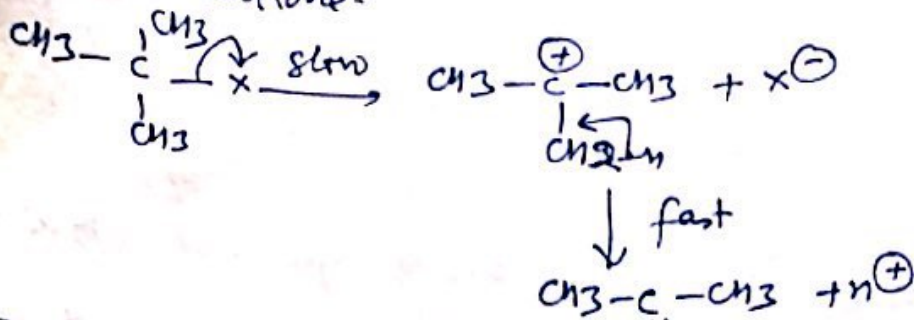


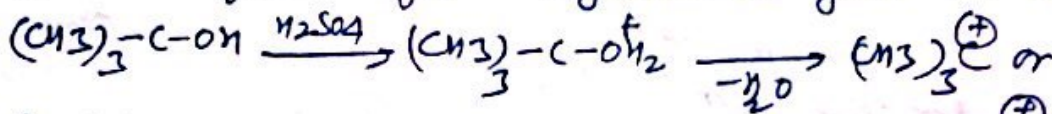
M.Sc. II sem. Elimination Reaction by P.K. Sharma 15-4-20

(2) In the second step, abstraction of proton from β -carbon atom produces alkene.

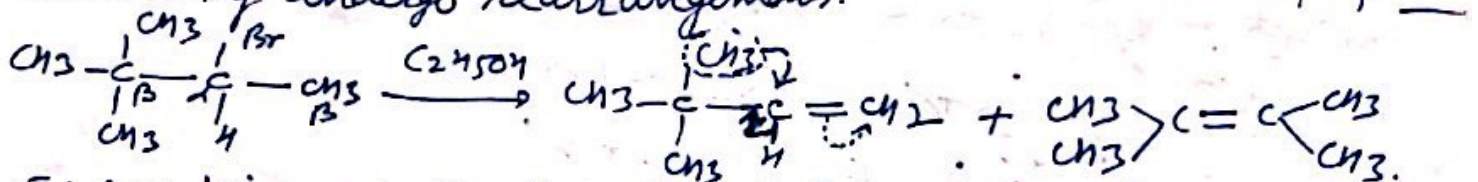


In case substrate is such that more than one alkenes can be formed then that alkene will be formed which has large no. of alkyl groups on doubly bonded carbon atoms. (Saytzeff Rule)

Acid catalysed dehydration of alcohols follows E1 mechanism.



In E1 mechanism, the rate of reaction is determined by the rate of formation of carbocation, due to formation of carbocation, these may undergo rearrangements.

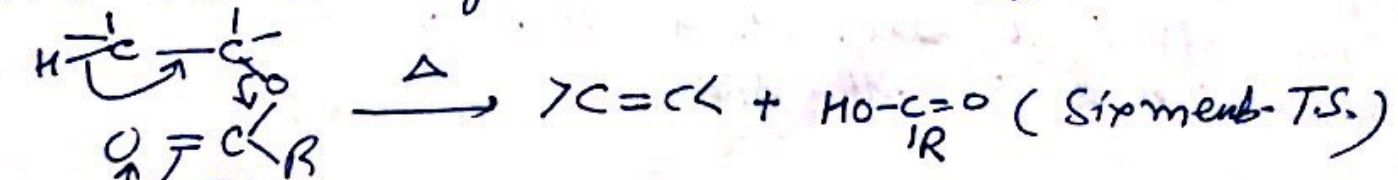


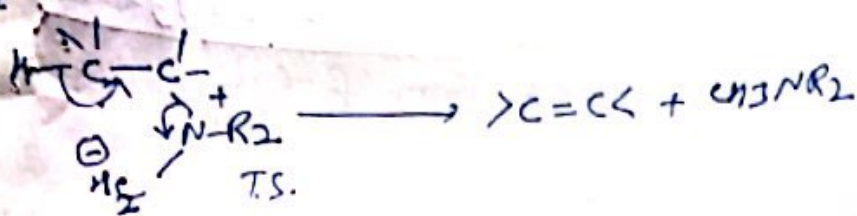
E1 reactions of both, the alkyl halides or amant. amrn. salts both give the same product. (More substituted alkene)

Pyrolytic SYN-Elimination or E_i Elimination (Elimination Internal)

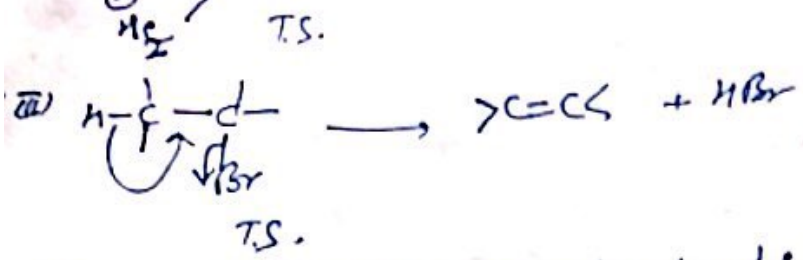
Acetates, xanthates and amine oxides, undergo such type of reaction, order being xanthates > Benzoates > acetates

A no. of compounds undergo elimination on heating, with no other reagent present. Mechanisms occurring in aqueous solutions are entirely different from those taking place in gaseous phase, pyrolytic eliminations. Two mechanisms have been found to operate - (A) Those involving four, five or six membered cyclic transition states - such as -





(Five memb. T.S.)



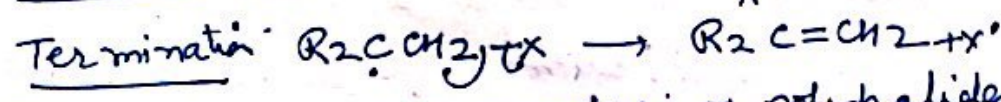
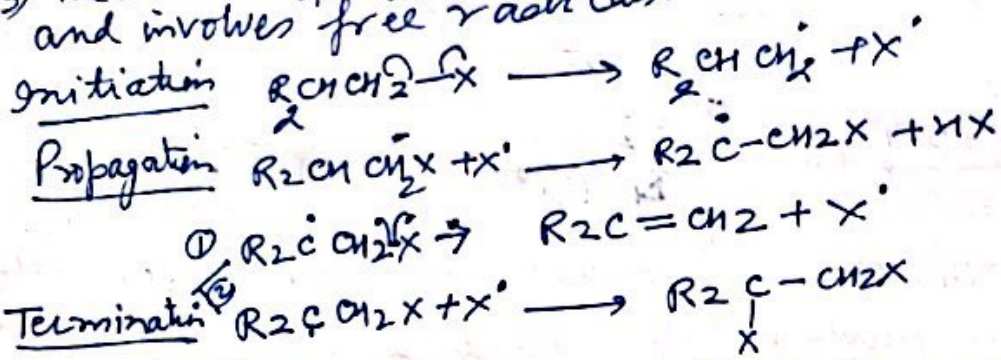
(Four memb. T.S.)

This mech. is called E_i-elimination. The two groups leave at about the same time.

Evidence for E_i-mech - (i) The Kinetics are first order, so that only one molecule is involved in the reaction.

- (ii) Free radical inhibitors do not slow the rate of reaction, so that no free radical mech. is involved.
- (iii) mech. predicts exclusive syn-elimination.
- (iv) C₁₄ vs. type effects for cope elimination show that both C-H and C-N bonds have been extensively broken in the T.S.

(B) The second type of pyrolysis mech. is quite different from E_i mech. and involves free radicals.



This mech. occurs in pyrolysis of polyhalides and of primary monohalides.

Orientation in Pyrolytic Elimination.

- (1) Orientation is statistical and is determined by β-hydrogens available, therefore, Hofman's rule is followed.
- 2) A cis-β-hydrogen is required.
- 3) In some cases, especially with cyclic compounds, the more stable olefine is formed.
- 4) Steric effect also plays role and steric interactions are minimized in transition state.

Reactivity = Effect of substrate structure, attacking base, leaving group and medium.

Now let us consider the effect of changes in the substrate structure attacking base, leaving group and the medium on overall reactivity.

E_1 vs E_2 vs E_1CB and elimination vs substitution.

① Effect of substrate structure. We refer carbon containing nucleophile as α and carbon containing proton as β . groups attached to these α and β carbons, exert four types of effects -

- ① They may stabilise or destabilise the appearing double bond.
- ② They may stabilise or destabilise the appearing negative charge affecting the acidity of proton.
- ③ They may stabilise or destabilise appearing +ve charge
- ④ They may exert steric effects

Effects ① and ④ can apply in all the three mechanisms; though steric effects are greatest for E_2 mechanism. Effect ② does not apply in E_1 and ③ does not apply in E_1CB mechanism. groups Ar and $C=C$, increase the rate by any mechanism. Electron withdrawing groups, increase the acidity when present in β -position. Thus Br, Cl, CN, TS, NO_2 in β -position will increase rate of reaction.

② Effect of attacking base. In E_1 mechanism, Additional base is not required. solvent acts as base. If external bases are added, mech shifts towards E_2 .

③ Effect of leaving group. E_2 -eliminations have been preferred with the following groups - $NR_3^+, SO_2R, OCOR, NO_2, F, Cl, Br, I, CN$. The only important leaving groups for preparative purposes are $OH_2^+ (E_1)$ and $Cl, Br, I, and NR_3^+ (E_2)$

④ Effect of Medium. With any reaction, a more polar environment enhances the mechanism, that involve ionic intermediates. Increasing polarity of solvent favours SN_2 reactions at the expense of E_2 . e.g. aq. KOH is used to effect elimination while more polar aq. KOH is used for substitution.

P.T.O.

Distinction between E₁, E₂ and E1cB mechanisms

E ₁	E ₂	E1cB
<ol style="list-style-type: none"> ① It is Two step reaction ② Reaction proceeds via formation of Carbocation. ③ Hydrogen leaves as proton from carbocation ④ Weak base is required for removal of proton ⑤ Reaction is Unimolecular ⑥ Main product is Saytzeff product. ⑦ Non stereospecific and non stereoselective ⑧ Reactivity depends upon stability of carbocation ⑨ Polar solvents increase rate of E₁ reaction ⑩ Basic strength has no effect on E₁ 	<ol style="list-style-type: none"> ① One step reaction ② proceeds via Transition state <li style="text-align: center;">— ④ Strong base is required for proton removal ⑤ Bimolecular ⑥ may be both Saytzeff or Hofmann product ⑦ Stereospecific and stereoselective ⑧ Reactivity depends upon stability of alkene ⑨ Polar aprotic solvents increase rate of E₂ reaction ⑩ Strong base increases rate of E₂ reaction 	<ol style="list-style-type: none"> ① Two step reaction ② Carbocation is formed ③ Leaving group leaves the Carbocation as either a neutral sp. ④ Strong base is required for removal of proton ⑤ unimolecular ⑥ Main product is Hofmann product ⑦ Non stereospecific and non stereoselective ⑧ Reactivity depends upon stability of carbocation ⑨ Polar solvents increase rate of E1cB reaction ⑩ Strong base increases rate of E1cB reaction