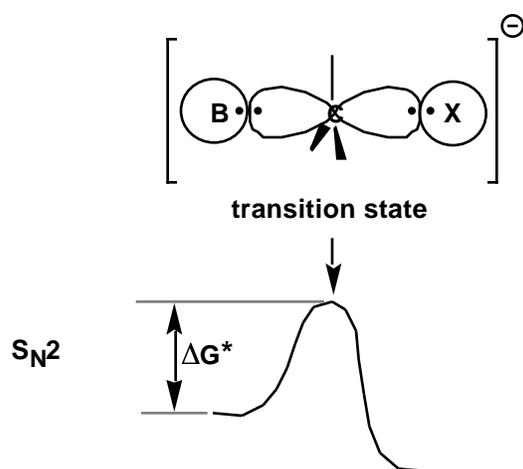
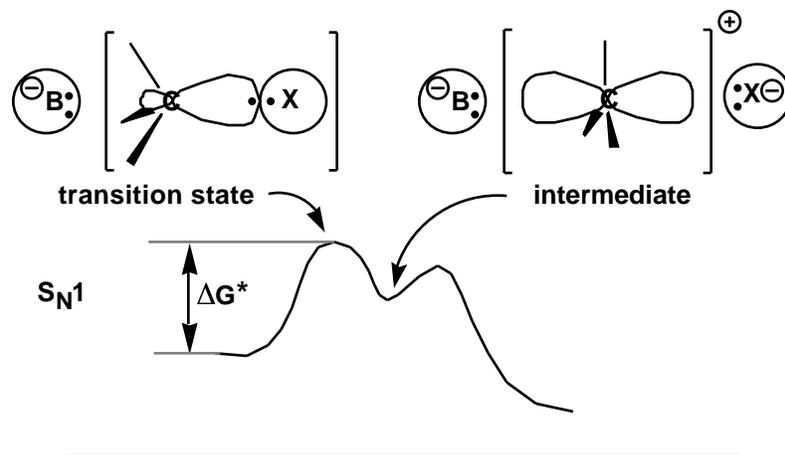


Text Related to Segment 14.02 ©2002 Claude E. Wintner

It is important to point out the similarity of the S_N1 picture introduced in the previous segment to the scenario already developed for the S_N2 mechanism. In each case the central actor is an electron deficient carbon atom having sp^2 hybridization and a perpendicular $2p_z$ orbital. *The difference lies entirely in the timing.* In the S_N1 case the leaving group leaves first, resulting in a trivalent electrophilic carbon intermediate — lying at relatively high energy, but at a *local energy minimum* — that only later reacts with a new nucleophile to replace the lost bond; hence, the first-order kinetic rate law. On the other hand, in the S_N2 mechanism the reaction is concerted: bond breaking and bond making are synchronous, the result being the formation of a transition state — *an energy maximum* — having the central electrophilic carbon atom half-bonded to each of the competing nucleophiles. Here the consequence is a second-order rate law, because both the attacking nucleophile and the substrate are incorporated in the transition state:



comparison of energetics of S_N1 and S_N2 mechanisms

How reasonable is it from the point of view of energy to postulate the involvement of such carbocation intermediates? By combining several experimental values, one can calculate enthalpies of reaction for the *gas phase* formation of the carbocations of interest to us, as listed in the figure below. While all of these enthalpy values are *extremely* unfavorable, the breadth of their spread nevertheless reflects the fact that, in the gas phase, tertiary carbocations are far more stable than secondary carbocations, which in turn are far more stable than primary carbocations, and in turn again are far more stable than the methyl carbocation. A second set of calculations, involving considerably more risky assumptions (but finally

defensible on the basis of agreement with observation!), estimates free energies of reaction in solution, *taking into account solvation*. Given that activation energies in the range of 20 kcal/mole are surmountable in solution in the neighborhood of room temperature, then on the basis of these results we can conclude that the S_N1 mechanism should be available for nucleophilic substitution for tertiary halides, and perhaps for secondary halides, but not for primary halides, and certainly not for methyl halides. Note that thus we are presented with a situation entirely complementary to that which obtains with the S_N2 mechanism: any observed substitution reaction for a primary halide will *not* be unimolecular, just as any observed substitution reaction for a tertiary halide will *not* be bimolecular.

	ΔH° for gas phase reaction, calculated from combination of experimental values, kcal/mole	ΔG° estimated for reaction in solution, taking into account solvation, kcal/mole	Attainable under "normal" solution reaction conditions?
$\text{CH}_3\text{-Br} \longrightarrow \begin{array}{c} \text{H} \\ \\ \text{C}^{\oplus}\text{-H} \\ \\ \text{H} \end{array} \quad \text{Br}^{\ominus}$	+215	+66	NO!
$\text{CH}_3\text{CH}_2\text{-Br} \longrightarrow \begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}^{\oplus}\text{-H} \\ \\ \text{H} \end{array} \quad \text{Br}^{\ominus}$	+180	+43	no
$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{CH}-\text{Br} \\ \\ \text{H}_3\text{C} \end{array} \longrightarrow \begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}^{\oplus}\text{-H} \\ \\ \text{H}_3\text{C} \end{array} \quad \text{Br}^{\ominus}$	+160	+28	perhaps
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{Br} \\ \\ \text{CH}_3 \end{array} \longrightarrow \begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}^{\oplus}\text{-CH}_3 \\ \\ \text{H}_3\text{C} \end{array} \quad \text{Br}^{\ominus}$	+140	+12	yes

thermodynamic values for formation of methyl, primary, secondary, and tertiary carbocations

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