

## Chapter 5. Reactions of Alkenes

### Learning objectives:

1. Differentiate primary, secondary, and tertiary carbocations, and recognize the order of stability for these carbocations.
2. Identify the followings from a potential energy diagram when applicable: endothermic or exothermic reactions, activation energy, heat of reaction, locations of transition states, locations of intermediates, and rate-limiting step.
3. Write the electron-pushing (arrow-pushing) mechanisms for the following reactions of alkenes: hydrohalogenation, hydration, and halogenation.
4. Draw the potential energy diagrams and provide all the applicable information listed in "1" for hydrohalogenation, hydration, and halogenation of alkenes.
5. Explain the regio- and stereoselectivity issues involving in hydrohalogenation, hydration, and halogenation of alkenes.
6. Write the *syn* addition from a dihydroxylation of alkenes, and explain the observed stereochemistry of products.
7. Write the *syn* addition from a halogenation of alkenes, and explain the observed stereochemistry of products.
8. Arrange the order of stability of substituted alkenes, and correlate this order to the heat of hydrogenation of these alkenes.

### Sections to be covered (in the order of delivery):

- 5.1 Introduction
- 5.2 Reaction Mechanisms\*
- 5.3 Electrophilic Addition Reactions\*
- 5.4 Oxidation of Alkenes – Formation of Glycols
- 5.5 Reduction of Alkenes - Formation of Alkanes

\* Sections that will be focused

# Sections that will be skipped

### Recommended additional problems

5.8 – 5.40

## 5.1 Introduction

*Know all the information in Table 5.1*

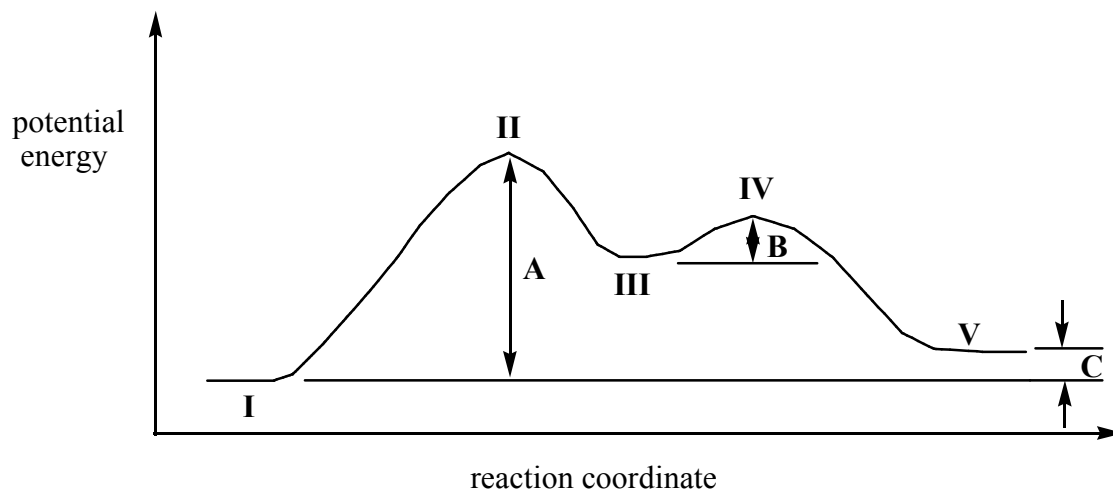
## 5.2 Reaction Mechanisms

### A. Energy Diagram and Transition States ( $\text{TS}^\ddagger$ )

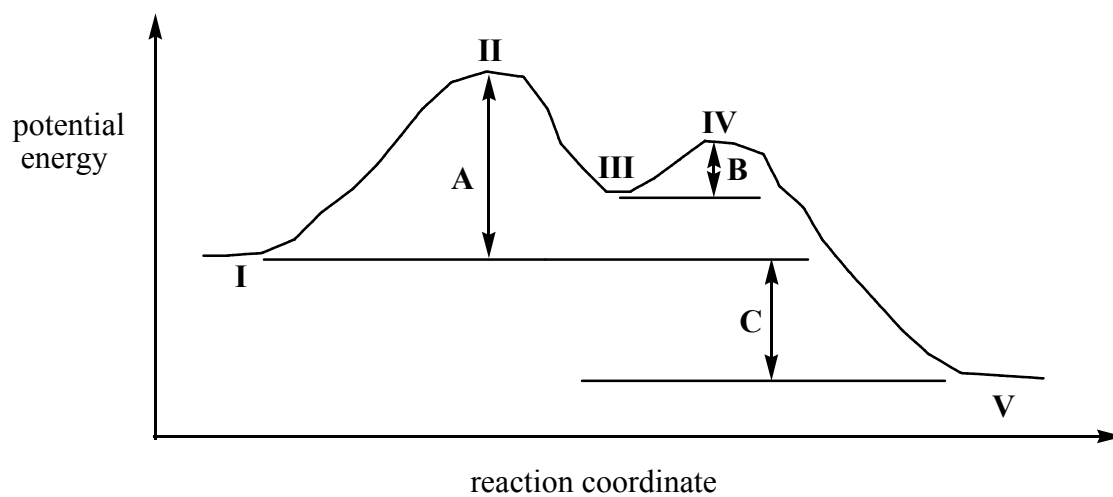
**Important Terminologies:** starting materials, products, reaction mechanism, energy diagram, reaction coordinate, heat of reaction ( $\Delta H$ ), exothermic reaction, endothermic reaction, activation energy ( $E_a$ ), reaction intermediate, rate-determining step (rate-limiting step) and transition state ( $\text{TS}^\ddagger$ ).

*Know the difference between reaction intermediate and transition state*

(i) Endothermic reaction



(ii) Exothermic reaction

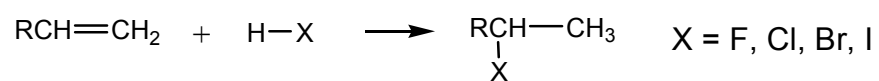


## B. Developing a Reaction Mechanism

### 5.3 Electrophilic Addition Reactions

#### A. Addition of Hydrogen Halides

(i) General Reaction:



R: alkyl group (example:  $\text{CH}_3-$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2-$ )

(ii) Markovnikov's rule:

(iii) Electron-pushing Mechanism:

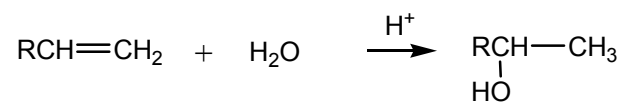
(iv) Carbocation and Electrophile ( $E^+$ )

(v) Reaction Energy Diagram

(vi) Stability of carbocation (Rationale for Markovnikov's rule)

## B. Addition of Water: Acid-Catalyzed Hydration

(i) General Reaction:



(ii) Variations in Representation of Available Acid

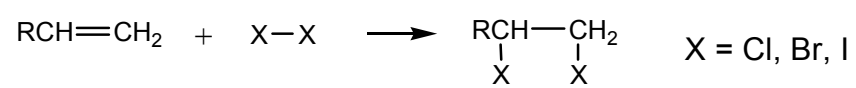


(iii) Electron-pushing Mechanism:

(iv) Reaction Energy Diagram

### C. Addition of Bromine and Chlorine

(i) General Reaction:



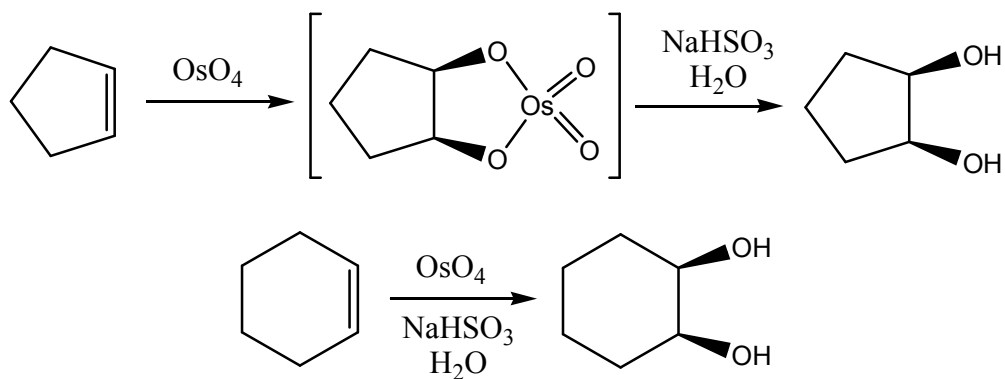
(ii) Electron-pushing Mechanism:

**(iii) Anti-selectivity (Anti addition): Issue in the Stereoselectivity of Halogenation**

## 5.4 Oxidation of Alkenes – Formation of Glycols

(i) Oxidation and reduction

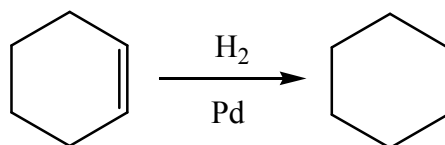
(ii) Reactions (Dihydroxylation):



(iii) Syn addition: Issue in the Stereoselectivity

## 5.5 Reduction of Alkenes - Formation of Alkanes

### (i) Catalytic Reduction (Hydrogenation)



### (ii) Variations in Available Metal Catalysts

Pd, Pt [Pt(0), Pt(II)], Ni (Raney Nickel), Rh

### (iii) Syn addition

### (iv) Heat of Hydrogenation and the Stabilities of Alkenes

*More substituted (alkyl group) alkenes, higher stability*

