❖ Reactivity – Effects of Substrate Structures, Attacking Base, the Leaving Group and The Medium

In this section, we will discuss the effects of substrate structures, attacking base, the leaving group, and the nature of the medium on the reactivity of elimination reactions.

➢ *Effect of Substrate Structure on the Reactivity of Elimination Reactions*

The effects of substrate structures on the reactivity of elimination reactions can be divided into the following categories.

1. Effect on the reaction Rate: Different Groups bonded to the α-carbon (C with nucleofuge i.e., C−X) or β-carbon (C that loses proton i.e., C−H) can primarily exercise four types of influences as discussed below.

i) The emerging double bond can be stabilized or destabilized by these groups.

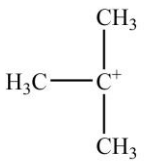
ii) The groups attached at β-carbon can affect the acidity of β-proton by stabilizing or destabilizing the emerging negative charge.

iii) The groups attached at α-carbon can affect the stability of the emerging positive charge.

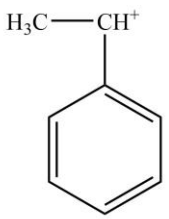
iv) The groups attached at α- and β-carbon can exert eclipsing effects (steric effects).

The first and fourth types of effects can affect all three kinds of elimination mechanisms, with steric effects as most dominant in E_2 reactions. Also, the second and third kinds of effects cannot be applied to E_1 and E_1CB, respectively. If the C=C bond formation is the rate-determining, the presence of C=C or aromatic ring enhances the reaction rate in all mechanisms. Finally, the presence of electron-withdrawing groups at β-position raises the acidity of leaving hydrogen but has little to no effect at α-sites provided that no multipole bond conjugation available; making CN, Br, Cl, NO_2, Ts, SR, and CN suitable E_2-kind reactions.

2. Effect on E_1 vs E_2 vs E_1CB: Since the presence of aryl or alkyl group at α-carbon can stabilize the carbocation via resonance or inductive effect, A shift towards the E_1 pathway should be observed in the same. Also, the same shift can also be carried out by Alkyl groups at β-position by decreasing the acidity of the hydrogen atom. Nevertheless, the presence of aryl groups at β-carbon will push the towards E_1CB pathway by carbanion's stabilization. Conclusively, it has been observed that the presence of any electron-withdrawing group at β-site always pushes the reaction E_1CB pathway. Finally, it should also be remembered that E_2C reactions are also favored by the presence of alkyl groups at α-sites.



Stablized via hyperconjugation or inductive effect (support E_1)



Stablized via Resonance (support E_1)

3. Effect on elimination vs substitution: In bimolecular elimination reaction, the rate of reaction increases as the branching increases. This behavior can easily be rationalized in terms of statistical and steric factors. In other words, the increased α-branching leads to more base-attackable hydrogens, and increased steric hindrance opposes the attack at the carbon simultaneously. Moreover, the increased α-branching also supports unimolecular elimination over unimolecular nucleophilic substitution. The E_2 pathway is also favored over SN_2 when branching at the β-carbon is raised because of the suppression of the latter. Similarly, The E_1 pathway is also favored over SN_1 when the branching at the β-carbon is raised because of the steric factors. If the leaving group has a charge on it, the branching at the β-carbon will slow down the rate of E_2 reactions (Hofmann's rule). Also, the presence of electron-withdrawing groups at the β-site supports E_2-pathway with the simultaneous shift towards the E_1CB route but (upsurging the elimination/substitution ratio).

- ***Effect of Attacking Base on the Reactivity of Elimination Reactions***

The effects of attacking base on the reactivity of elimination reactions can be divided into the following two categories.

1. Effect on E_1 vs E_2 vs E_1CB: The outside base isn't required in E_1 reaction under typical conditions because itself can act as the base. Therefore, the reaction pathway shifts from E_1 to E_2 when the outside bases is mixed. Furthermore, adding more outside stronger base will shift the pathway even towards E_1CB. Nevertheless, weak bases are also capable of yielding elimination reactions with some particular substrate-types. Bases (besides organic) yielding normal E2 reactions are given below.

$$NH_2^-, OR^-, OAr^-, CO_3^{2-}, LiAlH_4, CN^-, H_2O, NR_3, OH^-, OAc^-, I^-$$

It should also be noted that not all the bases are useful as far the practical synthetic route is concerned; for instance, NH_2^-, OR^- and OH^- are valuable for normal E_2 reaction; whereas the bases like OAc^-, Cl^- and RS^- are useful in preparing quaternary salts.

2. Effect on elimination vs substitution: Besides supporting E_2 over E_1, strong bases also assist elimination over substitution reactions. The concentrated solution of strong bases in a nonionizing solvent not only favors E_2 but also helps them to outrank the SN_2 pathway. On the other hand, dilute basic solutions in ionizing solvents not only favor E_1 but also help them to outrank the SN_1 pathway. It was also deduced from the nucleophilic substitution studies that stronger bases aren't necessarily stronger nucleophile; and therefore, a weaker nucleophile but stronger base will prefer elimination over substation. Nevertheless, weak bases can also lead to elimination if the solvent used is polar and aprotic.

- ***Effect of Leaving Group on the Reactivity of Elimination Reactions***

The effects of leaving-group on the reactivity of elimination reactions can be divided into the following categories.

1. Effect on the general reactivity: Despite the different nature of the pathways, the leaving groups in both cases behave pretty much similar. Leaving groups in E_2 are NO_2, F, Cl, Br, I, NR_3^+, OHR^+, SO_2R, PR_3^+, SR_2^+, OSO_2R, OOR, OCOR, OOH, and CN; leaving groups in E_1 are NR_3^+, OSO_2R, SR_2^+, OH_2^+, OHR^+, Br, I, OCOR, Cl, and N_2^+.

2. Effect on E_1 vs E_2 vs E_1CB: Since the better leaving groups make the ionization easier, they will move the pathway towards E_1 reactions, which can be confirmed via ρ-values. Furthermore, positively charged or poor leaving groups will shift the pathway towards the E_1CB reactions, which can be attributed to the increased acidity β-protons that arises from the strong field effects of electron-withdrawing nature. Finally, it has also been observed that good leaving groups support E_2C reaction.

3. Effect on elimination vs substitution: Since the reaction pathway (elimination or substitution) is decided only after the departure of the leaving group in the reactions following first-order kinetics, the leaving group will not be able to prefer elimination over substitution, and vice-versa. Nevertheless, if ion-pair formation had taken place, the leaving group will affect the final product. Therefore, the elimination to substitution ratio (e/s) is largely independent of a halide as leaving group with only a minor raise in elimination to Cl < Br < I. On the other hand, the substitution pathway is strongly favored if the leaving group is like OTs. For instance, *n*-$C_{18}H_{37}Br$ treated with t-BuOK results in 85% elimination, whereas *n*-$C_{18}H_{37}OTs$ gives rise to 99% substitution under similar experimental conditions. Conversely, leaving groups with a positive charge will increase the elimination yield.

- ***Effect of Medium on the Reactivity of Elimination Reactions***

The effects of the medium on the reactivity of elimination reactions can be divided into the following categories.

1. Effect on E_1 vs E_2 vs E_1CB: It is quite a well-known fact that reaction-rate increases with solvents polarity increases if the intermediates involved are ionic in nature. Furthermore, it has also been observed that the rate of E_1 and E_1CB pathways are also supported by increasing solvent's polarity and ionic strength, even if the leaving group is neutral in nature. Lastly, aprotic polar solvents encourage E_2C reactions with some particular substrates.

2. Effect on elimination vs substitution: The SN_2 pathway is favored at the cost of E_2 one if the solvent polarity is increased. For instance, KOH results in more elimination in alcohol but favors substitution in water as a solvent; which can partially be explained via the charge-dispersal phenomenon. On the other hand, the SN_1 pathway is encouraged over E_1 in most of the solvent mediums. Nevertheless, in the polar solvents with low nucleophilic character, the E_1 pathway become more prominent than the usual (like dipolar aprotic mediums). Finally, it has also been observed in the gas-phase studies (i.e., no medium) that when MeO^- reacts with1-bromopropane exclusively via the elimination-route even if the substrate used in the process are only primarily substituted.

3. Effect of temperature: It has been proven again and again that raising the reaction temperature almost always supports the elimination over substitution despite the order of the reaction (first or second-order). This behavior can simply be attributed to the higher activation energies of eliminations than those of substitutions, arising from larger bonding-alteration.

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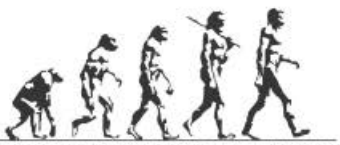

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