

Kinetics:

<u>Exp.</u>	<u>$[OH^-]$</u>	<u>$[+Cl]$</u>	<u>relative rate</u>
1	1	1	1
2	1	2	2
3	2	1	1
4	2	2	2

Rate is independent of the nucleophile conc.
 \Rightarrow ~~is~~ NOT S_N2 .

$$\text{rate} = k [+Cl]$$

1st order - S_N1

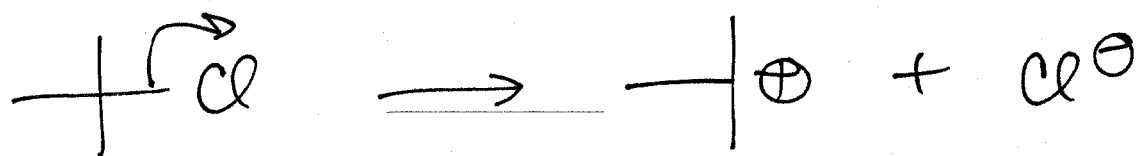
* must be
multistep mech.

substitution
nucleophilic
unimolecular

Proposed Mechanism for S_N1

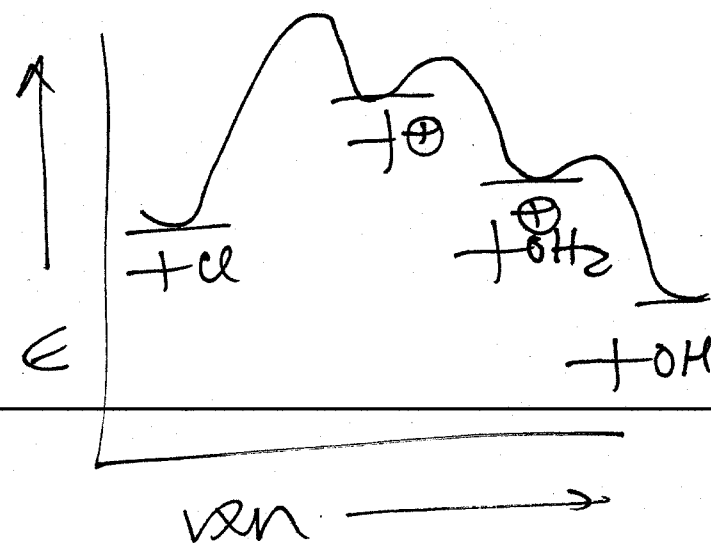
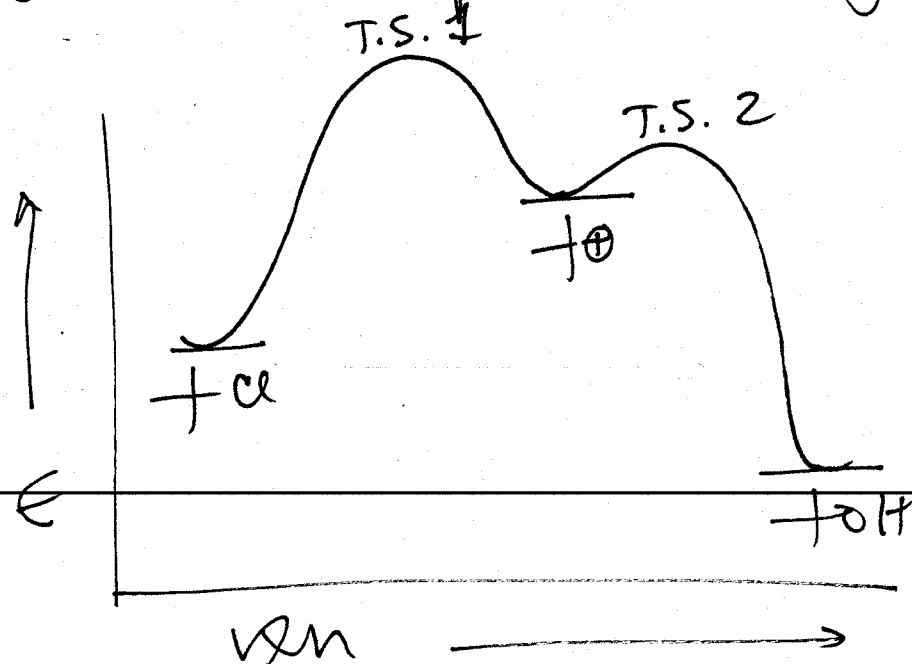
* 1. ionization of RX

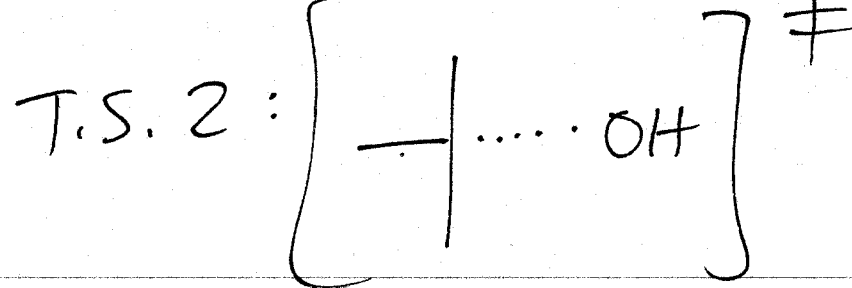
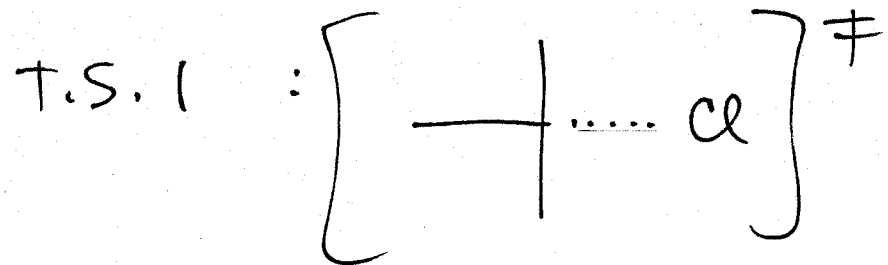
slow step



2. reaction of cation w/ nucleophile
(OH^- or H_2O - rxn goes just as fast in plain H_2O w/ no added OH^- .)

(3. loss of a proton to give neutral product)

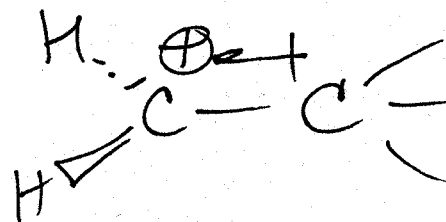
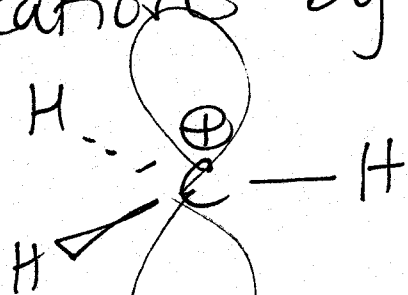




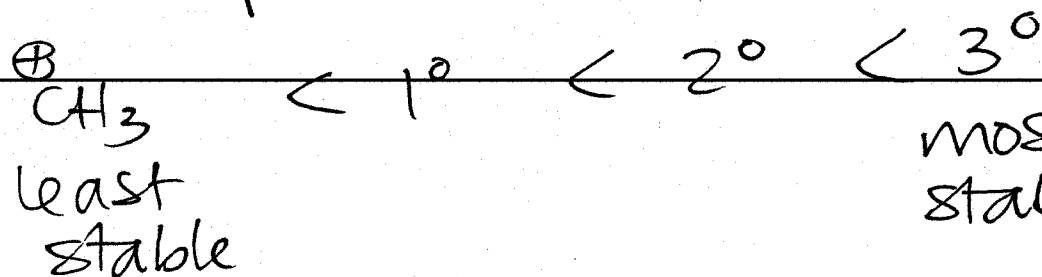
A word about cations...

structure: sp^2 , planar (120°)

stability: alkyl substitution stabilizes cations by induction (hyperconjugation)



nothing to help stabilize



Factors Affecting the Rate of S_N1 + S_N2

- structure of the alkyl group (RX)
- nature of the leaving group
- conc./reactivity of the nucleophile
- solvent effects

a. - S_N1 : stability of intermediate cation
 S_N2 : steric environment around RX.

methyl 1°
do not go S_N1 -
cations too unstable

2°

3°

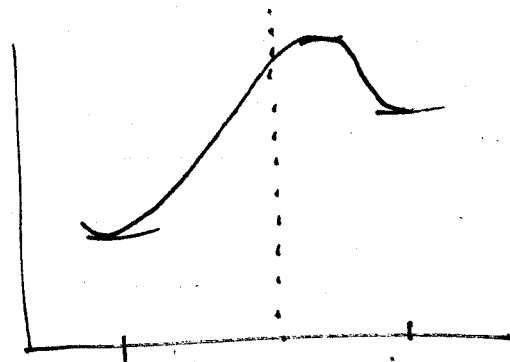
Does not go S_N2
too sterically
hindered!

S_N1 : $3^\circ > 2^\circ$ \sim $1^\circ/\text{CH}_3$

S_N2 : $\text{CH}_3/1^\circ > 2^\circ$ \sim 3°

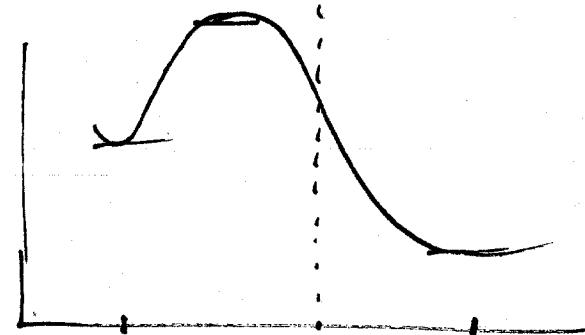
Note: vinyl,
aryl don't
follow either
mechanism.

Hammond-Leffler Postulate



endothermic - TS
resembles product

vs



exothermic: TS
resembles starting
material

cation formation is
endothermic \Rightarrow nature
of the cation is important.

b. Nature of LG (conj. base of strong acid)

of the halogens: $I > Br > Cl > F$

look at oxygen: OH is bad. (LG is OH^-
conj. acid is

protonation of OH turns
it into a good LG.

LG: H_2O
conj. H_3O^+

H_2O)