

Ch 4

Note Title

9/23/2005

Propagation steps:

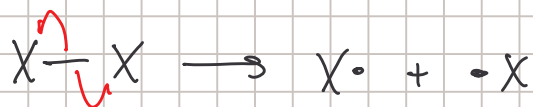


Thermodynamics

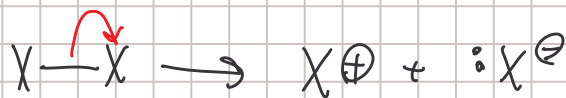
relative energies of reactants/
intermediates/products.

bond dissociation enthalpies

energy required to
split a bond



✓ homolytic bond cleavage

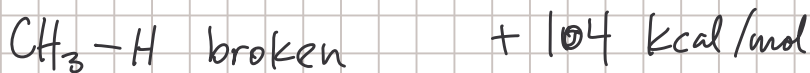


heterolytic bond cleavage

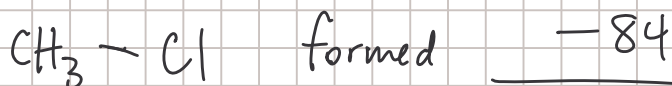
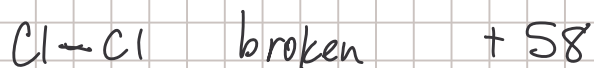
	BDE (kcal/mol)
$\text{CH}_3-\text{H} \rightarrow \text{CH}_3\cdot + \cdot\text{H}$	+104
$\text{H}-\text{Cl}$	+103
$\text{Cl}-\text{Cl}$	+58
CH_3-Cl	+84

Energy is absorbed when bonds are broken

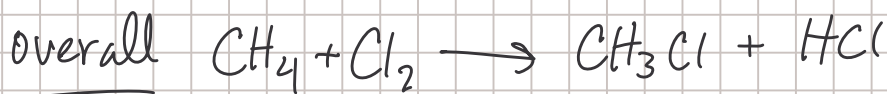
" " released " " " formed.



+1 kcal/mol
endothermic



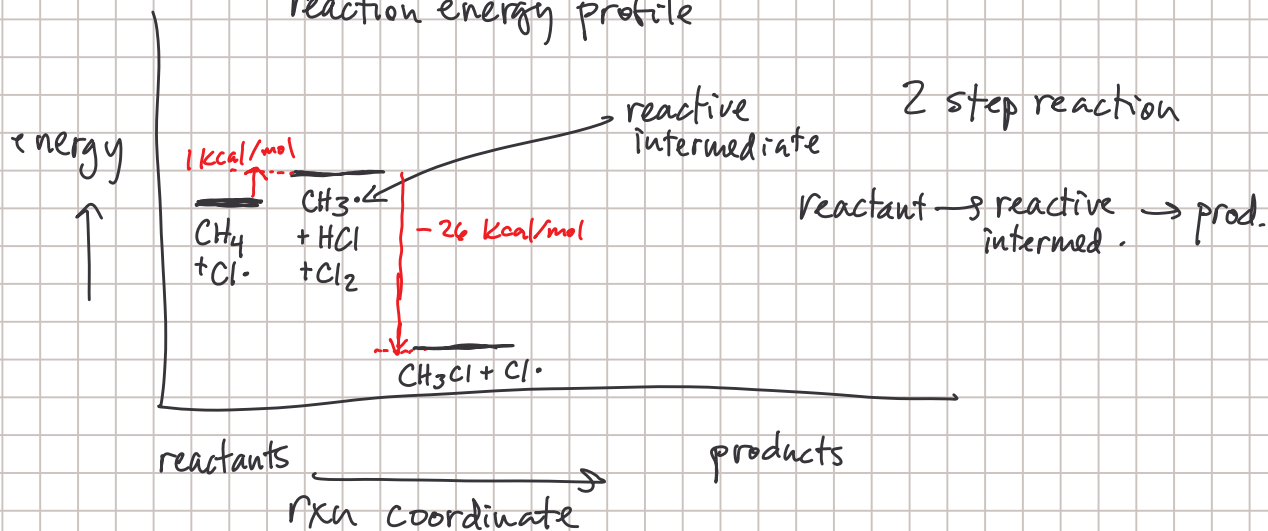
-26 kcal/mol
exothermic



$$+ 1 + -26 = \underline{-25 \text{ kcal/mol}}$$

exothermic

reaction energy profile



ΔH° = enthalpy (heat/energy absorbed/released in reaction)
standard conditions (room temp 1 atm) $\Delta H^\circ_{\text{rxn}} = -25 \text{ kcal/mol}$

ΔS° = entropy (measure of disorder usually not a major factor in organic reactions)

ΔG° = Gibbs free energy = measure of reaction spontaneity

$\Delta G^\circ < 0$: rxn is spontaneous

$\Delta G^\circ < -3 \text{ kcal/mol}$: rxn goes to completion

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \Delta G^\circ \approx \Delta H^\circ$$

exothermic rxns are usu. spontaneous in organic.

Kinetics

study of reaction rates

rate law \rightarrow $\text{rate} = k [A]^a [B]^b$

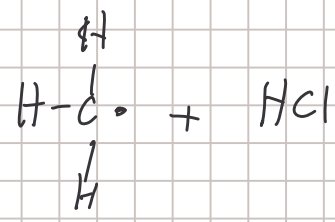
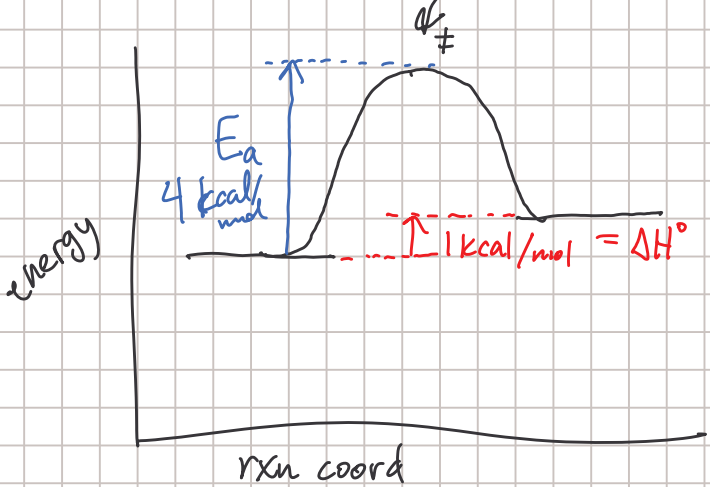
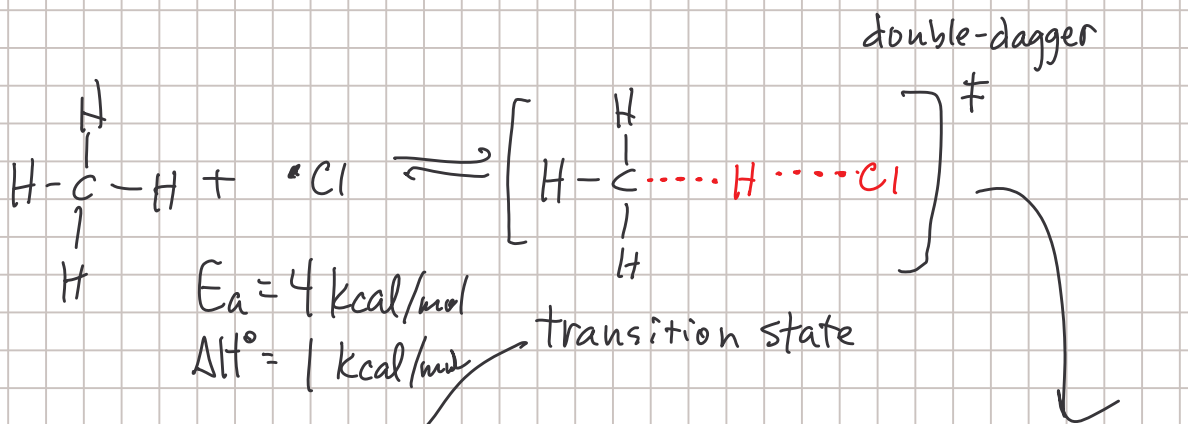
rate constant (unique to reaction)

Concentrations of reactants in rate-limiting step!

some power

rate law must be determined experimentally!
rate-limiting step: slowest step (bottleneck)

transition state: energy-maximum in reaction



$E_a = \text{activation energy}$

E_a is ^{inversely} ~~directly~~ related to k (rate constant)

Larger $E_a = \text{slower rate}$