Chapter 10 Problems

1. Consider the free radical bromination of 2,3-dimethylbutane to give the two isomers **A** and **B** shown below. Using the bond dissociation energy data provided, determine ΔH_i, ΔH_{ii} and ΔH_{rxn} for the formation of both **A** and **B**.

For RXN A

ΔH_i = +400 – 366 = +34KJ/mol

ΔH_{ii} = +193 – 263 = -70KJ/mol

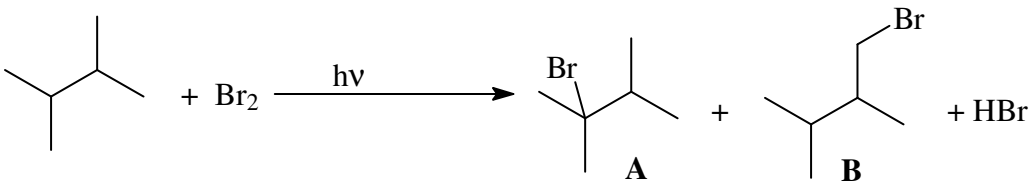
ΔH_{rxn}A = +34 - 70 = -36KJ/mol

For RXN B

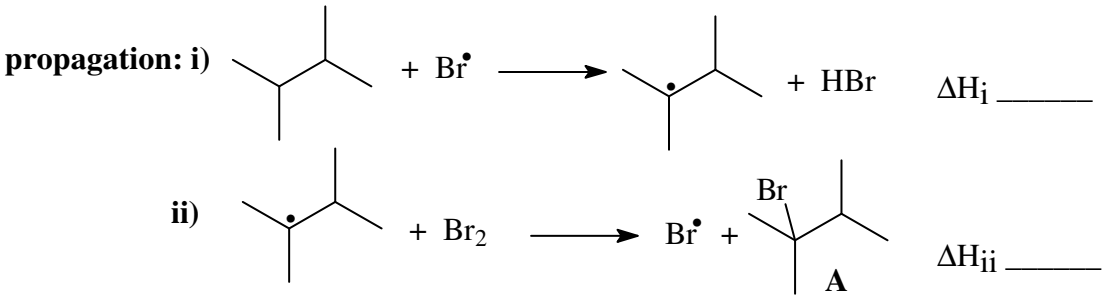
ΔH_i = +421 – 366 = +55KJ/mol

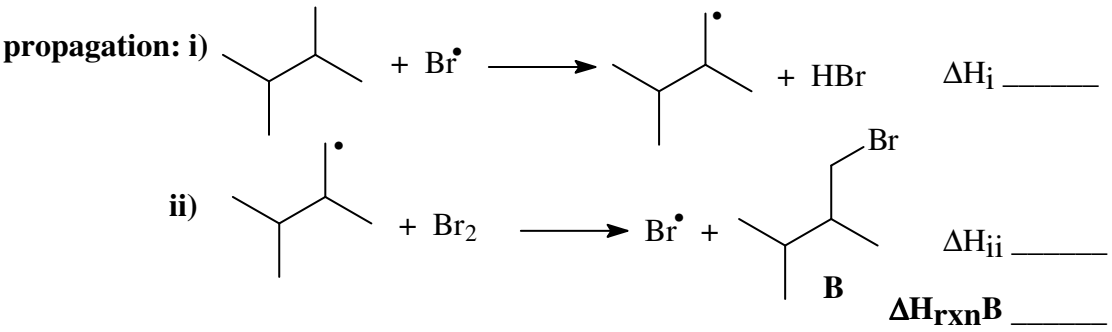
ΔH_{ii} = +193 – 295 = -102KJ/mol

ΔH_{rxn}A = +55 – 102 = -47KJ/mol



initiation: $Br_2 \longrightarrow 2\ Br^{\bullet}$



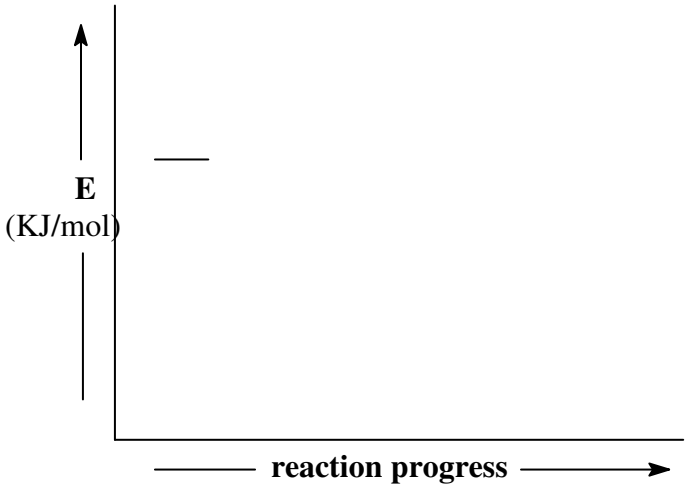


Which product, **A** or **B**, is more likely to be the major product? Explain.

Product **A** is more likely to form because the rate determining step has a lower ΔH_i therefore has a lower E_{act}. The overall ΔH_{rxn} has virtually no bearing on the product formation.

Bond	Bond Dissociation Energy KJ/mol
Br-Br	193
H-Br	366
3^{o} C-H	400
3^{o} C-Br	263
1^{o} C-H	421
1^{o} C-Br	295

2. On the axes below, draw the reaction profile for the 2 propagation steps in question #1 (use the horizontal line for the energy of the reactants) for the reaction that is likely to give the major product. Label with vertical arrows ΔH_i, ΔH_{ii} and ΔH_{rxn}. Try to keep it close to scale. Should be straight forward.



3. Consider the free radical halogenation (X_2) of **methane** with both **fluorine (F_2)** and **bromine (Br_2)**. Use the information below and the data table provided to answer the following questions.

$CH_4 + X_2 \text{ ----------} \rightarrow CH_3X + HX$

$X_2 \text{ ----------} > X^{\cdot} + X^{\cdot}$

	X=	**F**	**Br**
i) $X^{\cdot} + CH_4 \text{ ----------} > HX + CH_3^{\cdot}$	**ΔH_i**	-130	+74
ii) $CH_3^{\cdot} + X_2 \text{ ----------} > CH_3X + X^{\cdot}$	**ΔH_{ii}**	-302	-100
	ΔH_{rxn}	**-432**	**-26**

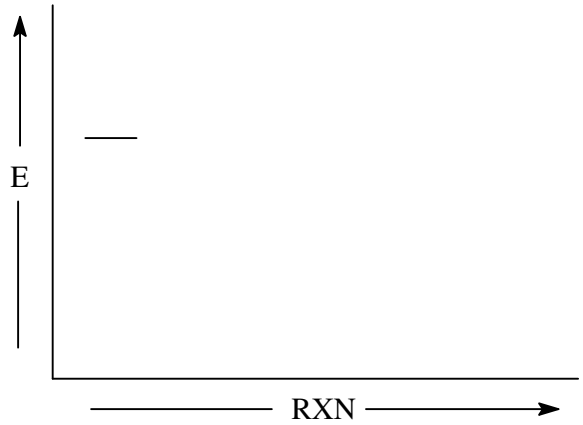
a) Using the two propagation steps shown above (i and ii), calculate ΔH_i and ΔH_{ii}. and ΔH_{rxn} for the reaction with both F_2 and Br_2 (see BDE values on next page).

b) Are the reactions endo- or exothermic overall? __exo_____

c) Which step is the rate determining step in the **bromination** reaction? Step i

d) Which reaction is likely *not* a safe reaction to carry out in the lab? Why? The fluorination is unsafe due to the highly exothermic first step – very small energy of activation with a huge amount of energy liberated.

e) On the axes below, construct a reaction profile for the **bromination** propagation steps. Keep your profile roughly to scale. With vertical arrows, **Label ΔH^o** for step i, ii, and for the overall reaction. You can do that…



Bond	Bond Dissociation Energy (KJ/mol)
CH_3-H	440
CH_3-Br	293
CH_3-F	461
H-Br	366
H-F	570
Br-Br	193
F-F	159