

Nucleophilic Substitution Bimolecular (S_N2)

Key points:
 - SN2 reaction is necessary if another functional group is nearby
 - SN2 reaction is very strong + irreversible + bimolecular + concerted
 - SN2 reaction proceeds through backside attack
 - SN2 reaction proceeds with inversion
 - Rate depends on concentration of both nucleophile and alkyl halide
 - Reaction occurs faster in polar aprotic solvents



1. The S_N2 Reaction is Sensitive to Steric Effects

in the S_N2 the nucleophile is the attacking species so you maximize the attacking ability with sterics you remove the bulk to the leaving group



2. The S_N2 Mechanism: The Backside Attack Leads to Inversion

The nucleophile (green part) attacks the empty antibonding orbital which is on the backside of the carbon-leaving group bond



3. The Rate Limiting Step of the S_N2 is Bimolecular

Rate	[R-X]	[Nu]	Rate = k [Substrate] [Nucleophile]
1	1	1	Doubling the concentration of either component will double the rate
2nd	1	1	
3rd	1	1	
4th	1	1	

4. Polar aprotic solvents are the best for the S_N2

Because of the charges involved in the S_N2 mechanism polar solvents are better than non-polar solvents

Two types of polar solvents: polar protic (have H-bond donors)
 Polar aprotic (no donors but accept H-bond)

Why? Polar protic solvents make a "cage" around nucleophiles through hydrogen bonding, decreasing the reactivity of the nucleophile.



What Makes a Good Leaving Group?

Key point: Good Leaving Groups are Weak Bases



Bad Leaving Groups:



With the exception of F^- these are all strong bases. Fluoride leaves only strong acids and is that a very bad leaving group?

Note how HO^- is not a good leaving group but OTf^- is. However, HO^- can be made into a good leaving group by adding a strong acid

How the Substrate Influences Reactivity



Note that hybridization in all cases here is sp³. These reactions do not occur for allylic and vinylic halides under normal conditions

What Factors Influence Nucleophilicity?

1. Charge: The conjugate base is often a better nucleophile than the conjugate acid
 $OH^- > H_2O$, $CH_3O^- > CH_3OH$, $CH_3S^- > CH_3SH$

2. Electronegativity: The less tightly held a pair of electrons are, the more readily they can be donated
 Nucleophilicity increases as we go to the LEFT along the periodic table (C > N > O > F)
 Nucleophilicity increases as we go DOWN the periodic table



Another term for how "loosely held" electrons are is polarizability. Nucleophilicity increases with polarizability.

3. Solvent: Polar protic solvents will hydrogen bond with nucleophiles (see above) and which decreases their nucleophilicity. More polarizable nucleophiles will be less affected by polar protic solvents, since hydrogen bonding ability is greatest for most electronegative nucleophiles. Polar aprotic solvents will not hydrogen bond, therefore they are good solvents for the S_N2

Note that in polar aprotic solvent reactivity of halides increases because there is no hydrogen bonding to them

4. Steric bulk: If a sterically bulky group surrounds the nucleophilic atom, the rate will decrease in nucleophilicity. Example: CH3O^- is more nucleophilic than (CH3)3CO^- for the reason



Elimination, Bimolecular (E2)

1. Key points:
 - Elimination is the loss of a leaving group from the β-carbon and a hydrogen from the α-carbon resulting in the formation of a double bond
 - The major product is the more substituted alkene ("Zaitsev product") and the fastest groups will be lost

- Loss of a bulky base will result in formation of more of the less substituted alkene (Hofmann alkene)
 - The leaving group and the hydrogen must be oriented anti-periplanar
 - Can occur with primary, secondary, tertiary substrates provided there is a hydrogen on the β-carbon that can orient itself anti to the leaving group
 - Rate determining step is bimolecular
 - Occurs in generally polar protic
 - Occurs if forced with heat



2. The Major Product is the Most Substituted Alkene

Why? Because alkenes become more thermodynamically stable as C=C bonds are replaced with C-C bonds

Exception: Bulky bases will give loss of the Hofmann product because steric repulsion on the less substituted carbon becomes favored

Exception #2: when the leaving group is bulky (e.g. OTf)

3. A Strong Base is Required

In order for the E2 reaction to occur, one must use a good base



Basicity increases going to the left along the periodic table (C > N > O > F)

Basicity increases going up the periodic table (I > Br > S > N > O > F)

4. The H and Leaving Group MUST be Anti-Periplanar



5. The E2 Can Occur With Primary, Secondary, and Tertiary Substrates



6. The Rate Limiting Step of the E2 is Bimolecular

Rate	[R-X]	[Nu]	Rate = k [Substrate] [Base]
1	1	1	Doubling the concentration of either component will double the rate
2nd	1	1	
3rd	1	1	
4th	1	1	

1. Solvent is Generally Polar Protic: not in all instances, but polar protic will favor E2 in cases where E competes with the S_N2 (see #1)
2. The E2 is Favored By Heat:
 Heat the E2 and when sterically substituted that could go E2 or S_N2 heat favors elimination due to higher entropy

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emphasize the important aspects of each chapter and will reinforce the key ideas without requiring memorization

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The Organic Chem Lab Survival Manual James W. Zubrick,2020-02-05
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these three bodies united to form the united congregational church of southern africa in 1967 it has approximately 500 000 members in 450 local congregations the united congregational church is a member of the world communion of reformed churches it has a synod in mozambique its office is located in maputo the igreja congregacional unida

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