

# CHAPTER 10

## Elimination Reactions

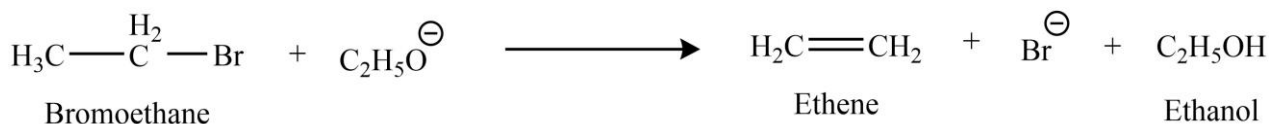
### ❖ The E<sub>2</sub>, E<sub>1</sub> and E<sub>1</sub>CB Mechanisms

No organic reaction is capable of giving 100% yield of a single product only, including nucleophilic substitutions. The reason for this type of behavior is the fact that nucleophilic substitution reactions are in direct competition with the elimination reactions; and if the reagent and substrate carefully with a fine-tuning of experimental conditions, elimination yield can even surpass the nucleophilic substitution product. In this section, we will discuss some important elimination mechanisms like E<sub>2</sub>, E<sub>1</sub>, and E<sub>1</sub>CB-type.

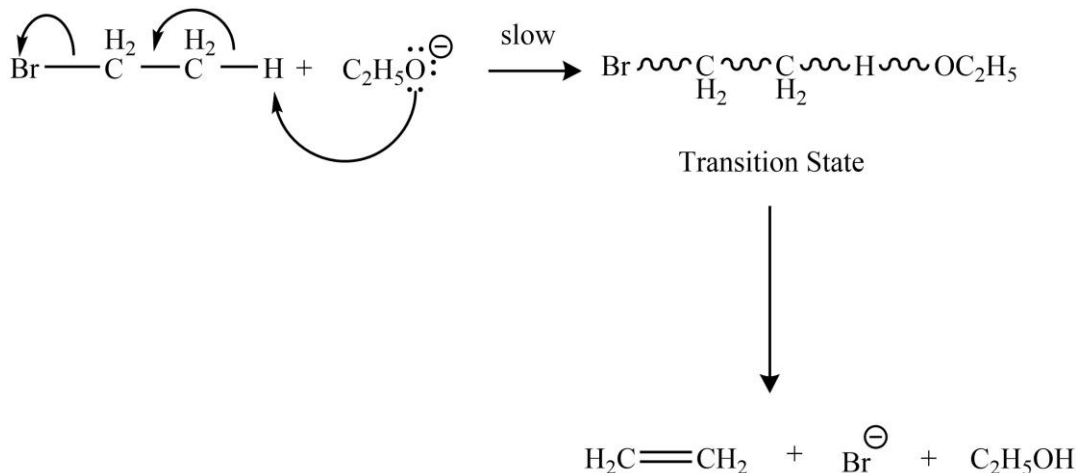
#### ➤ E<sub>2</sub> (Bimolecular Elimination) Mechanism

An E<sub>2</sub> elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in a one-step concerted mechanism. The numbers refer not to the number of steps in the mechanism, but rather to the kinetics of the reaction which means that E<sub>2</sub> is a bimolecular (second-order) reaction.

**Illustrative reaction:** The reaction of ethoxide ion with ethyl bromide falls into this category because the rate of reaction depends only upon the concentration of the substrate as well as of reagent.



**Mechanism involved:** The proposed mechanism for the reaction given above involves one step which must be discussed before we give salient features of the same.



It is worthy to recall that even though the reaction is shown as a two-step process, it is actually concerted in nature where the bond breaking and bond-making occur simultaneously.

**Salient Features:** The main features of the mechanism involved in bimolecular elimination reactions are given below.

i) E<sub>2</sub> reactions follow second-order kinetics with the rate law

$$\text{Rate} = k[\text{RX}][\text{B}]$$

Where  $k$  is the rate constant. The symbol  $[\text{RX}]$  and  $[\text{B}]$  represent the molar concentration of the alkyl halide and base, respectively.

ii) E<sub>2</sub> typically takes place with primary alkyl halides but is possible with some secondary alkyl halides.

iii) Because of the formation of a  $\pi$ -bond in the course of the E<sub>2</sub> mechanism, the two leaving groups (often a halogen and hydrogen) must be antiperiplanar. The reason for this is the fact that the antiperiplanar transition state will have lower energy (staggered-conformation) than a synperiplanar transition state (eclipsed conformation). In other words, the E<sub>2</sub> reactions are favored by staggered conformation whereas the E<sub>1</sub> by eclipsed one.

iv) E<sub>2</sub> typically uses a strong base. It must be strong enough to remove the weakly acidic hydrogen.

v) E<sub>2</sub> competes with the S<sub>N</sub>2 reaction mechanism if the base can also act as a nucleophile (true for many common bases).

➤ **E<sub>1</sub> (Unimolecular Elimination) Mechanism**

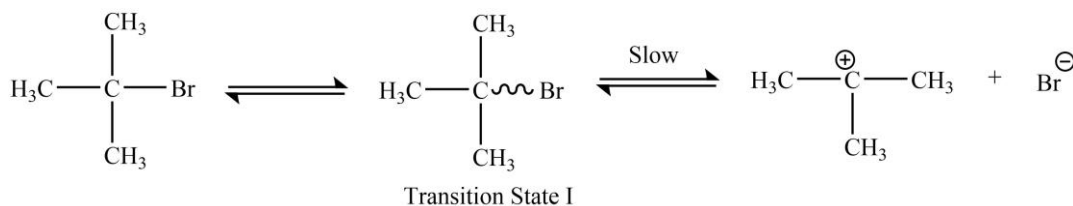
An E<sub>1</sub> elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in a two-step mechanism. The numbers refer not to the number of steps in the mechanism, but rather to the kinetics of the reaction which means that E<sub>1</sub> is a unimolecular (first-order) reaction.

**Illustrative reaction:** The reaction of NaOH with tert-butyl bromide falls into this category because the rate of reaction depends only upon the concentration of the substrate.

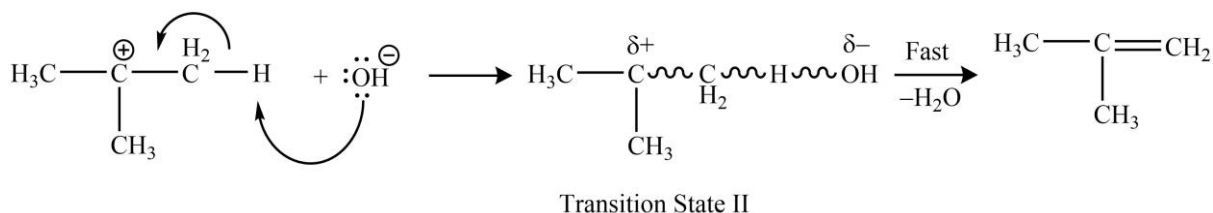


**Mechanism involved:** The proposed mechanism for the reaction given above involves two steps which must be discussed before we give salient features of the same.

i) *Generation of carbocation:* The alkyl halide accepts an electron from a radical initiator to form radical anion.



ii) Removal of proton:



**Salient Features:** The main features of the mechanism involved in unimolecular elimination reactions are:

i) E1 reactions follow first-order kinetics with the rate law

$$\text{Rate} = k[\text{RX}]$$

Where  $k$  is the rate constant. The symbol  $[\text{RX}]$  represents the molar concentration of the substrate.

ii) The E<sub>1</sub> reactions generally occur with tertiary alkyl halides but are possible with some 2° alkyl halides.

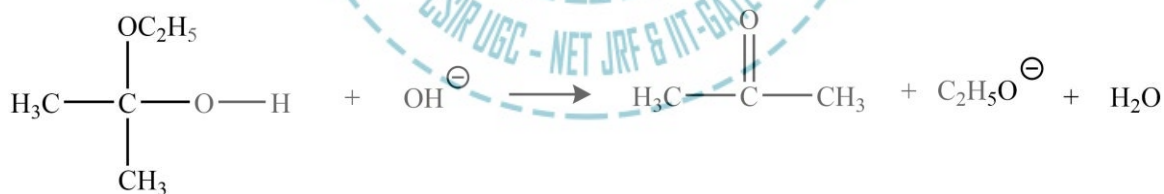
iii) The E<sub>1</sub> reaction typically takes place in the presence of a weak base or the base can be absent at all.

iv) E<sub>1</sub> reactions compete with S<sub>N</sub>1 reactions because they share the same intermediate.

➤ **E<sub>1</sub>CB (Conjugate Base Elimination) Mechanism**

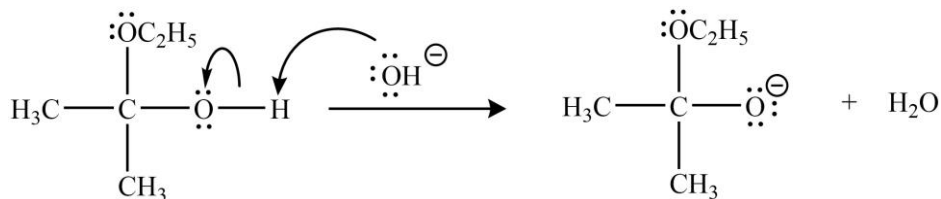
The E<sub>1</sub>CB elimination reaction is a type of chemical transformation where the elimination occurs in the presence of a strong base, and the hydrogen to be removed is comparatively acidic, while the leaving group (such as -OH or -OR) is a relatively poor one.

**Illustrative reaction:** An example of the E<sub>1</sub>CB reaction mechanism in the degradation of a hemiacetal under basic conditions.

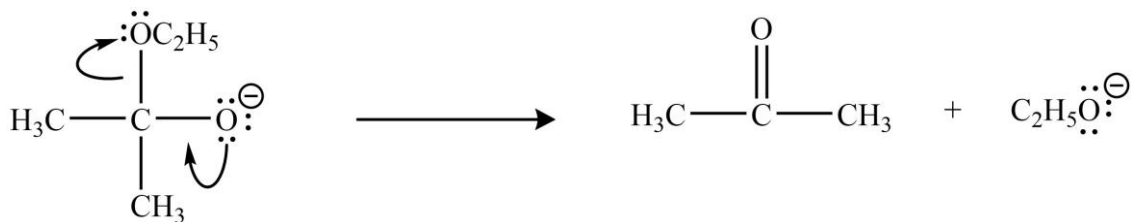


**Mechanism involved:** The proposed mechanism for the reaction given above involves two steps which must be discussed before we give salient features of the same.

i) *Proton abstraction:* The aryl halide accepts an electron from a radical initiator to form a radical anion.



ii) Detachment of leaving group:



**Salient Features:** The main features of the mechanism involved in unimolecular elimination conjugate-base reactions are:

i)  $E_1CB$  reactions follow first-order kinetics with the rate law

$$Rate = k[RX]$$

Where  $k$  is the rate constant. The symbol  $[RX]$  represents the molar concentration of the substrate.

ii) The substrate must have acidic hydrogen on its  $\beta$ -carbon and a relatively poor leaving group on the  $\alpha$ -carbon.

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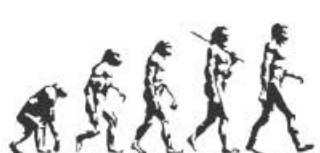
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