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ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audiotapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is methane. (SL)

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V. Zdravkovich

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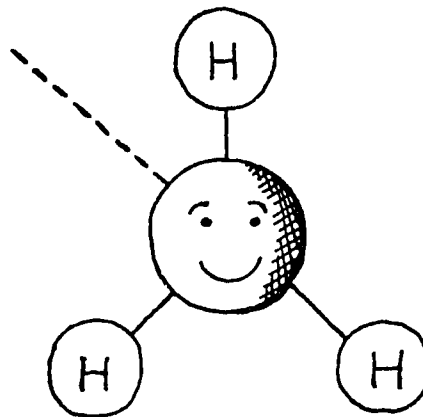
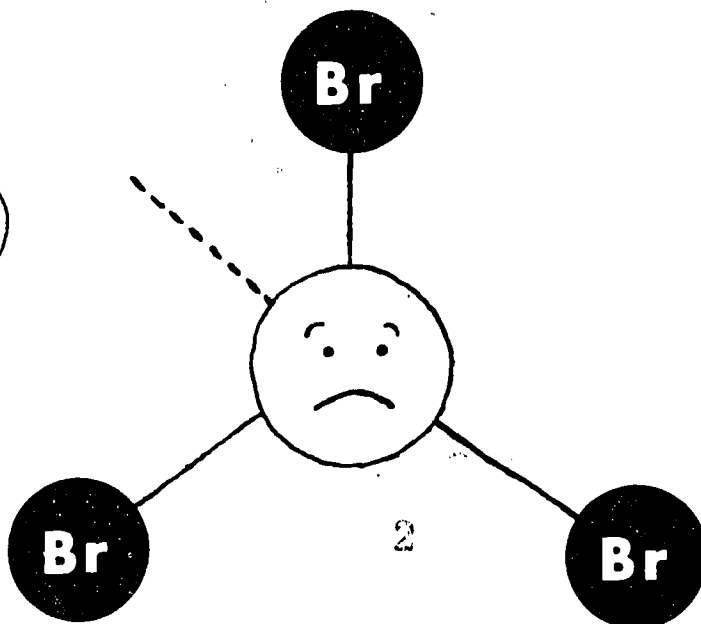
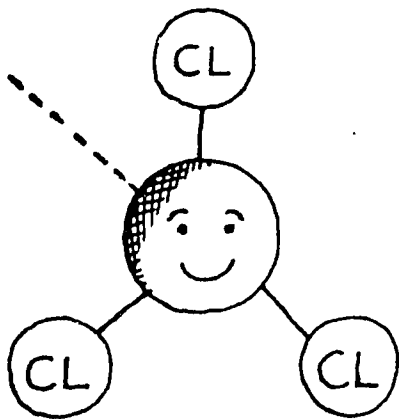
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METHANE



Self Instructional Sequence in

ORGANIC CHEMISTRY

"Copr.," V. Zdravkovich 1976

METHANE

Introduction

The very first statement that a student crossing the threshold of the fascinating and endless field of organic chemistry learns is: carbon is tetrahedral, it forms four identical bonds directed toward the corners of a tetrahedron. Such a simple, unequivocal and well supported statement! Yet only a hundred years ago, prior to 1874, eminent scientists of that era firmly believed in a concept of two dimensions. Organic chemistry has grown from a concept of no dimensions prior to the nineteenth century through a concept of one dimension to the concept of two dimensions. In September and November of 1874 two papers appeared in the scientific world--one written by Jacobus van't Hoff, a Dutch chemist, and another by Jules LeBel, a French chemist. These two scientists working independently in different countries came up with a very similar concept - that of a tetrahedral carbon. This concept was not accepted at once. It was opposed and attacked by eminent chemists of the day. Kolbe, the first chemist to synthesize acetic acid and a well known scientist by then, greeted the theory with the following comments:

"In a recently published paper I pointed out that one of the causes of the present day retrogression of chemical research in Germany is the lack of fundamental chemical knowledge. Under this lack no small number of our professors of chemistry are laboring, with great harm to the science. A consequence of this is the spread of the weed of the apparently scholarly and clever, but actually trivial and stupid natural philosophy, which was displaced fifty years ago by exact natural science, but which is now brought forth again out of the storeroom harboring the errors of the human mind by pseudo-scientists who try to smuggle it, like a fashionably dressed and freshly rouged prostitute, into good society where it does not belong. Anyone to whom this concern seems exaggerated may read the book by Messrs. van't Hoff and Herrmann on the Arrangement of Atoms in Space which has recently appeared and which overflows with fantastic foolishness...A Dr. J. H. van't Hoff of the Veterinary School at Utrecht has no liking, it seems, for exact chemical investigations. He has considered it more convenient to mount Pegasus (apparently borrowed from the Veterinary School) and to proclaim in his book how the atoms appear to him to be arranged in space when he is on the chemical Mt. Parnassus which he has reached by bold flight. It is indicative of the present day, in which critics are few and hated, that two practically unknown chemists, one from a veterinary school and the other from an agricultural institute, judge with such assurance the most important problems of chemistry, which may well never be solved--in particular, the question of the spatial arrangement of atoms--and undertake their answer with such courage as to astonish the real scientists."

METHANE

Definitions

The student will be able to define or explain and illustrate with appropriate examples where applicable the following terms: HYDROCARBON, MONOHALOMETHANE, DIHALOMETHANE, TRIHALOMETHANE, TETRAHALOMETHANE, METHYL FREE RADICAL, SUBSTITUTION REACTION, COMBUSTION REACTION, HEAT OF COMBUSTION, HEAT OF REACTION, ACTIVATION ENERGY, TRANSITION STATE, sp^2 HYBRIDIZATION, CHAIN INITIATING REACTION, CHAIN PROPAGATING STEPS, CHAIN TERMINATING STEPS.

Reactions

The student will be able to identify the reactants and the products in the combustion reaction of methane.

The student will be able to identify the reactants and the products in the halogenation reaction of methane, methylhalide, methylenehalide and haloform.

The student will be able to write the reaction for the incomplete oxidation of methane.

Mechanism

The student will be able to write the step by step mechanism for the halogenation of methane reaction.

The student will be able to identify the chain initiating, the chain propagating and the chain terminating steps in the halogenation reaction mechanism.

The student will be able to identify the rate determining step in the halogenation reaction mechanism.

The student will be able to calculate the ΔH 's for each step of the mechanism and for the overall reaction, utilizing the given bond energies.

The student will be able to draw the energy diagram for the halogenation reaction of methane identifying each step, individual ΔH 's and the overall ΔH .

The student will be able to identify the activation energy and the different ΔH 's on a given energy diagram.

The student will be able to write the structure for a transition state for different steps in the halogenation reaction mechanism.

The student will be able to describe the shape and explain the hybridization on the carbon atom in the methyl free radical.

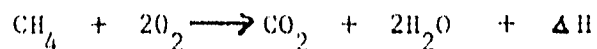
METHANE

You will fill out this exercise by blacking in the appropriate squares on an answer sheet. There may be more than one correct answer for each question.

1. In the following group of compounds identify hydrocarbons.
 - a) SiH_4
 - b) C_6H_6
 - c) CO_2
 - d) C_8H_{18}
2. The shape of methane is:
 - a) pyramidal
 - b) flat - square
 - c) trigonal planar
 - d) tetrahedral
3. The bond angle in methane is:
 - a) 120°
 - b) 90°
 - c) 180°
 - d) 109°
4. The low boiling temperature of methane is due to:
 - a) the strong intermolecular forces between methane molecules
 - b) the weak van der waals forces between methane molecules
 - c) the fact that bonds within methane molecules are nonpolar
 - d) the fact that the methane molecule is nonpolar

SIP No. 2
Form B - Self Evaluation Exercise

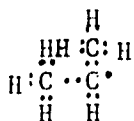
5. The following reaction of methane represents a typical:



- a) oxidation reaction
 - b) combustion reaction
 - c) substitution reaction
 - d) free radical reaction
6. Identify monohalomethane in the group of compounds given below:

- a) CH_2Br_2
- b) CF_4
- c) CH_3I
- d) CHCl_3

7. The following species



is a typical:

- a) positive ion
 - b) free radical
 - c) species with a tendency to give up one electron
 - d) species with a tendency to gain one electron
8. The rate determining step in the halogenation of methane consists of:
- a) homolytic cleavage of the halogen molecule
 - b) abstraction of a halogen atom by a methyl radical
 - c) reaction of methane with a halogen atom
 - d) formation of a methyl free radical and hydrogen halide

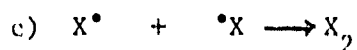
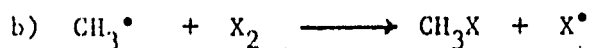
SIP No. 2
Form B - Self Evaluation Exercise

9. Halogenation of methane can be terminated via:
- reaction of two halogen atoms to form a halogen molecule
 - reaction of a halogen molecule with a methyl free radical to form a methyl halide and a halogen atom.
 - reaction of a methyl free radical and a halogen atom to form a methyl halide
 - reaction of two methyl free radicals to form an ethane molecule
10. Correct definitions and properties of activation energy are:
- It is the minimum amount of energy that must be provided by a collision for reaction to occur.
 - It is the difference in energy content between reactants and the transition state.
 - It is high for exothermic reactions.
 - It is at least as high as ΔH for endothermic reactions.
11. One factor which does not affect the rate of a chemical evaluation is the:
- heat released in the reaction
 - energy of activation
 - number of collisions per unit volume and unit time
 - probability that the reactants will be properly oriented
12. The explanation for the observed reactivity sequence in the halogenation of methane (Fluorine - most reactive; Iodine - least reactive) is:
- the low dissociation energy of fluorine
 - the highly exothermic abstraction of the fluorine atom by the methyl radical
 - the difference in activation energies for the abstraction of a halogen atom by a methyl radical expressed in kcal/mole:
$$\Delta H (\text{F}) = -71 \quad \Delta H = -23 \quad \Delta H (\text{Br}) = -21 \quad \Delta H (\text{I}) = -17$$
 - difference in activation energies for the abstraction of a hydrogen atom and formation of a methyl free radical

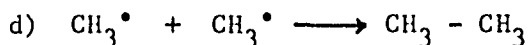
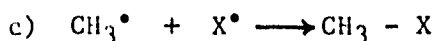
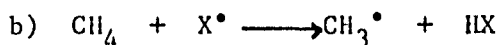
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Form B - Self Evaluation Exercise

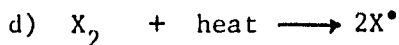
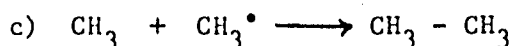
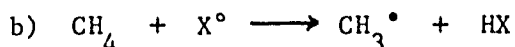
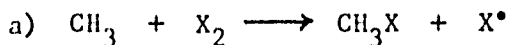
13. The following step or steps represent the chain terminating step in the halogenation of methane.



14. The following step or steps represent the chain propagating step in the halogenation of methane.



15. The rate determining step in the free radical halogenation of methane is:



16. Using the values given on the bond energy card you can calculate the ΔH for the monobromination of methane. This value is:

a) -25 kcal/mole

b) -8 kcal/mole

c) +16 kcal/mole

d) -24 kcal/mole

17. Using the same bond energy card one can calculate the ΔH for the rate determining step or the abstraction of a hydrogen atom from a methane molecule by the chlorine atom. This value is:

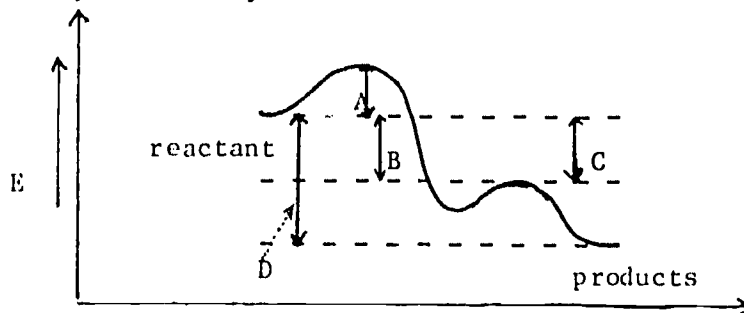
- a) +58 kcal/mole
- b) +1 kcal/mole
- c) -26 kcal/mole
- d) -25 kcal/mole

18. The following statements about an endothermic reaction are correct:

- a) It is a reaction in which energy is released.
- b) It is a reaction for which energy is required.
- c) In an endothermic reaction, the products possess lower amounts of potential energy or "they have a lower potential energy valley" than the reactants.
- d) In an endothermic reaction products possess a higher amount of potential energy or "they have a higher potential energy valley" than the products.

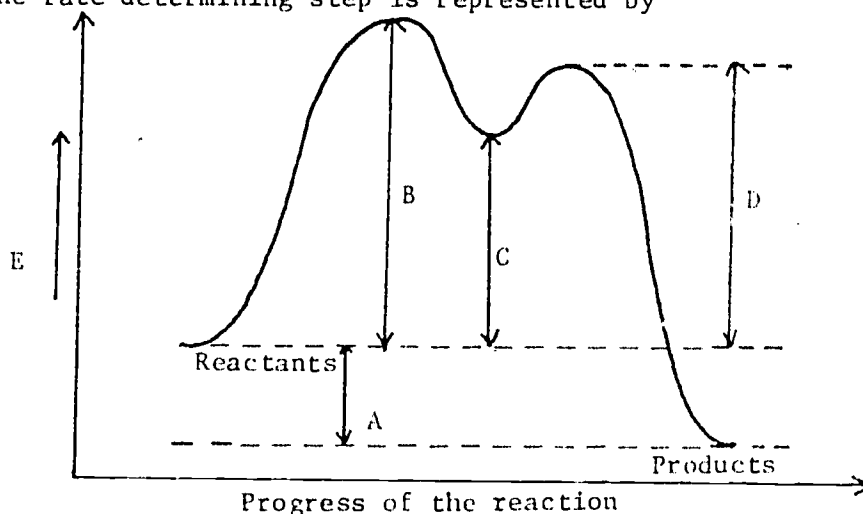
19. In the energy diagram for the chlorination reaction given below the heat of reaction ΔH is represented by distance:

- a) A
- b) B
- c) C
- d) D



20. In the energy diagram for the bromination reaction given below the activation energy for the rate determining step is represented by distance:

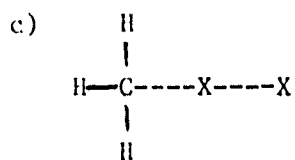
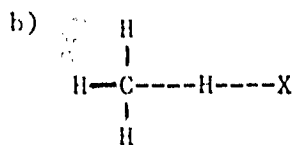
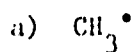
- a) A
- b) B
- c) C
- d) D



21. Inhibitors are:

- a) compounds which speed up a chemical reaction.
- b) compounds which slow down a chemical reaction.
- c) an example of inhibitors is halogen in the halogenation of methane reaction.
- d) an example of inhibitors is oxygen in the halogenation of methane reaction.

22. Identify one of the species below as the transition state for the rate determining step or the abstraction of the hydrogen atom from methane by the halogen atom.



23. The shape of the methyl free radical CH_3^\bullet is:

- a) flat trigonal
- b) pyramidal
- c) tetrahedral
- d) square

METHANE

The reference guide should be used in conjunction with Form B or the Self Evaluation Exercise. The references given are geared specifically toward the questions on Form B.

Question 1	Chapter 2	Section 1
Questions 2, 3	Chapter 2	Section 2, S.I.P. No. 1 - Tape 1
Question 4	Chapter 2	Section 3
Question 5	Chapter 2	Section 6
Question 6	Chapter 2	Sections 7, 9
Question 7	Chapter 2	Section 12
Questions 9, 13, 14,	Chapter 2	Section 13
Questions 16, 17, 18	Chapter 2	Sections 15, 17
Questions 8, 10	Chapter 2	Section 16
Questions 19, 20	Chapter 2	Section 17
Question 12	Chapter 2	Section 20
Question 11	Chapter 2	Sections 18, 19
Question 8	Chapter 2	Section 20
Question 21	Chapter 2	Section 14
Question 22	Chapter 2	Sections 22, 23
Question 23	Chapter 2	Section 21

Morrison and Boyd Organic Chemistry

For Questions 2 and 3, additional explanation can be found in the S.I.P. No. 1 - Tape 1 - sp^3 Hybridization on the Carbon Atom.

For Questions 6, 7, 9, 13, 14, 15 additional explanation and examples can be found in Tape 1 - Methane - Halogenation Reaction.

For Questions 16, 17, 18 additional explanation and examples can be found in Tape 2 - Methane - Energy Aspect of the Halogenation Reaction.

For Questions 8, 10, 12, 19, 20, 22 additional explanation and examples can be found in Tape 3 - Energy Diagram for the Halogenation Reaction.



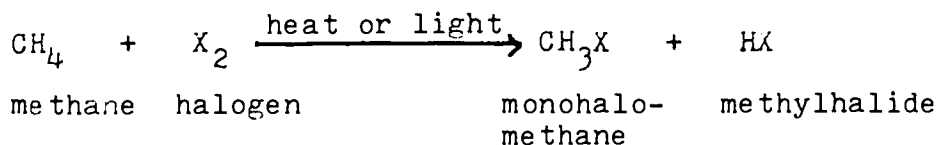
Self Instructional Package 2
Tape 1 - Worksheet

OBJECTIVES:

1. To learn the halogenation reaction of methane.
2. To learn the mechanism of the halogenation reaction of methane.
3. To learn the concept of free radicals.

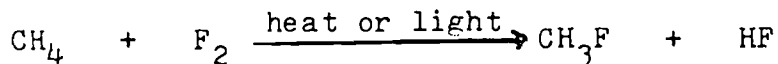
Example 1.

Monohalogenation of Methane



Example 2.

Monofluorination of Methane



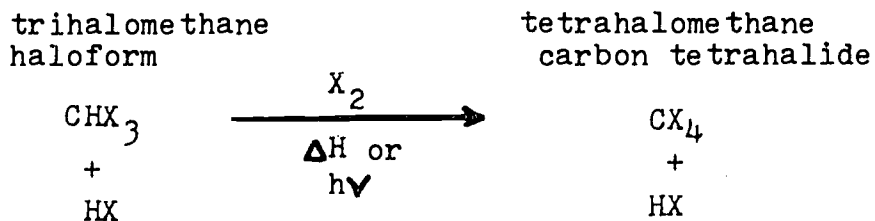
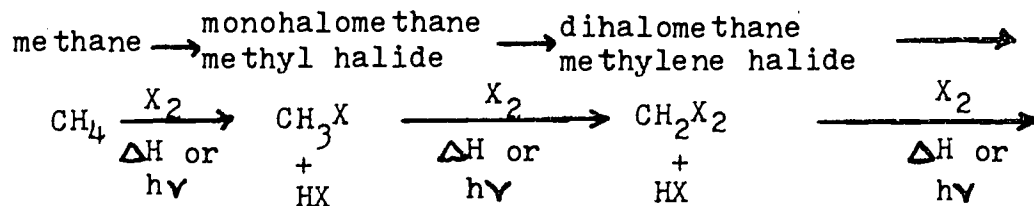
(Heat is conventionally depicted by a small triangle followed by a capital H. Light is conventionally depicted by the letters hv.)

ASSIGNMENT 1. Write the overall reactions for:

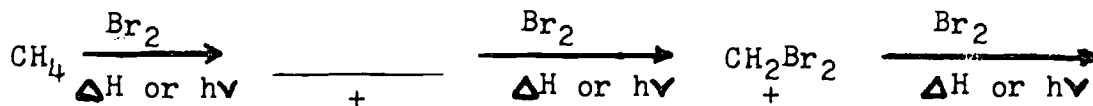
- a) Monochlorination of methane:
- b) Monobromination of methane :
- c) Monoiodination of methane :

Self Instructional Package 2
Tape 1 - Worksheet cont.

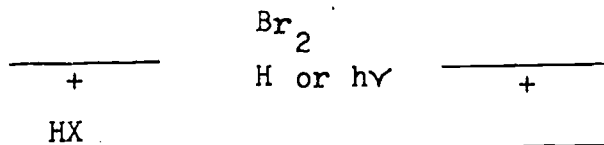
Example 3. Mono, di, tri, and tetrahalogenation of methane



ASSIGNMENT 2. Fill in the blanks for the bromination of methane reaction.



Names:



Names:

Self Instructional Package 2
Tape 1 - Worksheet cont.

ASSIGNMENT 3. Write all the possible products for the following reactions:

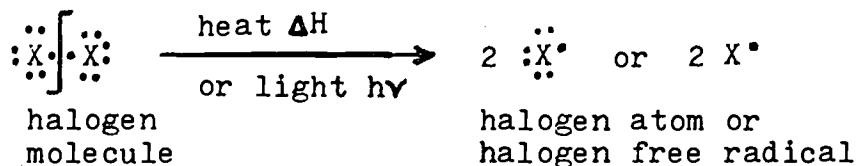
a) Fluorination of methane:

b) Chlorination of methane:

c) Iodination of methane :

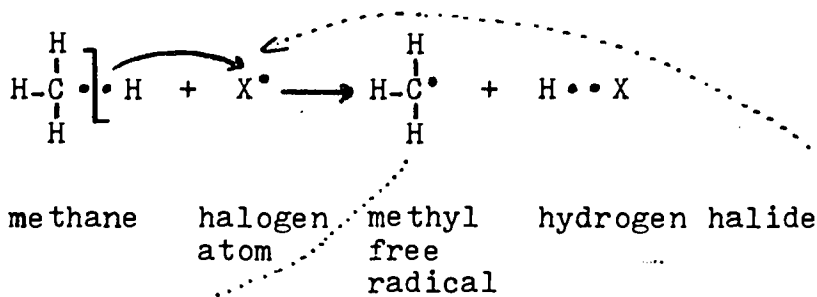
Example 4. Step-by-step mechanism for the free radical halogenation of methane.

I Step 1. Homolytic cleavage - CHAIN INITIATING STEP:

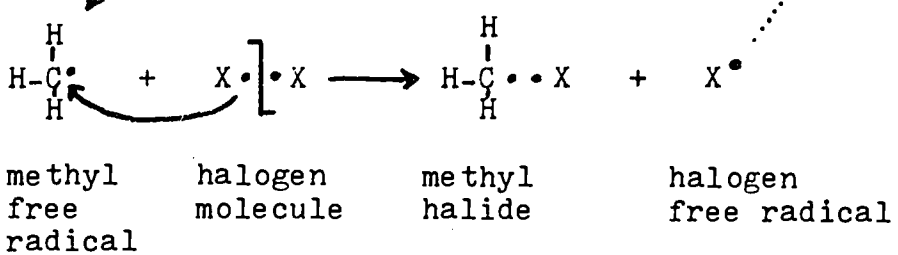


II CHAIN PROPAGATING STEPS:

Step 2.



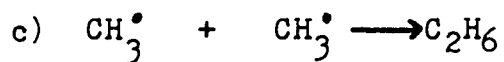
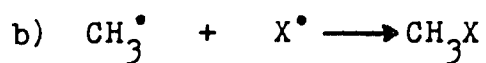
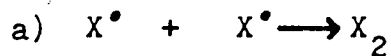
Step 3.



Self Instructional Package 2
Tape 1 - Worksheet cont.

III

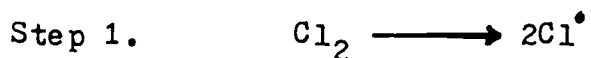
CHAIN TERMINATING STEPS:



ASSIGNMENT 4. Write the step-by-step mechanism for the monobromination of methane.

ASSIGNMENT 5-a Step-by-step mechanism for the monochlorination of methane.

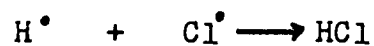
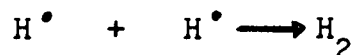
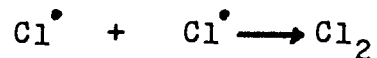
CHAIN INITIATING STEP:



CHAIN PROPAGATING STEPS:

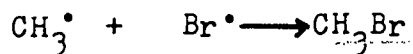
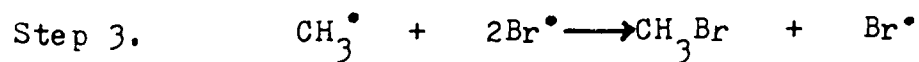
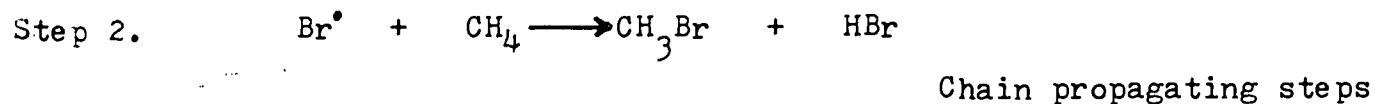
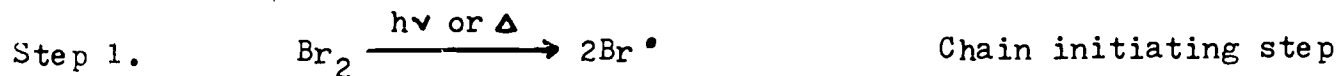


CHAIN TERMINATING STEPS:



Self Instructional Package 2
Tape 1 - Worksheet cont.

ASSIGNMENT 5-b Step-by-step mechanism for the monobromination of methane.



ASSIGNMENT 6. Definition for homolytic cleavage:

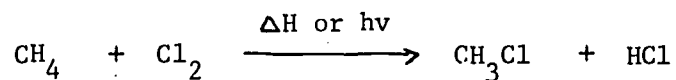
Examples of a typical homolytic cleavage:

METHANE

HALOGENATION REACTION

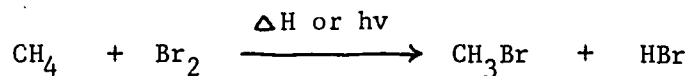
Assignment No. 1

a) Monochlorination of methane:



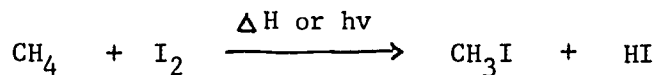
monochloromethane or
methyl chloride

b) Monobromination of methane:



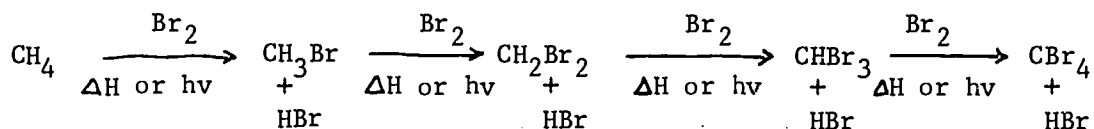
monobromomethane or
methyl bromide

c) Moniodination of methane:



monoiodomethane or
methyl iodide

Assignment No. 2



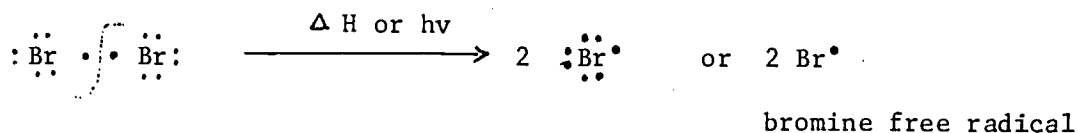
Names: monobromomethane dibromomethane tribromomethane
or
 methyl bromide or methylene bromide or bromoform

 tetrabromomethane
or
 carbontetrabromide

Assignment No. 4

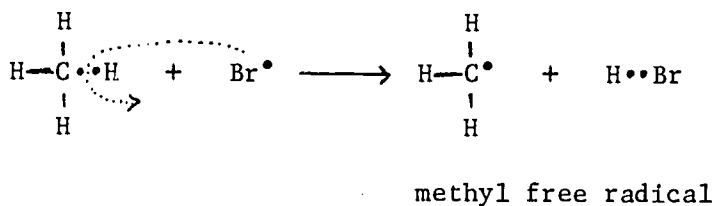
Step-by-step mechanism for the monobromination of methane

I - Chain initiating step

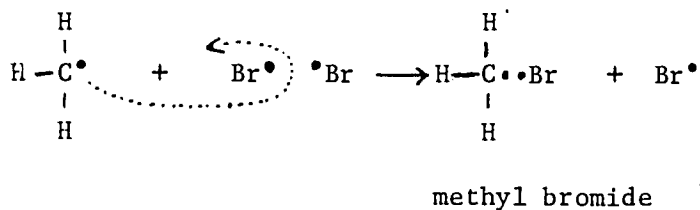


II - Chain propagating steps

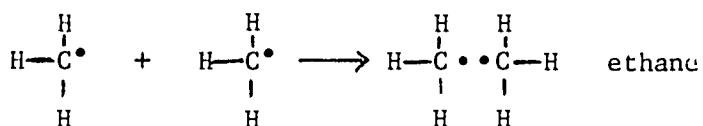
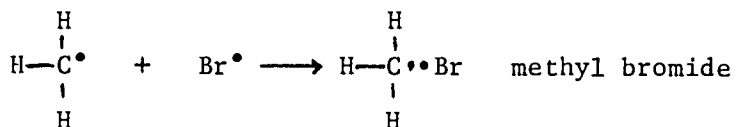
Step 2:



Step 3:



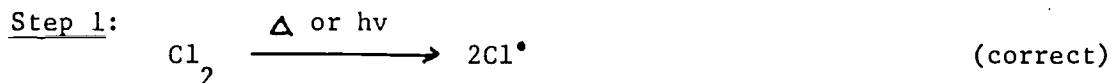
III. Chain terminating steps



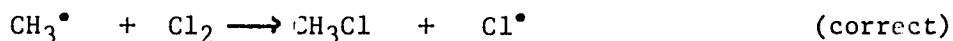
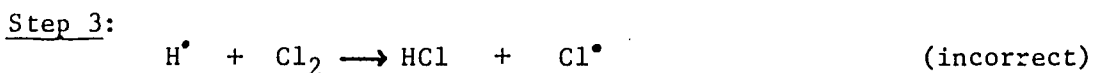
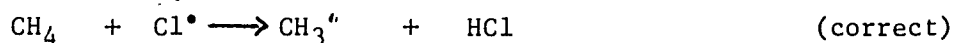
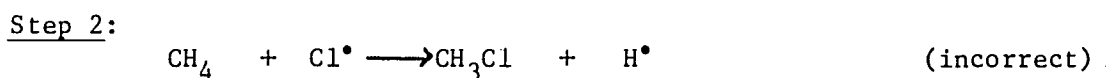
Assignment No. 5

a) Step by step mechanism for the monochlorination of methane

Chain initiating step:



Chain propagating steps:

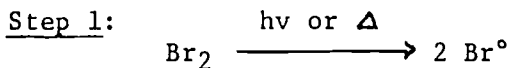


Chain terminating steps:

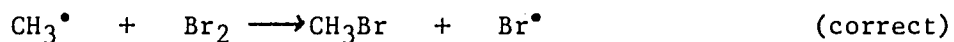
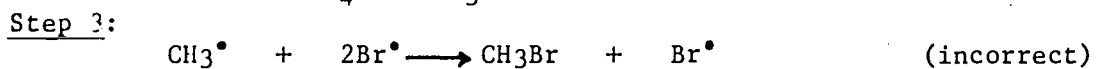
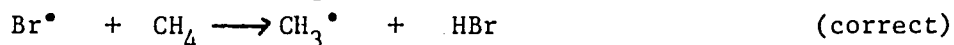
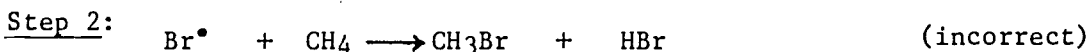


b) Step-by-step mechanism for the monobromination of methane

Chain initiating step:

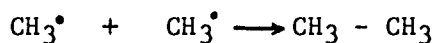


Chain propagating steps:



Assignment No. 5 (continued)

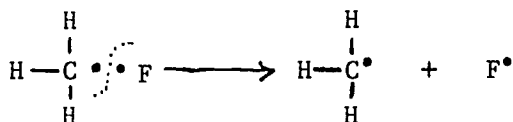
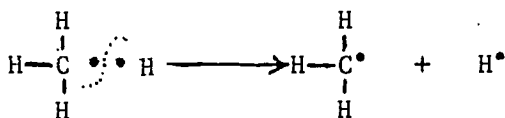
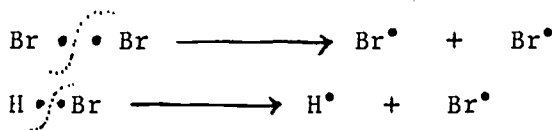
Chain terminating steps:



Assignment No. 6

Homolytic cleavage or homolysis is the bond dissociation in which the two electrons making up the covalent bond break in such a manner that one electron goes to each fragment. Homo in Greek means the same; lysis means a loosening.

Examples of a typical homolytic cleavage:

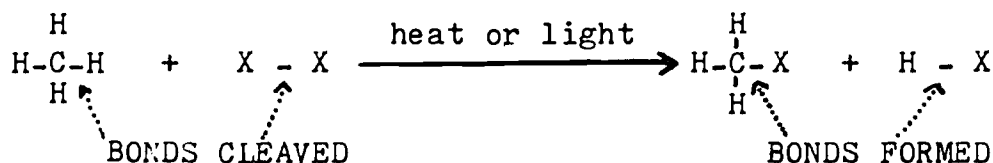


Self Instructional Package 2
Tape 2 - Worksheet

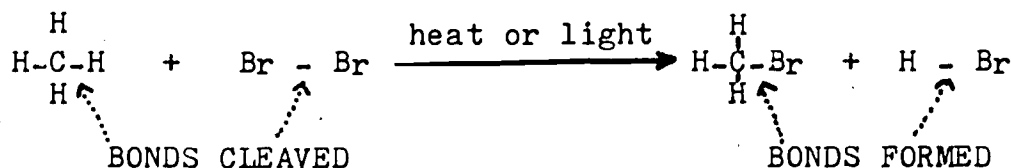
OBJECTIVES:

1. To learn how to calculate the energy or ΔH for the overall halogenation reaction.
2. To learn how to calculate the energy or ΔH for each step of the mechanism.
3. To learn how to calculate the energy or ΔH for the overall reaction from the energies calculated for the individual steps of the mechanism.

Example 1. Halogenation of methane



Example 2. Bromination of methane



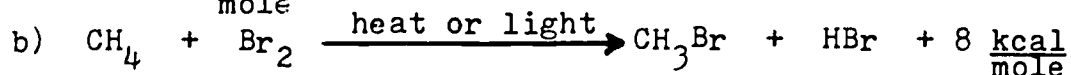
$$104 \frac{\text{kcal}}{\text{mole}} + 46 \frac{\text{kcal}}{\text{mole}}$$

$$70 \frac{\text{kcal}}{\text{mole}} + 88 \frac{\text{kcal}}{\text{mole}}$$

$$150 \frac{\text{kcal}}{\text{mole}} \quad (\text{E required})$$

$$158 \frac{\text{kcal}}{\text{mole}} \quad (\text{E released})$$

a) $\Delta H = -8 \frac{\text{kcal}}{\text{mole}}$ (E is released in the overall reaction.)



ASSIGNMENT 1. Chlorination of methane



a) Bond energies: $\frac{\quad}{\text{C}-\text{H}} \quad \frac{\quad}{\text{Cl}-\text{Cl}} \quad \frac{\quad}{\text{C}-\text{Cl}} \quad \frac{\quad}{\text{H}-\text{Cl}}$

Bonds cleaved:

Bonds formed:

E required:

23

E released:

22

Self Instructional Package 2
Tape 2 - Worksheet cont.

ASSIGNMENT 1. cont.

- b) ΔH for the chlorination reaction.
- c) Chlorination of methane is an ENDOTHERMIC, EXOTHERMIC (circle one) reaction.
- d)

ASSIGNMENT 2. $\Delta H = 102$ for the fluorination of methane reaction.

- a) Write the reaction:
- b) The value for ΔH given above is correct, incorrect (circle one).
If the answer in part a) is incorrect, the correct value is: $\Delta H =$ _____
- c)

ASSIGNMENT 3. Esterification reaction.



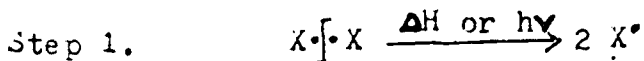
Bond energies: _____

- a) $\Delta H =$
- b) Reaction above is ENDOTHERMIC, EXOTHERMIC (circle one).
- c) Reaction WILL, WILL NOT (circle one) take place spontaneously.

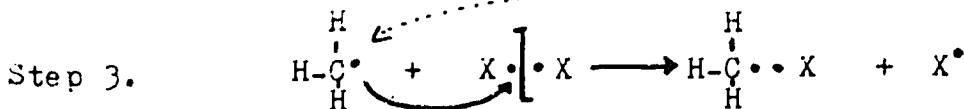
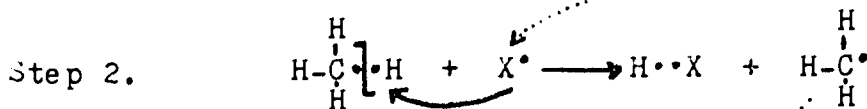
Self Instructional Package 2
Tape 2 - Worksheet cont.

Example 3. Mechanism of the halogenation of methane.

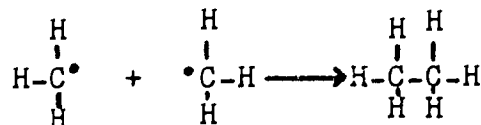
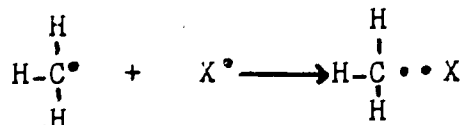
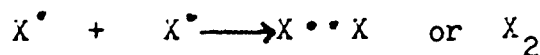
I CHAIN INITIATING STEP:



II CHAIN PROPAGATING STEPS:

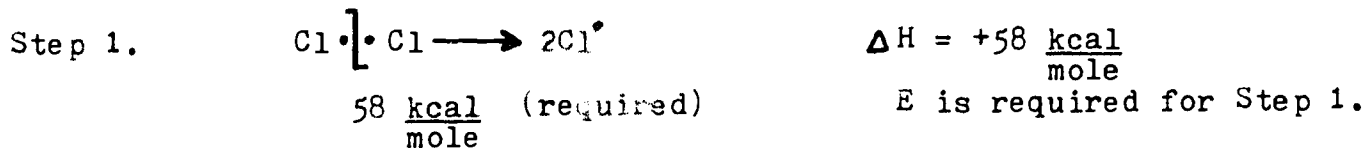


III CHAIN TERMINATING STEPS:

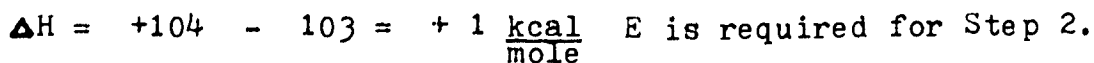
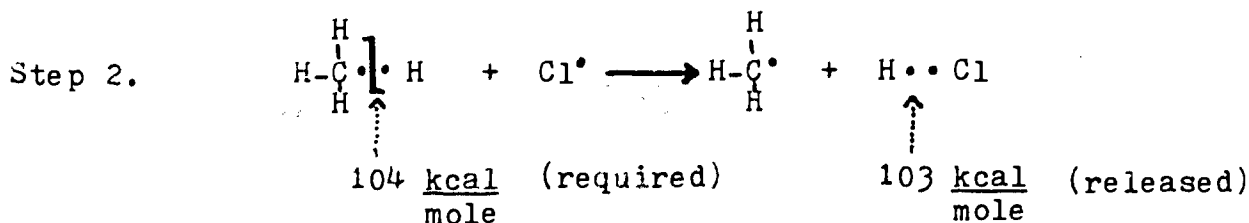


Example 4. Mechanism

I Chain Initiating Step

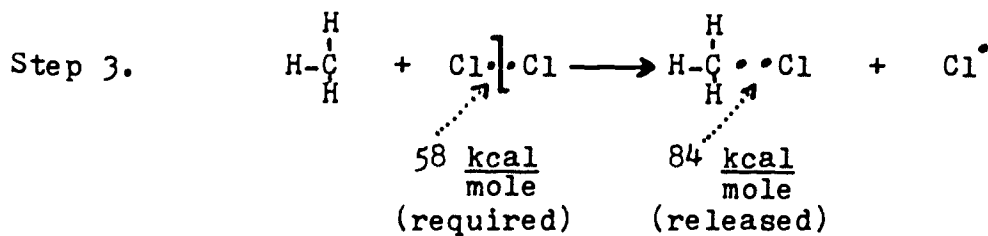


II Chain Propagating Steps



Self Instructional Package 2
Tape 2 - Worksheet cont.

Example 4. cont.



$$\Delta H = +58 - 84 = -26 \frac{\text{kcal}}{\text{mole}} \quad \text{E is released in Step 3.}$$

ASSIGNMENT 4. Monobromination of methane

I Chain initiating step

Step 1.

$$\Delta H = \underline{\hspace{2cm}}$$

Step 1. is **ENDOTHERMIC**
EXOTHERMIC

II Chain propagating steps

Step 2.

$$\Delta H = \underline{\hspace{2cm}}$$

Step 2. is **ENDOTHERMIC**
EXOTHERMIC

Step 3.

$$\Delta H = \underline{\hspace{2cm}}$$

Step 3. is **ENDOTHERMIC**
EXOTHERMIC

ASSIGNMENT 5. Monoiodination of methane

$$\begin{array}{l}
 \Delta H_1 = + 56 \frac{\text{kcal}}{\text{mole}} \\
 \Delta H_2 = - 36 \frac{\text{kcal}}{\text{mole}} \\
 \Delta H_3 = + 20 \frac{\text{kcal}}{\text{mole}} \\
 \Delta H_4 = + 33 \frac{\text{kcal}}{\text{mole}}
 \end{array}$$

Self Instructional Package 2
Tape 2 - Worksheet cont.

ASSIGNMENT 5. cont.

ΔH_1 corresponds to step _____. It should be properly written with a + or a - sign _____.

ΔH_2 corresponds to step _____. It should be properly written with a + or a - sign _____.

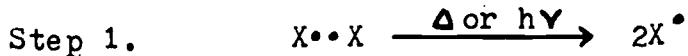
ΔH_3 corresponds to step _____. It should be properly written with a + or a - sign _____.

ΔH_4 corresponds to step _____. It should be properly written with a + or a - sign _____.

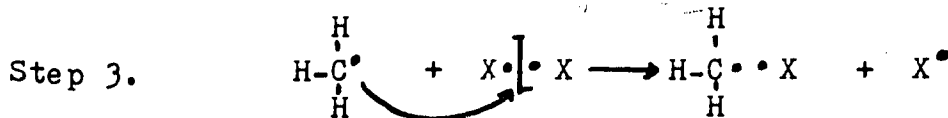
Example 5. Halogenation of methane



I Chain initiating step



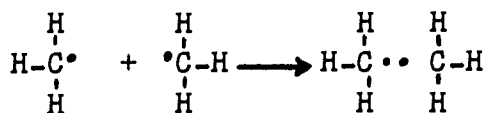
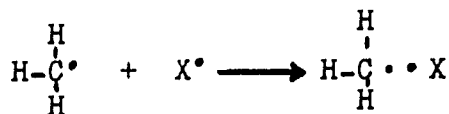
II Chain propagating steps



Self Instructional Package 2
Tape 2 - Worksheet cont.

Example 5. cont.

III Chain terminating steps



The combination of the two chain propagating steps:

_____ \longrightarrow _____
Combined left sides of
steps 2 and 3.

_____ \longrightarrow _____
Combined right sides of
steps 2 and 3.

ASSIGNMENT 6. Monobromination reaction of methane

Utilizing the ΔH 's for the individual steps of the reaction mechanism as calculated in ASSIGNMENT 4, the ΔH for the overall reaction is: $\Delta H = \underline{\hspace{2cm}}$.
SHOW WORK!

Monoiodination reaction of methane

Utilizing the ΔH 's for the individual steps of the reaction mechanism as calculated in ASSIGNMENT 5, the ΔH for the overall reaction is: $\Delta H = \underline{\hspace{2cm}}$.
SHOW WORK!

Self Instructional Package 2
Tape 2 - Worksheet cont.

ASSIGNMENT 7.



Fluorination of methane

Answer provided by Forgetful Flora is:

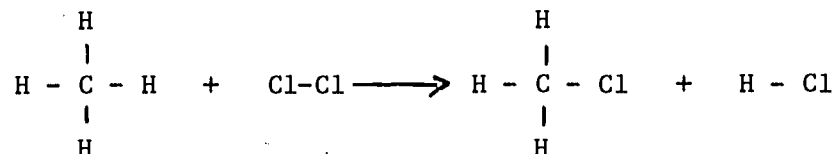
$\Delta H = 64 \text{ kcal/mole.}$

- a) Mark her answer correct or incorrect.
- b) Supply the correct sign.
- c) If the answer is not correct, find how the student arrived at her answer. Explain the mistake she made.
- d) Show all the work which the student failed to show.

METHANE

Assignment No. 1 - Energy aspect of the halogenation reaction

Chlorination of methane:



a) Bond Energies 104 kcal/mole 58 kcal/mole 84 kcal/mole 103 kcal/mole

Bonds cleaved: C - H Bond and Cl - Cl Bond

Bonds formed: C - Cl Bond and H - Cl Bond

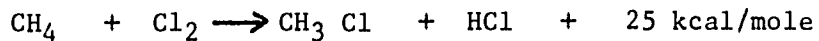
E Required: 162 kcal/mole

E Released: 187 kcal/mole

b) ΔH for the chlorination reaction is: $162 - 187 = -25$ kcal/mole

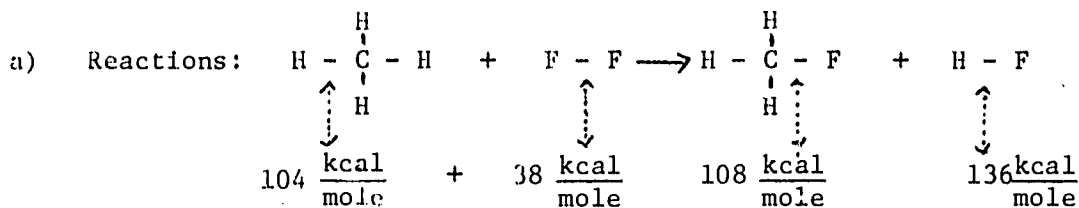
c) Chlorination of methane is an exothermic reaction

d) $\Delta H = -25$ kcal/mole



Assignment No. 2

Fluorination of methane: $\Delta H = 102$



$$\Delta H = (104 + 38) - (108 + 136) = 142 - 244 = -102 \frac{\text{kcal}}{\text{mole}}$$

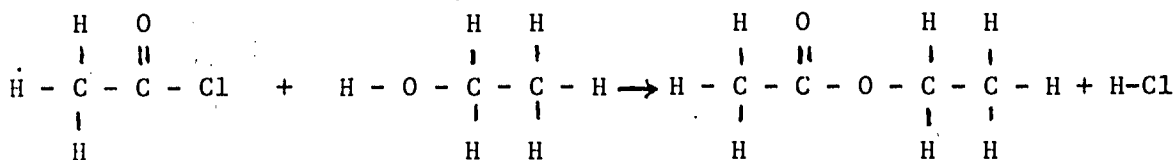
$$\Delta H = -102 \frac{\text{kcal}}{\text{mole}}$$

The missing factors are: 1. Sign indicating that the reaction is exothermic

2. Unit

Assignment No. 3

Esterification reaction:



$$\text{Bond Energies: } 74 \frac{\text{kcal}}{\text{mole}} \quad 104 \frac{\text{kcal}}{\text{mole}} \quad 36 \frac{\text{kcal}}{\text{mole}} \quad 103 \frac{\text{kcal}}{\text{mole}}$$

a) $\Delta H = (74 + 104) - (36 + 103) = 178 - 139 = +39 \frac{\text{kcal}}{\text{mole}}$

b) Esterification reaction above is an endothermic reaction

c) It will NOT take place spontaneously

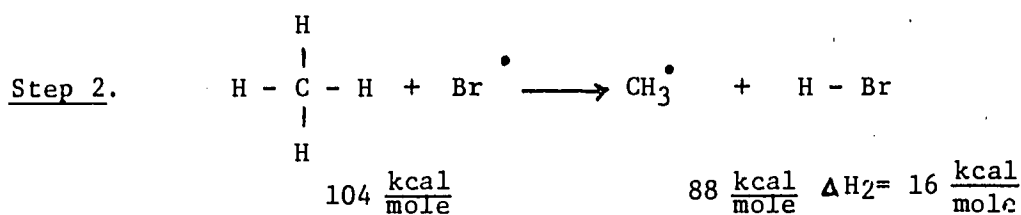
Assignment No. 4

Monobromination of methane:

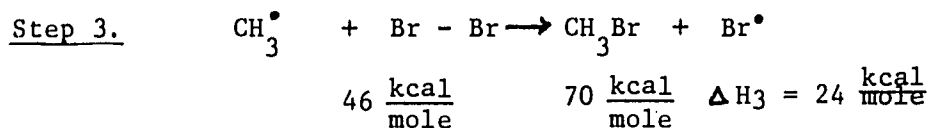
Chain initiating step



Chain propagating steps:



Endothermic



Exothermic

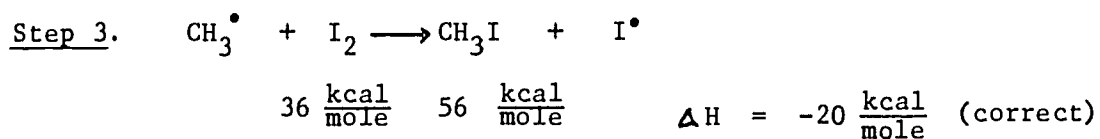
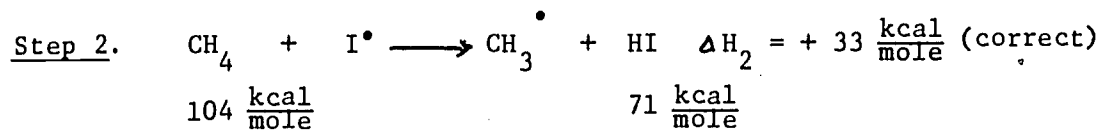
Assignment No. 5

Monoiodination of methane:

Chain initiating step

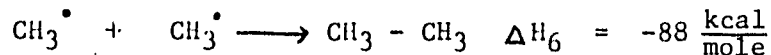
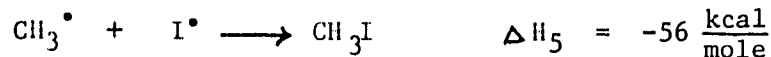


Chain propagating steps:



Assignment No. 5 (continued)

Chain terminating steps:



ΔH_1 corresponds to Step 5. It should be properly written with a (+) or a (-) sign (-).

ΔH_2 corresponds to Step 1. It should be properly written with a (+) or a (-) sign (+).

ΔH_3 corresponds to Step 3. It should be properly written with a (+) or a (-) sign (-).

ΔH_4 corresponds to Step 2. It should be properly written with a (+) or a (-) sign. (+).

Assignment No. 6

Monobromination of methane:

$$\text{From Assignment 4: } \Delta H_2 \text{ (Step 2)} = + 16 \frac{\text{kcal}}{\text{mole}}$$

$$\Delta H_3 \text{ (Step 3)} = - 24 \frac{\text{kcal}}{\text{mole}}$$

$$\Delta H \text{ (overall)} = \Delta H_2 + \Delta H_3 = + 16 - 24 = -8 \frac{\text{kcal}}{\text{mole}}$$

Monoiodination of methane:

$$\text{From Assignment 5: } \Delta H_2 \text{ (Step 2)} = + 33 \frac{\text{kcal}}{\text{mole}}$$

$$\Delta H_3 \text{ (Step 3)} = -20 \frac{\text{kcal}}{\text{mole}}$$

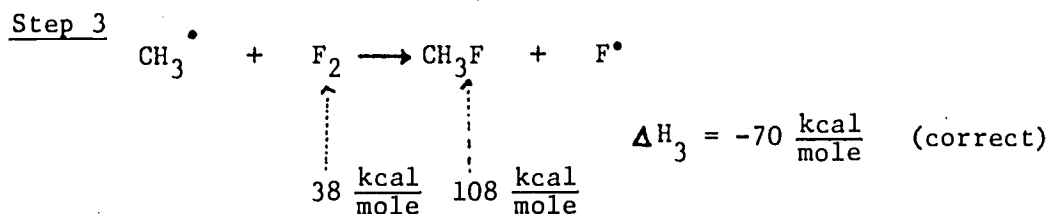
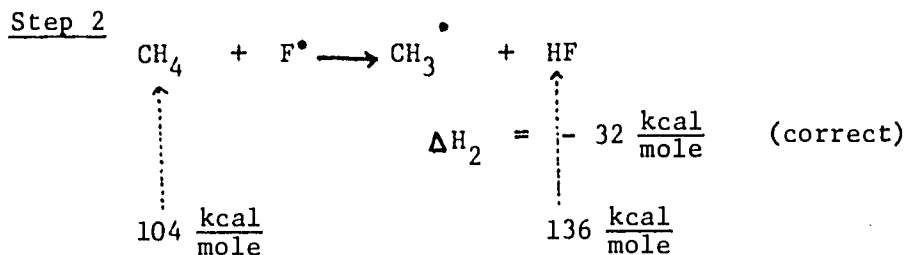
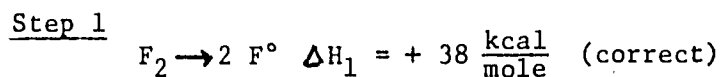
$$\Delta H \text{ (overall)} = \Delta H_2 + \Delta H_3 = + 33 - 20 = + 13 \frac{\text{kcal}}{\text{mole}}$$

Monofluorination of methane:

Answer submitted by Forgetful Flora:

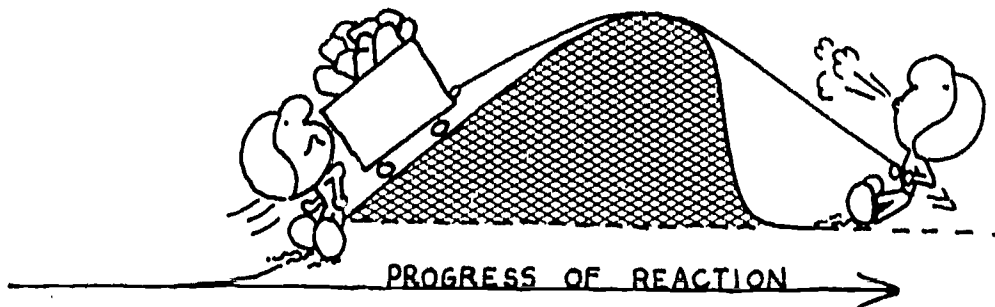
$$\Delta H = 64 \frac{\text{kcal}}{\text{mole}}$$

- a) Incorrect
- b) Forgetful Flora has combined the ΔH 's of not only the two chain propagating steps as she was supposed to do, but she combined the chain initiating step or Step 1 and the two chain propagating steps or Steps 2 and 3. She has also forgotten the sign which should have been (-).



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = + 38 - 32 - 70 = -64 \frac{\text{kcal}}{\text{mole}} \quad (\text{incorrect})$$

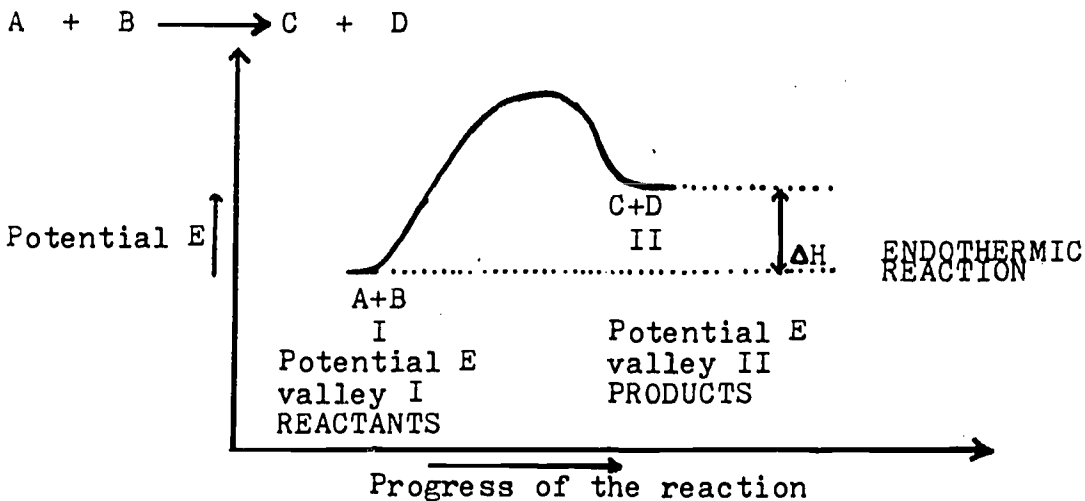
$$\Delta H = \Delta H_2 + \Delta H_3 = -32 - 70 = -102 \frac{\text{kcal}}{\text{mole}} \quad (\text{correct})$$



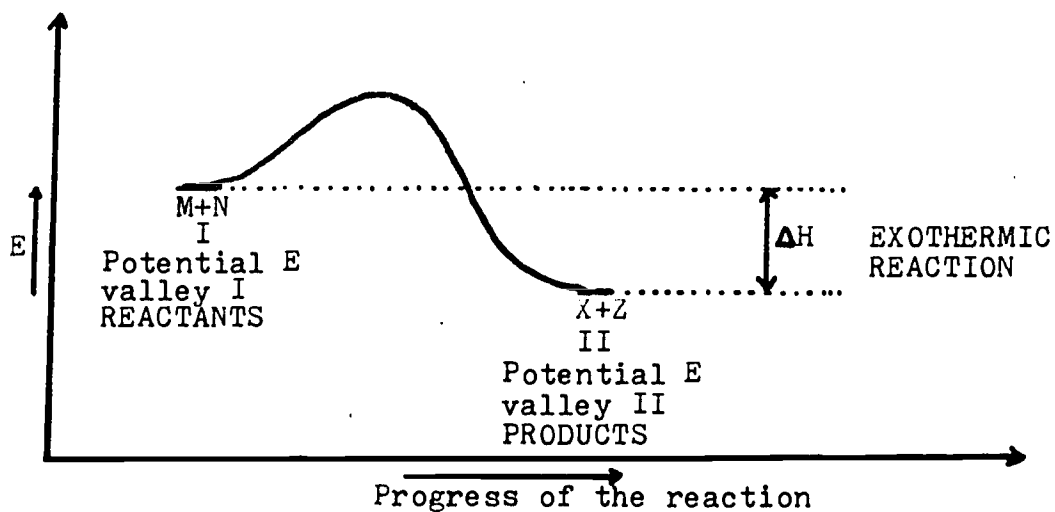
Self Instructional Package 2
Tape 3 - Worksheet

- OBJECTIVES:
1. To learn how to draw an energy versus progress of reaction diagram (E diagram) for a given halogenation reaction.
 2. To learn how to interpret a given E diagram.
 3. To learn the meaning and the definition for the ACTIVATION ENERGY - E_{act}
 4. To learn the meaning and the definition for the TRANSITION STATE.

Example 1.



Example 2.



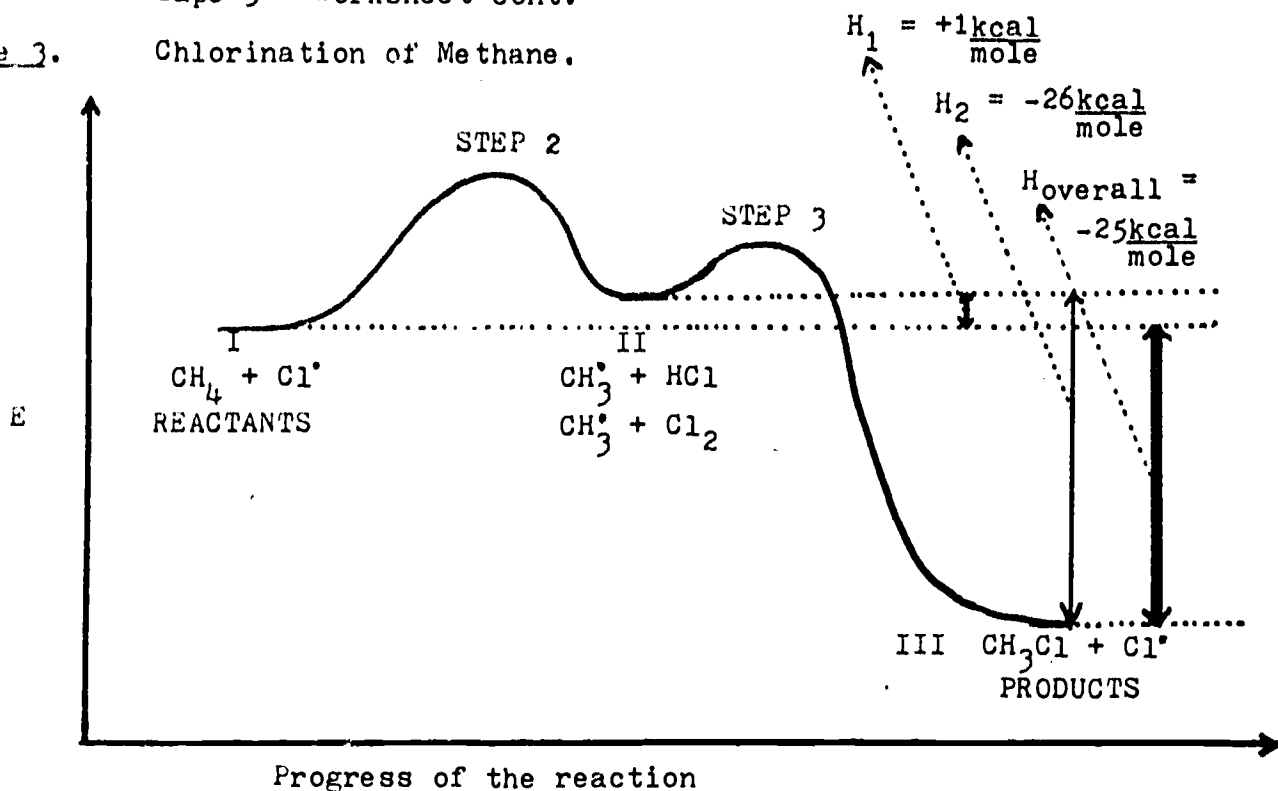
Self Instructional Package 2
Tape 3 - Worksheet cont.

ASSIGNMENT 1. Draw the potential E versus progress of reaction diagram for the rate determining step for: a) the chlorination and b) the bromination reaction.

ASSIGNMENT 2. Draw the potential energy versus progress of reaction diagram for step 3 (formation of methyl chloride) for the chlorination reaction.

Example 3.

Chlorination of Methane.

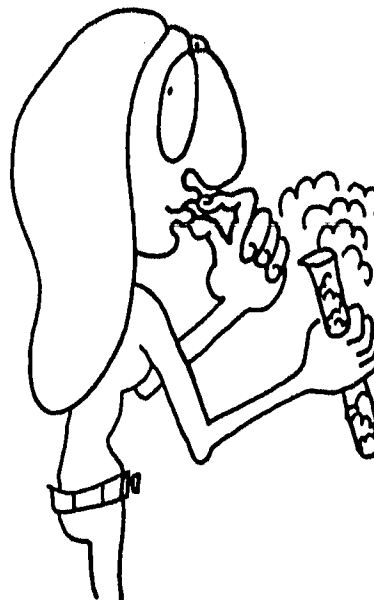


$$\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 = +1 \text{ kcal/mole} - 26 \text{ kcal/mole}$$

$$\Delta H_{\text{overall}} = -25 \text{ kcal/mole.}$$

ASSIGNMENT 3.

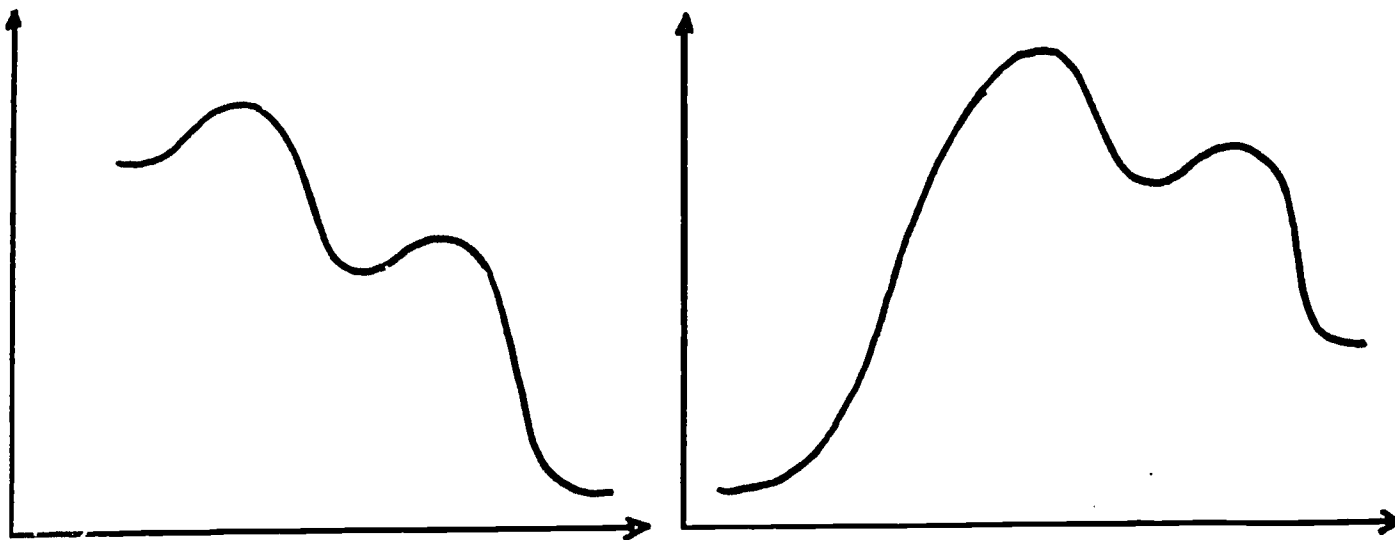
- a) Draw the potential E versus reaction progress diagram for the bromination of methane.
- b) Indicate all particles involved i.e. reactants, products, and intermediate species.
- c) Identify ΔH_1 , ΔH_2 , and the overall ΔH .



ASSIGNMENT 4.

Forgetful Frieda has been asked to draw energy diagrams for the iodination and fluorination reaction. Absent-mindedly she failed to label anything on either diagram. Your task is:

- to identify the given diagram as the diagram for the fluorination or the iodination reaction.
- to indicate all the particles involved and label them correctly on the diagram.
- to assign the correct values for the ΔH 's or heats of reaction for EACH STEP OF BOTH REACTIONS, and to clearly identify and label them on the diagram.
- to assign the correct values for the ΔH 's for the overall reactions and to identify them on the diagram.

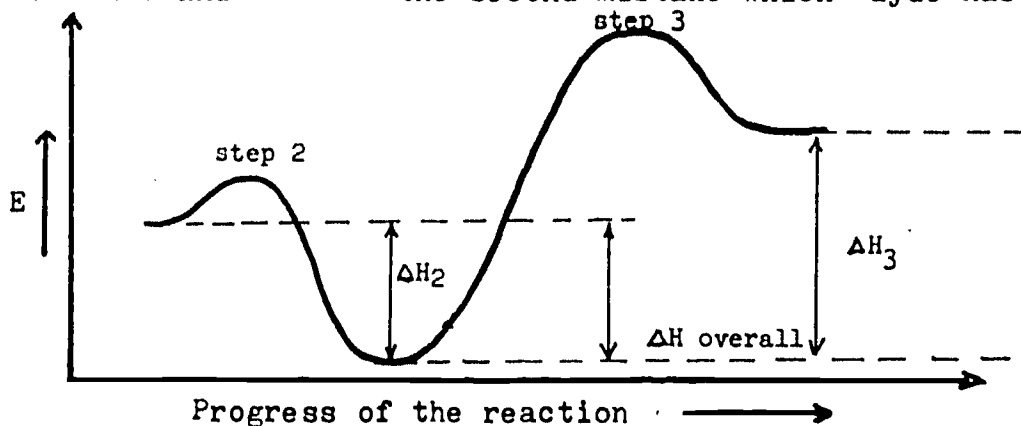


ASSIGNMENT 5.



Confused Clyde was asked to correctly draw the potential energy versus progress of reaction diagram for the monobromination reaction. He has diligently and meticulously completed his assignment. However, being confused, as usual, he has made TWO mistakes. One is that he failed to indicate the particles and energies involved and to write them in their proper places on the diagram. It is your task now to:

- complete Clyde's diagram with all the necessary notations and missing particles.
- find and EXPLAIN the second mistake which Clyde has made.



$$\Delta H_2 = -16 \text{ kcal/mole}$$

$$\Delta H_3 = +24 \text{ kcal/mole}$$

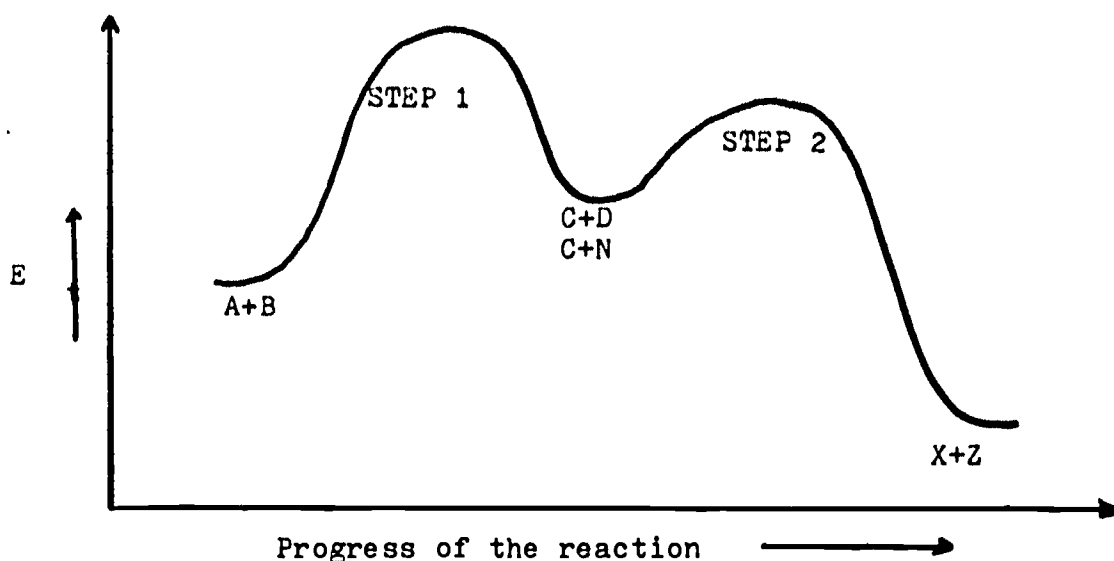
$$\Delta H_{\text{overall}} = +8 \text{ kcal/mole}$$

Self Instructional Package 2
Tape 3 - Worksheet cont.

ASSIGNMENT 6. On the energy diagram from example three, identify and point out the E_{act} - activation energy - for the reaction:

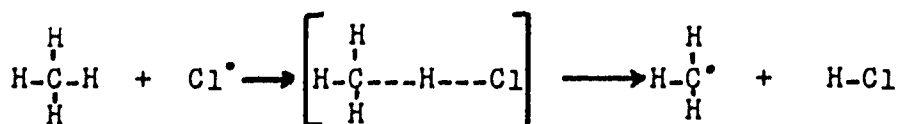
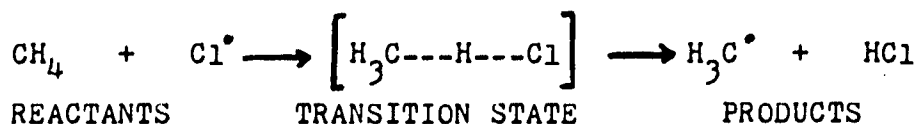


ASSIGNMENT 7. On the energy diagram below, identify:
a) the activation energies for step 1 and step 2.
b) ΔH_1 and ΔH_2 .
c) overall ΔH .



ASSIGNMENT 8. Label and assign the correct E_{act} for each step in the diagrams from the first five assignments.

Example 4.



ASSIGNMENT 9. a) Draw the transition states for the chain initiating and the chain propagating steps for the monobromination reaction.
b) Identify the transition states for the two chain propagating steps on the diagram from assignment three.

METHANE
ENERGY DIAGRAM OF THE HALOGENATION REACTION

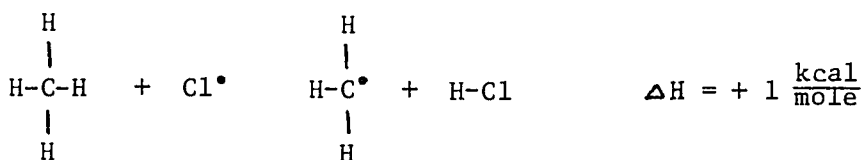
Assignment No. 1

Monochlorination reaction

The rate determining step or "The Difficult Step" in the mechanism is:

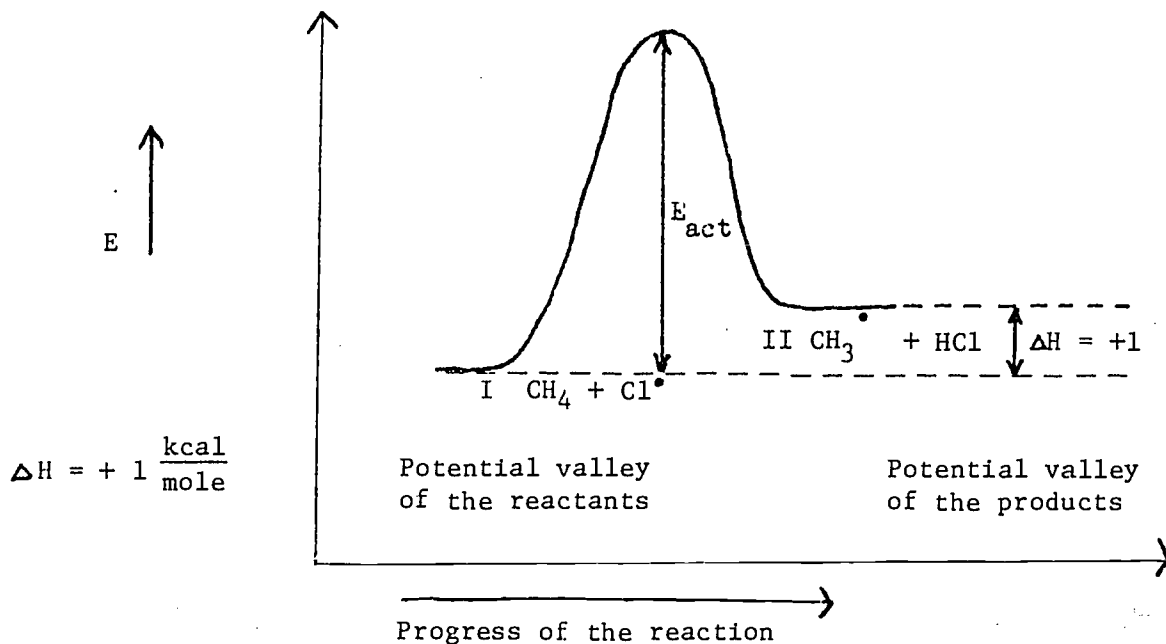
Step 1. (abstraction of H atom by the chlorine atom and the formation of methyl free radical)

Step 2.



104 kcal/mole

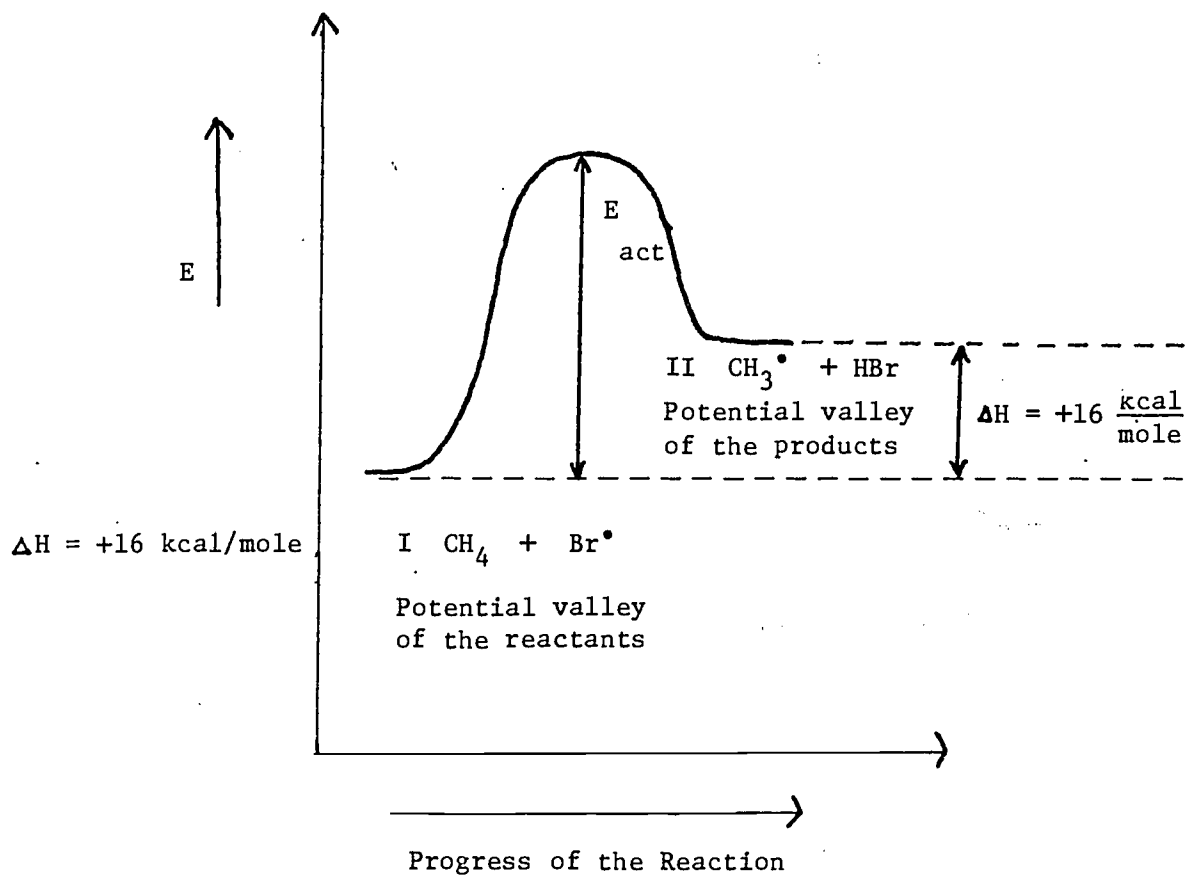
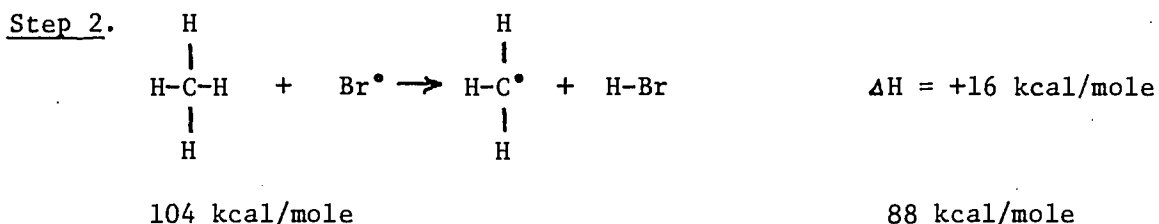
103 kcal/mole



Assignment No. 1 (continued)

Monobromination reaction

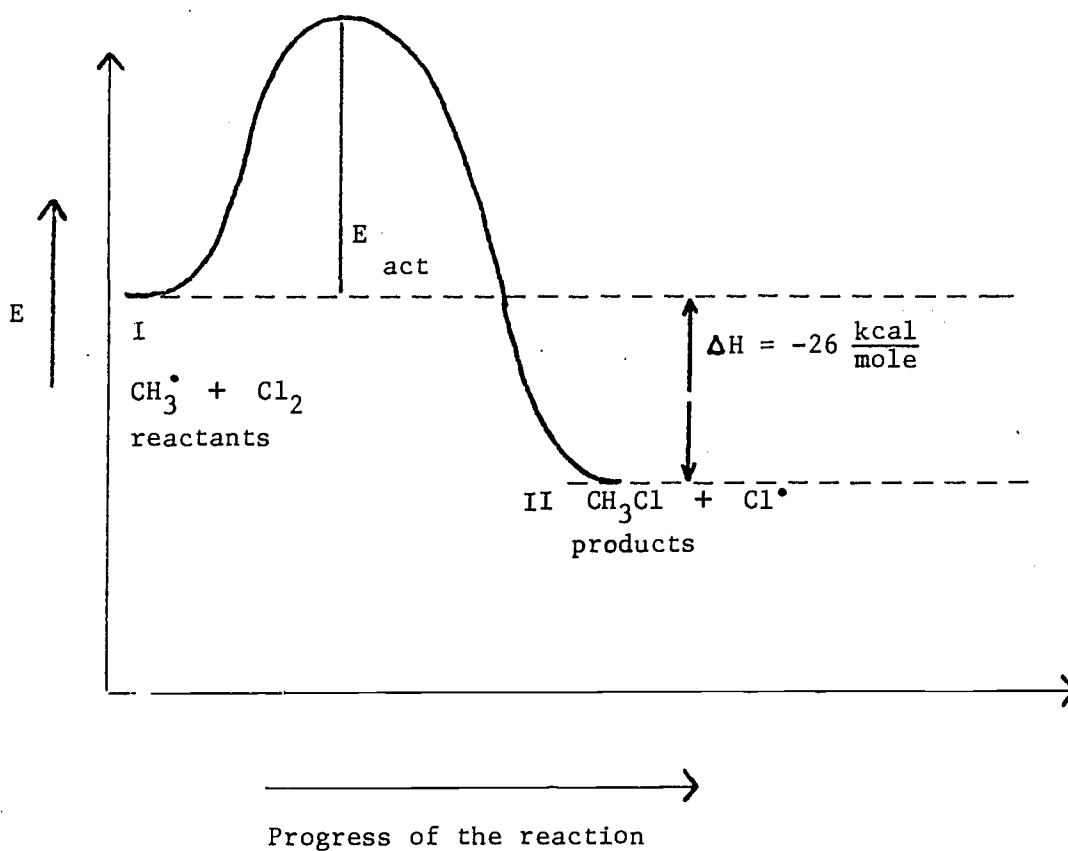
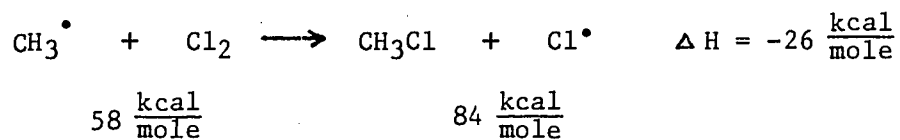
The rate determining step is the Step 2 (abstraction of H atom by the bromine atom and the formation of methyl free radical).



Assignment No. 2

Monochlorination reaction:

Step 3:



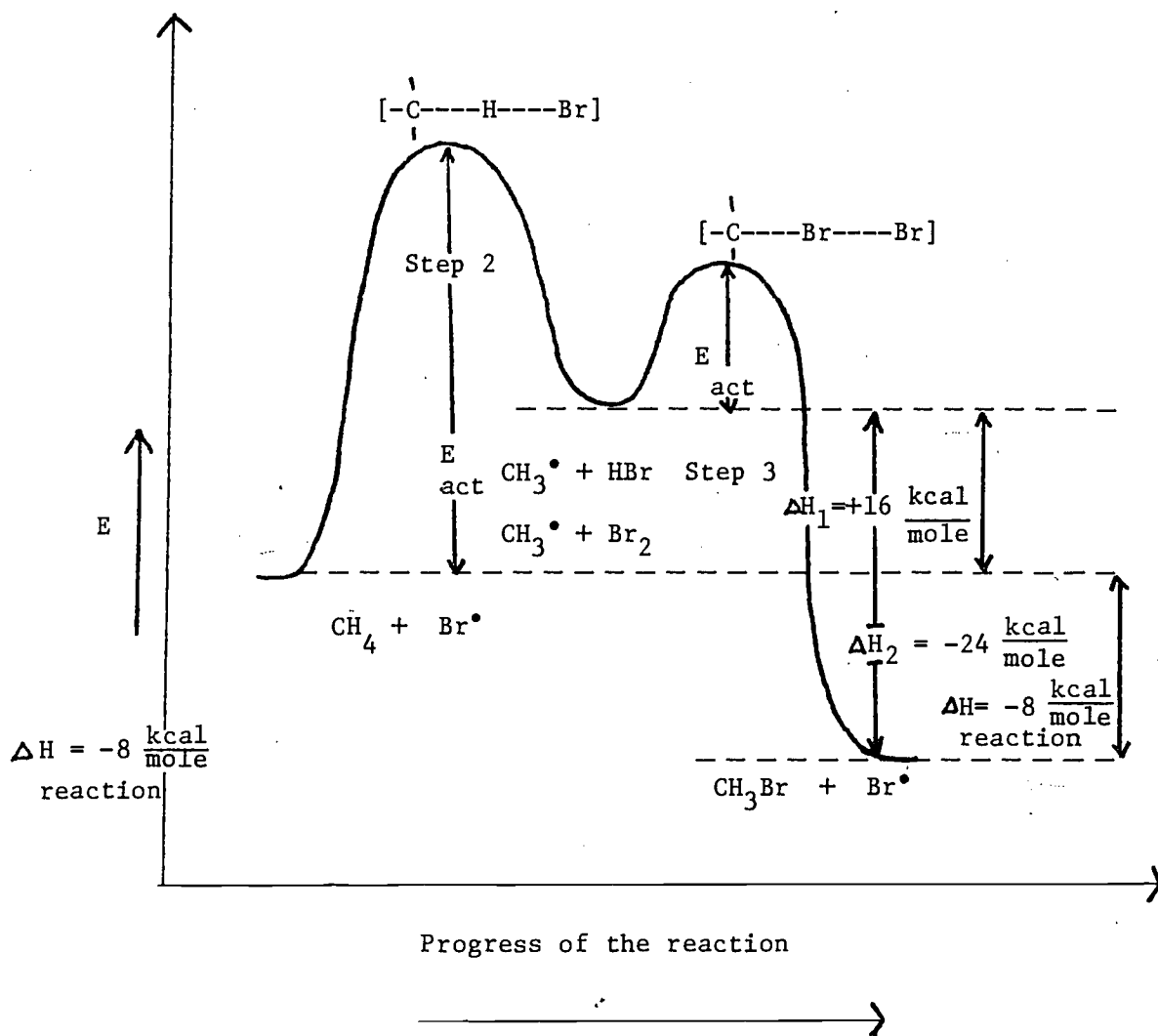
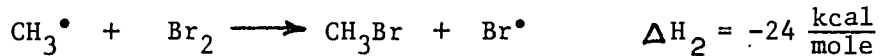
Assignment No. 3

Potential E diagram for the bromination of methane

Step 2

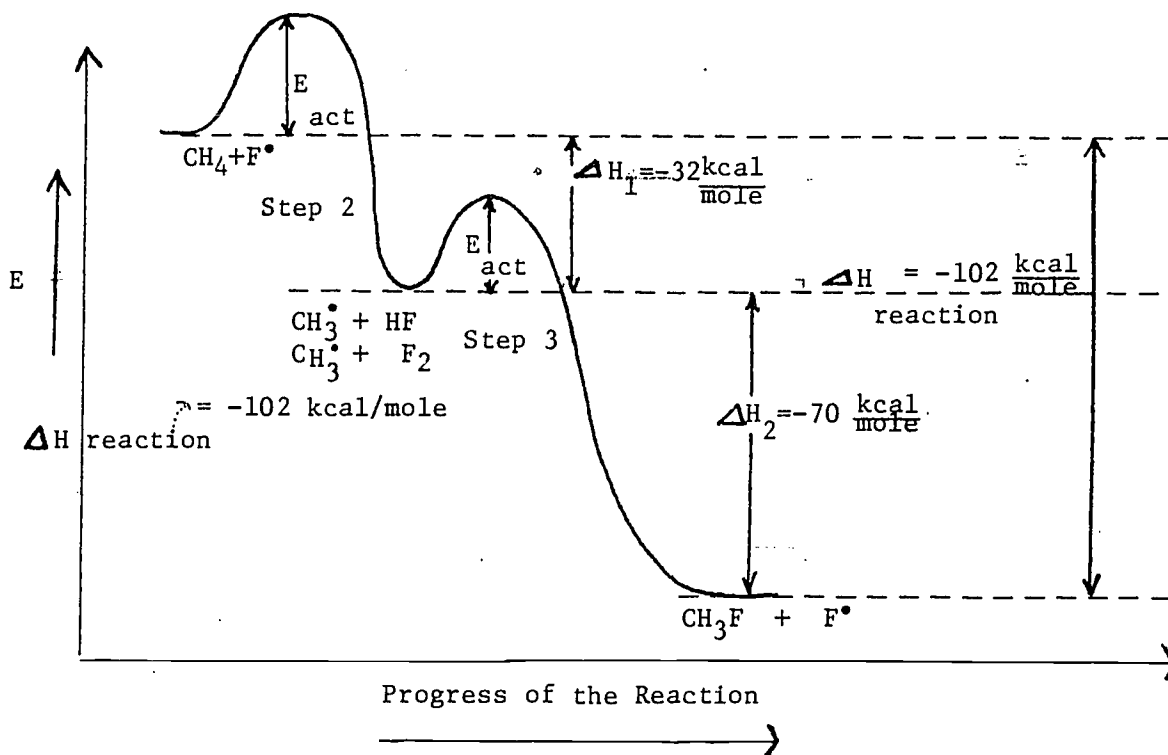


Step 3

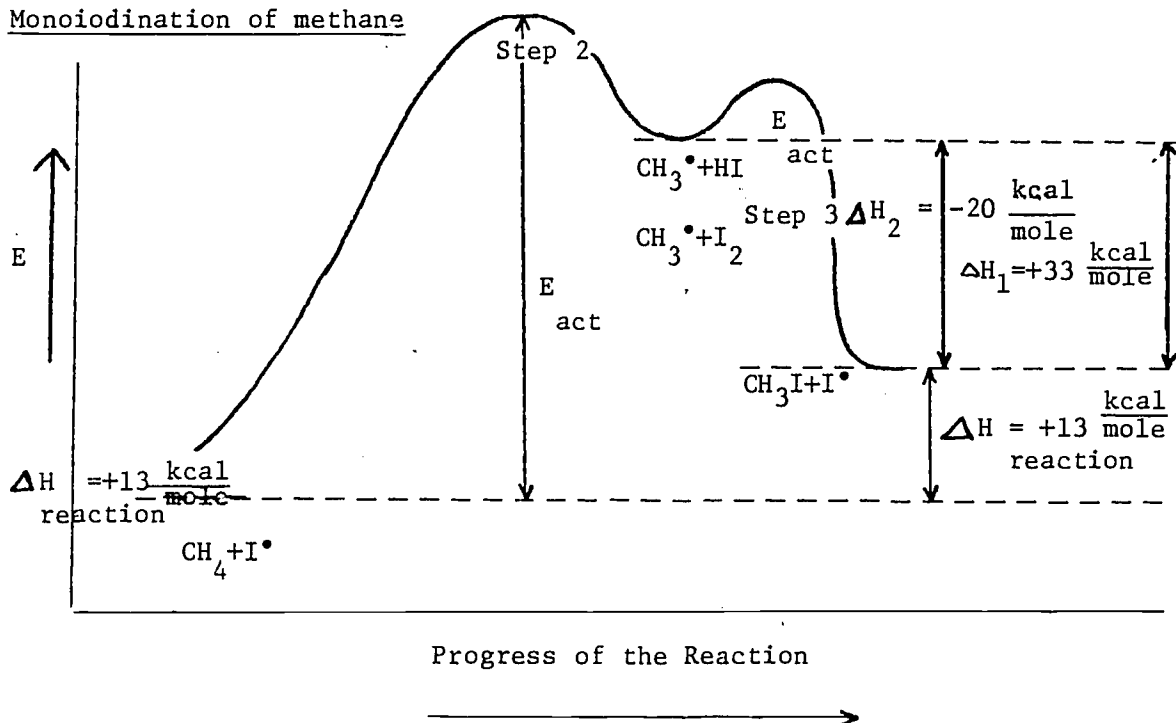


Assignment 4

Monofluorination of methane

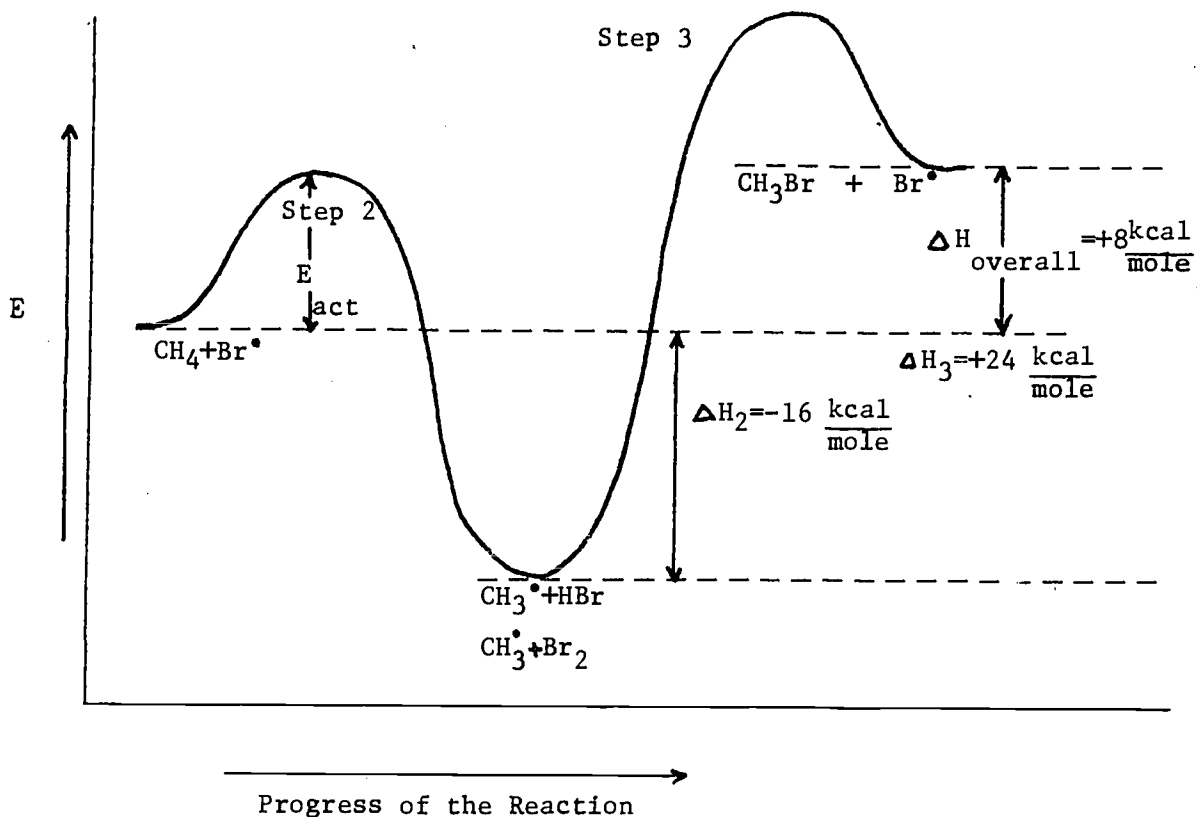


Monoiodination of methane



Assignment No. 5

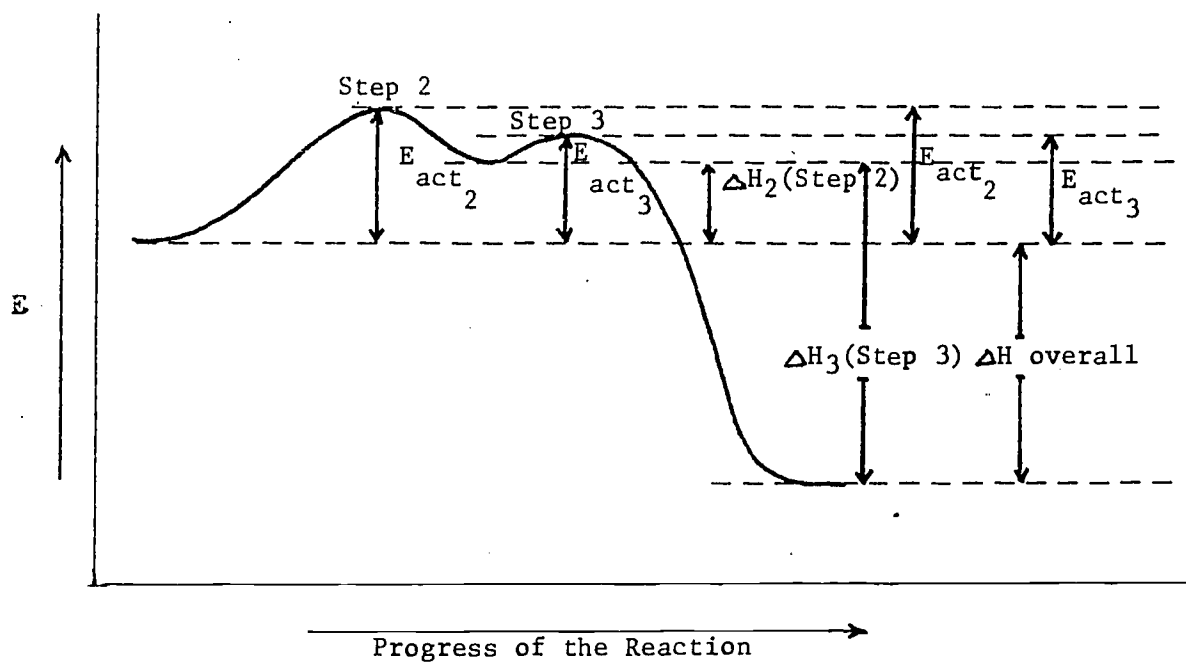
monobromination of methane



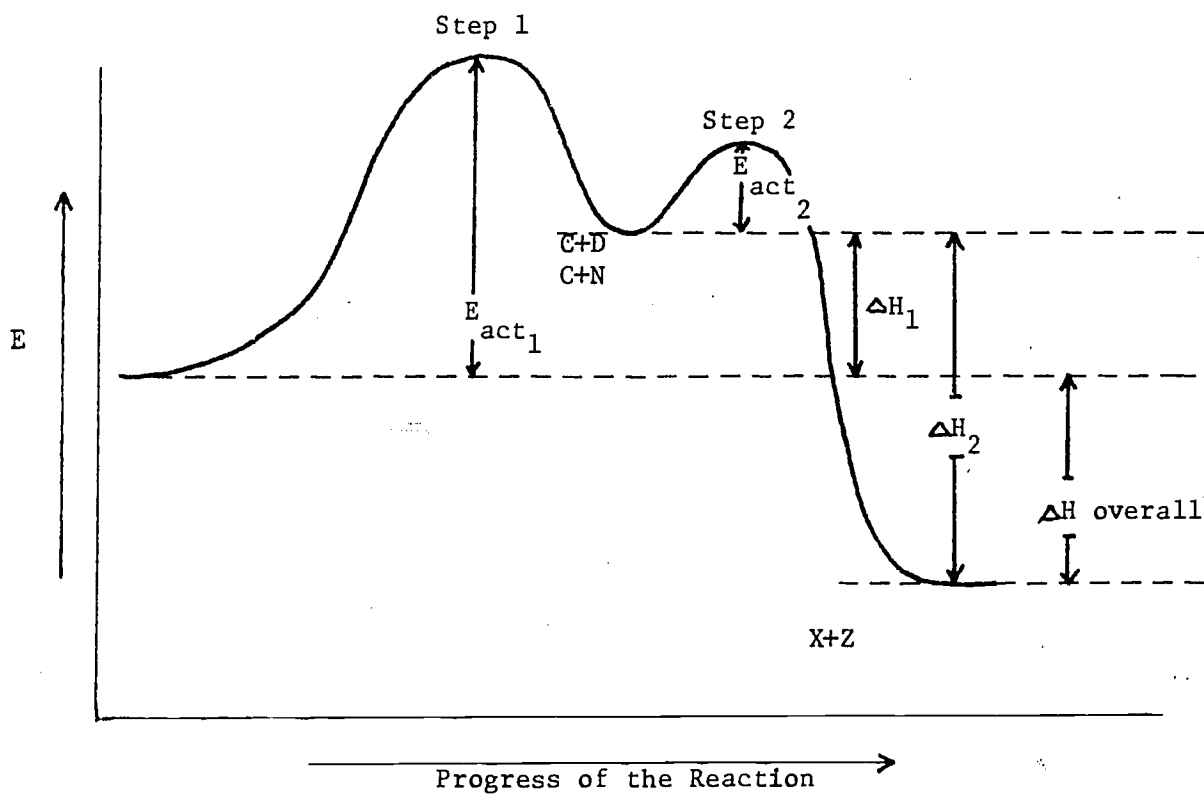
The diagram above is incorrect. The values assigned to ΔH , (Step 1) and (Step 2) have the opposite signs, consequently ΔH overall is incorrect. Compare this diagram to the correct diagram given the answer to Assignment No. 3.

ΔH_2	=	$-16 \frac{\text{kcal}}{\text{mole}}$	(incorrect)	ΔH_2	=	$+16 \frac{\text{kcal}}{\text{mole}}$	correct
ΔH_3	=	$+24 \frac{\text{kcal}}{\text{mole}}$	(incorrect)	ΔH_2	=	$-24 \frac{\text{kcal}}{\text{mole}}$	correct
ΔH overall	=	$+8 \frac{\text{kcal}}{\text{mole}}$	(incorrect)	ΔH overall	=	$-8 \frac{\text{kcal}}{\text{mole}}$	correct

Assignment No. 6



Assignment No. 7

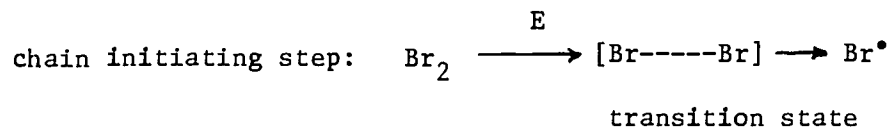


Assignment No. 8

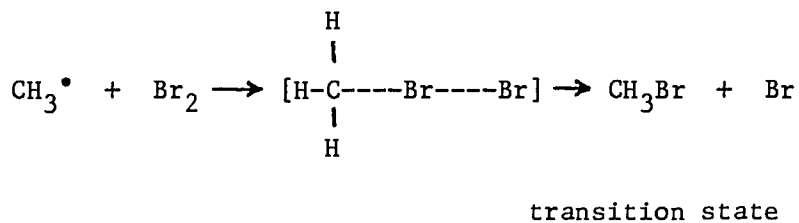
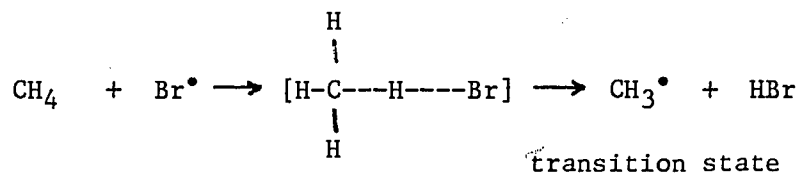
All the activation energies are indicated on each diagram.

Assignment No. 9

a) monobromination of methane



chain propagating steps:



b) Refer back to the Assignment 3 - the transition states are identified in the diagram.

METHANE

You will fill out this exercise by blacking in the appropriate squares on an answer sheet. There may be more than one correct answer for each question.

1. Correct statements pertaining to methane are:
 - a) The angles in methane are 109° .
 - b) C in methane has sp^3 hybrid orbitals, consequently methane is pyramidal.
 - c) C in methane has sp^2 hybrid orbitals, consequently methane is tetrahedral.
 - d) The hybridization on the C atom in methane is sp^3 .
2. Methane is a gas at room temperature due to:
 - a) the weak intermolecular forces between methane molecules.
 - b) the fairly strong Van der Waals forces between methane molecules.
 - c) the tetrahedral shape of methane.
 - d) the fact that methane is a nonpolar molecule.
3. Correct statements pertaining to methyl free radical are:
 - a) C atom in the methyl free radical has sp^2 hybridization, consequently methyl free radical is flat trigonal.
 - b) The angles in the methyl free radical are 120° because of the sp^3 hybridization on the C atom.
 - c) The angles in the methyl free radical are 109° .
 - d) The unpaired electron in the methyl free radical is located in the p atomic orbital.
4. From the compounds given below identify the trihalomethane.
 - a) CH_2I_2
 - b) $CHBr_3$
 - c) CH_3Cl
 - d) CF_4

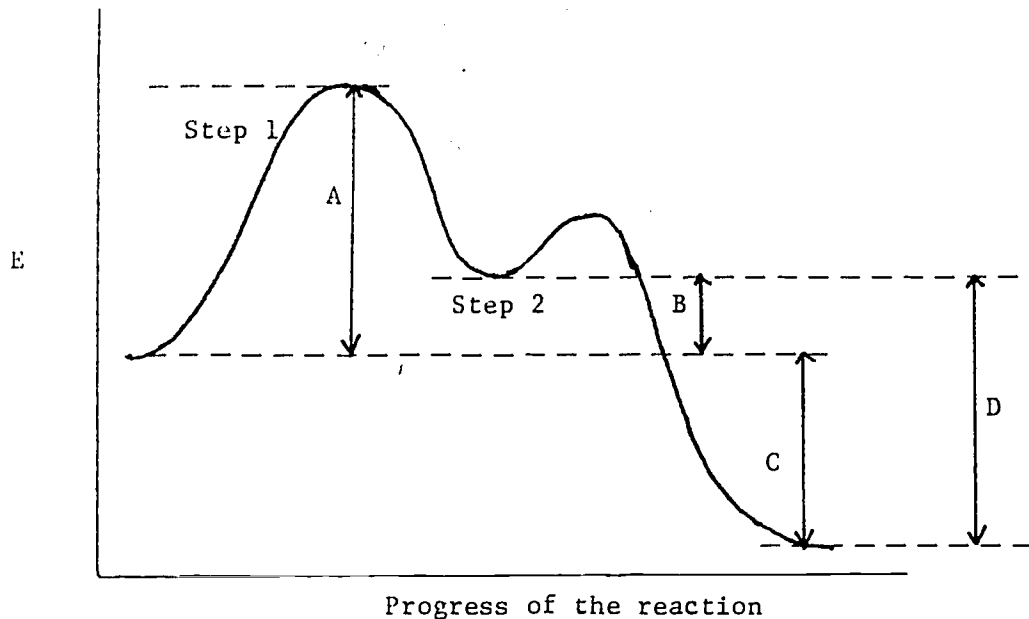
5. A typical substitution reaction of methane is a reaction:
- which results in the formation of monohalomethane.
 - in which a hydrogen atom is substituted by any other atom.
 - in which methane is converted into carbon dioxide and water.
 - which is highly exothermic.
6. In order to minimize the formation of the di, tri and tetrasubstituted halogen derivatives of methane and obtain the highest percent of the monohalo derivative, the following should be done:
- Low concentration of halogen should be used.
 - Excessive amount of methane should be used.
 - Monohalomethane should be removed from the mixture.
 - Limited amount of energy should be applied.
7. The correct statements about the rate of reaction are:
- It is independent of the concentration of the reactants.
 - It is independent of the concentration of the products.
 - It is directly proportional to the concentration of the reactants.
 - It is dependent on the heat of the reaction.
8. Which one of the following is/are free radicals?
- a) Na^\bullet b) $\text{:}\ddot{\text{S}}\text{:}^{\ominus\ominus}$ c) K^+ d) $\text{C}_2\text{H}_5^\bullet$
9. Reaction of halogen atom with methyl free radical is:
- a chain terminating step
 - a chain propagating step
 - a chain initiating step
 - the rate determining step

10. Chlorine atom reacts with methane to produce:
- a) Methyl chloride and hydrogen chloride
 - b) Methyl chloride and chlorine atom
 - c) Methyl free radical and chlorine atom
 - d) Methyl free radical and hydrogen chloride
11. Methyl free radical reacts in the chain propagating step with:
- a) chlorine atom to produce methyl chloride.
 - b) chlorine molecule to produce methyl chloride and hydrogen chloride.
 - c) chlorine molecule to produce methyl chloride and chlorine atom.
 - d) hydrogen chloride to produce methyl chloride and hydrogen atom.
12. The rate determining step in the monohalogenation of methane reaction is:
- a) dissociation of halogen molecule to produce halogen atoms.
 - b) reaction of methyl free radical with halogen atom.
 - c) reaction of methyl free radical with halogen molecule.
 - d) reaction of methane with halogen atom.
13. In the rate determining step of the monohalogenation of methane reaction, the products are:
- a) two halogen atoms.
 - b) halogen atom and methyl halide.
 - c) hydrogen halide and methyl free radical.
 - d) halogen atom and methyl free radical.
14. Dissociation of halogen molecule to produce two halogen atoms is:
- a) a chain terminating step
 - b) a chain propagating step
 - c) a chain initiating step
 - d) the rate determining step

SIP No. 2
Form D - Progress Check Evaluation

15. A reaction of methane with halogen atom is:
- a) a chain terminating step
 - b) a chain propagating step
 - c) a chain initiating step
 - d) the rate determining step
16. A reaction of halogen atom with methane to produce methyl halide and hydrogen halide is:
- a) a chain terminating step
 - b) a chain propagating step
 - c) incorrect
 - d) the rate determining step
17. The function of the heat or light in the halogenation of methane reaction is:
- a) to initiate the reaction
 - b) to catalyze the reaction
 - c) to inhibit the reaction
 - d) to keep the reaction going
18. Oxygen if present in the halogenation of methane will:
- a) speed up the reaction
 - b) slow down the reaction
 - c) catalyze the reaction
 - d) inhibit the reaction
19. The activation energy can be defined or described as:
- a) the difference in the energy content of reactants and the products.
 - b) the difference in the energy content of reactants and the transition state.
 - c) the minimum amount of energy required for a productive collision.
 - d) the energy required for the reaction to take place.

The following four questions refer to the diagram below:



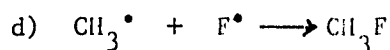
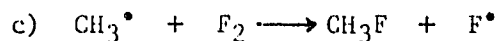
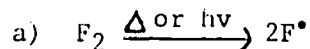
20. The energy difference A on the diagram is the:
- a) ΔH or heat of the overall reaction.
 - b) activation energy of the first step.
 - c) activation energy of the overall reaction.
 - d) ΔH or heat of the first step.
21. The heat of the overall reaction depicted by the diagram above is the energy difference:
- a) A
 - b) B
 - c) C
 - d) D

22. The correct statements about the reaction depicted by the diagram above are:
- a) The rate determining step in this reaction is Step 1.
 - b) The overall reaction is an endothermic reaction.
 - c) ΔH for the overall reaction will have a negative sign.
 - d) Step 2 of the mechanism is exothermic.
23. The energy difference D is:
- a) the difference in the energy content of the reactants and the products.
 - b) the ΔH or the heat for Step 1.
 - c) the ΔH or the heat for Step 2.
 - d) the value which may be obtained by subtracting B from C.

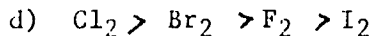
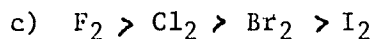
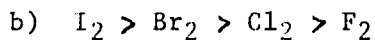
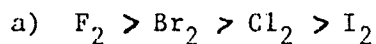
Use the bond energy card in order to correctly answer the following three questions.

24. ΔH or heat for the rate determining step of the monobromination of methane reaction is:
- a) +46 kcal/mole
 - b) +16 kcal/mole
 - c) -24 kcal/mole
 - d) -8 kcal/mole
25. ΔH or heat for the iodination reaction is:
- a) +36 kcal/mole
 - b) +13 kcal/mole
 - c) $\Delta H_1 + \Delta H_2 + \Delta H_3$ or +36 + 33 - 20
 - d) $\Delta H_2 + \Delta H_3$ or +33 - 20

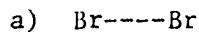
26. -108 kcal/mole in the monofluorination reaction is the ΔH or heat for the following step of the mechanism.



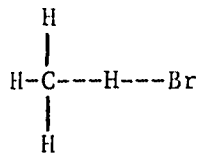
27. From the values for the activation energy for the rate determining step of the monohalogenation reaction, which are: $F_2 + 1$ kcal/mole; $Cl_2 + 4$ kcal/mole; $Br_2 + 18$ kcal/mole; $I_2 + 35$ kcal/mole; the reactivity of these halogens is expected to be:



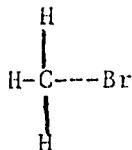
28. Transition state for the rate determining step of the monobromination reaction can be written as:



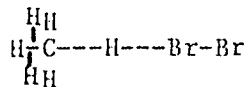
b)



c)



d)



Self Instructional Package No. 2
Form B¹ - Self Evaluation Exercise - Answer Sheet

METHANE

- | | |
|-------------|-------------|
| 1. d | 13. a, c, d |
| 2. d | 14. a, b |
| 3. d | 15. b |
| 4. b | 16. b |
| 5. b | 17. b |
| 6. c | 18. b, d |
| 7. b, d | 19. d |
| 8. c, d | 20. b |
| 9. a, c, d | 21. b, d |
| 10. a, b, d | 22. c |
| 11. a | 23. a |
| 12. d | |

Self Instructional Package No. 2
Form D' - Progress Check Evaluation - Answer Sheet

METHANE

- | | |
|------------|-------------|
| 1. a, d | 15. b, d |
| 2. a | 16. c |
| 3. a, d | 17. a |
| 4. b | 18. b, d |
| 5. b | 19. b, c |
| 6. a, b, c | 20. b |
| 7. b, c | 21. c |
| 8. a, d | 22. a, c, d |
| 9. a | 23. c |
| 10. d | 24. b |
| 11. c | 25. b, d |
| 12. d | 26. d |
| 13. c | 27. a |
| 14. c | 28. d |

S.I.P #2 - ERRATA

CORRECT STATEMENTS AND ANSWERS

FORM B - 18 d In an endothermic reaction products possess a higher amount of potential energy or "they have a potential energy valley" than the reactants.

FORM B¹ - Answer Sheet
1. d, b
5. a, b
22. b

FORM D¹ - Answer Sheet
5. a, b
27. c
28. b

TAPE 3 - Answer Sheet

Assignment #4. Monoiodination of methane: ΔH_1 is missing on the diagram.

$\Delta H_1 = +33$ kcal/mole -- the line should be drawn from the first valley of the products to the reactants at the beginning of the reaction. (it should connect the two dotted lines.)

