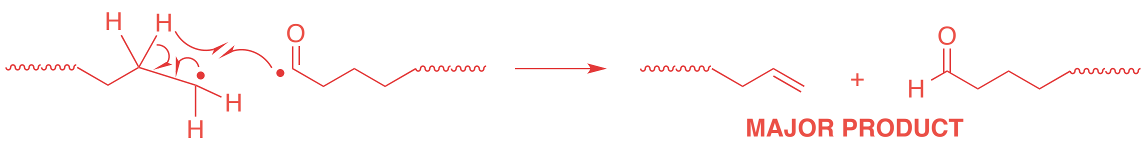




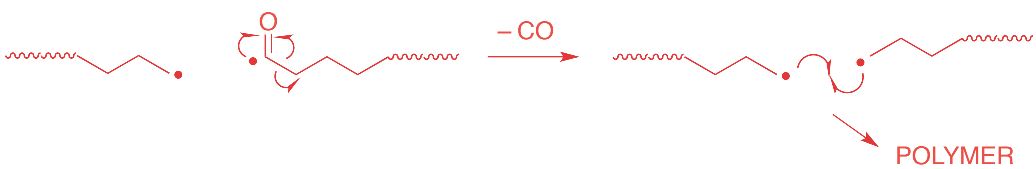
The 4 possible pathways (not all need to be shown):

1. recombination

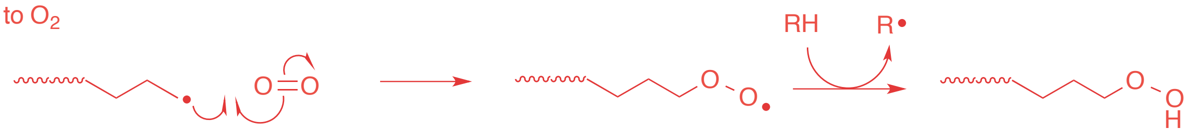
2. disprop'n



3. decarbonylation



4.addition to O_2



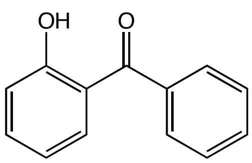
--QUESTION CONTINUED ON NEXT PAGE--

3. CONTINUED…

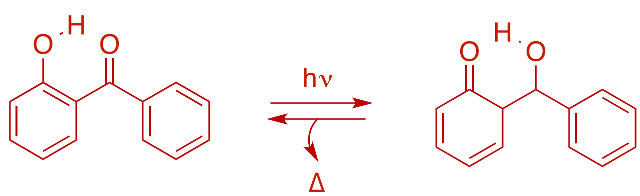
(b) In both cases, what is the principal effect on the polymer's mechanical properties?

Rupture of main polymer backbone = sharp decrease in polymer molecular weight = loss of mechanical properties

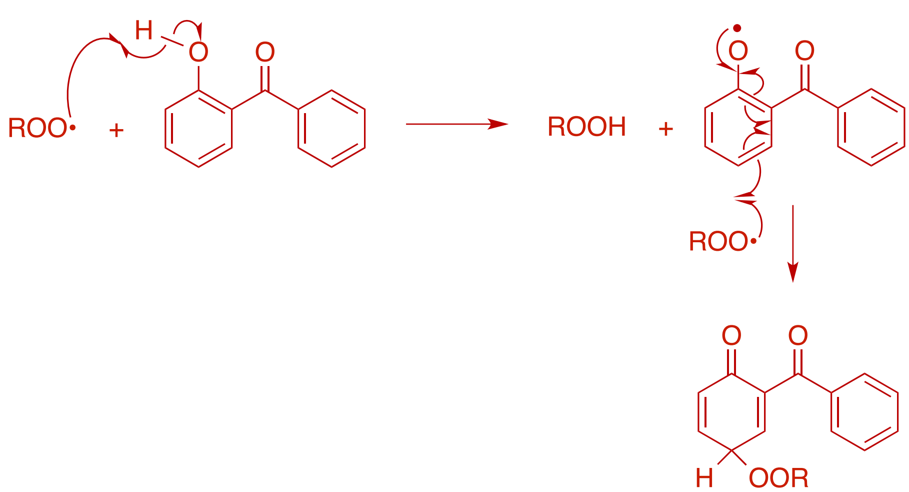
(c) This photochemical degradation can be reduced by the addition of *ortho*-hydroxybenzophenone (shown below). Explain the two roles this additive plays in protecting against UV damage. You may use chemical equations to support your answer.



Role #1: Sunscreen
The molecule acts as a sunscreen by absorbing UV light and then wastes the energy in non-free radical producing pathways (e.g. converts the energy to heat).

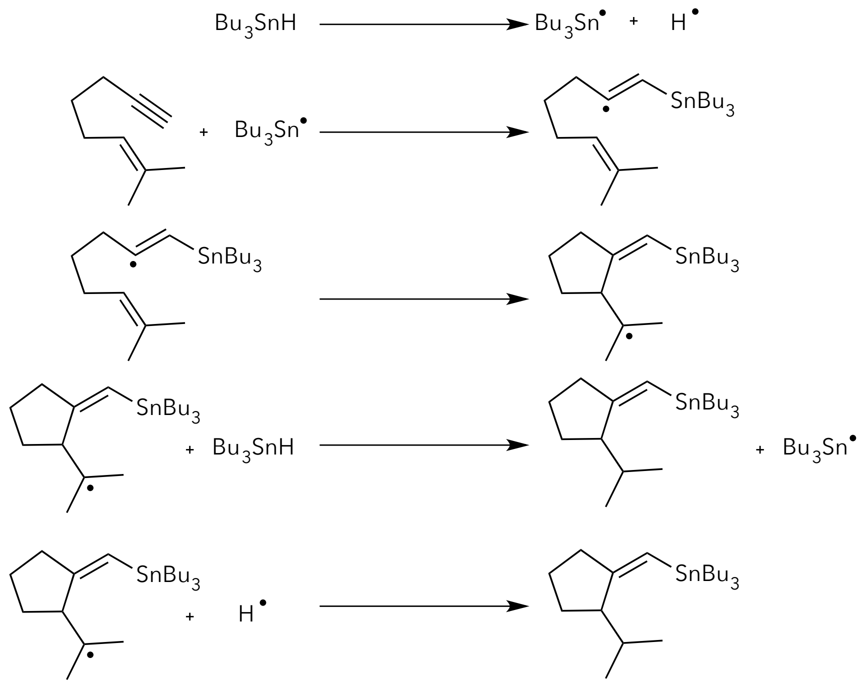


Role #2: Anti-oxidant
The molecule acts as a free radical scavenger, because it is a good hydrogen donor (weak PhO-H bond) which creates a free radical that is unreactive towards O_2 (PhO•).



4. (10 POINTS) FREE RADICALS

Consider the following tin-mediated free radical chain reaction:



INITIATION

PROPAGATION 1

PROPAGATION 2

PROPAGATION 3 (RDS)

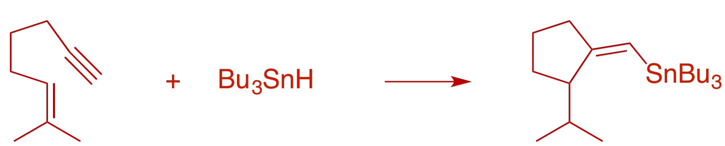
TERMINATION

(a) (3 pts) Label each step of the chain reaction and indicate the RDS.

(b) (2 pts) What is the driving force of the third step?

3rd step = the ring closing step (5 membered ring, so only a small amount of ring strain)
Driving force = formation of a more stable free radical: change a SECONDARY radical on an SP² HYBRIDIZED atom to a TERITARY radical on an SP³ HYBRIDIZED atom.

(b) (2 pts) What is the overall reaction?



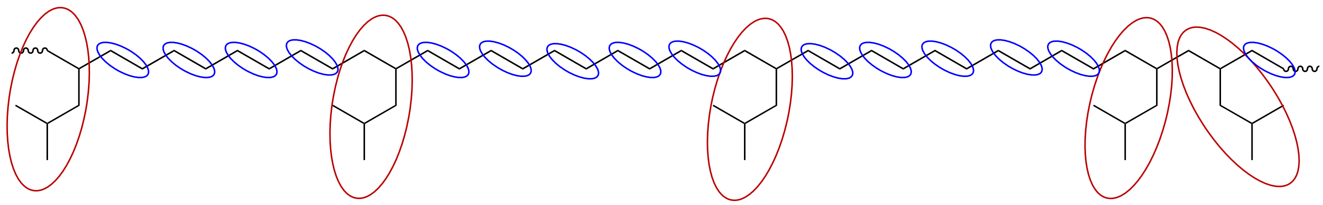
(c) (3 pts) The product of the reaction might be used as an additive for increasing the octane number of gasoline. Name three attributes of this compound that would be responsible for this behavior.

- cyclic
- branched
- unsaturated (double bond)
- contains tin (Sn is one row above Pb)

lead to increased octane number!

5. (10 POINTS) POLYMER CHEMISTRY

LLDPE is a copolymer made from the reaction of ethylene (monomer 1) with 2-methyl-1-pentene (monomer 2):



(a) (4 pts) Provide approximate values of r_1 and r_2, based on the representative polymer shown above, and thoroughly explain your reasoning.

Monomer 1 and 2 units are circles in blue and red, respectively. R values are based on the ratio of self-propagation to cross-propagation. Using the additions seen above to derive estimates, we obtain:

r_1 ~ 12/3 ~ 4 (a number greater than 1 makes sense due to the preponderance of monomer 1 in the overall polymer)

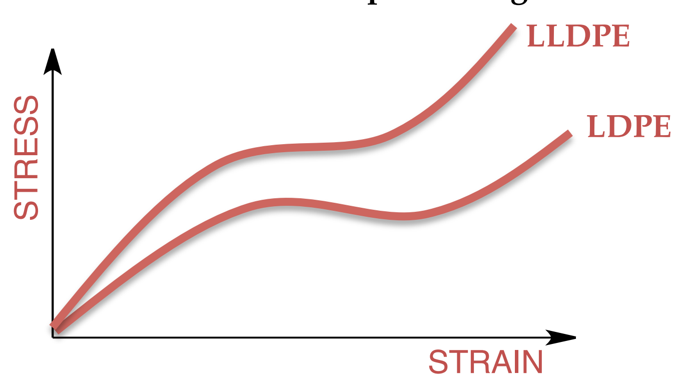
r_2 ~ 1/4 ~ 0.25 (a number less than 1 makes sense due to the lack of monomer 2 in the overall polymer)

(b) (3 pts) What does LLDPE stand for? How would its physical properties (e.g. T_g etc.) differ from LDPE? Explain, drawing structures if necessary.

LLDPE = linear low density polyethylene
LDPE = low density polyethylene

LDPE is made via FRVP and has extremely high levels of branching (much more so than the controlled branching in LLDPE, which is made by Ziegler-Natta polymerization). Lots of branching means LDPE has much lower crystallinity than LLDPE. So, LDPE would have all of the physical properties of a more amorphous material (lower T_g, lower density, lower modulus, etc.).

(c) (3 pts) Draw and label representative stress-strain curves for the two plastics mentioned in part (b). Do not forget to label the axes. Which plastic might be more appropriate for use in grocery bags?



Grocery bags: You can either say "LLDPE, because it is a stronger material (higher crystallinity)" or "LDPE, because it will be easier to recycle (lower T_g)". Both are acceptable.

6. (10 POINTS) POLYMER AND SURFACTANT APPLICATIONS

(a) (5 pts) Choose one of the following common polymers discussed in class (circle your selection) and fill in the spaces below with details about the polymer you've chosen.

POLYBUTADIENE	POLYETHYLENETEREPHTHALATE
POLYDIMETHYLSILOXANE	POLYTETRAFLUOROETHYLENE

Monomer Formula: **Polymer Formula:**

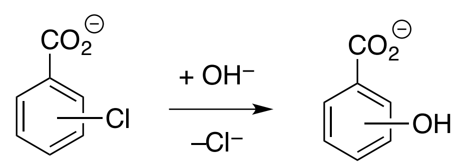
Polymerization Method Used:

Polymer Properties (at least two):

*****Answers based on selection above*****

(b) (5 pts) In the 1980's, Broxton studied the effects of cetyltrimethylammonium bromide (CTAB) micelles on the hydroxy-dehalogenation of benzoates (overall reaction shown). Provide an explanation for the trends in his experimental data, shown in the table.

Substrate	Rate constant, in pure water ($M^{-1}\ s^{-1}$)	Rate constant, in 40 mM CTAB ($M^{-1}\ s^{-1}$)
p-chlorobenzoate	0.0635	1.505
o-chlorobenzoate	0.965	12.20



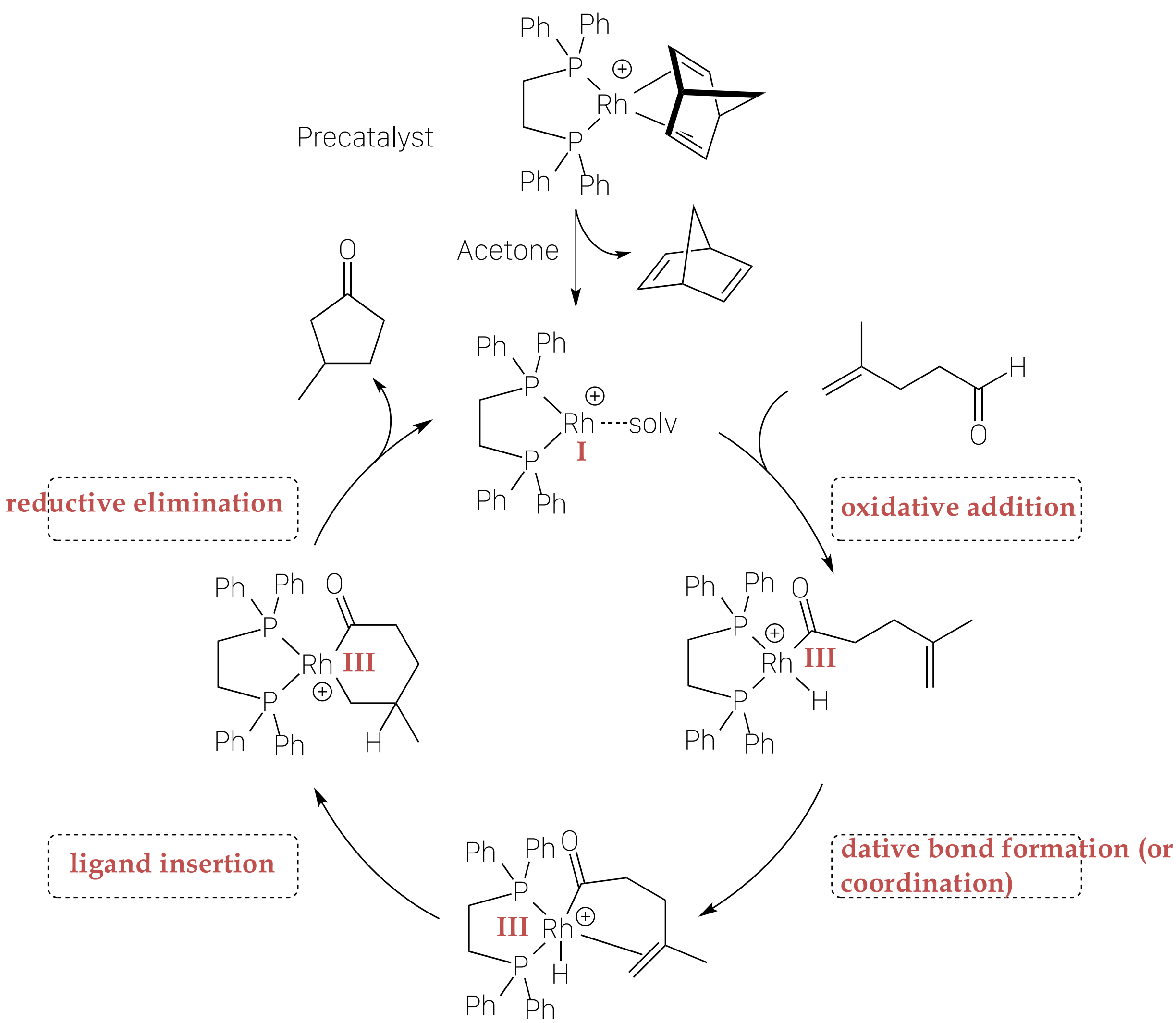
Looking horizontally: the reactions are faster in micellar solution. This is due to ELECTROSTATIC EFFECTS: this is an S_NAR reaction, where the nucleophile is negatively charged. Electrostatic attraction to the positively charged CTAB micelles hence accelerates the rate.

Looking vertically: the ortho isomer reacts faster than the para isomer. This is due to an ORIENTATION EFFECT: the substrate behaves slightly like a surfactant because of its anionic "head" and nearly non-polar body, and will thus align itself in the micelle like a surfactant molecule. This means that the reactive site for the ortho isomer is closer to the surface, but buried deeper in the micelle for the para isomer. Therefore, the more accessible ortho isomer reacts faster.

7. (10 POINTS) INDUSTRIAL CATALYTIC CYCLES

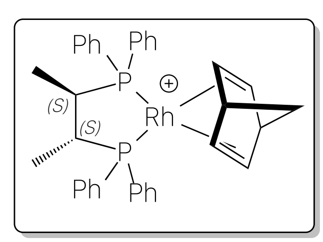
Shown below is the catalytic cycle for <u>intramolecular hydroacylation</u> using a modified Wilkinson's-type catalyst.

(a) (6 pts) In the boxes, write the name of each type of reaction step, and write the oxidation state of the rhodium centre below each intermediate.



(b) (2 pts) What is the overall reaction?

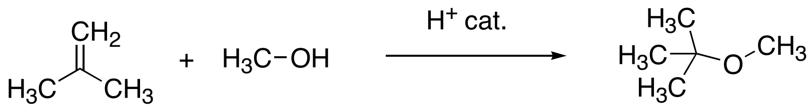
(c) (2 pts) Suppose we changed the precatalyst to the one shown in the box at right. How might it affect the product of the reaction?



Since this is a catalyst with an enantiomerically pure ligand, it is likely that this will act as a DIRECTING GROUP for the ligand insertion step and form preferentially either the R or S enantiomer of the cyclic product.

8. (10 POINTS) ASSORTED QUESTIONS

(a) (4 pts) Using group additivity values, estimate the ΔHº of the following reaction.



ΔH^o_f(methanol)

1 x C-$(H)_3$(O)= 1 x (-10.1 kcal/mol) = -10.1 kcal/mol
1 x O-(C)(H) = 1 x (-37.9 kcal/mol) = -37.9 kcal/mol
ΔH^o_f(methanol) = -48.0 kcal/mol

ΔH^o_f(*iso*-butane)

2 x C-$(H)_3(C_d)$ = 2 x (-1.72 kcal/mol) = -3.44 kcal/mol
1 x C_d-$(C)_2$ = 1 x (10.34 kcal/mol) = +10.34 kcal/mol
1 x C_d-$(H)_2$ = 1 x (6.26 kcal/mol) = +6.26 kcal/mol
ΔH^o_f(*iso*-butane) = +13.16 kcal/mol

ΔH^o_f(MTBE)

3 x C-$(H)_3$(C) = 3 x (-10.20 kcal/mol) = -30.60 kcal/mol
1 x C-$(C)_3$(O) = 1 x (-6.6 kcal/mol) = -6.6 kcal/mol
1 x O-$(C)_2$ = 1 x (-23.2 kcal/mol) = -23.2 kcal/mol
1 x C-$(H)_3$(O) = 1 x (-10.1 kcal/mol) = -10.1 kcal/mol
ΔH^o_f(MTBE) = -70.5 kcal/mol

ΔH^o_{rxn} = ΔH^o_f (pdts) - ΔH^o_f (rxts)
= ΔH^o_f(MTBE) – [ΔH^o_f(*iso*-butane) + ΔH^o_f(methanol)]
= (-70.5 kcal/mol) - (-48.0 kcal/mol + 13.16 kcal/mol)
= -35.7 kcal/mol

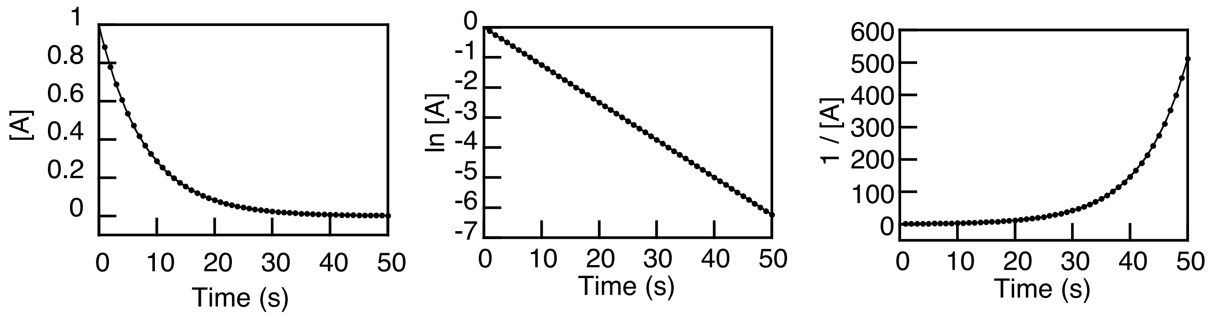
Answer: ______________________

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) (3 pts) The reaction A + B → 2 C is followed for 50 seconds and the following graphs are made using the experimental data. What would [A] be after 45 seconds, if its initial concentration is 0.780 M?



Find k from Graph #1 (using $t_{1/2}$) or from Graph #2 (k = –slope): k ~ 0.12 s^{-1}

$\ln[A]_t = \ln[A]_o - kt$
$\ln[A]_t = \ln(0.780) - (0.12\ s^{-1})(45\ s) = -5.648$

$[A]_t = e^{-5.648} = 3.5 \times 10^{-4}$ mol/L

(c) (3 pts) Depict using an overall scheme (no mechanisms) the reaction steps that one would need in order to convert *toluene* to *cumene*. Include all reagents, relative reaction conditions, and important byproducts where applicable.

(can be shown as a flow chart or as a series of reaction instead):

1. HYDRODEALKYLATION OF TOLUENE TO BENZENE
   - thermally crack toluene at high temperatures in the presence of high pressure hydrogen to produce benzene and methane

OR
   - catalytically crack toluene at medium temperature with a metal catalyst and high pressure hydrogen to produce benzene and methane

2. ALKYLATION OF BENZENE TO CUMENE
   - treat excess cumene with propylene (from the catalytic cracking of petroleum) at medium pressure with an acid catalyst (can be Bronsted or Lewis) in a Friedal-Crafts reaction