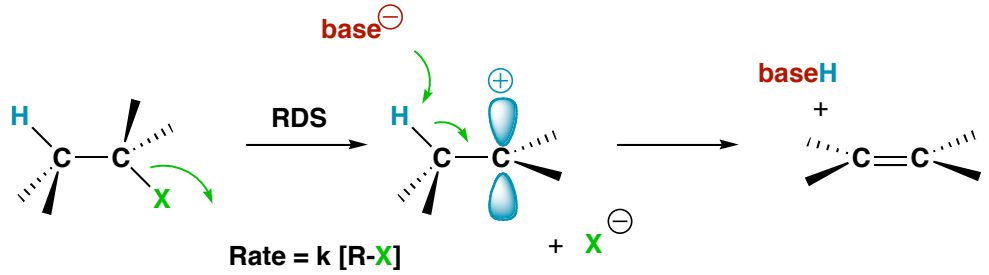
Chapter 11 - Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations

E1 Elimination

If the elimination reaction takes place in a two step process, this is called an E1 elimination. Similar to a S_N1 substitution reaction, the rate of the reaction depends on how easily a carbocation can be formed. Thus, the rate expression indicates the reaction is unimolecular. There is no requirement for antiperiplanar alignment of a hydrogen with the leaving group as the hydrogen is not taken off in the rate determining step. Once the carbocation is formed, an adjacent hydrogen can align with the p-orbital and be taken off. Since the base is not involved in the RDS, it's strength is less important than that for an E2 elimination. Usually E1 and S_N1 pathways are in competition with each other and a mixture is often formed.



E1 Elimination Characteristics - Substrate

Exactly like the S_N1 reaction, the E1 reaction depends on easily forming a carbocation. Thus, 3° will work best and secondary allylic substrates can react. Secondary is slower and primary is very unlikely.

E1 Elimination Characteristics - Base

Strong bases are not required. Weaker bases will work just fine.

E1 Elimination Characteristics - Leaving Groups

Since the leaving group is departing in the reaction, it is important just like in the S_N1 reaction. Better leaving groups that form more stable anions are best for elimination reactions.

E2 Elimination Characteristics - Solvent

Polar protic solvents are best. Polar solvents help to stabilize the carbocation intermediate and protic solvents help to stabilze the leaving group anion.

Summary of Substitution and Elimination Reactions

Sometimes it is difficult to tell what mechanism will be the predominant pathway in a reaction. Usually the most important factor is the substrate. For competing elimination reactions, the base strength (vs. nucleophile) is key.

R-X	S_N1	S_N2	E1	E2
1°	X	favored with good nucleophile	X	favored with strong base
2°	can occur best if allylic	can occur with good nucleophile	can occur best if allylic	favored with strong base
3°	favored competes with E1	X	favored if basic competes with S_N1	favored with strong base
Stereochem	racemic	100% inversion	doesn't matter	antiperiplanar required