

FREE RADICAL REACTIONS

A STUDENT WHO HAS MASTERED THE MATERIAL IN THIS SECTION SHOULD BE ABLE TO:

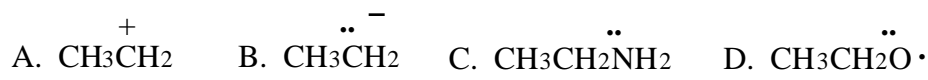
1. Define, recognize, and give examples of: homolytic cleavage (homolysis), heterolytic cleavage, free radical, exothermic and endothermic reactions.
2. Given homolytic bond dissociation energies (enthalpies), calculate heats (enthalpies) of reaction. Bond forming is an exothermic process (ΔH is negative); bond breaking is endothermic (ΔH is positive). The heat of reaction equals the sum of the bond dissociation enthalpies of the bonds broken minus the sum of the enthalpies of the bonds formed.
3. Predict the relative stabilities of free radicals and the relative rates of reactions that give rise to free radicals. The order of free radical stabilities is: $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\cdot$. Relatively stable species are relatively easy to form (and difficult to destroy).
4. Predict the product(s) of free radical reactions. Important reactions include:
 - Halogenation of alkanes. I_2 does not react, the order of reactivity is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2$, and the order of selectivity is $\text{Br}_2 > \text{Cl}_2 > \text{F}_2$. Stereochemistry of reactions (these occur via a planar intermediate) is important.
 - Anti-Markovnikov addition of hydrogen bromide to alkenes and alkynes.
 - Free radical polymerization of alkenes.
5. Propose mechanisms for free radical reactions, and predict and explain experimental results using a knowledge of these mechanisms. Important reactions include:
 - Halogenation of alkanes
 - Anti-Markovnikov addition of HBr
 - Free radical polymerization of alkenes

Important concepts include:

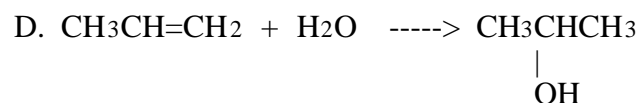
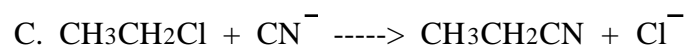
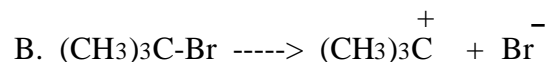
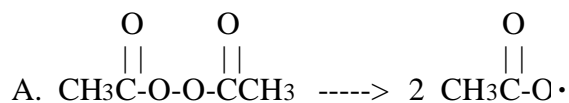
- Energy of activation (effect of temperature changes)
- For reactions in which bonds are both broken and formed, E_{act} must be greater than both zero and ΔH .
- Collision frequency (effects of temperature and concentration)
- Initiation, propagation, and termination steps

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

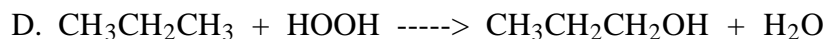
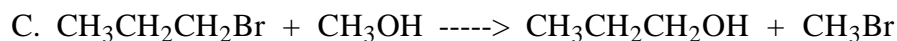
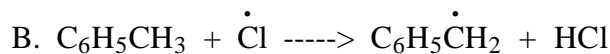
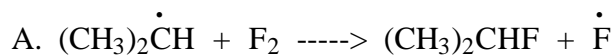
1.1 Which of the following is a free radical?



1.2 Which of the following is a homolytic cleavage?



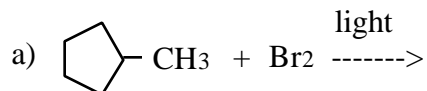
2. Calculate the value of ΔH for each of the following reactions using the table of bond dissociation energies in your textbook.

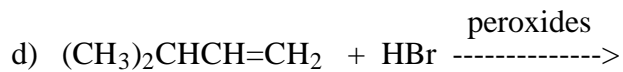
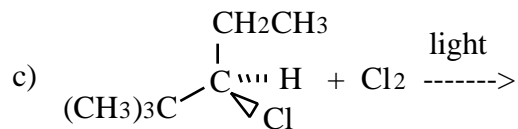
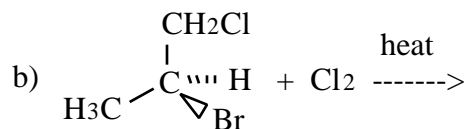


3. Which of the following free radicals is the most stable? Which is the least stable?

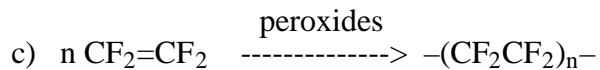
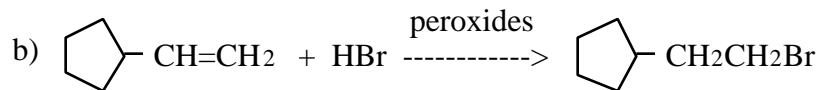
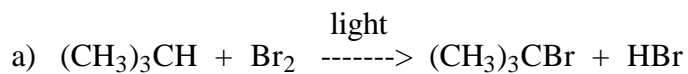


4. Predict the product(s) of each of the following reactions. Indicate stereochemistry where appropriate.





5.1 Propose a mechanism for each of the following reactions.



5.2 For which of the following reactions is E_{act} (A) equal to zero, (B) greater than zero, and (C) equal to $\dot{\text{H}}$?

- a) $\text{Cl}_2 \text{ -----} > 2 \dot{\text{Cl}}$
 b) $\text{CH}_3\text{CH}_3 + \dot{\text{Cl}} \text{ -----} > \text{CH}_3\dot{\text{C}}\text{H}_2 + \text{HCl}$
 c) $\text{CH}_3\dot{\text{C}}\text{H}_2 + \text{Cl}_2 \text{ -----} > \text{CH}_3\text{CH}_2\text{Cl} + \dot{\text{Cl}}$
 d) $\text{CH}_3\dot{\text{C}}\text{H}_2 + \dot{\text{Cl}} \text{ -----} > \text{CH}_3\text{CH}_2\text{Cl}$

SOLUTIONS TO SAMPLE PROBLEMS:

1.1 D

1.2 A

2. a) -280 kJ mol^{-1}

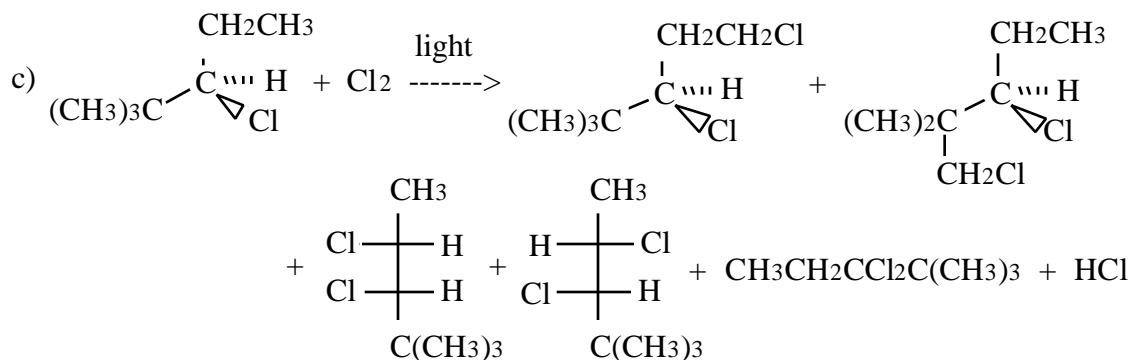
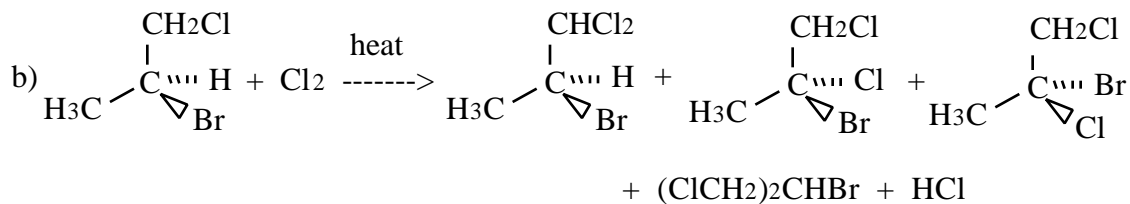
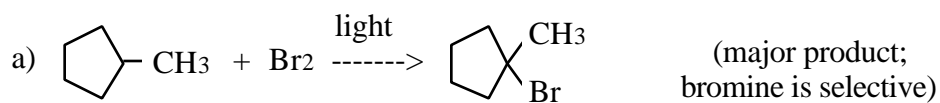
b) -57 kJ mol^{-1}

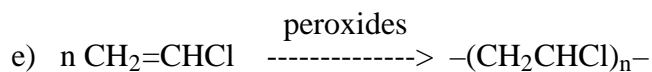
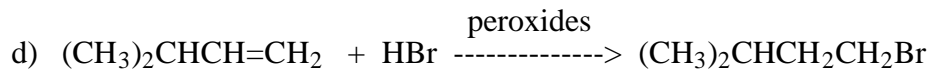
c) -7 kJ mol^{-1}

d) -257 kJ mol^{-1}

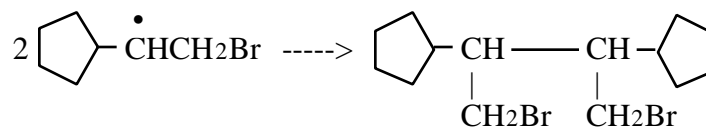
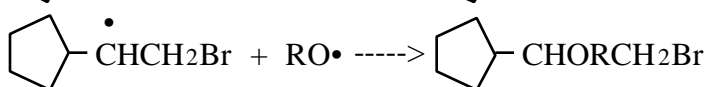
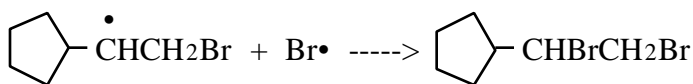
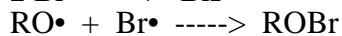
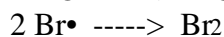
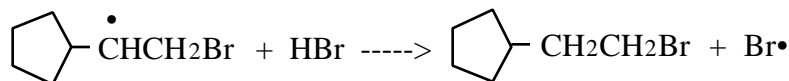
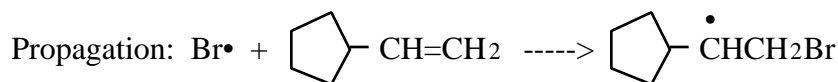
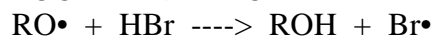
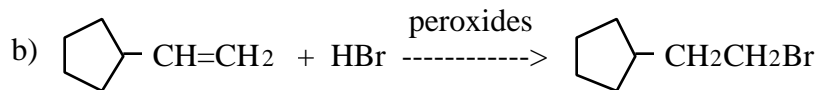
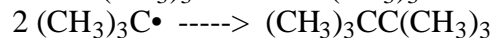
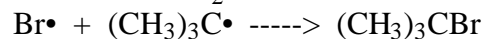
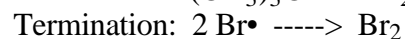
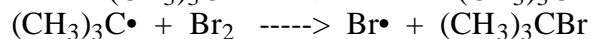
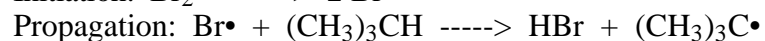
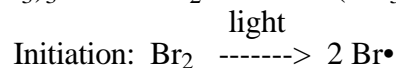
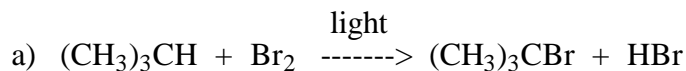
3. most stable: A; least stable: C

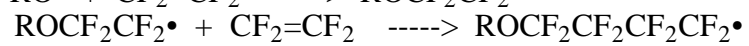
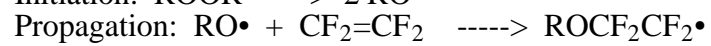
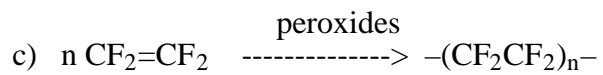
4. Predict the product(s):





5.1 Propose a mechanism for each of the following reactions.

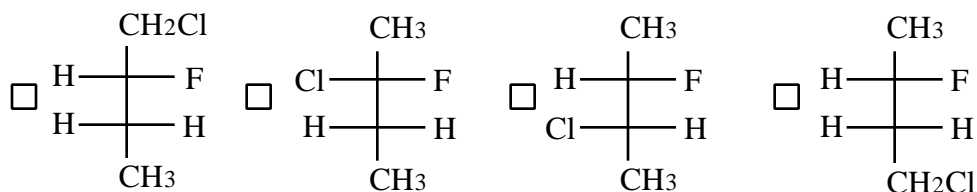
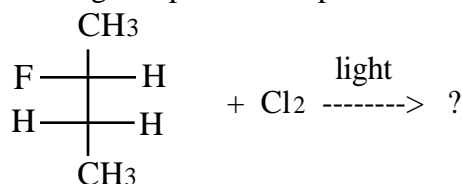




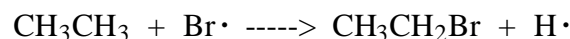
etc.

- 5.2 $E_{\text{act}} = 0$: d
 $E_{\text{act}} > 0$: a, b, c
 $E_{\text{act}} = H$: a

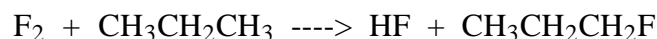
1. Which of the following compounds is a product of the reaction shown?



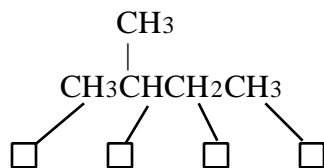
2. What is ΔH in kJ mol^{-1} for the process shown? Some bond dissociation energies in kJ mol^{-1} are: CH_3-CH_3 , 368; $\text{CH}_3\text{CH}_2-\text{H}$, 410; $\text{CH}_3\text{CH}_2-\text{Br}$, 289.



- A. -121 B. -79 C. 79 D. 121
3. What is ΔH in kJ mol^{-1} for the reaction shown? Some bond dissociation energies in kJ mol^{-1} are: $\text{CH}_3\text{CH}_2\text{CH}_2-\text{H}$, 410; $(\text{CH}_3)_2\text{CH}-\text{H}$, 395; $\text{F}-\text{F}$, 159; $\text{CH}_3\text{CH}_2\text{CH}_2-\text{F}$, 444; $(\text{CH}_3)_2\text{CH}-\text{F}$, 439; $\text{H}-\text{F}$, 569.



- A. -444 B. -439 C. -458 D. -454
4. Which of the indicated hydrogens reacts most RAPIDLY with Cl_2 in the presence of light?



5. Which of the following reactions proceeds by way of a free radical mechanism?

