LEC (13) CHEM 30A Nov 1st

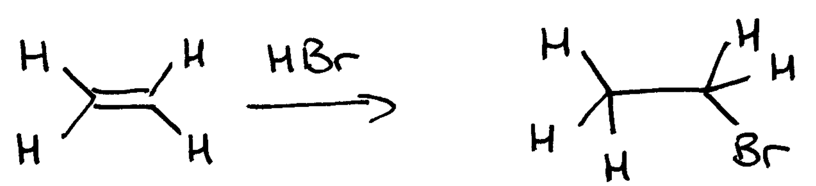
ORGANIC REACTIONS
1. TYPES
2. MECHANISMS
3. ENGRGY DIAGRAMS

READ: Ch5 6.1–6.3   PBLMS: 5.2, 5.6–5.10, 5.13–5.19 6.1, 6.2

1. TYPES OF REACTIONS

a) ADDITION (A + B ⟶ C)

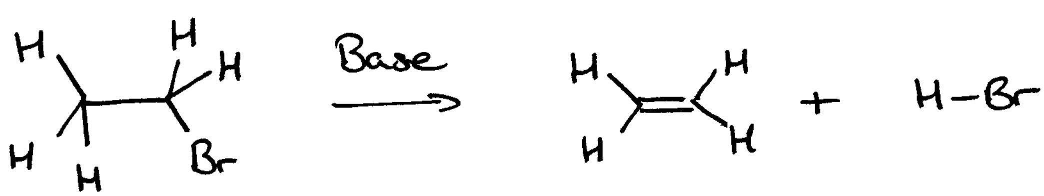
e.g



alkene   alkylhalide

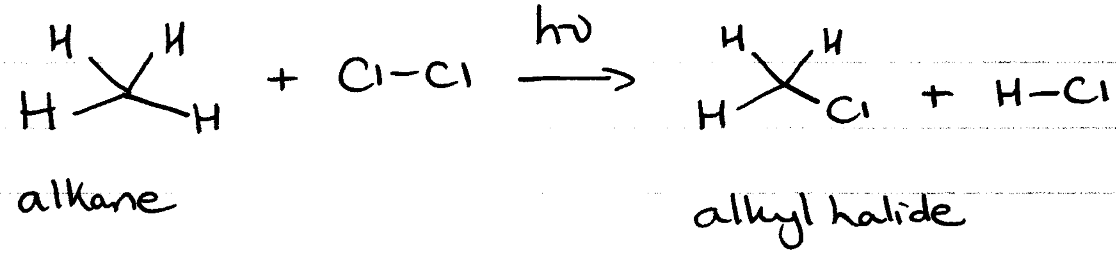
b) ELIMINATION (A ⟶ B + C)

e.g.

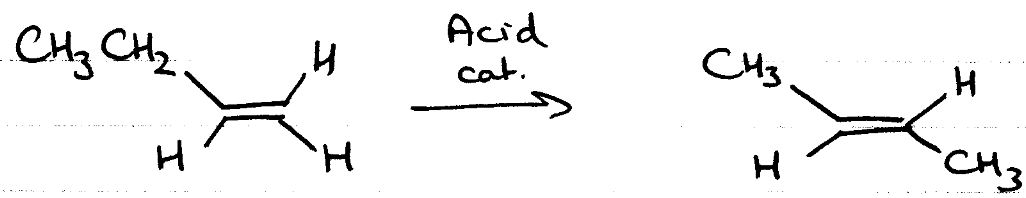


c) SUBSTITUTION (A-B + C-D → A-C + B-D)

e.g.

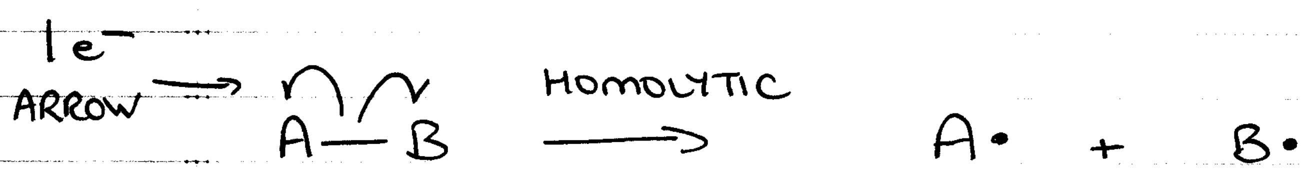


d) REARRANGEMENT (A → B)



(2) MECHANISMS

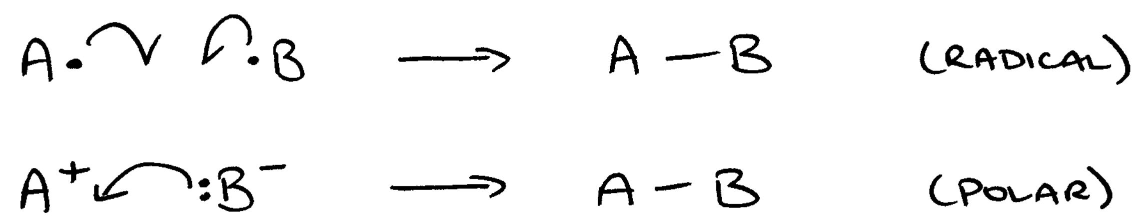
BOND MAKING / BOND BREAKING



Radical reactions → radical is a neutral chemical species that contains a single unpaired electron

POLAR REACTIONS

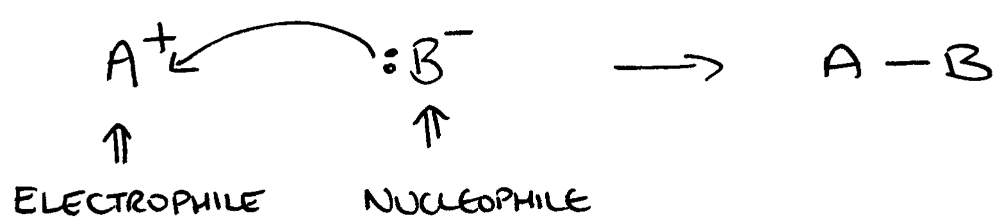
Bond making



(Radical rxns later in course)

- Polar reactions

e^- rich sites in one molecule react with e^- poor sites in another molecules

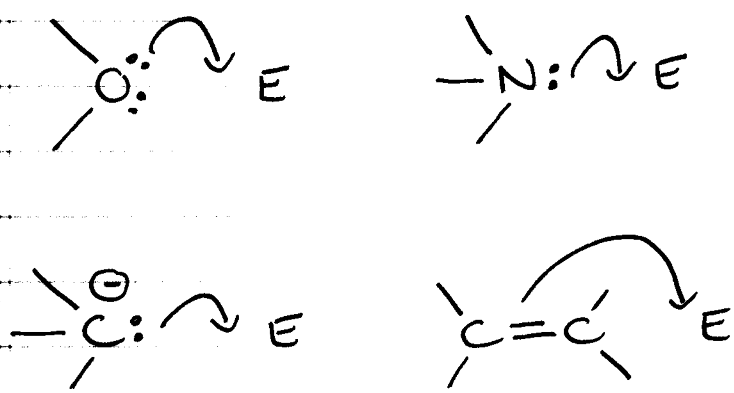


Nucleophiles: have an e^- rich atom and are NEUTRAL or −VELY charged.

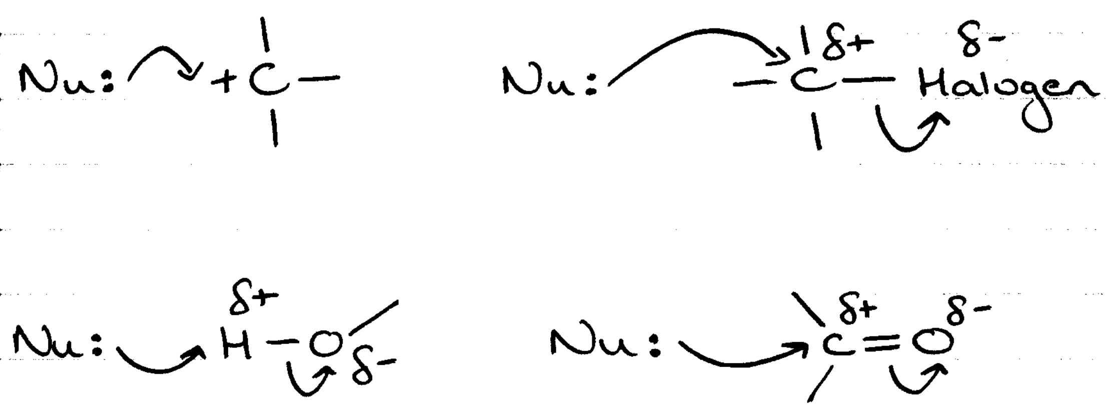
Electrophiles: have an e^- poor atom and are NEUTRAL or +VELY charged

Patterns

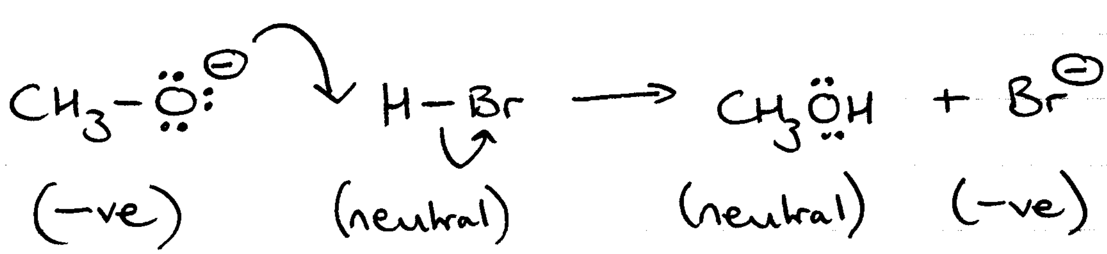
Electrons flow from nucleophiles:

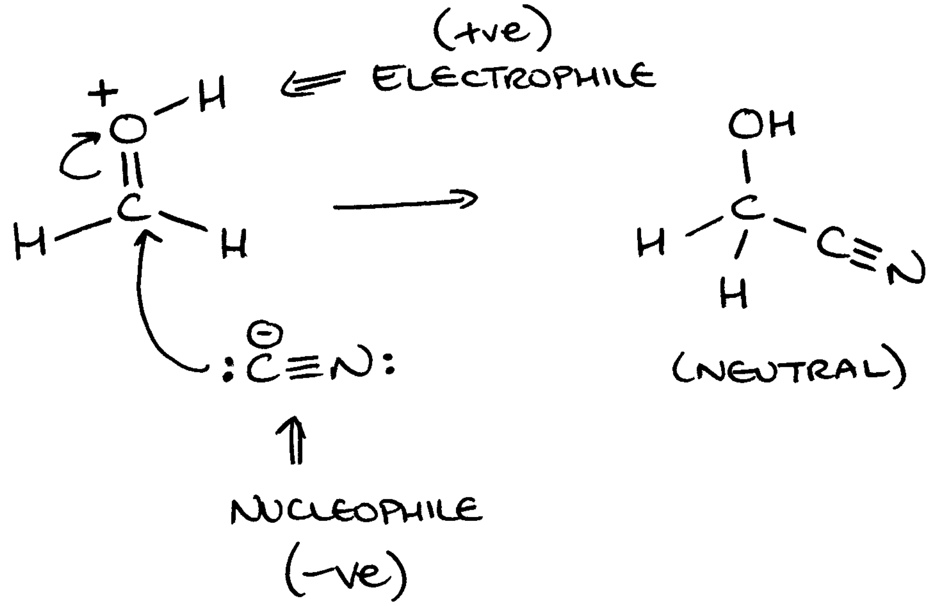


Electrons flow to electrophiles:

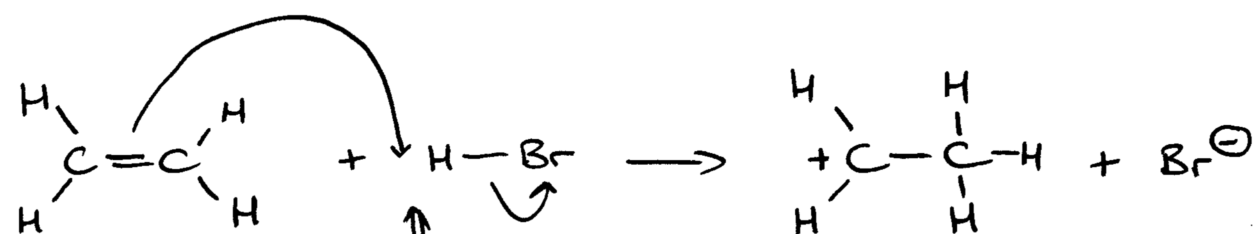


Conserve charge:



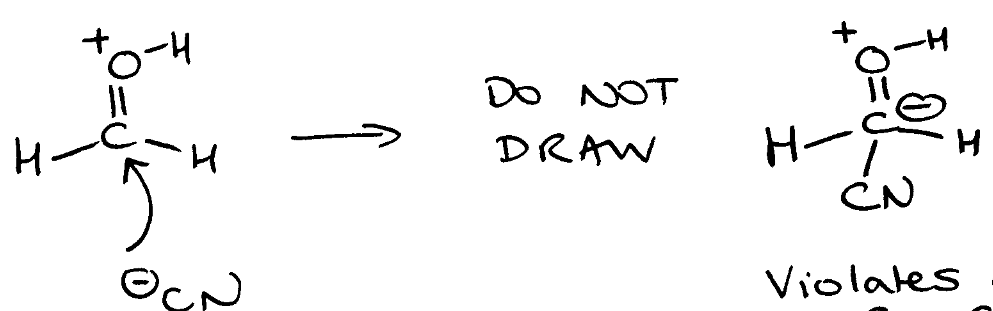


Octet Rule must be followed



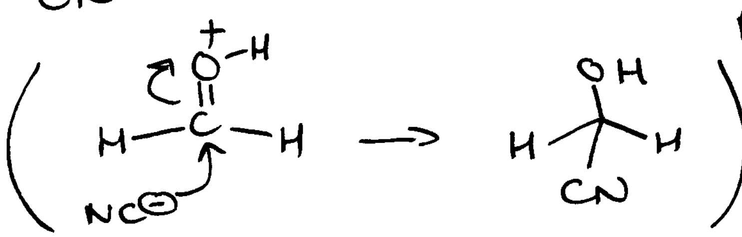
Cannot have 2 BONDS to H, so H-Br bond breaks

note that charge is conserved



DO NOT DRAW

Violates octet RULE

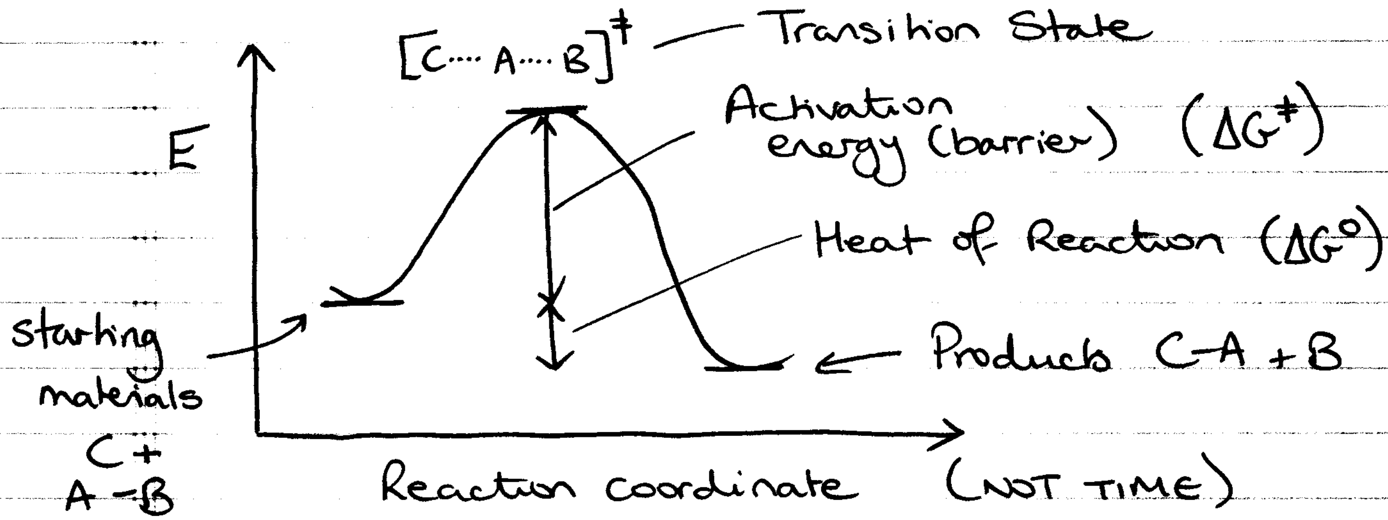


← CORRECT

(3) ENERGY DIAGRAMS

- ONE-STEP REACTION

$C + A-B \longrightarrow C-A + B$



For a reaction to occur as written,

$\Delta G^\circ < 0$ (proceeds spontaneously)

If $\Delta G^\circ > 0$ reaction does not proceed

- Heat of reaction

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ← change in entropy (more significant at higher T)

↑ change in enthalpy (CAN BE MEASURED DIRECTLY)

ΔH^o -ve EXOTHERMIC Reaction
ΔH^o +ve ENDOTHERMIC Reaction

- Transition State

Energy maximum on reaction co-ordinate

- definite geometry and arrangement of atoms

CANNOT BE ISOLATED, STRUCTURE CANNOT BE DETERMINED

- Sometimes we can infer structure, or use computational techniques

- Activation energy

Difference in energy between starting materials and the transition state

$\Delta G^{\ddagger}$ or E_A

Arrhenius equation

$$K = Ae^{\left(\frac{-E_A}{RT}\right)}$$

A ← pre-exponential factor

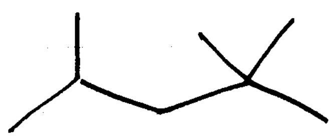
K ← reaction rate constant

KINETICS vs THERMODYNAMICS

↓ How fast will it happen

↓ Will a reaction happen?

e.g.

 $+ O_2 \rightleftharpoons 8CO_2 + 9H_2O$

isooctane

$$\Delta G^0 = -1000 \text{ kJ mol}^{-1}$$

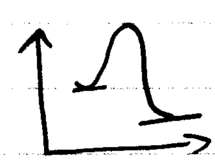
$K_{eq} = 10^{175}$ at 298K

(10^{86} atoms in the observable universe)

BUT

ISOOCTANE is stable
(YOU PUT IT INTO YOUR CAR)

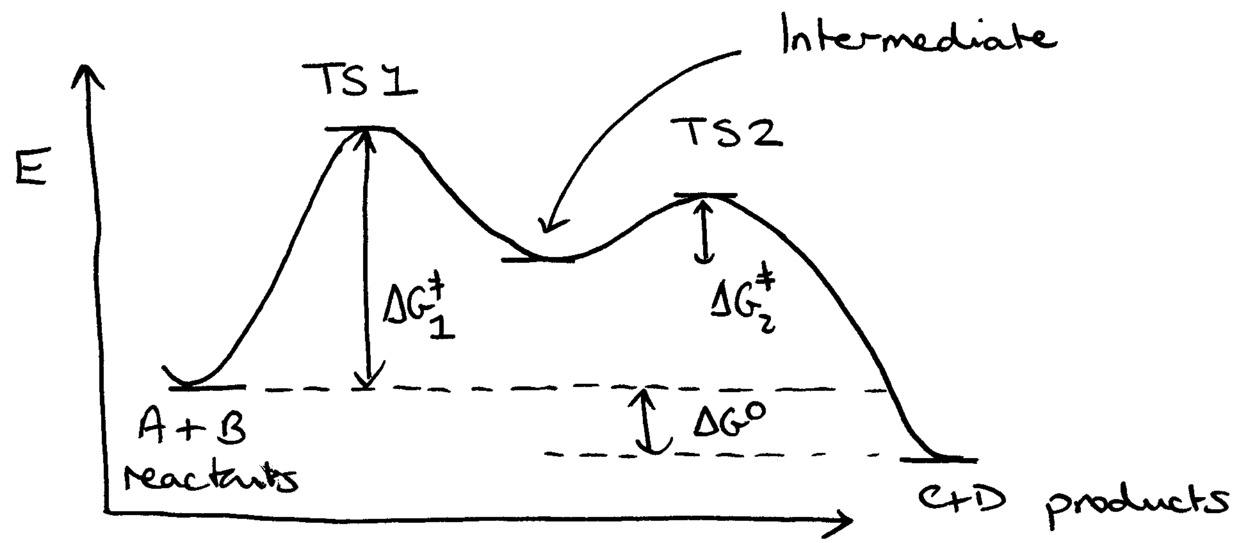
So, energy is required to start reaction
⇒ activation energy

DRAW GRAPH 

So, octane + oxygen
THERMODYNAMICALLY UNSTABLE BUT KINETICALLY STABLE

By contrast, if you applied the same burst of energy to the H_2O and CO_2 that is formed, it WILL NOT revert back to octane and oxygen.

TWO-STEP REACTION



Reaction intermediate → energy minimum between two transition states

SLOWEST step in a multi-step reaction (one with highest barrier) is called the RATE DETERMINING STEP (RDS)