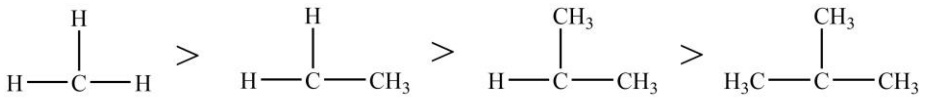
## ❖ Effect of Substrates, Leaving Group and the Solvent Polarity on the Reactivity

The reactivity of aliphatic electrophilic substitution reactions is affected by many factors that can be better understood via experimental data and theoretical treatment combined. In this section, we will discuss some major factors that greatly influence the electrophilic substitution's rate in aliphatic compounds like substrate structure, leaving group and reaction medium.

### ➢ *Effect of Substrate Structure*

The electron-donating groups of the substrate decrease the rate of $SE_1$ reactions whereas electron-withdrawing groups show an opposite trend. This declining rate in the $SE_1$ pathway with electron-donating groups is quite normal for a reaction-type where the proton's dissociation is the rate-determining step (like in the case of acidic character). Jensen and Davis proved that the reactivity of alkyl groups is similar in $SE_2$-back as that for the $SN_2$ pathway, which can be attributed to the backside attack and steric hindrance, simultaneously.



Reactivity of alkyl groups for $SE_2$-back pathway

Furthermore, it has also been observed that the rate of front-mode electrophilic substitution in aliphatic compounds increases as the branching in the substrate increases increased, which can be attributed to the electron-releasing effect of the alkyl groups that makes the electron-deficient transition state more stable. However, it is also worthy to note that β-branching will reduce the substitution rate in $SE_2$-front because of the steric hindrance.

### ➢ *Effect of Leaving Group*

The ease of electrofuge's detachment in both types ($SE_1$ and $SE_2$) increases with the increasing polarity of the C−X bond. Nevertheless, if the leaving group is metallic in nature and metal has a valence greater than one, then any group attached to the metal center will affect its electrofugal ability. For instance, consider the case of $Me_3C-Hg-W$ (organomercurials) where the rate of reaction has decreased. The reason lies in the fact that although Hg and W have less electronegativity than carbon (which is why the C−Hg bond is polar), the C−Hg bond becomes less polar due to the higher electronegativity W than Hg. In other words, carbon will have a lower negative charge in the C−Hg bond when W is attached to Hg because tungsten will support Hg to hold the shared pair more firmly. Therefore, −HgMe will be a better leaving group than −HgCl.

Hg–*t*-Bu > Hg–*i*Pr > HgEt > HgMe

Leaving-group order

Furthermore, it is also worthy to note that carbon-based leaving groups support the $SE_1$ mechanism, whereas $SE_2$ or $SE_i$ mechanisms are favored by metal-based leaving groups.

➢ ***Effect of Solvent Polarity***

Just like the case of aliphatic nucleophilic substitution reactions, the raise in solvent polarity boosts the chances of the $SE_1$ pathway by supporting the ionization because of the better solvation of carbanions. However, if $SE_2$ and $SE_1$ reactions are competing with each other in parallel propagation, then less polar solvents favor the $SE_2$ pathway and polar solvents favor the $SE_1$ mechanism. Finally, If the nucleophilic character of the solvent is very small, the electrophile with properly placed assisting functionality might support the reaction; and therefore, motivating the reaction towards the $SE_i$ pathway; otherwise, solvent polarity has little to no effect upon $SN_i$ reactions.

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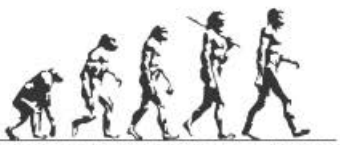

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