(2) **Today**

Sections 11.1 - 11.6: Substitution Reactions

Next Class (3)

Sections 11.1 - 11.6: Substitution Reactions

Sections 10.5, 17.6: Alcohols in Nucleophilic Substitution Reactions

(4) **Second Class from Today**

Sections 10.5, 17.6: Alcohols in Nucleophilic Substitution Reactions

Third Class from Today (5)

Sections 11:7 - 11:11: Elimination Reactions

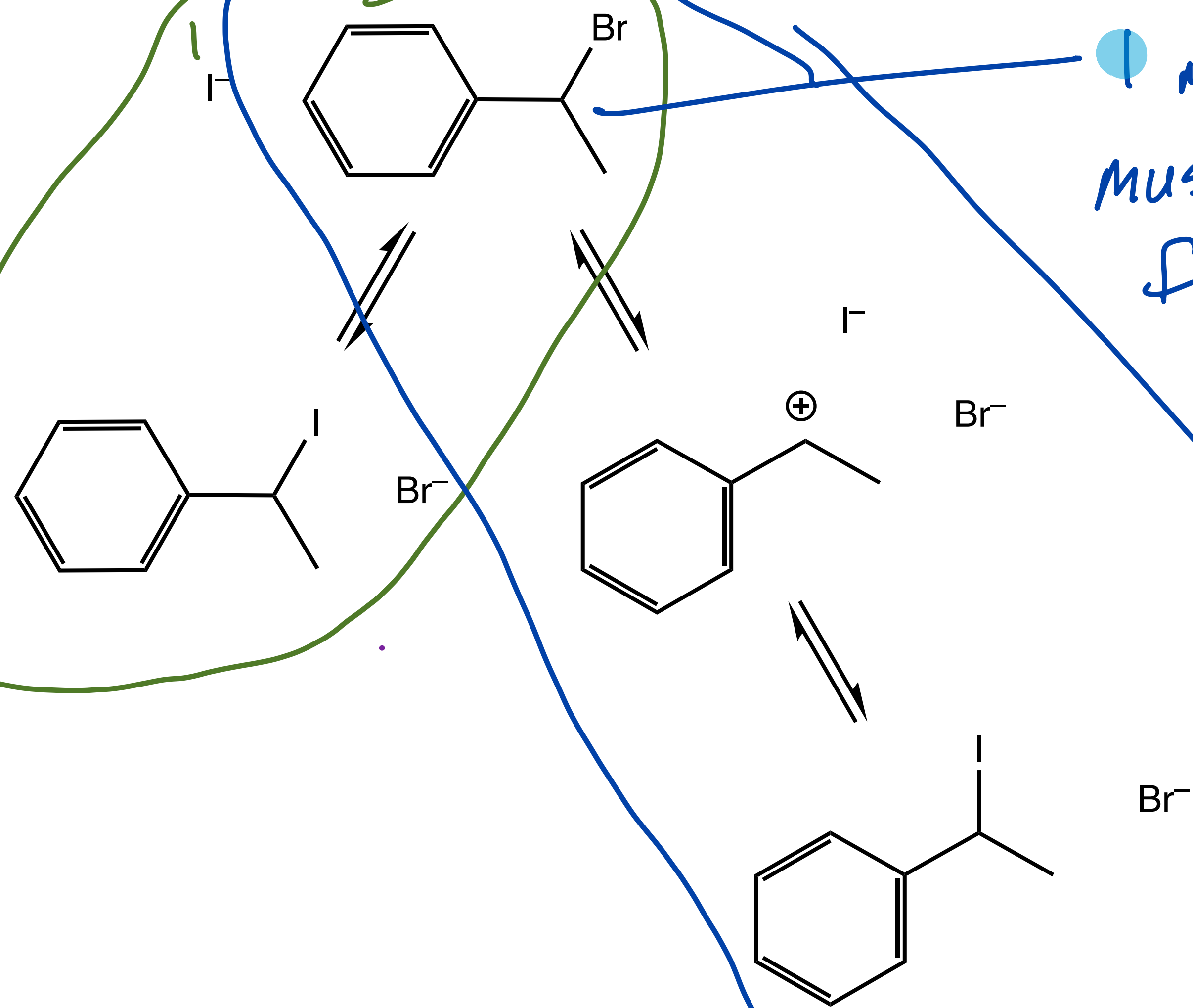
Mechanisms of Nucleophilic Substitution: S_N1 and S_N2

2 molecules collide

bimolecular

in rate determining step (RDS)

S_N2



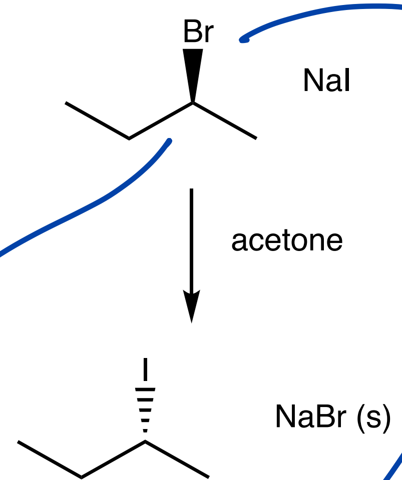
1 molecule must ionize first in RDS

S_N1

S_N+

Evidence for S_N2 and S_N1

S_N2

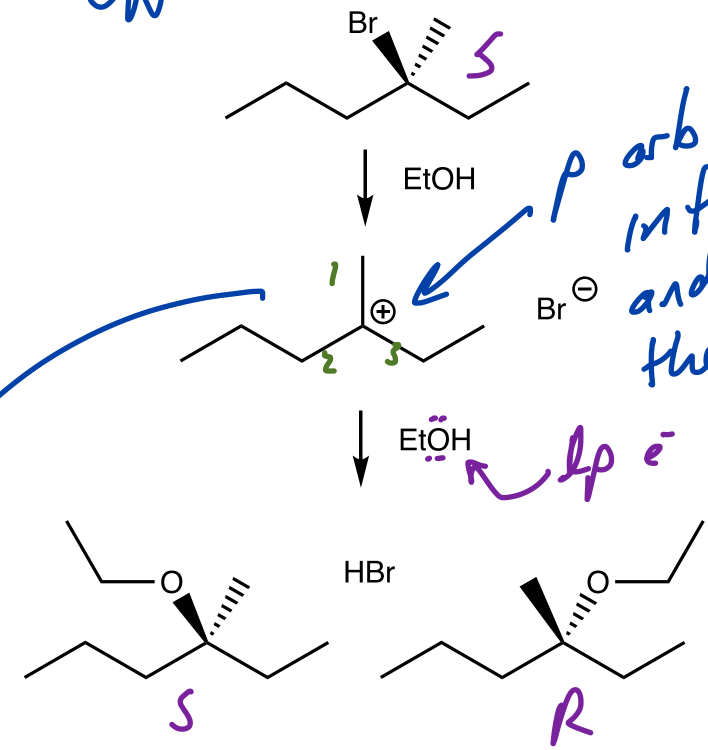


Nu must come in from behind

I⁻ cannot come in from the front, the Br is in the way

Inversion of stereochemistry

S_N1



p orb exists in front of and behind the screen

lp e⁻ make alcohols nucleophilic

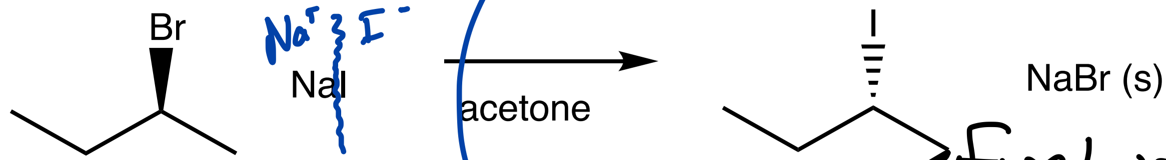
planar C⁺ ...
Nu can come in from either side

Mixture of stereoisomers

Evidence for S_N2 and S_N1

Section 11.2 and 11.4

S_N2



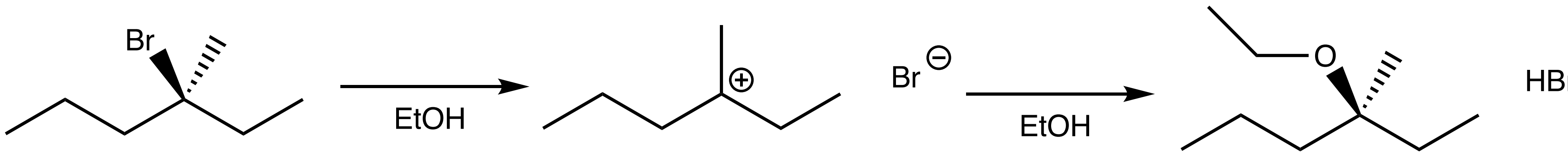
predicted rate law
1st order in [Nu] + the [substrate]

rate = k [$CH_3CH_2CH_2CH_2Br$][I^-]

First order w.r.t [substrate]

First order w.r.t. [Nu]

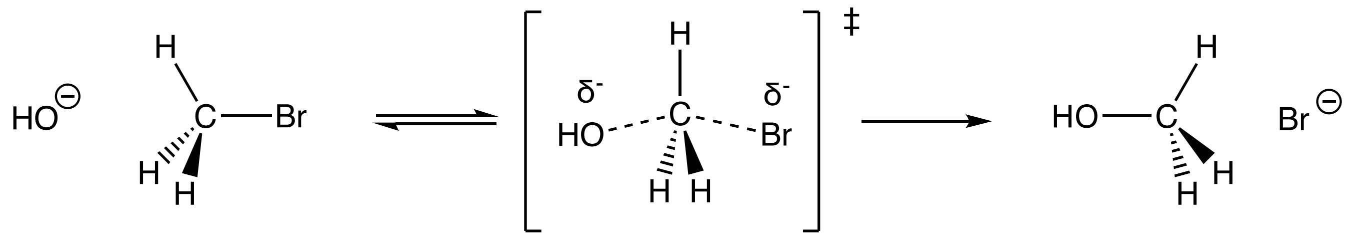
α-C + I^- must collide... double one conc should double rate of rxn

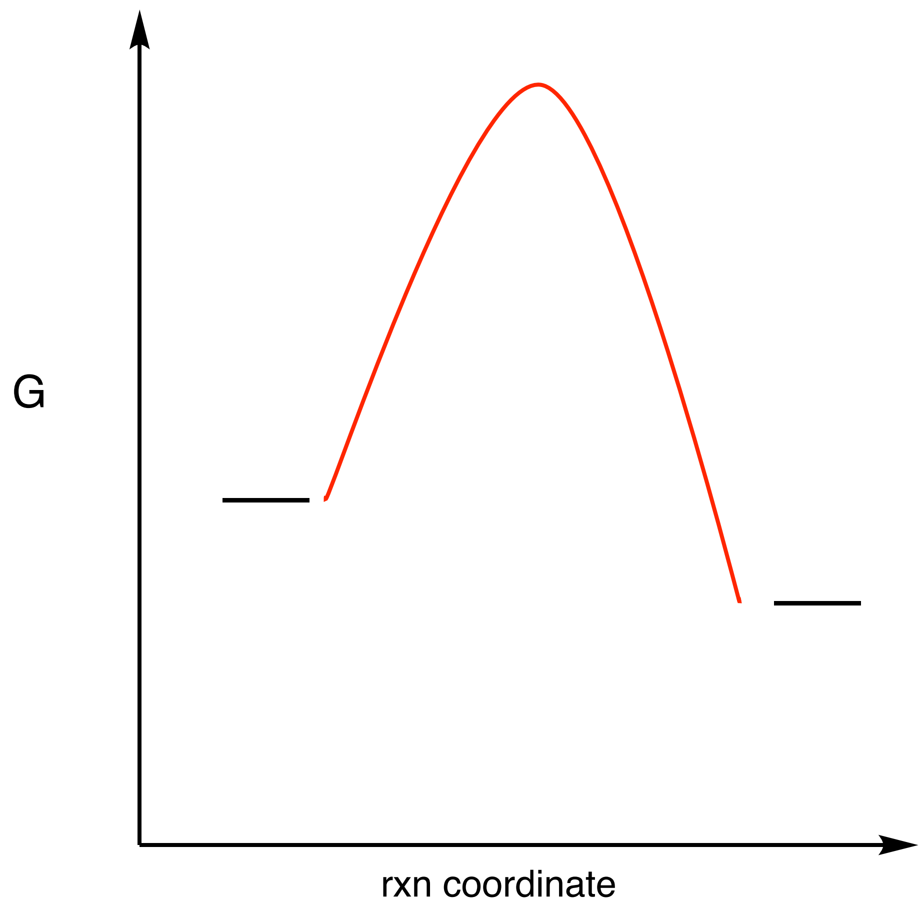


rate = k [$CH_3CH_2CH_2C(CH_3)BrCH_3$]

S_N1

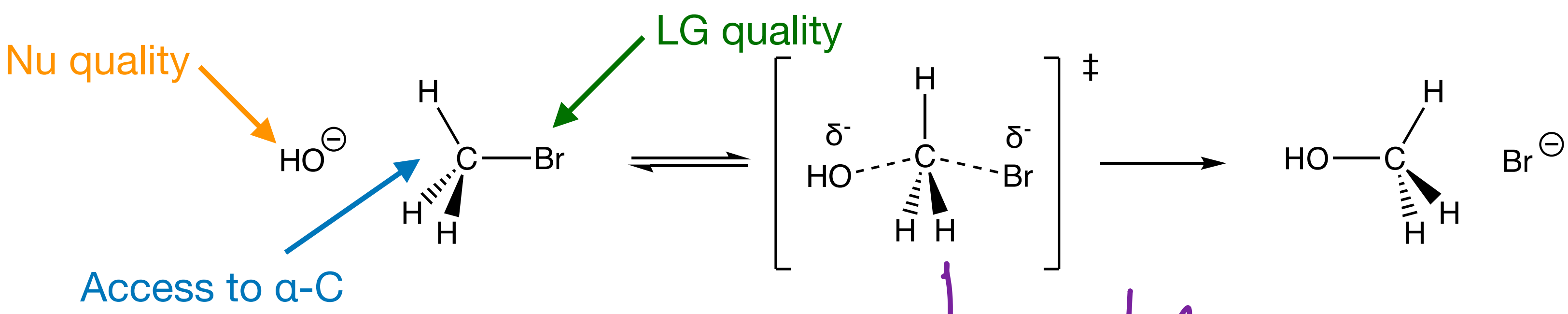
nucleophile not involved in RDS so rxn zero order w.r.t. $[Nu]^0$


HO
H
C
Br
H
H
δ-
HO
H
C
δ-
Br
H H
‡
HO
C
H
H
H
Br


G
rxn coordinate

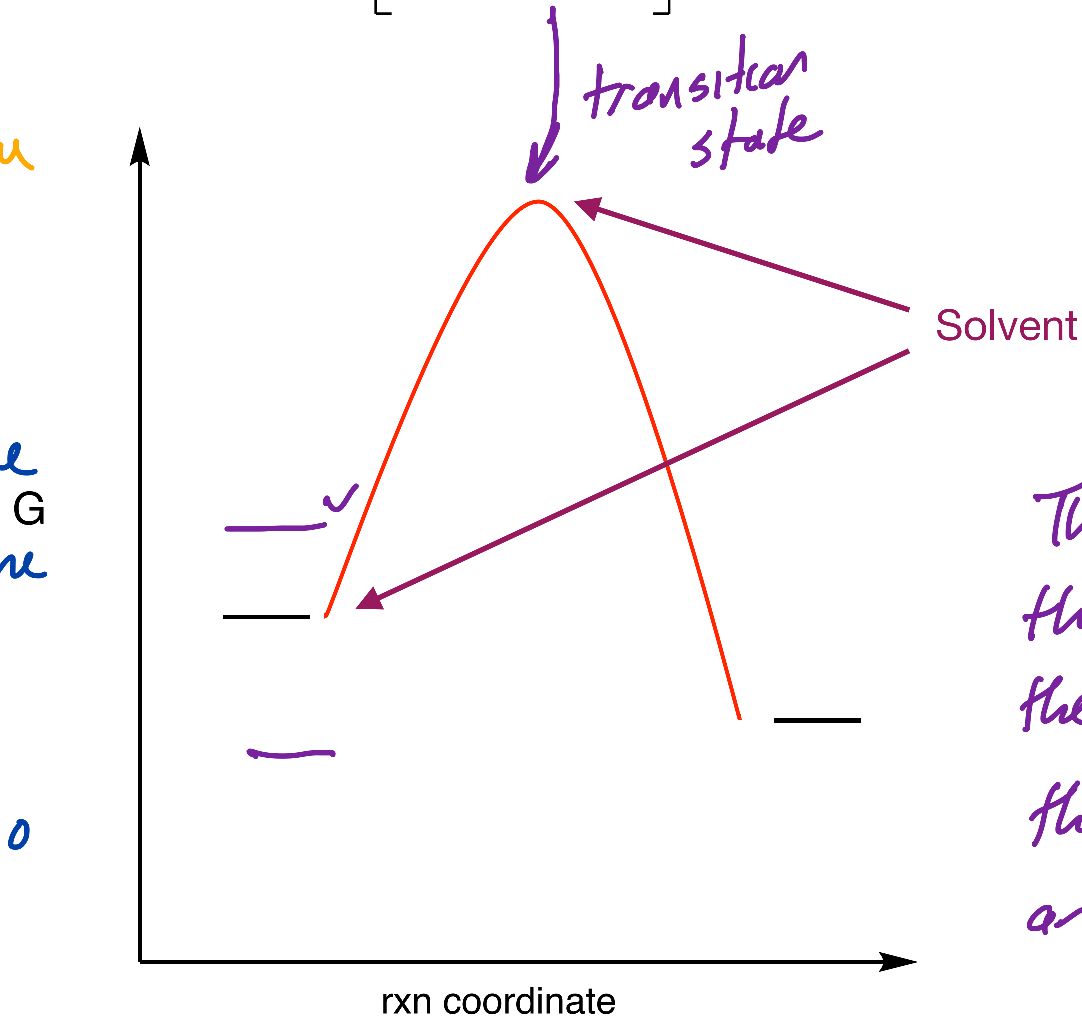
Factors Affecting S_N2 Reactions

Section 11.2 and 11.3



The better the Nu the faster the rxn will go

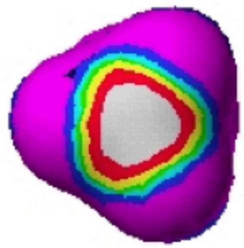
The more easily the Nu can access the backside of the α-C the faster the rxn will go

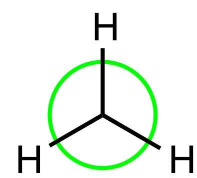


The better the LG the faster the rxn

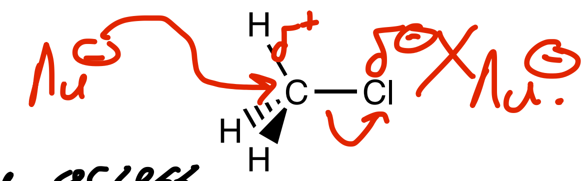
The solvent affects the energies of the reactants, the transition, and products

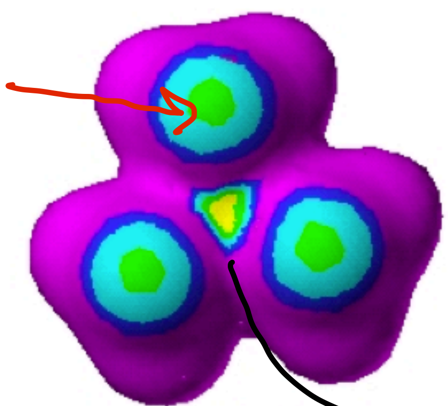
Newman projection from C to Cl

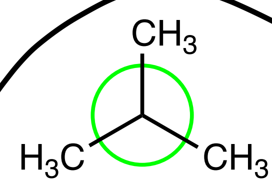




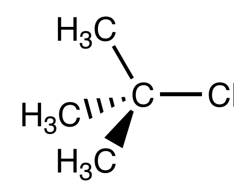
big bullseye showing easy access to the back side of the α-C







bullseye on the back of the 3° α-C is essentially non existant

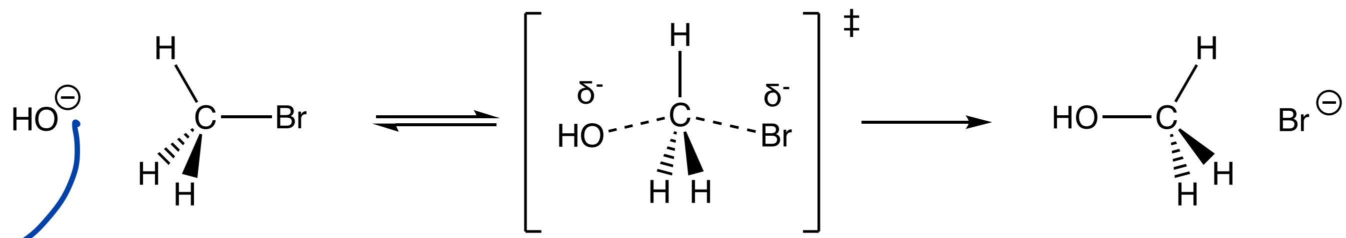


S_N2 depends on easy access to the backside of the α-C

methyl > 1° > 2° > 3°

good for S_N2 (methyl)

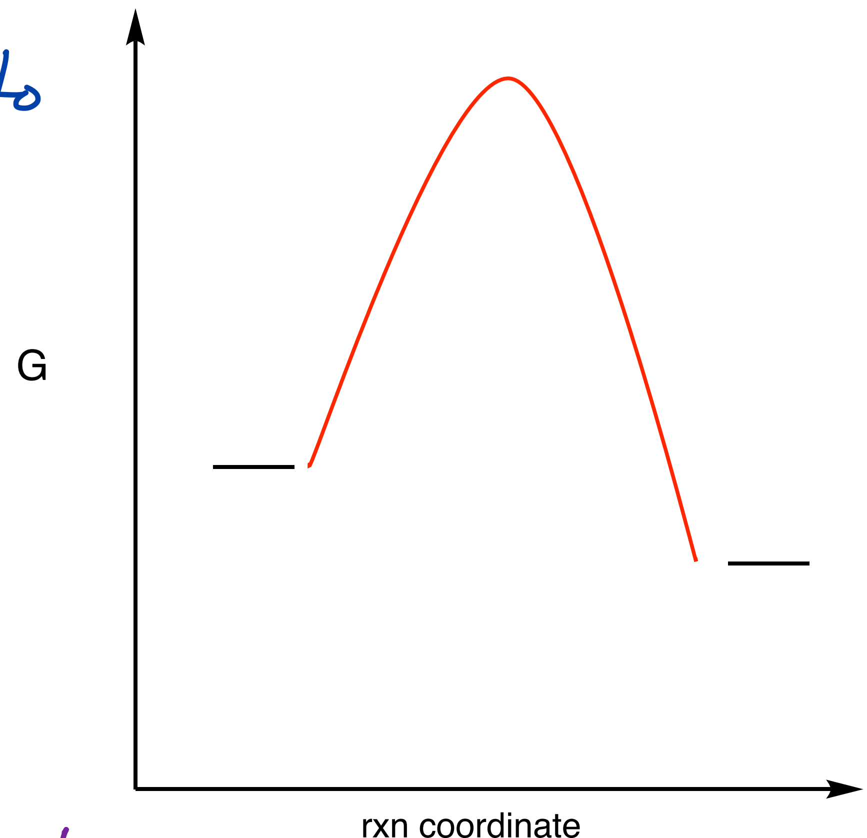
cannot do S_N2 (3°)



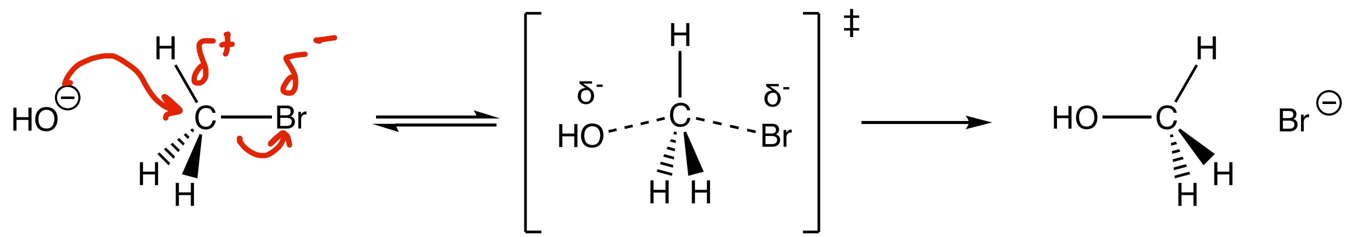
rate = k [$CH_3CH_2CH_2CH_2Br$][Nu^-]

More e^- rich
more attracted to
δ^+ of α-C

the more easily
the e^-'s are
moved around
the easier it is
to form the
bond

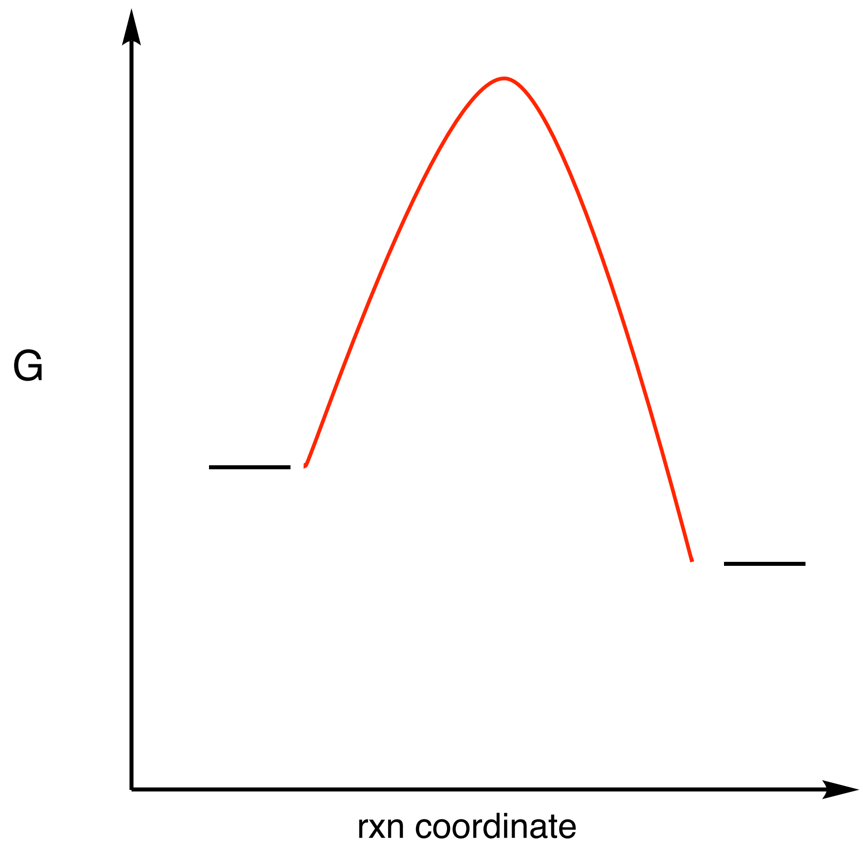


polarizability ... larger atoms are more polarizable



The more e⁻ rich the Nu is the more likely it is to be attracted to the δ+ C

rate = k [$CH_3CH_2CH_2CH_2Br$][Nu^-]



The more easily the e⁻'s on the nucleophile are moved the easier it is to form the new bond

polarizability

large atoms - polarizable make for good Nu

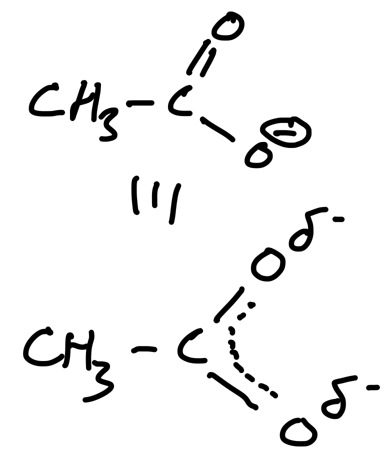
Factors affecting S_N2: Nucleophile Quality – Section 11.3

* no change in polarizability

* no change in charge only a change in polarizeability

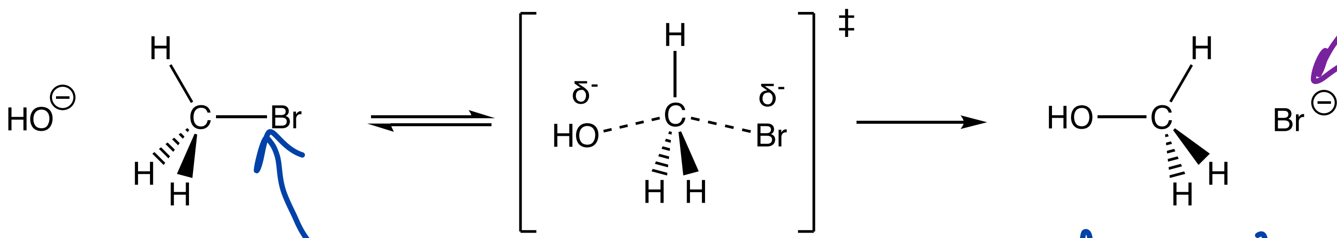
$$Nu:^- + CH_3Br \rightarrow CH_3Nu + Br^-$$

Nucleophile		Product		Relative rate of reaction
Formula	Name	Formula	Name	
H_2O	Water	$CH_3OH_2^+$	Methylhydronium ion	1
$CH_3CO_2^-$	Acetate	$CH_3CO_2CH_3$	Methyl acetate	500
NH_3	Ammonia	$CH_3NH_3^+$	Methylammonium ion	700
Cl^-	Chloride	CH_3Cl	Chloromethane	1,000
HO^-	Hydroxide	CH_3OH	Methanol	10,000
CH_3O^-	Methoxide	CH_3OCH_3	Dimethyl ether	25,000
I^-	Iodide	CH_3I	Iodomethane	100,000
^-CN	Cyanide	CH_3CN	Acetonitrile	125,000
HS^-	Hydrosulfide	CH_3SH	Methanethiol	125,000



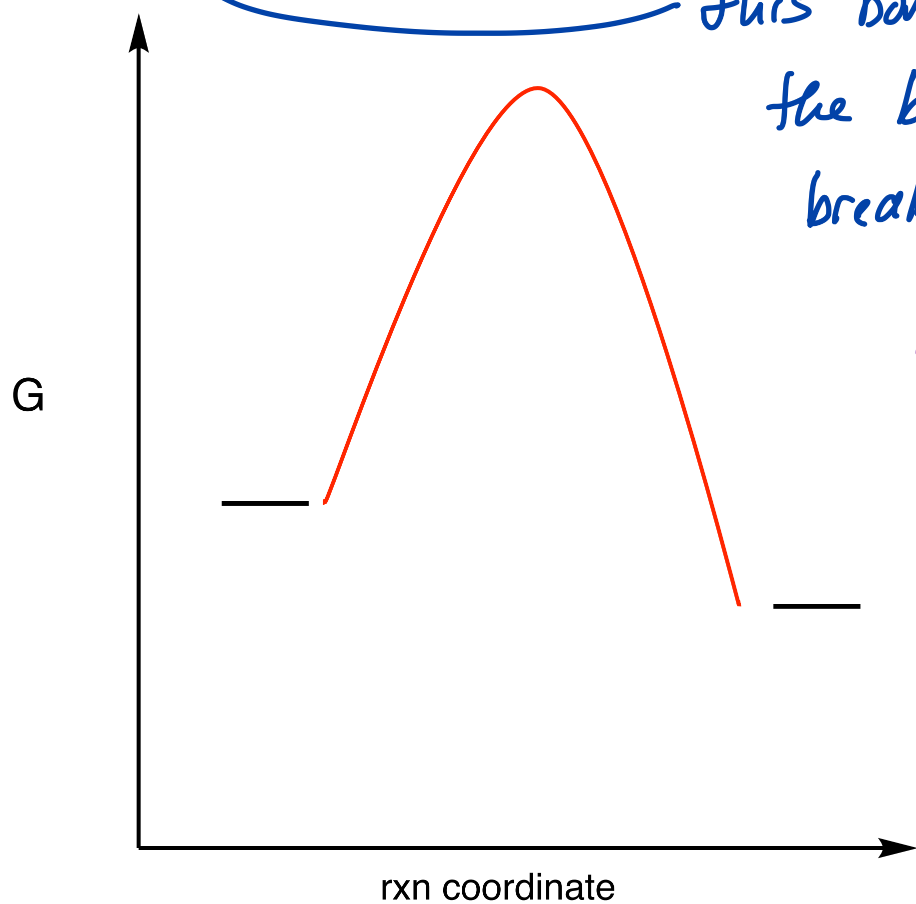
12.5 × faster than OH^- rxn ... same charge as OH^- but more polarizable

Organic Chemistry, a Tenth Edition. McMurry, OpenStax.



needs to be low in E

this bond must break... the weaker the bond the easier it is to break



LG needs to be low in E...

weak base that forms when the LG leaves the easier it is for the LG to leave

extremely weak bases

I^- Br^- Cl^- very weak base F^- weak base

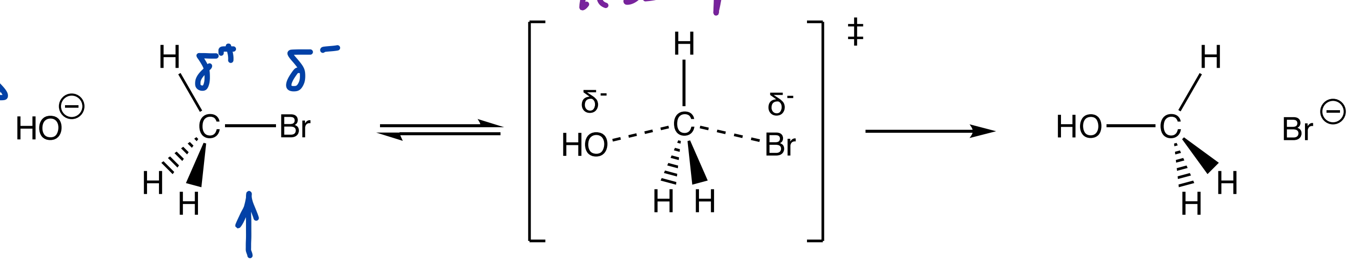
Relative reaction rates from Bruice, McMurry I^- : Br^- : Cl^- : F^- 30,000 : 10,000 : 200 : 1

HI HBr HCl HF

Factors Affecting S_N2 Reactions: Solvent

polar or ionic

less polar



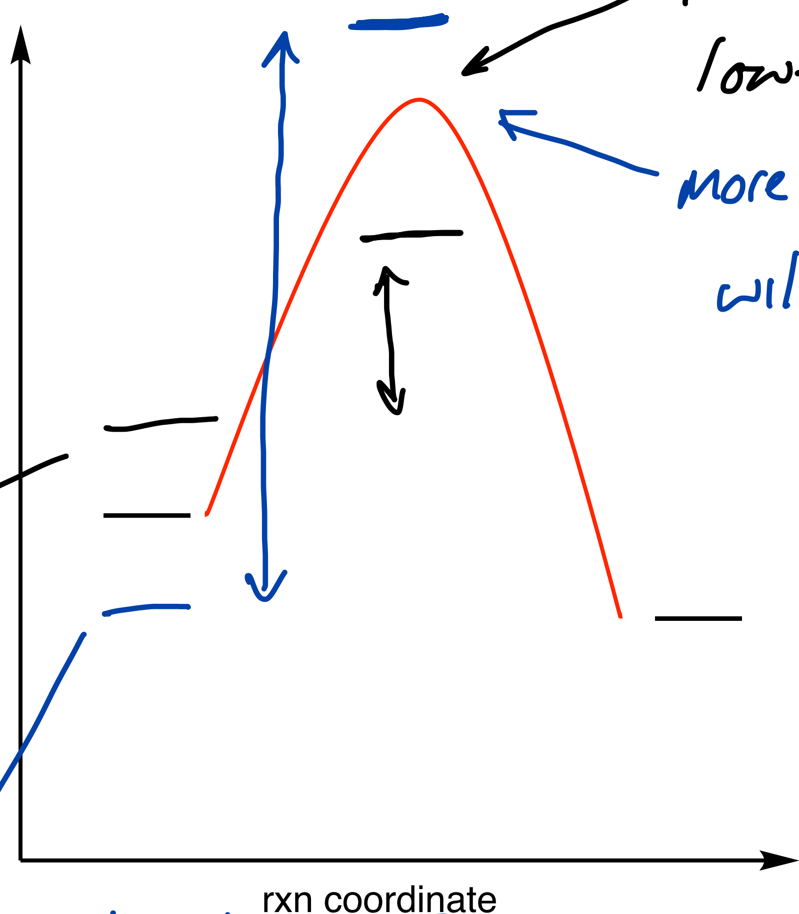
polar

polar solvents needed to get reactants to dissolve

TS is less polar

less polar solvents lower the E of the TS

more polar solvents will will raise the energy



less polar solvents raise E of reactants

more polar lower E