<u>Last Lecture (10k)</u>

Chemical bonds and AOc → hybrid AO → MO

<u>Today</u> Thermodynamics and Kinetics

$A + B \rightleftharpoons C + D$

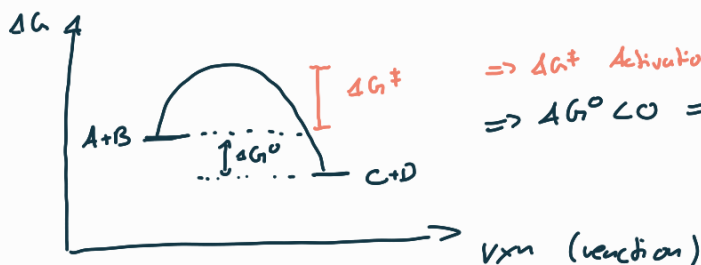$k = \dfrac{[C][D]}{[A][B]}$ zero order , relate Thermodynamics to rate constant

$\Rightarrow \Delta G^{\circ} = -RT \ln(k)$

$\Delta G^{\circ} = \Delta H - T\Delta S$ (2nd law of thermody)

to see weather a reaction is spontaneous look at free
energy

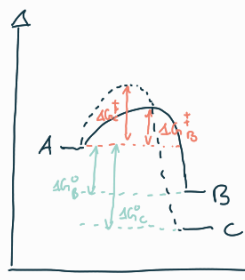Reaction coordinate   (H bond 4 $\frac{kJ}{mol}$)

$\Rightarrow \Delta G^{\ddagger}$ Activation free energy

$\Rightarrow \Delta G^{\circ} < 0 \Rightarrow$ gain in Energy = Exothermic

$\Rightarrow$ Arrhenius :   rate $= A e^{-\frac{E_a}{RT}}$ (also Eyring eq) $E_a = \Delta G^{\ddagger}$
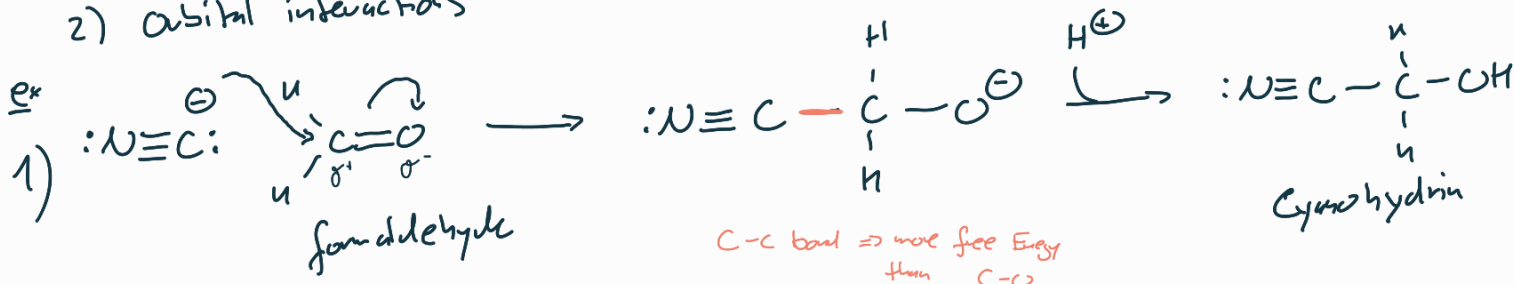
Increase T by 10°C
$\Rightarrow$ rate will $\approx$ 2x

<u>Ex</u>

$\Delta G^{\circ}_C < \Delta G \Rightarrow C$ is Thermodynamical product (higher yield with time ; T↑)
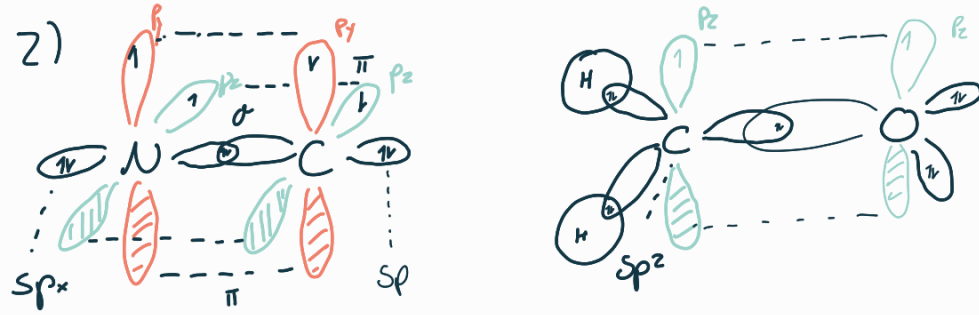
$\Delta G^{\ddagger}_B < \Delta G^{\ddagger}_C \Rightarrow B$ is kinetic product (higher yield when cooled and reaction stop)

<u>Nucleophilic additions to carbonyl groups</u> (ch. 6, 9 - 11)

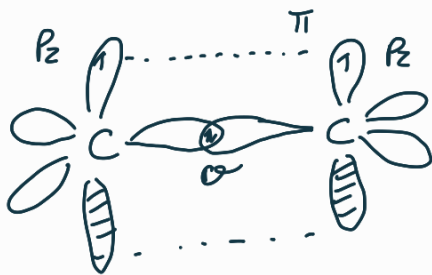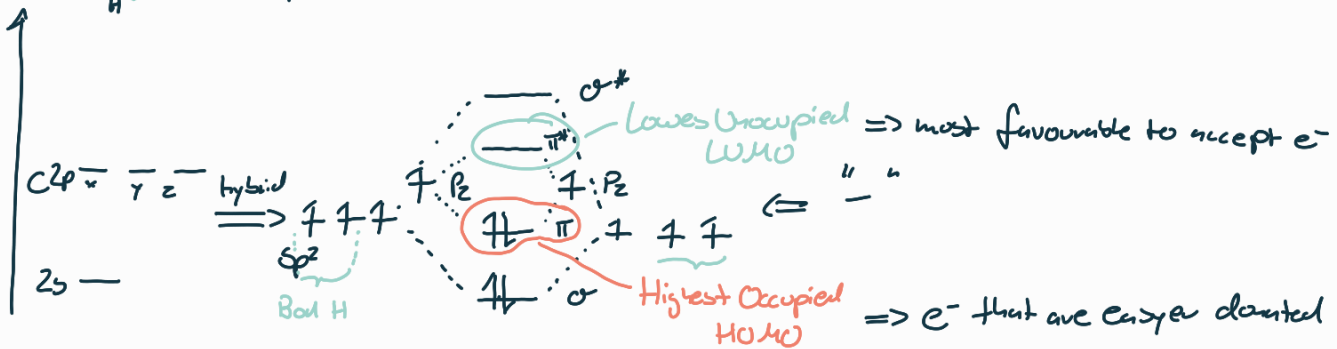## <u>Mechanisms</u>

1) curly arrows
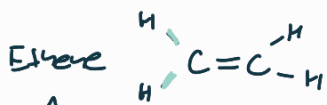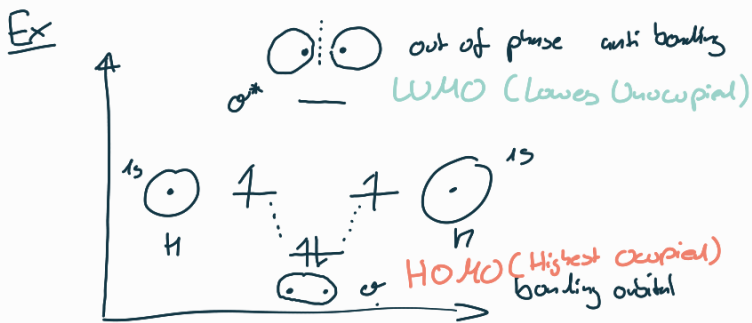2) orbital interactions

ex

1)

formaldehyde

$:N \equiv C - \overset{H}{\underset{H}{C}} - O^{\ominus} \xrightarrow{H^{\oplus}} :N \equiv C - \overset{H}{\underset{H}{C}} - OH$

Cyanohydrin

C-C bond $\Rightarrow$ more free Energy
than   C-O

2)

one p hybridized with s orbital => two left

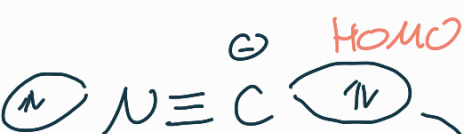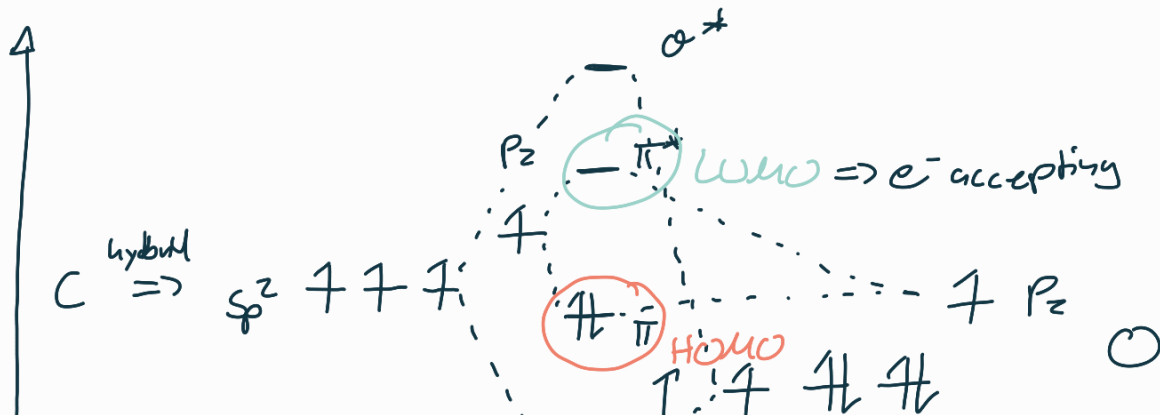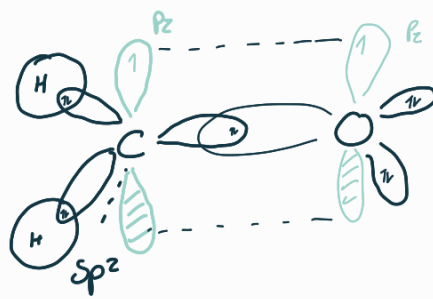## FMO   Frontier molecular orbital theory

HOMO – Highest Occupied Molecular Molecular Orbital   = Weakest bond, highest in Energy density has e^-

LUMO – lowes Unoccupied   "   –   "   = Lowest e^-, can accept more e^-

Ex

out of phase   anti bonding
σ^* ___ LUMO (Lowes Unocupial)

HOMO (Highest Occupied)
bonding orbital

Ethene $C=C$ with H's

σ^*

___ π^* – Lowes Unocupied => most favourable to accept e^-
LUMO

$C2p_x$ $\overline{y}$ z^- hybrid
=> $\uparrow\uparrow\uparrow$ $\uparrow$ P_z $\uparrow$ P_z
sp^2
Bod H

$\uparrow\downarrow$ π $\uparrow$ $\uparrow\uparrow$ $\Leftarrow$ "–"

$\uparrow\downarrow$ σ – Highest Occupied HOMO => e^- that are easyer donated

$2s$ ___

Formaldehyde ?

sp_x   π   sp

Homo

H
 \
  C = O
 /
H

sp²

C $\xrightarrow{hybrid}$ sp² ⇅ ⇅ ⇊

σ*
P_z — π* LUMO ⇒ e⁻ accepting

⇅ π HOMO   ⇊ P_z   O

σ ⇅   sp² ⇊ ⇅ ⇅
          lone pairs

e⁻ "freely" donatable from this orbital
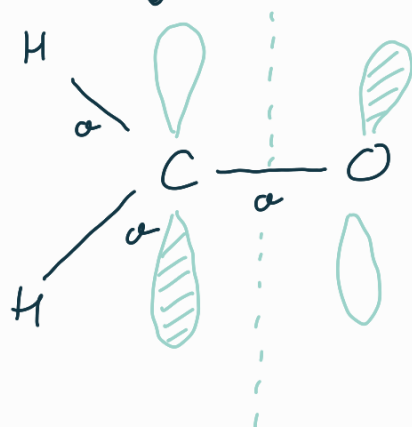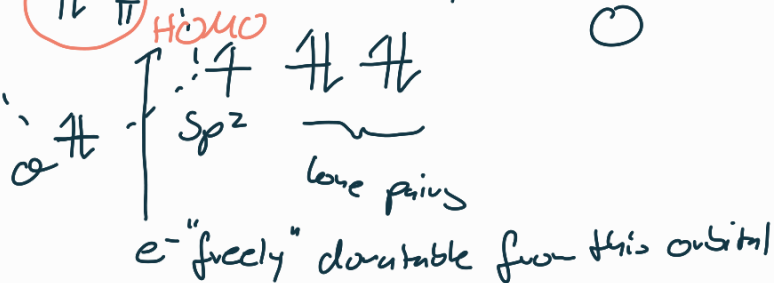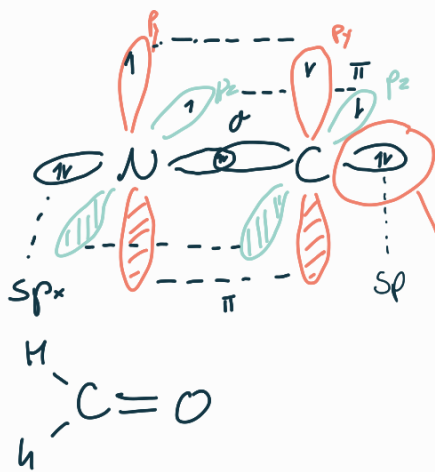
LUMO = antibonding, out of phase

⊖
N ≡ C   HOMO ⇊

H
   \
    C — O
   /
H

σ   σ

node (no e⁻, since no overlap)

⇒ b - Attack must come from above

HOMO (sp) starts occupying LUMO π*

N ≡ C
      \
       C — O ⊖
      / \
    H   H
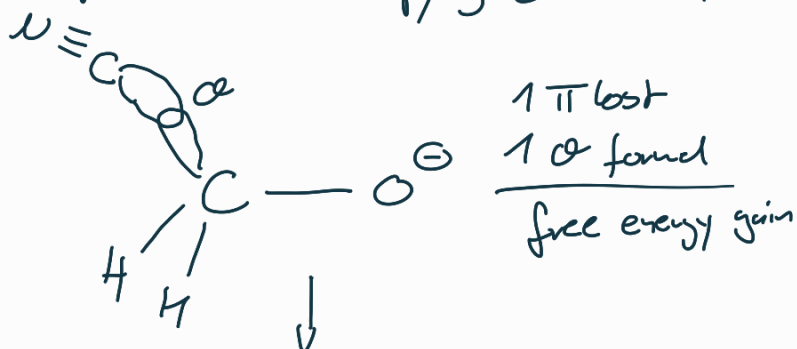
1 π lost
1 σ formed
―――――――――
free energy gain

...

Angle of attack is 107°
= Bürgi - Dunitz angle

Compromise between:
- Optimal AO overlap (90°)
- Oxygen repulsion