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E1 REACTION MECHANISM

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The substitution reactions of alkyl halides are often accompanied by an elimination reaction in which the elements of a hydrogen halide are removed and a carbon – carbon double bond is formed.

The hydroxide ion can either act as a nucleophilic reagent, donating an electron pair to the α - carbon, thus facilitating substitution, or as a base, donating an electron pair to the hydrogen attached to the β carbon, thus facilitating elimination.

The substitution and elimination reactions are similar in many respects. Elimination may occur by two main mechanisms:
(i) a bimolecular, one-step mechanism, E2,
(ii) a unimolecular, two-step mechanism, E1

The unimolecular, two-step mechanism, E1 will be considered first:

Kinetics:

- Unimolecular, two-step Mechanism
- $Rate = k[R - X]$ where, k = rate constant

Comparison to Other Reactions:

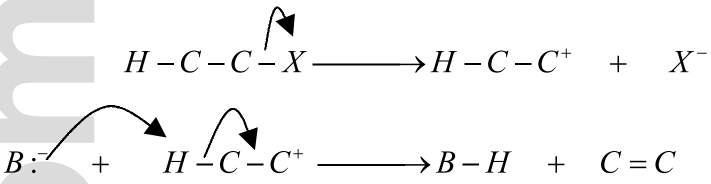
- Similar to S_N1: The rate determining step in both E1 and S_N1 is the slow ionization of the alkyl halide to form a carbocation intermediate. The fast step is the elimination reaction in which a proton is lost to the hydroxide ion acting as a base.
- The stronger the base, greater the branching in the halogenoalkane and by carrying out the reaction in a polar solvent, will all contribute to promoting the E1 reaction to take place.
- Under given experimental conditions either substitution or elimination may occur or the two reactions may effectively compete with each other. The structure of the halogenoalkane and the reaction conditions both have a considerable effect on the relative amounts of the two reactions. In general, primary halogenoalkanes tend to give high yields of substitution products with little or no elimination, while tertiary halogenoalkanes undergo elimination almost exclusively to give an alkene. Secondary halogenoalkanes are intermediate I behaviour and give a mixture of substitution and elimination products: the elimination reaction can, however be promoted by using a strong base in high concentration at a higher temperature.

Conditions:

- Good leaving group
- Stable carbocation
- Hot, concentrated alkali. (The elimination reaction has a higher activation energy than the competing substitution reaction and the elimination/substitution ratio can, therefore, be increased by raising the reaction temperature.)

Reaction Mechanism:

[Note: B refers to a base, such as $OH^{-}, CH_3COO^{-1}, NH_2^{-1}$]



Step 1: A carbocation is generated by the loss of a halide leaving group.
Step 2: A base reacts with the carbocation, causing the carbocation to lose a proton in order to form a $\pi-bond$.

Tertiary halogenoalkanes undergo this type of reaction because the intermediate carbocation is more stable due to the positive inductive effect of the other attached alkyls.

A movie of this reaction can be found at:
http://www.jbpub.com/organic-online/movies/e1.htm