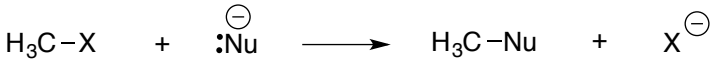
Chemistry 233
Chapter 11 Handout – Substitution Reactions

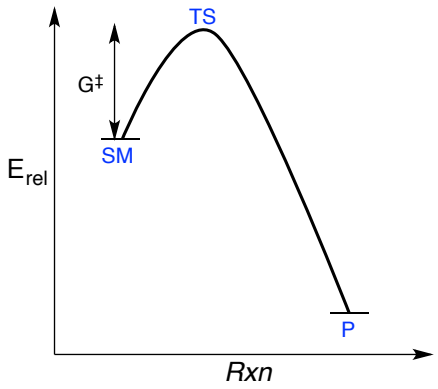
S_N2 Reaction - Substitution Nucleophilic Bimolecular

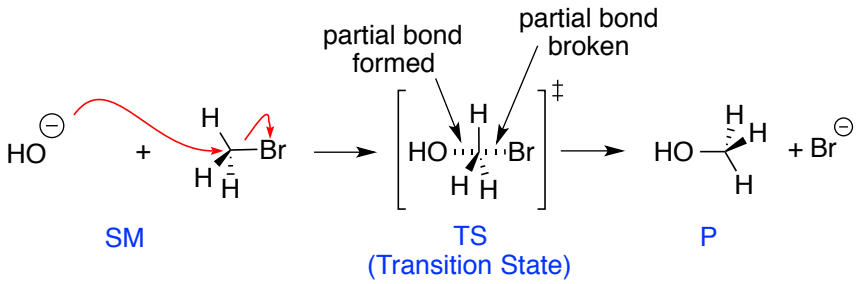


Only a single step in the reaction
This single step must then = slow step

Rate = $k[H_3C-X][Nu^-]$

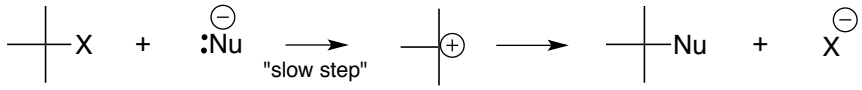
Reaction Coordinate:





G‡ = energy required to get to the transition state

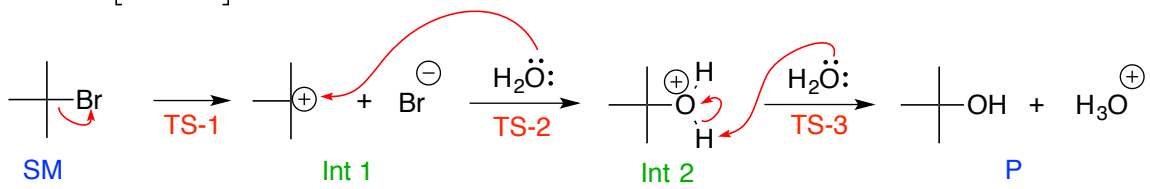
S_N1 Reaction - Substitution Nucleophilic Unimolecular

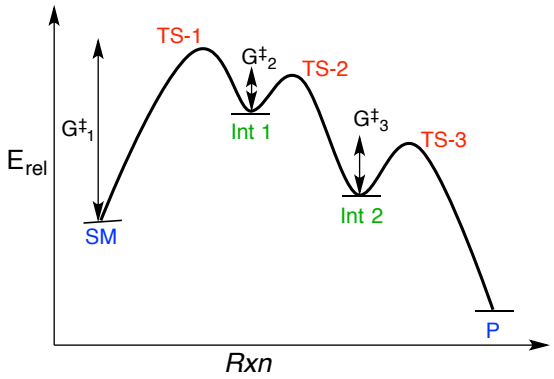


More than one step involved in the reaction with discrete intermediate
Carbocation formation is the rate determining step
Only a single reactant (the alkyl) halide is involved in the rate determining step = unimolecular

Rate = k [X]

Changing the concentration of R-X changes the reaction rate
Chaing the concentration of any other reactants will not affect the rate

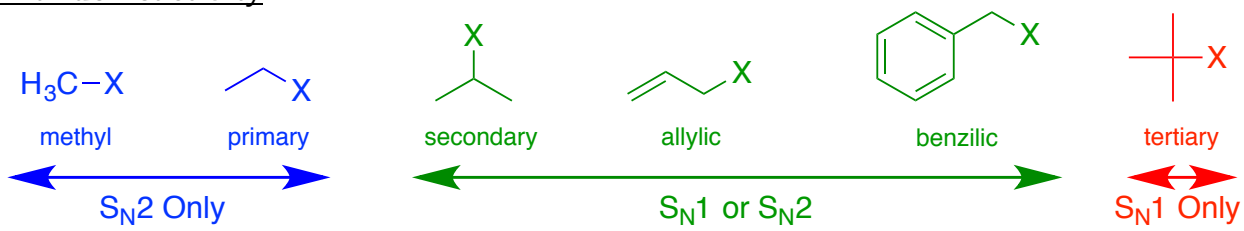




$G^{\ddagger}_1 > G^{\ddagger}_2$ and $G^{\ddagger}_3$

Requires the most energy therefore = slow step of the reaction

Alkyl Halide Reactivity



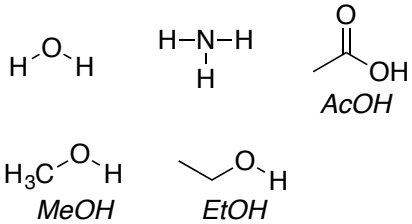
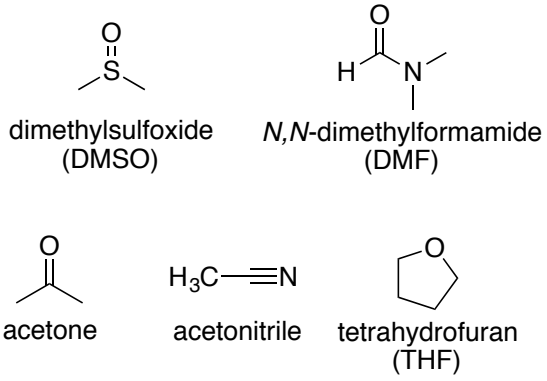
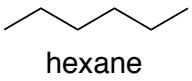
Common Nucleophiles

Strong					Weak
X	$Cl^{\ominus}$	$Br^{\ominus}$	$I^{\ominus}$		$F^{\ominus}$
S	$HS^{\ominus}$	$RS^{\ominus}$	H_2S	RSH	H_2O
O	$HO^{\ominus}$	$RO^{\ominus}$			ROH
C	$N{\equiv}C^{\ominus}$	$R{-}C{\equiv}C^{\ominus}$			

Good Leaving Groups

R—I R–Br R–Cl $R{-}\overset{\oplus}{O}H_2$ R–OTs
(we will talk about this one later on)

Common Solvents

Polar Protic	Polar Aprotic	Non-Polar
 *AcOH*; *MeOH*; *EtOH*	 dimethylsulfoxide (DMSO); *N,N*-dimethylformamide (DMF); acetone; acetonitrile; tetrahydrofuran (THF)	 hexane; CCl_4 carbontetrachloride
Used in S_N1 Reactions	Used in S_N2 Reactions	Not Used in Substitution Reactions

Differentiating Between S_N1 and S_N2

Factor	Favoring S_N2	Favoring S_N1
Substrate	Methyl or primary	Tertiary
Nucleophile	Strong nucleophile	Weak Nucleophile
Leaving Group	Good leaving group	Very good leaving group
Solvent	Polar Aprotic	Polar Protic