Recall from last lecture - importance of nucleophile to S_N1 vs S_N2 reactions

Nu: - Not so critical for S_N1

- Quite important for S_N2

Q - what makes a good Nucleophile?

- Needs e^- pair, often anionic

i) In same row of Periodic Table, Nucleophilicity parallels Basicity

$H_2N^- > HO^- > F^-$

$H_3N: > H_2O:$

$CH_3O^- > HO^- > CH_3-\overset{O}{\overset{\|}{C}}-O^-$

(by a bit)

ii) As you go down a column in Periodic Table, Nucleophiles get better

$I^- > Br^- > Cl^- > F^-$

$HS^- > HO^-$

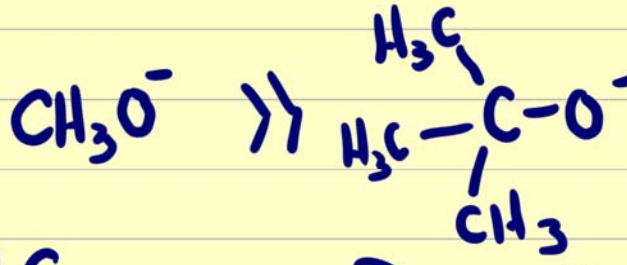
- REASON - SOLVENT EFFECTS; DETAILS BEYOND SCOPE OF COURSE

iii) NEGATIVELY CHARGED Nu⁻ IS STRONGER THAN A NEUTRAL Nu:

$HO^- > H_2O$

$H_2N^- > H_3N:$

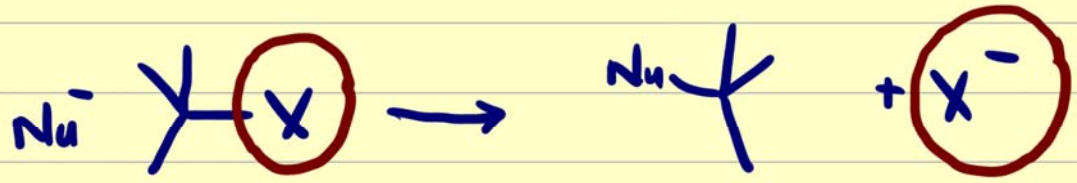
iv) STERIC EFFECTS CAN HINDER A NUCLEOPHILE



CH_3O^- >> $H_3C-C(CH_3)_2-O^-$

V. GOOD — POOR - TOO STERICALLY HINDERED

LEAVING GROUP



IMPORTANT FOR BOTH S_N1 & S_N2, BUT ESP. S_N1

- USUALLY, S_N1'S HAVE EXCELLENT LEAVING GROUPS

- TREND - LOOK AT ACID STRENGTH
  IF HX IS A STRONG ACID, X^- IS A GOOD LEAVING GRP.

ACIDITY

$HI > HBr > HCl > HF > H_2O > NH_3$

∴ L.G. ABILITY

$I^- > Br^- > Cl^- > F^- > HO^- > \bar{N}H_2$

NOTE: H_2O IS EXCELLENT NEUTRAL L.G.

SOLVENT

POLARITY OF SOLVENT HAS AN IMPORTANT EFFECT

LOW POLARITY, = LOW DIELECTRIC CONSTANT

HEXANE, BENZENE, TOLUENE, CH_2Cl_2

HIGH POLARITY

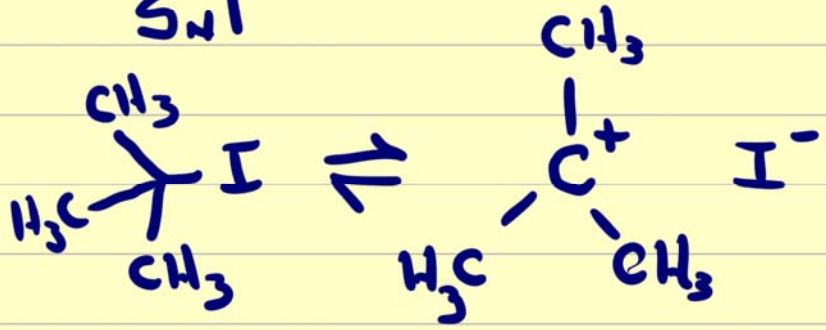
H_2O, CH_3OH, $CH_3C{\equiv}N$

ACETONE - MEDIUM POLARITY.

HIGH POLARITY SOLVENTS
- STABILIZE CHARGED SPECIES.

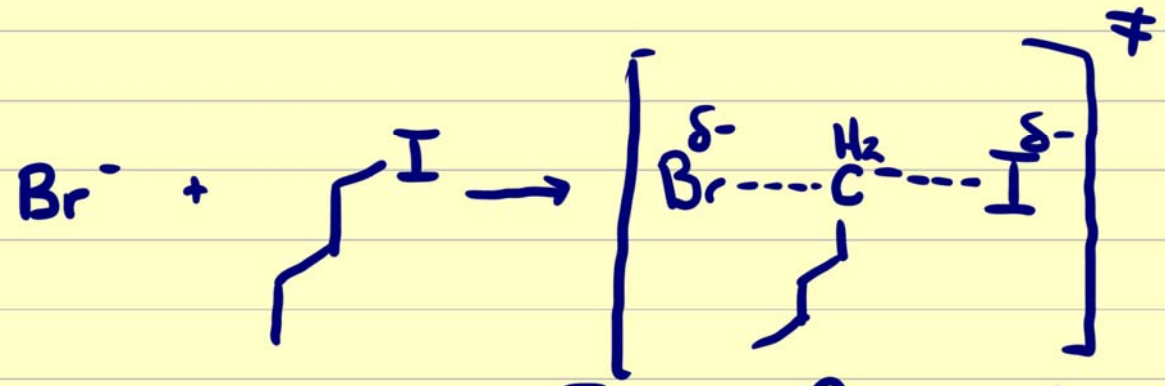
LOW POLARITY SOLVENTS
- DESTABILIZE CHARGED SPECIES

S_N1



SLOW STEP.

POLAR SOLVENT STABILIZES THIS, SPEEDS UP S_N1.



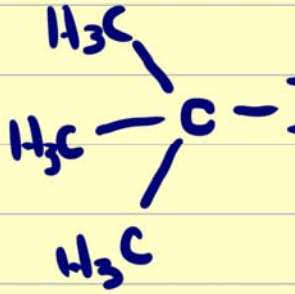
IN TRANSITION STATE, CHARGE DENSITY IS LOWER

∴ SLOWED IN POLAR SOLVENTS.

PUTTING THEM ALL TOGETHER

$CH_3CH_2CH_2-Br + H_2O \longrightarrow$?

$CH_3CH_2CH_2-Br + H_3N \longrightarrow$?



$+ H_2O \longrightarrow$?

$CH_3CH_2CH_2-I + H_2O \longrightarrow$?