$$\text{\textemdash}Cl + NaOH \xrightarrow[\text{water}]{\text{acetone}} \text{\textemdash}OH + NaCl$$

Kinetics:

Exp.	[OH⁻]	[⊢Cl]	relative rate
	1	1	1
1	1	2	2
2	1	1	1
3	2	2	2
4	2		

Rate is independent of the nucleophile conc.

⇒ NOT S$_N$2.

rate = K [⊢Cl]
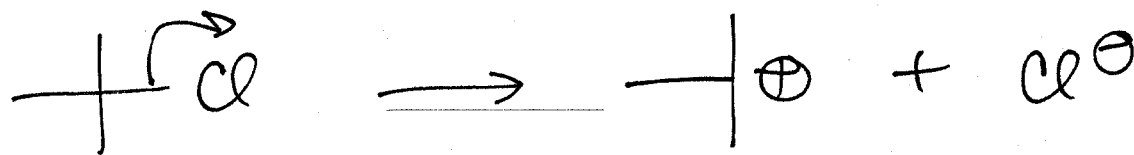
1st order – S$_N$1

* must be
  multistep mech.

substitution
nucleophilic
unimolecular

Proposed Mechanism for S_N1
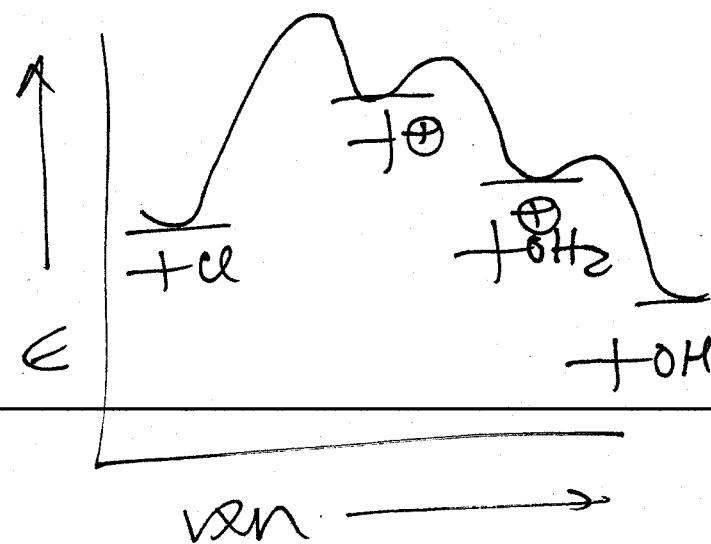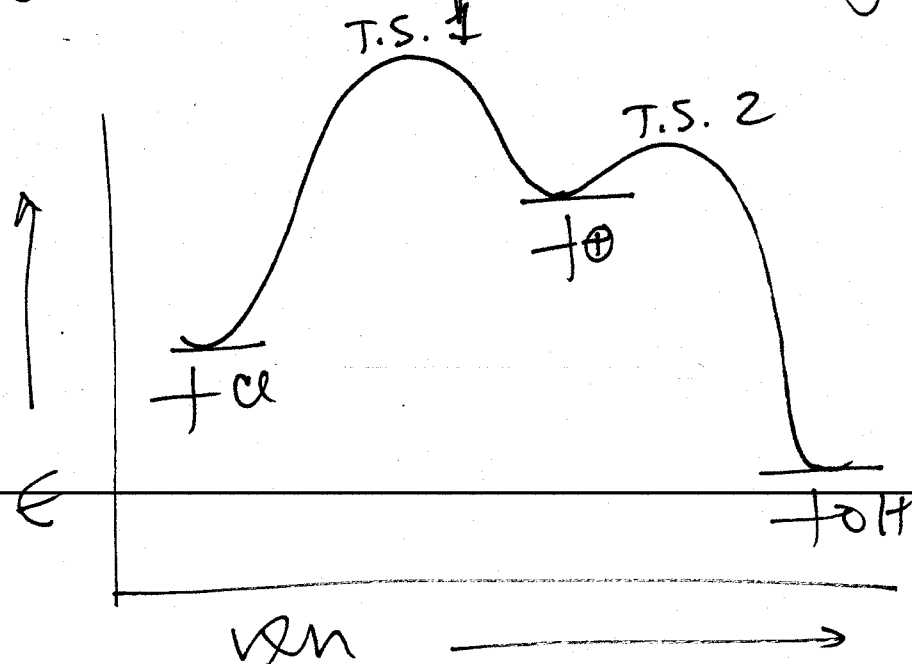
*1. ionization of RX

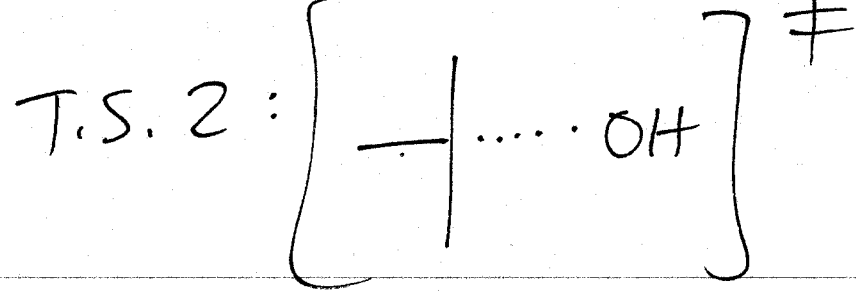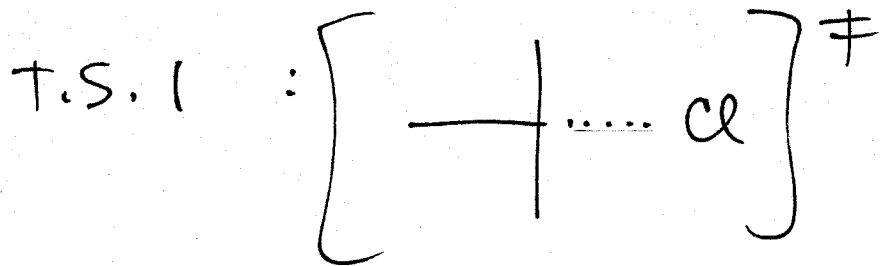$$\underset{}{+}\overset{\curvearrowright}{Cl} \implies \underset{}{+}\oplus + Cl^{\ominus}$$

slow step

2. reaction of cation w/ nucleophile
(OH$^{\ominus}$ or H_2O — rxn goes just as fast in plain H_2O w/ no added $^{\ominus}$OH.)

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

T.S. 1 : $\left[\begin{array}{c} \diagup\!\!\!\!\!\!\top\!\!\!\!\!\!\diagdown \cdots\cdots Cl \end{array} \right]^{\ddagger}$ T.S. 2: $\left[\begin{array}{c} \diagup\!\!\!\!\!\!\top\!\!\!\!\!\!\diagdown \cdots\cdots OH \end{array} \right]^{\ddagger}$
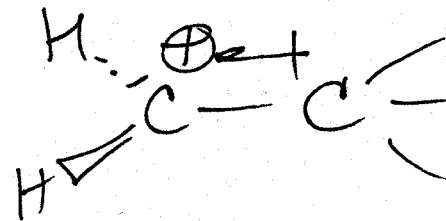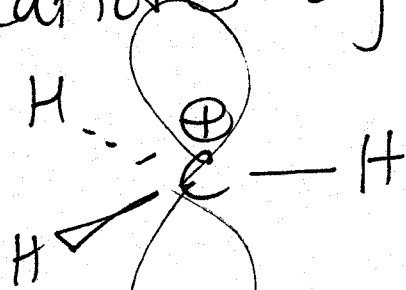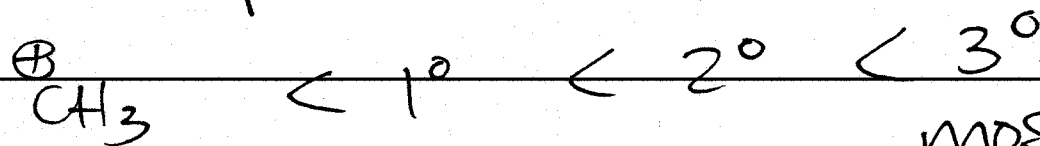

A word about cations...

structure: sp^2, planar $(120°)$

stability: alkyl substitution stabilizes
cations by induction (hyperconjugation)

nothing to
help stabilize

$\overset{\oplus}{CH_3}$ < 1° < 2° < 3°

least   most
stable   stable

Factors Affecting the Rate of S_N1 + S_N2

a. structure of the alkyl group (RX)
b. nature of the leaving group
c. conc./reactivity of the nucleophile
d. solvent effects

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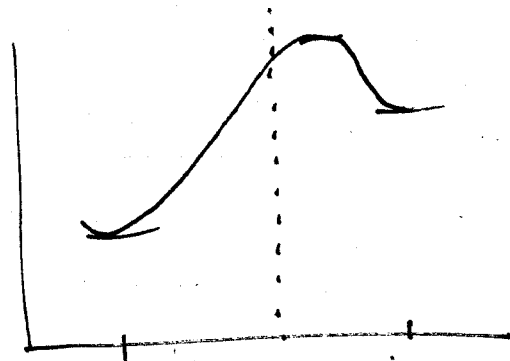S_N2: steric environment around RX.

methyl   1°   2°   3°

Do not go S_N1-
cations too unstable

Does not go S_N2
too sterically
hindered!

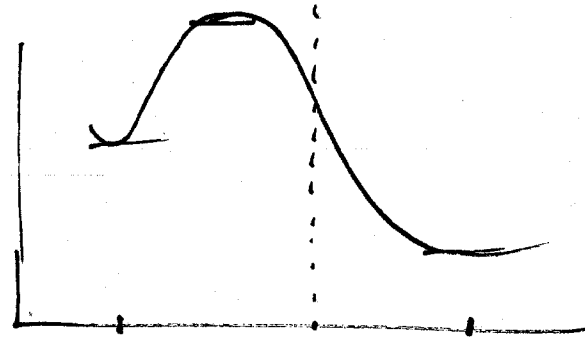S_N1: 3° > 2° { 1°/CH_3

S_N2: CH_3/1° > 2° { 3°

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

Hammond-Leffler Postulate

vs.

endothermic — TS
resembles product

exothermic: TS
resembles starting
material

cation formation is
endothermic ⇒ nature
of the cation is important.

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b. Nature of LG (conj. base of strong acid)
    of the halogens: $I > Br > Cl > F$

look at oxygen: OH is bad. (LG is $OH^{\ominus}$
                                              conj. acid IS
protonation of OH turns H_2O)
it into a good LG.   LG: H_2O
                      conj. H_3O^+