CHAPTER

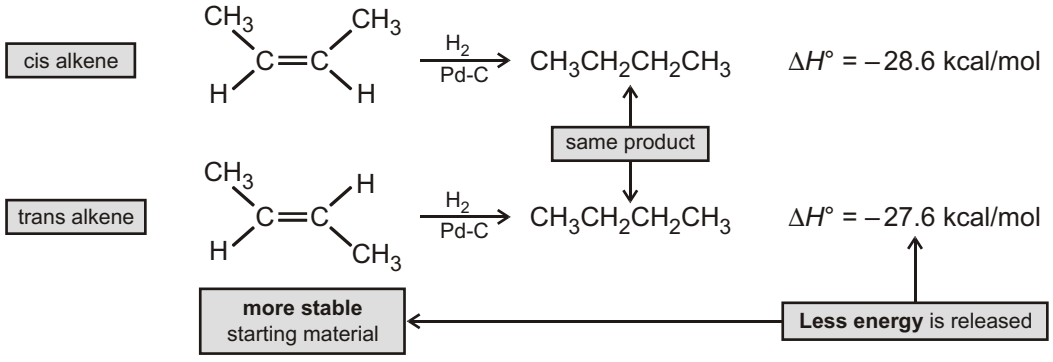
19

Heat of Hydrogenation and Heat of Combustion

HEAT OF HYDROGENATION

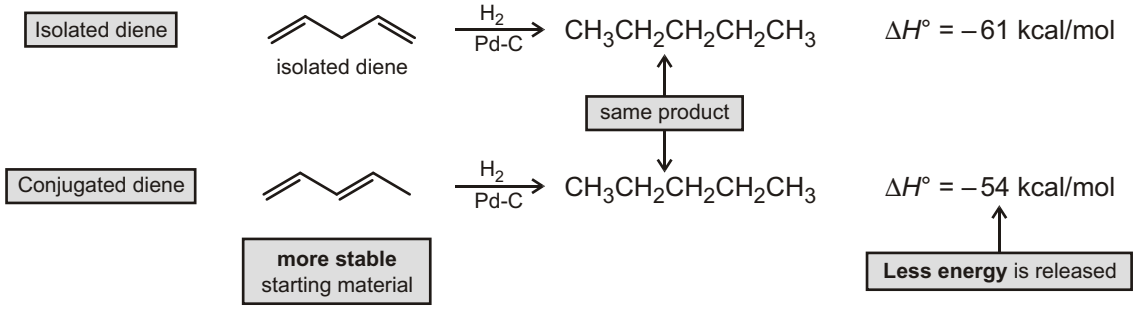
Hydrogenation reactions are exothermic because the bonds in the product are stronger than the bonds in the starting materials, making them similar to other alkene addition reactions. The H for hydrogenation, called the **heat of hydrogenation**, can be used as a measure of the relative stability of two different alkenes that are hydrogenated to the same alkane.

☞ For example, both cis- and trans-2-butene are hydrogenated to butane, and the heat of hydrogenation for the trans isomer is less than that for the cis isomer. Because less energy is released in converting the trans alkene to butane, it must be lower in energy (more stable) to begin with. The relative energies of the butene isomers are illustrated in figure.



☞ When hydrogenation of two alkenes gives the same alkane, the more stable alkene has the smaller heat of hydrogenation.

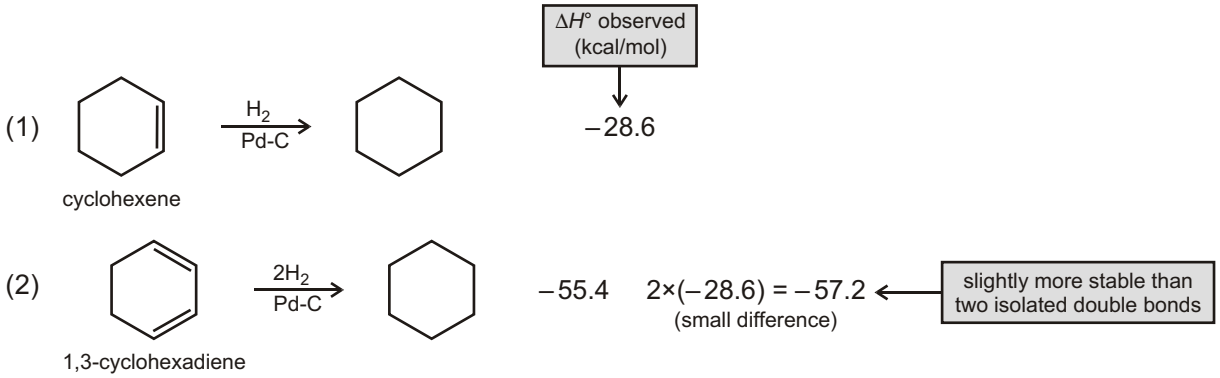
Heat of hydrogenation $\propto \frac{1}{\text{Stability}}$



☞ When one compound have more -bonds than other, its heat of hydrogenation is also more.

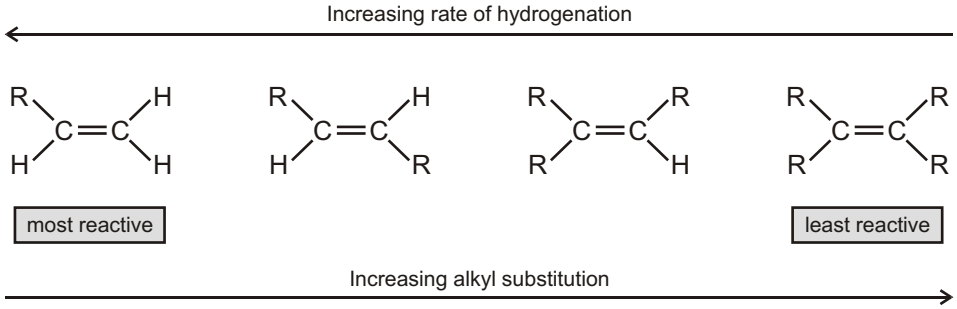
Heat of hydrogenation number of -bonds present in compound.

For Example :



☞ Rapid, sequential addition of H_2 occurs from the side of the alkene complexed to the metal surface, resulting in syn addition. (syn addition means same side addition)

☞ Less crowded double bonds complex more readily to the catalyst surface, resulting in faster reaction.

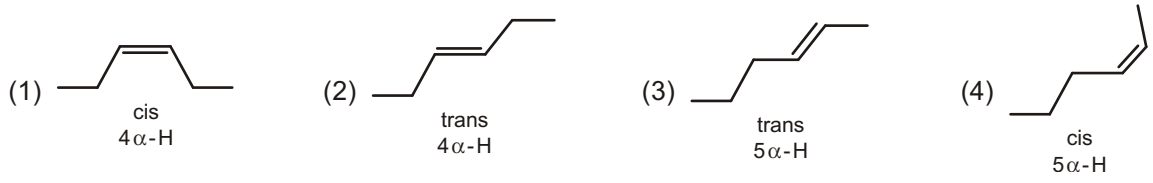


Solved Example

- Correct order of heat of hydrogenation of the below compounds?

Ans. 1 > 2 > 4 > 3

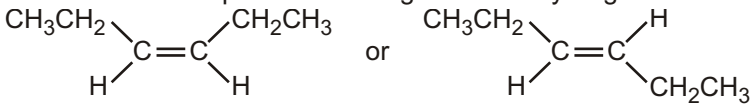
Sol.

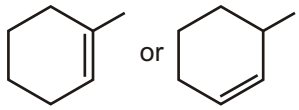


Stability order 3 > 4 > 2 > 1

Heat of hydrogenation 1 > 2 > 4 > 3

- Which alkene in each pair has the larger heat of hydrogenation?

(I) 

(II) 

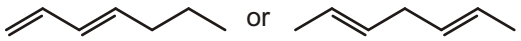
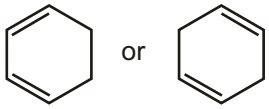
Sol. (I) a > b (II) b > a

In pairs (I) stability b(trans) > a(cis)

Number of H a(7) > b(3)

Heat of hydrogenation $\frac{1}{\text{Stability}}$

- Which diene in each pair has the larger heat of hydrogenation?

(a)  (b) 

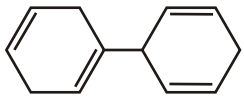
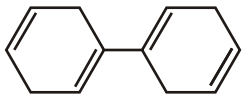
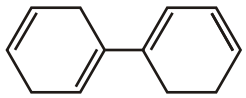
Sol. (a) II > I (b) II > I

Heat of hydrogenation $\frac{1}{\text{Stability}}$

In pair (a) compound I is resonance stabilized

In pair (b) compound I is resonance stabilized

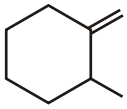
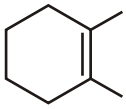
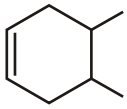
- Rank the following compounds in order of increasing stability.

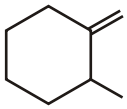
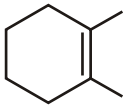
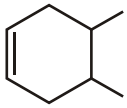
(a)  (b)  (c) 

Sol. c > b > a

In compound (c) more number of -bonds (3) are in resonance thats why it is most stable.

- Decreasing order of heat of hydrogenation?

(I)  (II)  (III) 

Sol. (I)  (II)  (III) 

αH = 3 αH = 10 αH = 4

Stab. order II > III > I

HOH order II < III < I

HEAT OF COMBUSTION(HOC)

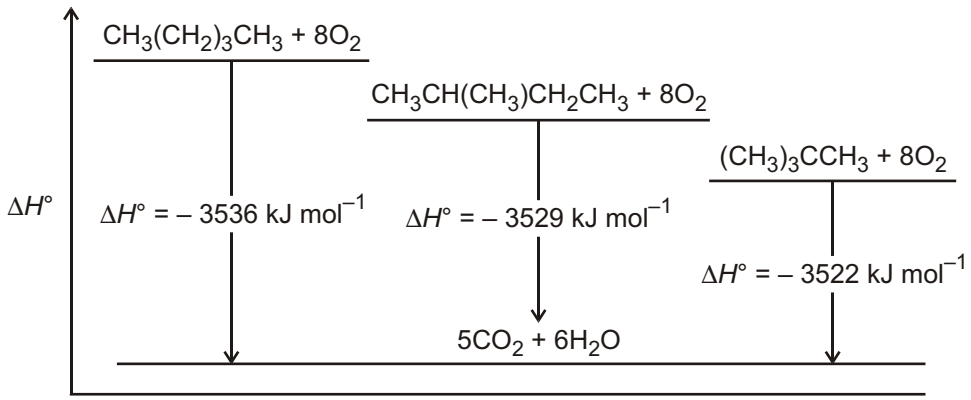
The heat of combustion is the total energy released as heat when a substance undergoes. Complete combustion with oxygen under standard conditions. The chemical reaction is typically a hydrocarbon or other compound with oxygen to form carbon dioxide and water and release heat.

Ex. : $C_3H_8 \quad 5O_2 \quad 3CO_2 \quad 4H_2O \qquad H \quad 2202 \text{ KJ mol}^{1}$

Heat of combustion is more of that isomer which is less stable since it has more potential energy.

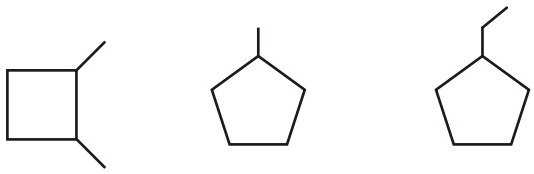
HOC $\dfrac{1}{\text{Stability}}$

Ex. : $(CH_3)_3CCH_3$ is the most stable isomer of pentane (*i.e.*, it is the isomer with the lowest potential energy) because it evolves the least amount of heat on a molar basis when subjected to complete combstion.



Solved Examples

- Heat of combustion of following compounds is :



I II III

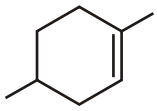
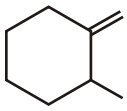
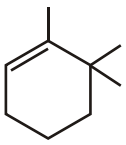
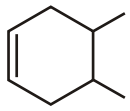
Ans. III > I > II

Sol. Heat of combustion increases with the number of carbons is the compound which is maximum is case of (III)
In case number of carbon is same, heat released is inversely related to stability.

EXERCISE

SINGLE CHOICE QUESTIONS

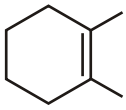
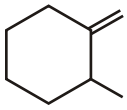
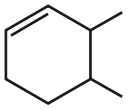
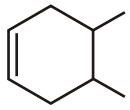
1. Correct order for the heat of combustion of the following is :

(I)  (II)  (III)  (IV) 

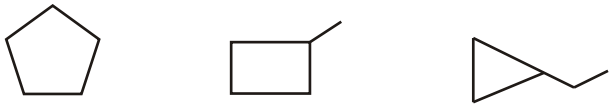
(A) I > II > IV > III (B) IV > I > II > III

(C) III > I > IV > II (D) III > II > IV > I

2. Which of the following compound have least Heat of Cumbustion :

(A)  (B)  (C)  (D) 

3. Which of the following will have largest heat of combustion?



(I) (II) (III)

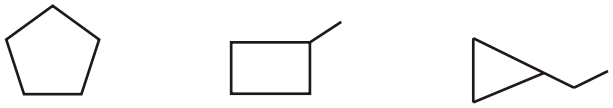
(A) I

(B) II

(C) III

(D) All will have same heat of combustion because DBE = 1 for all.

4. Which of the given is most stable?



(I) (II) (III)

(A) I

(B) II

(C) III

(D) All are equally stable because DBE = 1 for all.

5. Which of the following alkene have maximum heat of combustion?

(A) 2, 4-Dimethyl-1-pentene (B) 1-Heptene

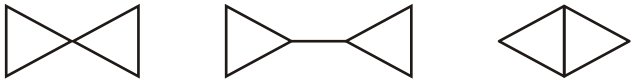
(C) 2, 4-Dimethyl-2-pentene (D) 4, 4-dimethyl-2-pentene

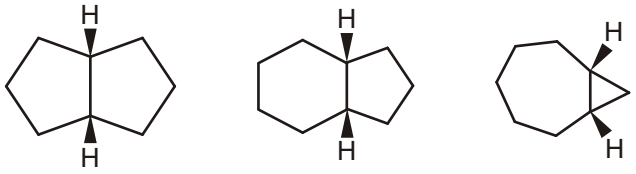
WORK SHEET

1. In each of the following groups of compounds, identify the one with the largest heat of combustion and the one with the smallest. In which cases can a comparison of heats of combustion be used to assess relative stability?

(a) Cyclopropane, cyclobutane, cyclopentane

(b) cis-1,2-Dimethylcyclopentane, methylcyclohexane, 1,1,2,2-tetramethylcyclopropane

(c) 

(d) 

2. In each of the following groups of compounds, identify the one with the largest heat of combustion and the one with the smallest. (Try to do this problem without consulting Table).

(a) Hexane, heptane, octane

(b) Isobutane, pentane, isopentane

(c) Isopentane, 2-methylpentane, neopentane

(d) Pentane, 3-methylpentane, 3,3-dimethylpentane

(e) Ethylcyclopentane, ethylcyclohexane, ethylcycloheptane

Answers

Single Choice Questions

1. (D) **2.** (A) **3.** (C) **4.** (A) **5.** (B)

1. Stability of compound I > IV > II

So heat of combustion III > II > IV > I

compound III have more number of carbon atoms so its HOC is maximum

2. More the stability least is HOC

3. Compound C is least stable due to ring strain so HOC is maximum.

4. Compound C is least stable due to ring strain.

5. H.O.C $\frac{1}{\text{Stability}}$, if number of 'C' are same.

Work Sheet

1. (a) c > b > a (b) c > a > b (c) b > a > c (d) b > c > a

2. (a) c > b > a (b) b > c > a (c) b > a > c (d) c > b > a (e) c > b > a

❑❑❑