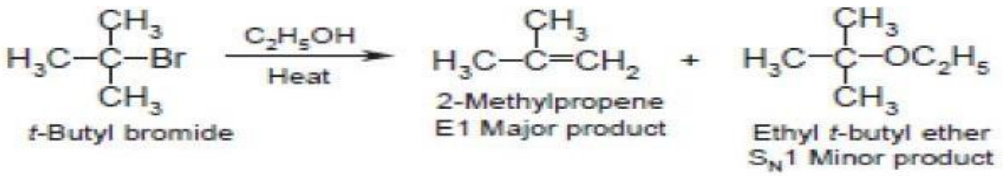
Elimination reaction

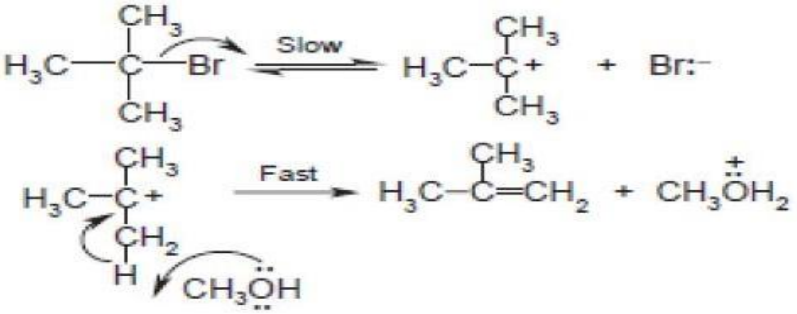
- Elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-stepmechanism.
- The one-step mechanism is known as the E2 reaction, and the two-stepmechanism is known as the E1 reaction.
- In most organic elimination reactions, at least one hydrogen is lost toform the double bond: the unsaturation of the molecule increases.
- It is also possible that a molecule undergoes reductive elimination, by which the valence of an atom in the molecule decreases by two, thoughthis is more common in inorganic chemistry.
- There are three fundamental events in these elimination reactions:
    - removal of a proton
    - formation of the CC π bond
    - breaking of the bond to the leaving group

• E1 reaction or first order of HX: preparation of alkenes

- E1 reaction or first order elimination results from the loss of a leaving group to form a carbocationintermediate, followed by the removal of a proton to form the C═C bond.
- This reaction is most common with good leaving groups, **stable carbocation's** and **weak bases** (strongacids)



Mechanism.



- In the E1 mechanism which is also ***known as unimolecular elimination***, there are usually two steps involved – ionization and deprotonation.
- During ionization, there is a formation of **carbocation as an intermediate**. In deprotonation, a proton is lost by the carbocation.
- This happens in the presence of a base which further leads to the formation of a pi-bond in the molecule.
- In E1, the reaction rate is also proportional to the concentration of the substance to be transformed.
-

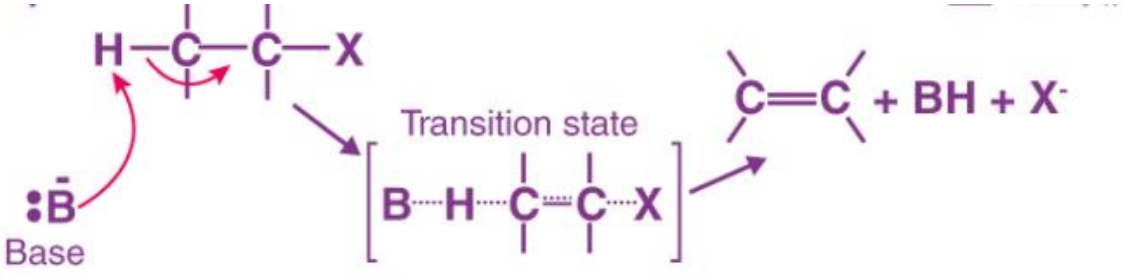
- It exhibits ***first-order kinetics***.
- **For example**, ter-butyl bromide (3^0 alkyl halide) reacts with water to form 2-methylpropene, followingan E1 mechanism.

Characteristics of an E1 Reaction

- Kinetics – First order
- Mechanism – Two step process

- Identity of R group – More substituted halides react faster
  - Rate: $R_3CX > R_2CHX > RCH_2X$
  - Strength of the base – Favored by weaker bases such as H_2O and ROH
  - Leaving group – Better leaving group leads to faster reaction rates. The rate determining stepinvolves the C—X bond cleavage
  - Type of solvent – Favored by **polar Protic solvents,** which can stabilize the ionic intermediates
- **E_2 REACTION or second order elimination of HX (formation of alkenes)Characteristics of an E2 Reaction**
  - Kinetics – Second order
  - Mechanism – Single step
  - Identity of R group – More substituted halides react faster
  - Rate: $R_3CX > R_2CHX > RCH_2X$
  - Strength of the base – Stronger bases favor the reaction
  - Leaving group – Better leaving group leads to faster reaction rates
  - Type of solvent – Favored by polar aprotic solvents
  - E2 reactions are stereo selective, resulting in the formation of trans-double bonds preferably.

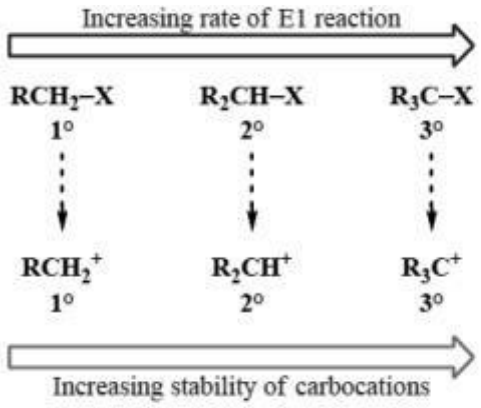
- Dehydrohalogenation of sec- and ter- alkyl halides undergo both E1 and E2 reactions. However, prim-halides undergo only E2 reactions.
- They cannot undergo E1 reaction because of the difficulty of forming primary carbocations.
- E2 elimination is stereospecific,
- The E2 reaction is the most effective for the synthesis of alkenes from primary alkyl halides.
  - In an E2 mechanism which refers to bimolecular elimination is basically a one-step mechanism.
  - Here, the carbon-hydrogen and carbon-halogen bonds mostly break off to form a new double bond.
  - However, in the E2 mechanism, a base is part of the rate-determining step and it has a huge influence on the mechanism.
  - The reaction rate is mostly proportional to the concentrations of both the eliminating agent and the substrate.
  - It exhibits second-order kinetics.
  - The E2 mechanism can generally be represented as below. In the below-mentioned representation, B stands for base and X stands for halogen.

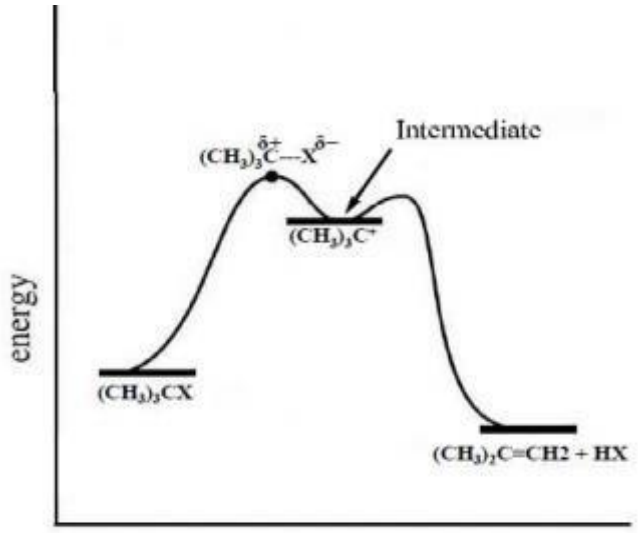


E1 Reaction influence the reaction pathway:

- E1 mechanistic pathway is most common with:
  - ✓ Good leaving groups
  - ✓ Stable carbocations
  - ✓ Weak bases.
- -E1 Reactions is Non-stereospecific- follows Zaitsev (Saytseff) Rule -Does NOT occur with primary alkyl halides (leaving groups)

  Effect of R-
- Reactivity order: (CH3)3C- > (CH3)2CH- > CH3CH2- > CH3-
- In an E1 reaction, the rate determining step is the loss of the leavinggroup to form the intermediate carbocation.
- The more stable the carbocation is, the easier it is to form, and the fasterthe E1 reaction.
- -The rate of an E1 reaction increases as the number of R groups on thecarbon with the leaving group increases.





Energy Profile for an E_1 Reaction

(ii) Leaving Group (LG)

- ✓ The only event in the rate determining step of the E1 is breaking the C- LG bond. Therefore, there is a very strong dependence on the nature of the leaving group, the better the leaving group, the faster the E1 reactionwill be.

- ✓ In the acid catalysed reactions of alcohols, the -OH is protonated first togive an oxonium ion, providing the much better leaving group, a water molecule.

(iii) Base (B)

- ✓ Since the base is not involved in the rate determining step, the nature ofthe base is unimportant in an E1 reaction.
- ✓ Favored by weaker bases such as H2O and ROH.

(iv) Type of Solvent

- ✓ Favored by polar protic solvents, which can stabilize the ionic intermediates.

E2Reaction influence the reaction pathway:

Kinetics – Second order

Mechanism – Single step

Stereospecific (Anti-periplanar geometry preferred, Syn-periplanar geometry possible)0

Concerted - all bonds form and break at same time.

Bimolecular - rate depends on concentration of both base and substrate - Favoured by strong bases.

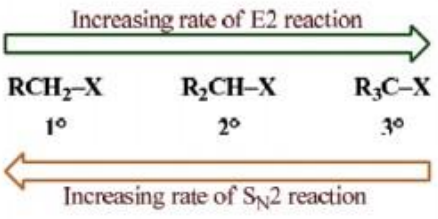
Favored by polar aprotic solvents.

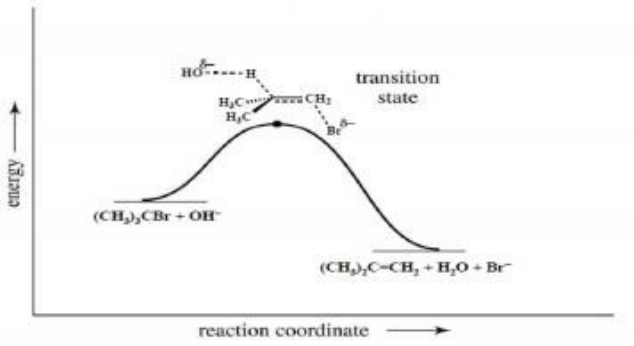
Better leaving group leads to faster reaction rates.

Identity of R group - More substituted halides react faster Rate: R3CX > R2CHX > RCH2X

(i) Effects of R-

- ✓ Reactivity order: (CH3)3C-> (CH3)2CH- > CH3CH2- > CH3- -
- ✓ In an E2 reaction, the reaction transforms 2 sp3 C atoms into sp2 C atoms. This moves the substituents further apart decreasing any steric interactions.
- ✓ So more highly substituted systems undergo E2 eliminations more rapidly. This is the same reactivity trend as seen in E1 reactions.
- ✓ As the number of R groups on the carbon with the leaving group increases, the rate of the E2 reaction increases.





Energy Profile for an E_2 Reaction

(ii) Leaving Group (LG)

The C-LG bond is broken during the rate determining step, so the rate does depend on the nature of the leaving group.

However, if a leaving group is too good, then an E1 reaction may result. -Rate of reaction follows the order Rate of reaction follows the order, **R−I**

> R−Br > R−Cl > R−F

(iii) Base (B)

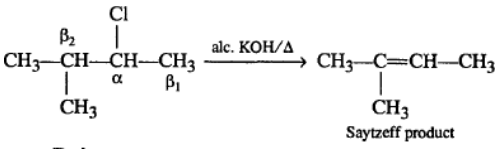
Stronger bases favor the reaction. Since the base is involved in the ratedetermining step, the nature of the base is very important in an E2 reaction.

More reactive bases will favor an E2 reaction.

Characteristics of E1 reaction	**Characteristics of E2 reaction**
Unimolecular reaction	Biomolecular reaction
Two step reaction	Single step reaction
Carbocation intermediate formed	Hydrogen removes from beta carbon.
Reactivity order of RX is 3°>2°>1°	Trans elimination because low energy consumption.
No stereospecific.	Anti periplanar attack
Follow ziatsev rule	Polar aprotic solvent best
Polar protic solvent good because stabilized ionic intermediate.	Phenyl group influence elimination because product alkene further stabilised by resonance.
Rate of reaction increases when concentration of substrate increases.	Reactivity order 3°>2°>1°. No steric effect
Rearrangement may take place.	Strong nucleophile influence elimination
	No intermediate formed.

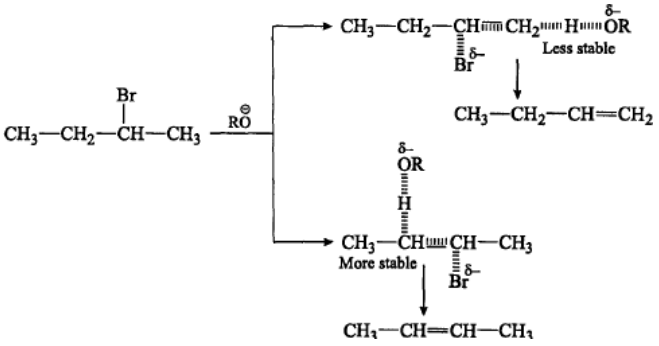
Saytzeff Rule (Zaitsev Rule):

According to this rule, major product is the most substituted alkene, *i.e.*,the most stable alkene. Thus, the major product is obtained by elimination of H^+ from that β-carbon whichhas the least number of hydrogen. Product of the reaction in this case is known as Saytzeff product.



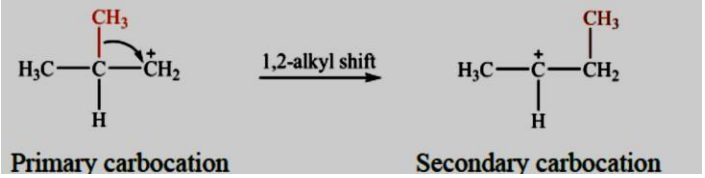
Theoretical Explanation for Saytzeff Rule

- Explanation for the more stable alkene (Saytzeff product) being formed in preference to the less stablealkene, is avail.lble from the transition states leading to these two alkenes.
- In either transition state, the removal of a proton and the formation of the double bond is taking placesimultaneously.
- The transition state has some double-bond character which is represented by the dotted line.

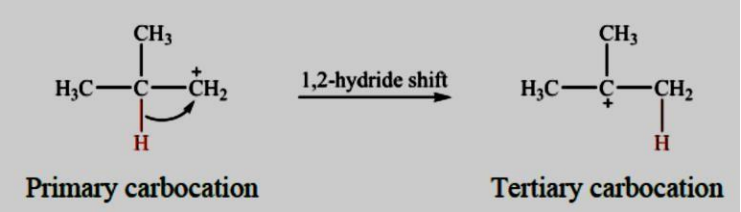


Rearrangement of carbocation:

- The bonding electrons of a carbocation may shift between adjacent atoms to form a more stablecarbocation.
- For example, rearrangement will occur if a secondary carbocation can be formed from a primarycarbocation because a secondary carbocation is more stable than the primary carbocation.
- There can be two types of rearrangements-
  1. Shift of an alkyl group is called a 1, 2-alkyl shift.
  2. 1, 2-hydride shift
  - In the following example the migrating methyl group-



  - Shift of a hydrogen atom is called a 1, 2-hydride shift (or a 1,2-H shift).
  - Hydride ion = H:-. In the following example the migrating hydrogen atom and the associated electron pair-



- Of these two rearrangement examples, hydride shift leads to a tertiary carbocation whereas alkyl shift leads to a secondary carbocation. Because a tertiary carbocation is more stable than a secondary carbocation, the hydride shift is favored in preference to the alkyl shift.

- Any C–H or C–C bond adjacent to a carbocation may shift (including C–C bonds that are part ofa ring), but only C–C and C–H bonds can migrate during carbocation rearrangement.
- The most common carbocation rearrangements involve a carbocation rearranging into a more stable carbocation, such as $2^o \rightarrow 3^o$ with resonance. (So use these rearrangements with impunity.)
- Rearrangements that transform a carbocation into another of apparently equal stability are lesscommon, but they do occur.
- Rearrangement to a less stable carbocation is very unusual, but also does occur.