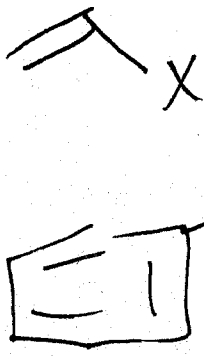
Ch. 6 - Ionic Rxns – Alkyl Halides

an alkyl halide is a halogen on an $\underline{sp^3}$ carbon.



vinyl halide

aryl halide (phenyl halide)

} NOT these.

Nucleophilic Substitution Rxns.

$$Nu:^{\ominus} + RX \longrightarrow Nu\text{-}R + X^{\ominus}$$

$$Nu: + RX \longrightarrow Nu\text{-}R^{\oplus} + X^{\ominus}$$

Questions:

* What is the mechanism?
* Does the C–Nu bond form 1st, and then the C–X bond breaks? or is it simultaneous? Or the other way around?
* What makes a good nucleophile?
* Does the size/nature of R matter?
* Does X matter?
* Can we use something besides X?

Definitions:

Nucleophile – nucleus loving – basically, anything with a lone pair. Can have ⊖ charge but don't have to.

Electrophile – electron loving – e⁻deficient. Often cations; always at least partial ⊕

leaving group - the conjugate base of a strong acid. Able to handle a neg. charge w/o difficulty. Halides are good L.G.'s - remember. HCl acid; $Cl^{\ominus}$ conj. base.

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sample Rxn: $CH_3Cl + NaOH \rightarrow CH_3OH + NaCl$

Experiment	[NaOH]	$[CH_3Cl]$	Relative Rate
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	4

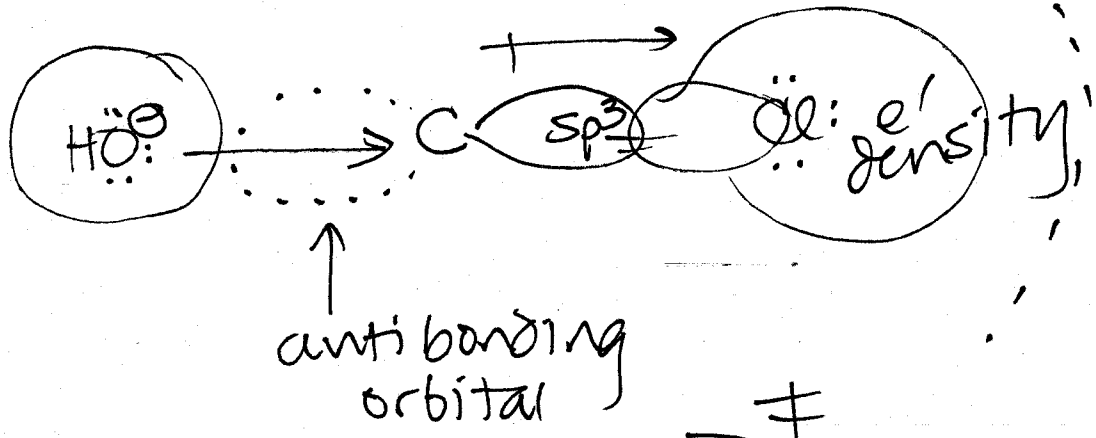
Rate = $k[OH^-][CH_3Cl]$ 2nd order kinetics

2nd order rxn means both species are involved in rate-det. step. (bimolecular)

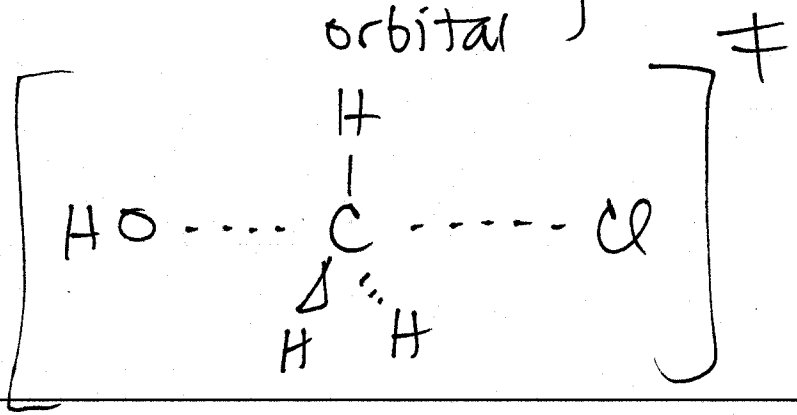
This is an S_N2 rxn.

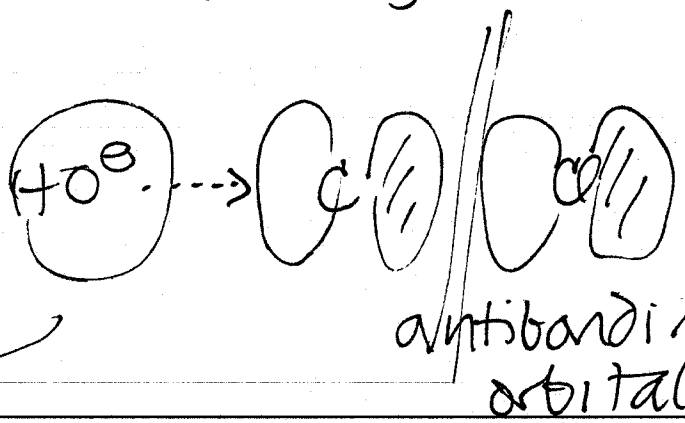
substitution, nucleophilic, bimolecular

consider the orbitals on the carbon.



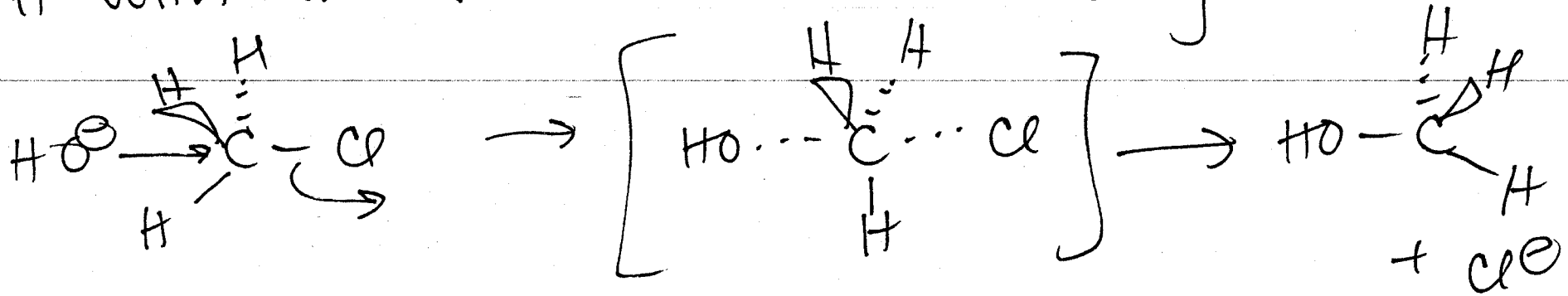
⊖ it won't attack from this side - too many e's repelling it.





pentacoordinate transition state

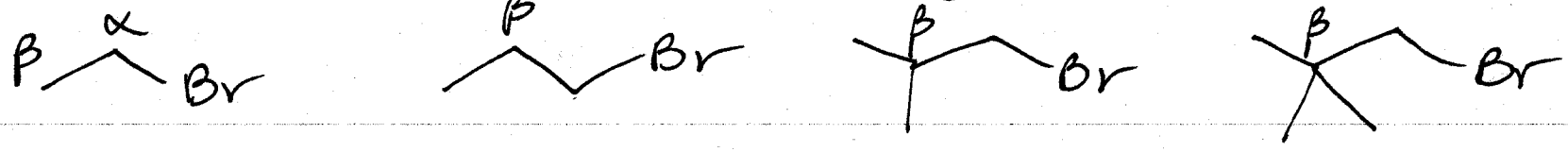
steric effects - look at TS. - replacing a H with an R will cause crowding.



$$R\text{-}Cl + {}^{\ominus}OH \rightarrow R\text{-}OH + Cl^{\ominus}$$

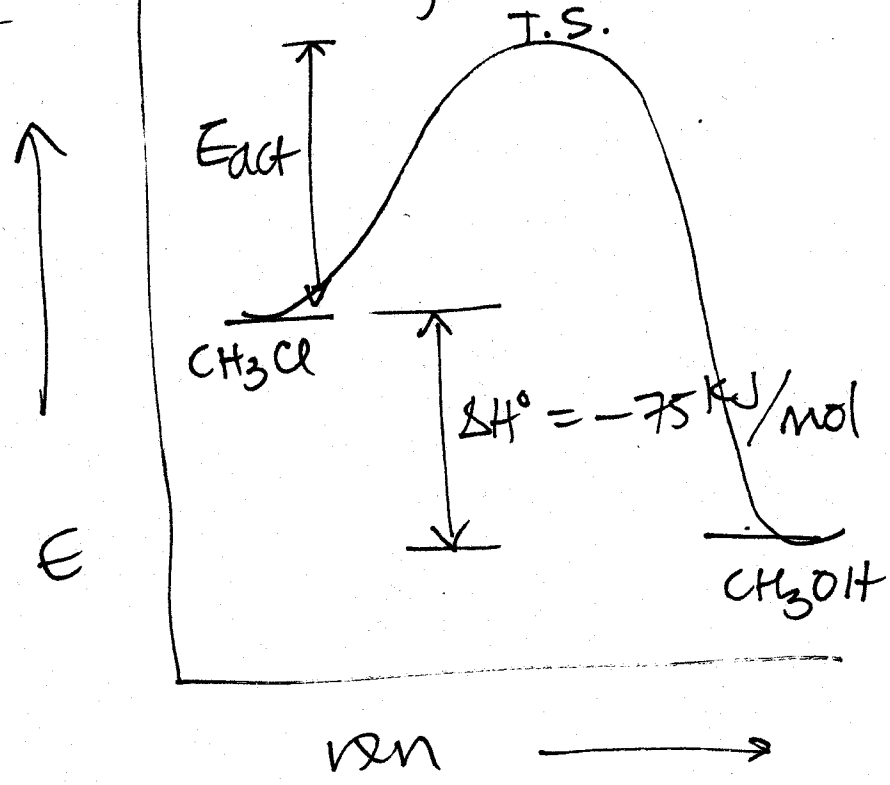
R:	CH_3-	Et-	Pr-	iPr-	tBu-
Nature of R:	methyl	1°	1°	2°	3°
Relative rate:	100	1.31	0.81	0.015	0.004 (essentially no reaction)

more sterics: β-branching



rate:	1	0.8	0.003	1.3×10^{-5} (NRX)

(still looking at $CH_3Cl + NaOH$)



This rxn has

$\Delta G^\circ = -100$ kcal/mol

calc. $K_{eq} = 5 \times 10^{15}$

Eact = activation energy

Generally if Eact < 84 kJ/mol the rxn will go.