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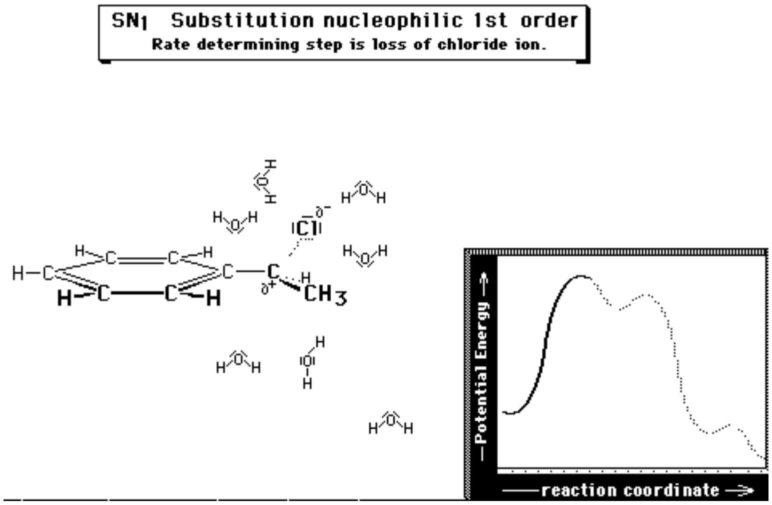
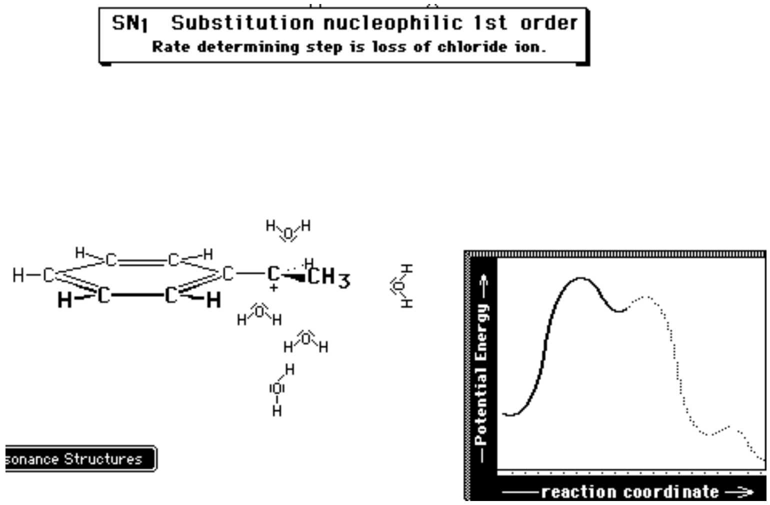
*Chemistry 0310 - Organic Chemistry 1*

# $S_N1$ & Elimination Reactions

$S_N1$ reactions are first order with respect to the concentration of the electrophile and independent of the concentration of the nucleophile. The reaction proceeds via a rate-limiting ionization of the electrophile to give an $sp^2$-hybridized planar carbocation intermediate. Subsequent reactions with nucleophiles or solvents occur commonly under overall racemization. Hyperconjugation stabilizes the intermediate carbocation.



**SN1 Substitution nucleophilic 1st order**
Rate determining step is loss of chloride ion.

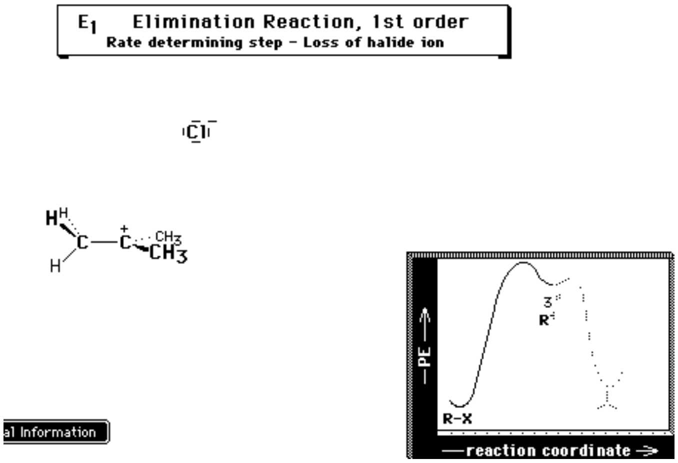


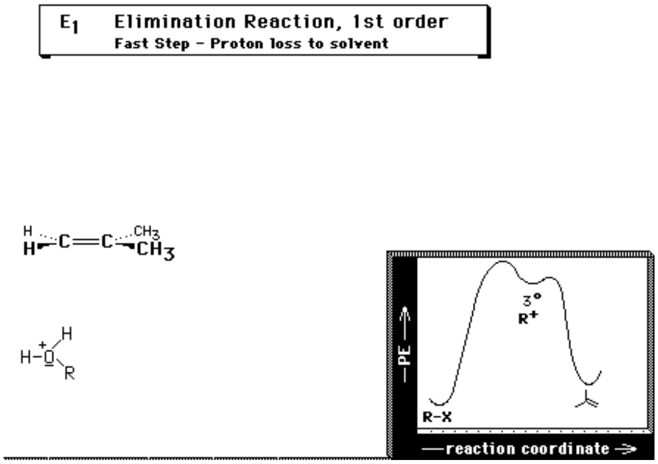
**SN1 Substitution nucleophilic 1st order**
Rate determining step is loss of chloride ion.

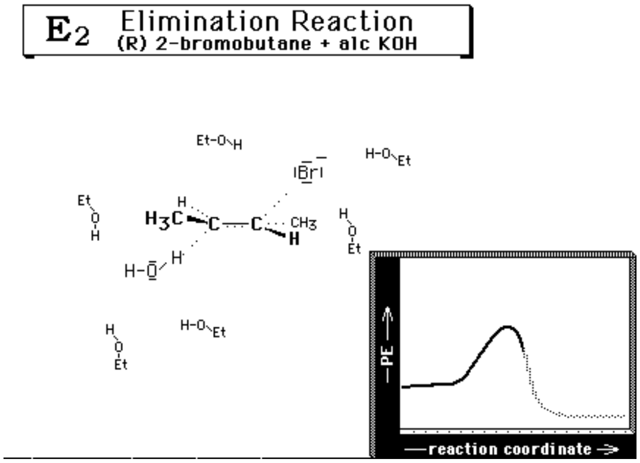
The order of reactivity for alkyl halides and alkyl sulfonates in $S_N1$ reactions is 3°>2°>1°>$CH_3$.

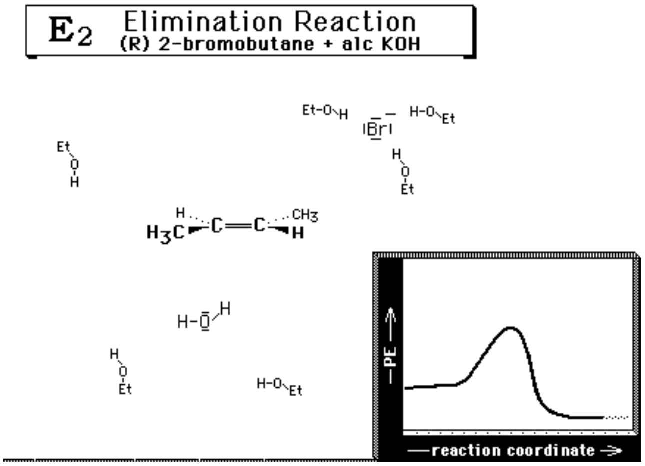
Polar protic solvents favor $S_N1$ by stabilization of the intermediate carbocation and solvation of nucleophiles. Polar aprotic solvents favor $S_N2$. Vinylic (alkenyl) halides and vinylic (alkenyl) sulfonates are generally extremely unreactive in substitution reactions.

An elimination reaction may be either $E_1$, involving a carbocation intermediate, or $E_2$, which is a second-order reaction. Eliminations occur in competition with substitutions and are promoted by strong and sterically hindered bases (poor nucleophiles), high temperatures, and steric hindrance in electrophiles. For elimination reactions that can give rise to more than one alkene, the more highly substituted alkene is the major product. $E_2$ reactions proceed via anti-orientation of the leaving group and the proton that is removed. The order of reactivity for alkyl halides and alkyl sulfonates in elimination reactions is 3°>2°>1°.


$E_1$ Elimination Reaction, 1st order
Rate determining step – Loss of halide ion


$E_1$ Elimination Reaction, 1st order
Fast Step – Proton loss to solvent


$E_2$ Elimination Reaction
(R) 2-bromobutane + alc KOH


$E_2$ Elimination Reaction
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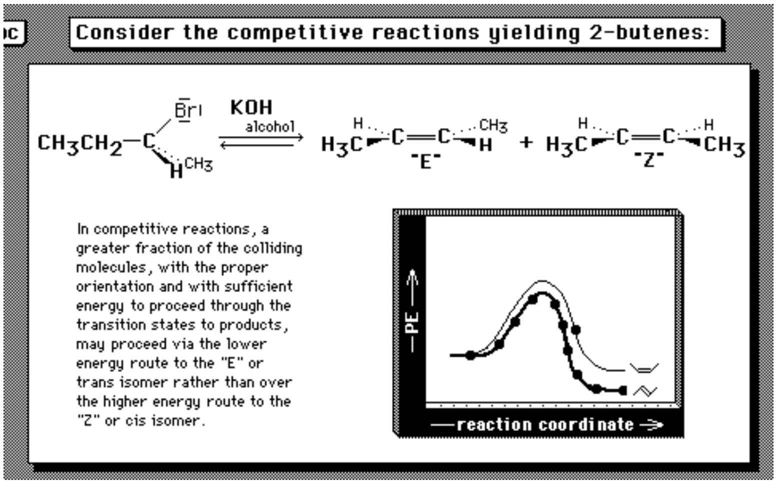
Consider the competitive reactions yielding 2-butenes:

In competitive reactions, a greater fraction of the colliding molecules, with the proper orientation and with sufficient energy to proceed through the transition states to products, may proceed via the lower energy route to the "E" or trans isomer rather than over the higher energy route to the "Z" or cis isomer.