CH203 Lecture 9

September 30, 2010

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Administrative Announcements

Exam I: Thursday October 7th 8 am – 9:20 am

- Exam locations will be as follows:

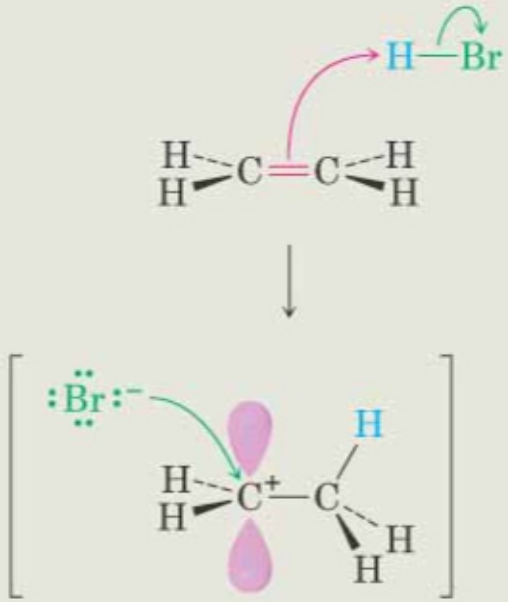
A-S STO B50
T-Z CAS 227

- Exam 1 will cover lectures 1-9 (Chapters 1- 5)

- Sample exam #1 will be posted on the course website by Friday October 1st.

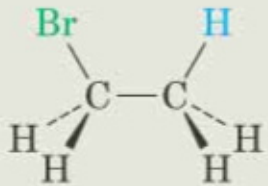
- *Exam # 1 Review Session*: Monday October 4th 7-8:15 pm in SCI 115

The electrophile HBr is attacked by the π electrons of the double bond, and a new C–H σ bond is formed. This leaves the other carbon atom with a + charge and a vacant *p* orbital.



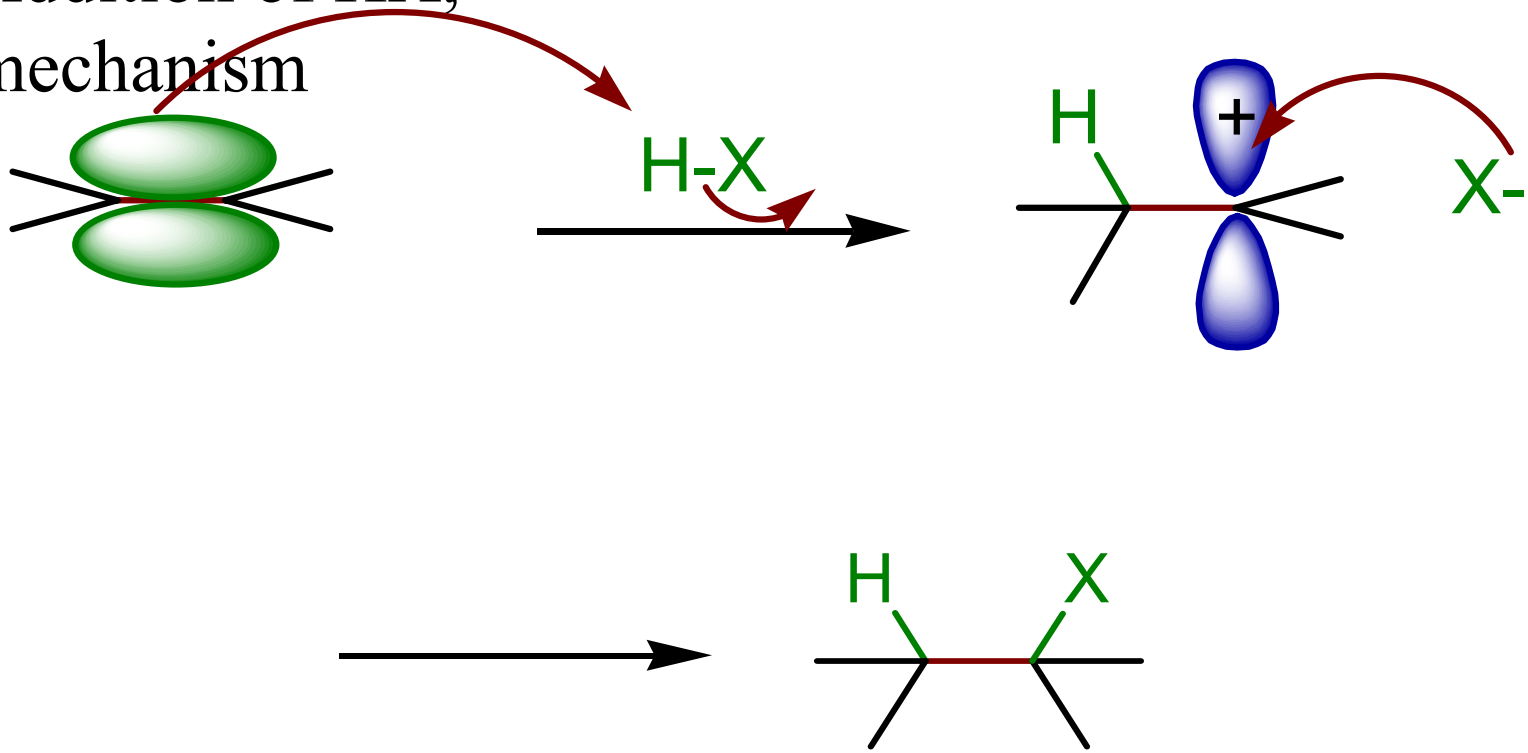
Carbocation intermediate

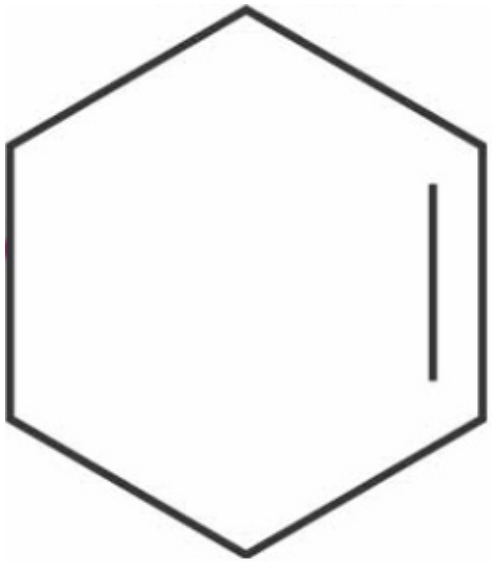
Br^- donates an electron pair to the positively charged carbon atom, forming a C–Br σ bond and yielding the neutral addition product.



Addition to Alkenes

- Addition of HX, mechanism





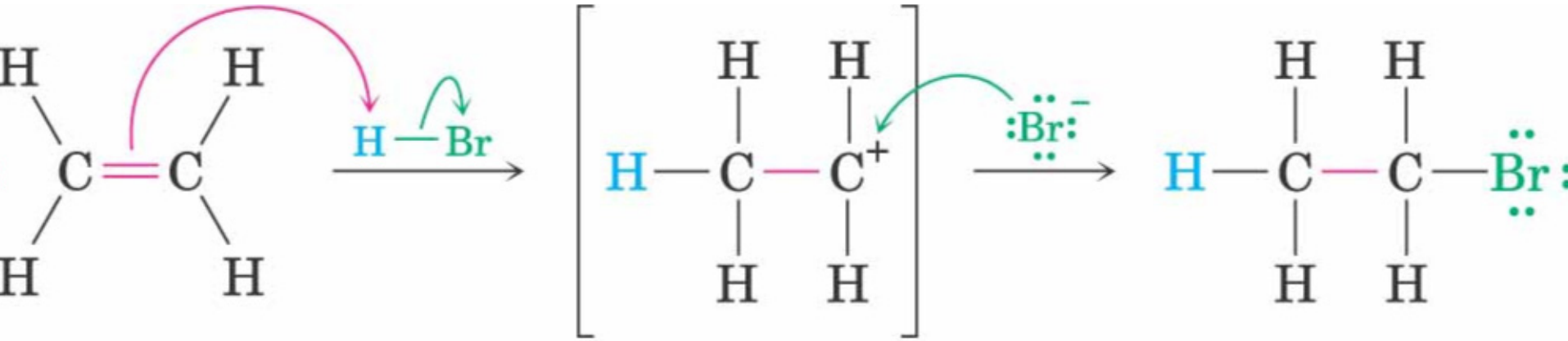
+ HBr ⟶ ?

What is
The product ?

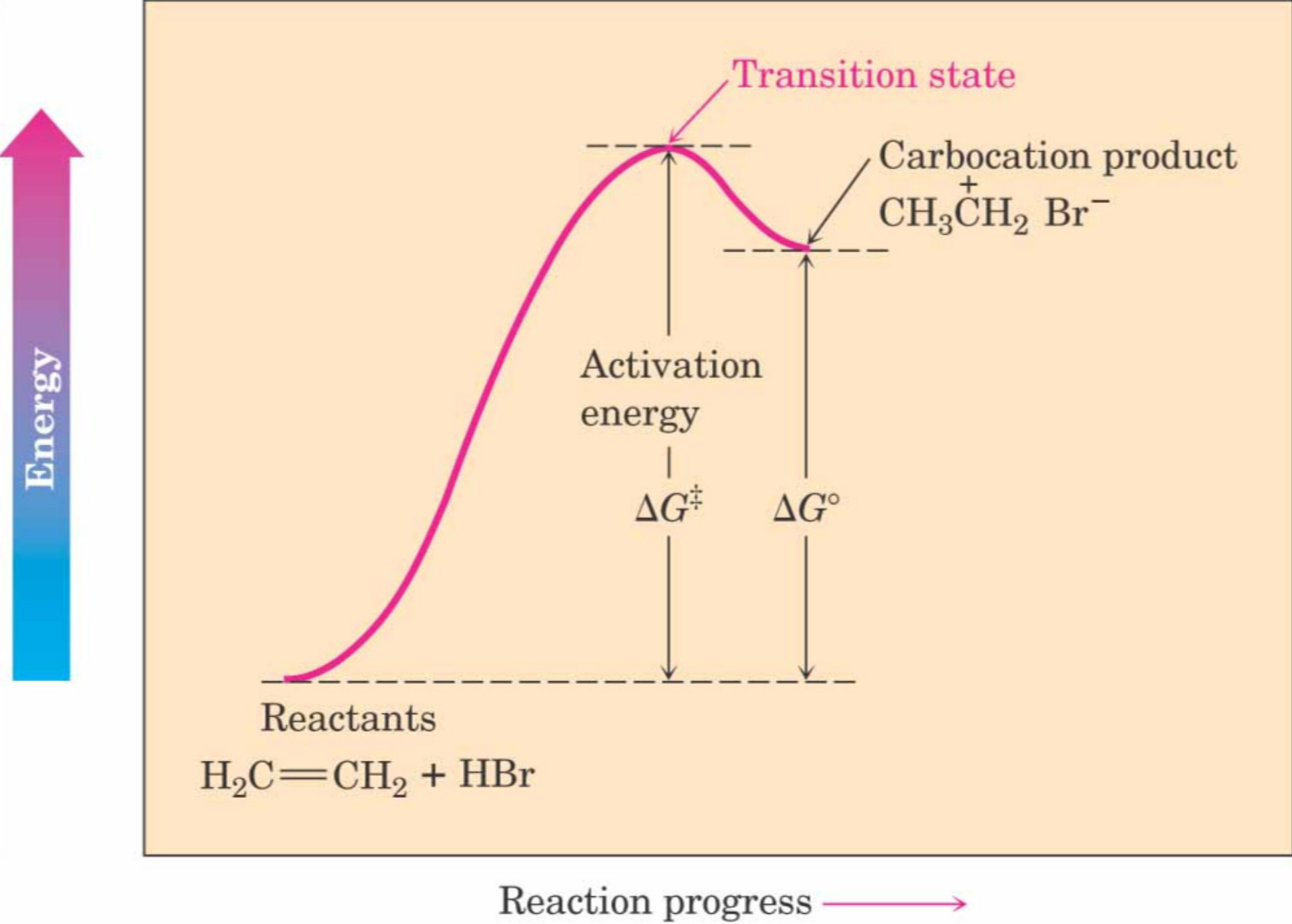
cyclohexene

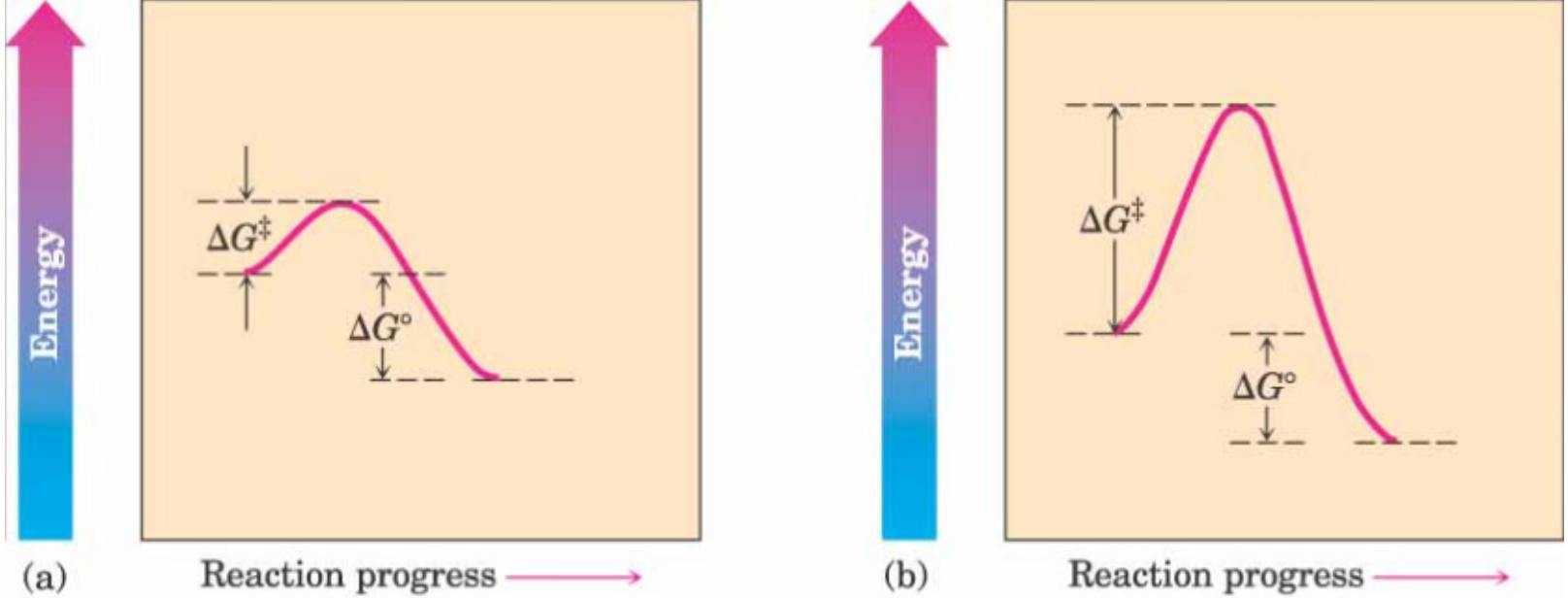
Changes in Energy at Equilibrium

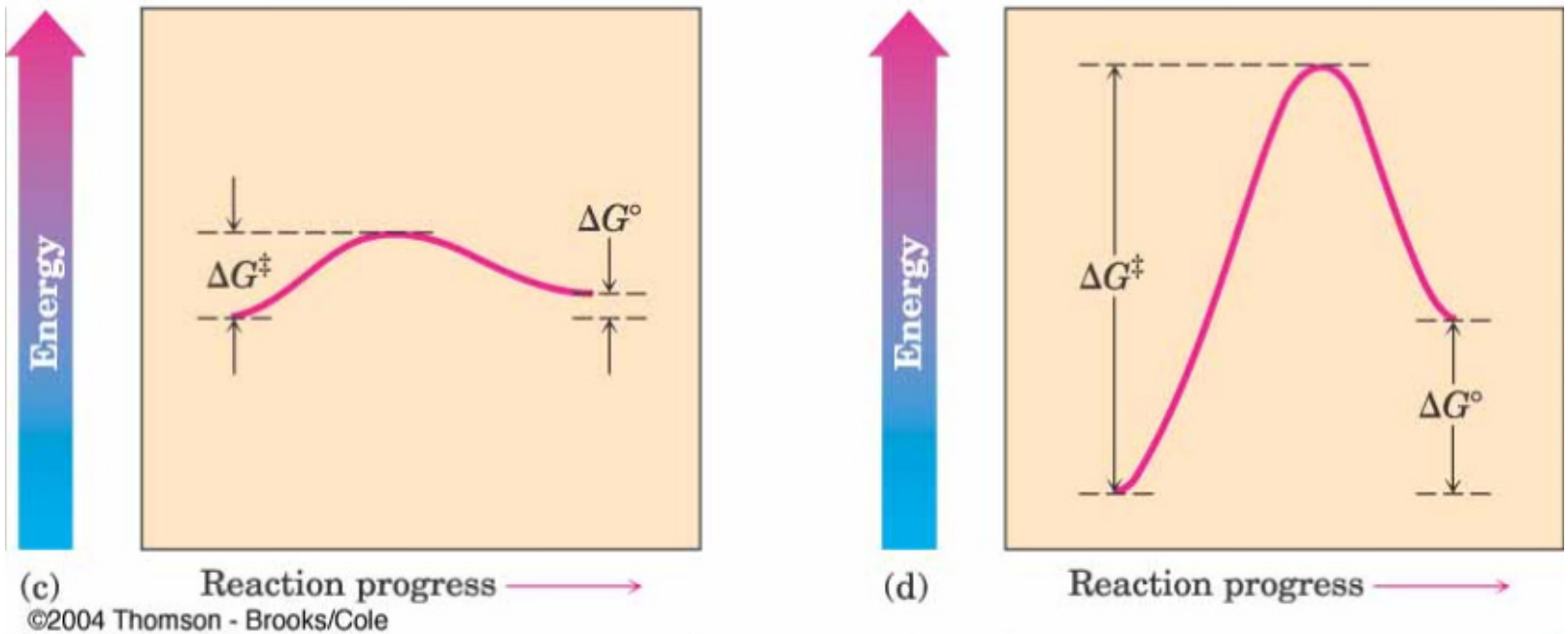
- Free energy changes (ΔG^o) can be divided into
  - a temperature-independent part called **entropy** (ΔS^o) that measures the change in the amount of disorder in the system
  - a temperature-dependent part called **enthalpy** (ΔH^o) that is associated with heat given off (exothermic) or absorbed (endothermic)
- Overall relationship: $\Delta G^o = \Delta H^o - T\Delta S^o$



Carbocation

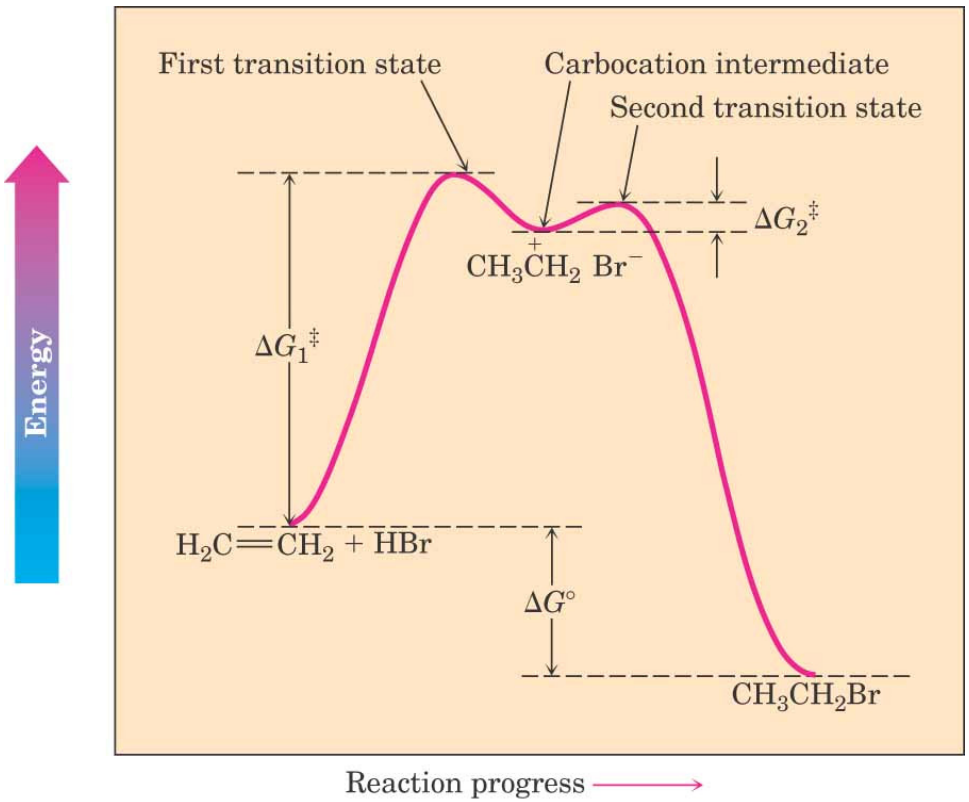






Reaction Diagram for Addition of HBr to Ethylene

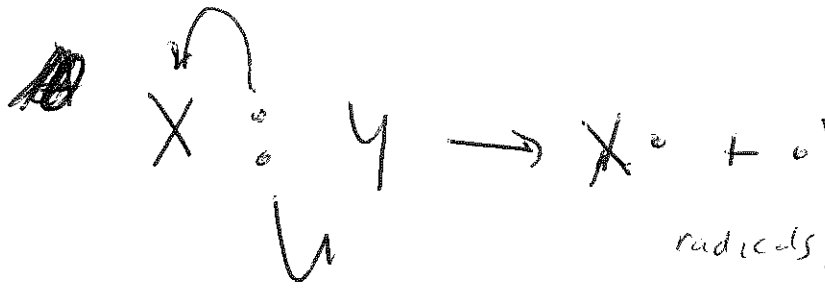
- Two separate steps, each with a own transition state
- Energy minimum between the steps belongs to the carbocation reaction intermediate.



Review

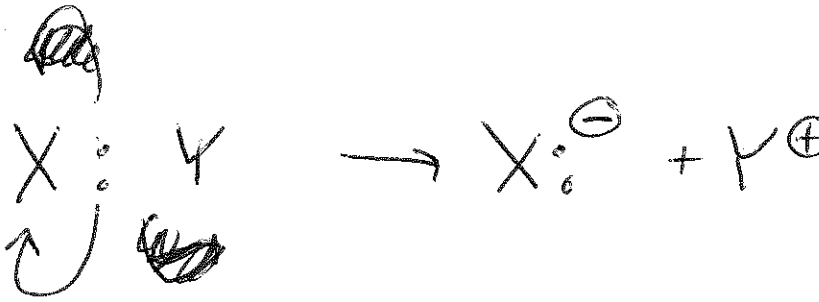
Reaction mechanisms

X–Y



radicals, unpaired e⁻s

Symm. bond breaking (radical)



unsymm. bond breaking (polar)

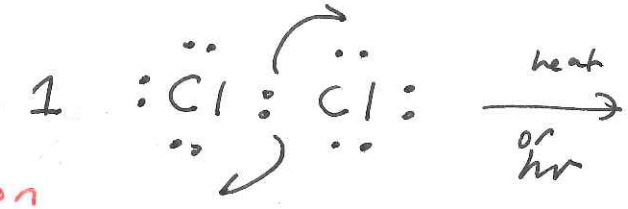
radical reactions : symm. bond breaking + taking

polar reactions unsymm. " " "

Mechanism for Radical Chlorination of methane

Rx: $CH_4 + Cl_2 \xrightarrow[\text{or } h\nu]{\text{heat}} CH_3-Cl + HCl$

Mechanism

Step 1  

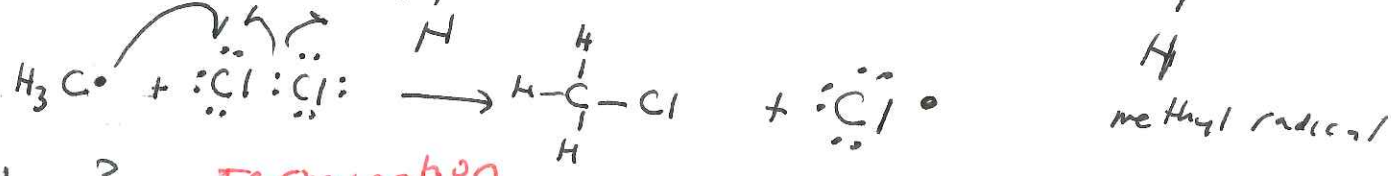
Initiation

each atom takes one b.e.

2 Cl "radicals"

Step 2 Propagation

(1) 

(2) 

methyl radical

Step 3 Termination

$CH_3\cdot + Cl\cdot \rightarrow CH_3-Cl$

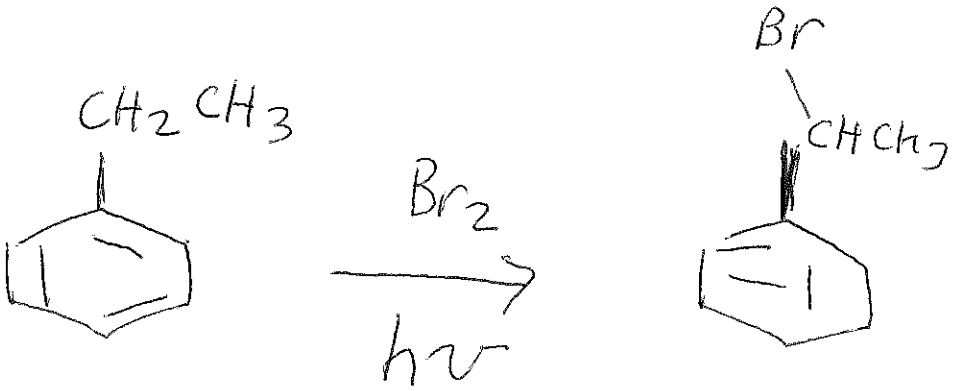
$CH_3\cdot + \cdot CH_3 \rightarrow CH_3-CH_3$

$Cl\cdot + Cl\cdot \rightarrow Cl_2$

Probably occurs least frequently and simply may undergo homolysis again

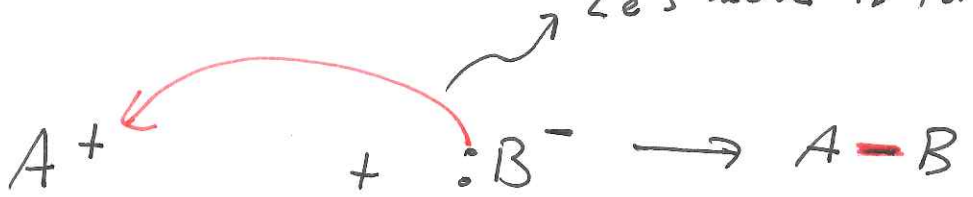
Problems / Mechanisms

include init + prop steps

1) 

2) How many distinct dichlorination products can result when isobutane is subjected to free radical chlorination?

Polar Reactions



generalized equation

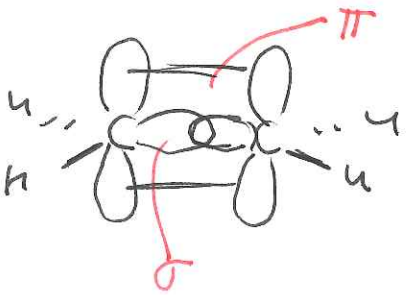
greek philos "to love"

Nucleophile ("nucleus loving") – e⁻ rich atom forms bond by donating e⁻ pair to an e⁻ poor atom

Electrophile "electron loving") – forms a bond by accepting e⁻ pair from nucleophile

e.g. H+ donors, $-\overset{\overset{O}{\|}}{C}-$, $-\overset{|}{C}-Br$

Take case of an alkene e.g. ethylene

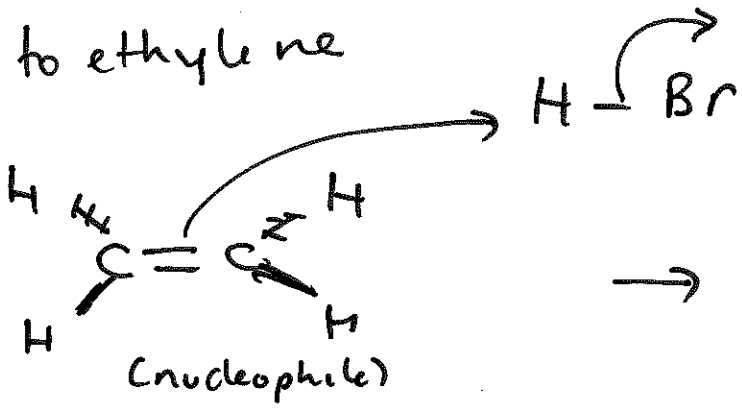


- σ bonding e⁻s relatively inaccessible
- The π bond is particularly susceptible to e⁻ seeking reagents (electrophiles)

Polar reaction : Addition of HBr

Example.

to ethylene



HBr – H+ donor (electrophile)

(nucleophile)

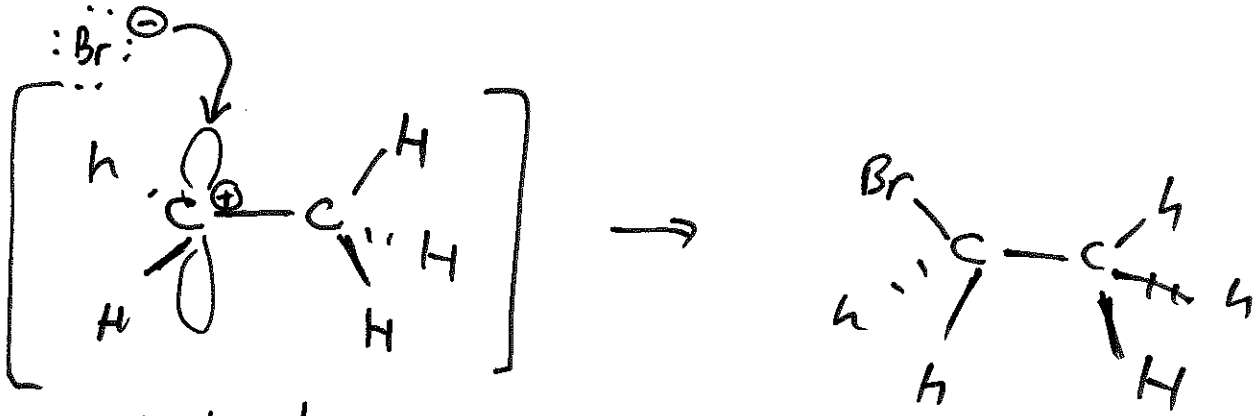
→ σ bond

sp^2–sp^2

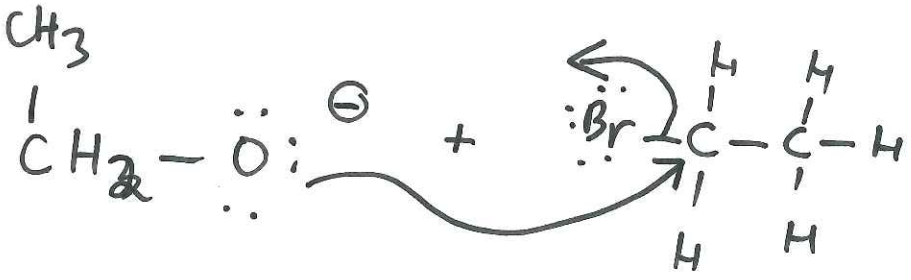
• e⁻s in π bond located above & below plane of d.b and are accesible to approaching reactants

π bond

p–p overlap



carbocation (also electrophile)



indicates flow of e^-s

$$Et-O-CH_2-CH_3 + :\ddot{B}r:^{\ominus}$$

Polar reaction, SN_2

Substitution Nucleophilic

Second order

Reactions: Equilibria & Free energy

rxs can go in forward or rev. dir.

$CH_2=CH_2 + HBr \rightleftharpoons CH_3-CH_2-Br$

$K_{eq} > 1$ most material pres. as products

$$K_{eq} = \frac{[CH_3CH_2Br]}{[HBr][CH_2=CH_2]} = 7.5 \times 10^7 \text{ (at 25°C)}$$

K_{eq} equil const.

> 99.99999% ethylene converted to bromoethane

Magnitude of equi. K_{eq} depends on rel. energy of prod. + react.

Energy of products must be lower than reactants

ΔG gibbs free energy → controls ratio of products to reactants

energy change during a chem rx

ΔG (−) exergonic ↗ energy rel. to surrounds

ΔG (+) endergonic

rel. between free energy chg & K_{eq}

$$\Delta G^\circ = -RT \ln K_{eq}$$

so for $C=C + HBr$

$\Delta G^\circ = -44.8$ kJ/mol

Free energy change ΔG° divi. into

ΔG° → standard gibbs free energy change; 1 atm and usually 298K

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

ΔH°: enthalpy; $T\Delta S^\circ$: temp dep. entropy; ΔS°: change in amt of disorder in the system

$\Delta H^\circ = -84.1$ kJ/mol

ΔH heat of reaction

$\Delta H(-)$ (exothermic) → bonds in products more stable than reactants

$\Delta H(+)$ (endothermic)

heat given off or absorbed

+ ΔS° associated with a change from a more ordered to a less ordered system

$A \rightarrow B + C$ net incr in entropy

− ΔS° reverse process

$A + B \rightarrow C$ net decr in entropy

ΔS (entropy change)

$A \rightarrow B + C$ (e.g. elim.)
net incr in entropy (+)

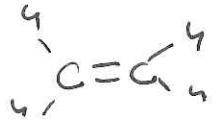
$A + B \rightarrow C$ (e.g. add rx)
ΔS (−)

std change in overall free energy

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

change in enthalpy; entropy

∴ A + entropy change makes a negative contribution to ΔG° and is energetically favorable for formation



+ HBr ⟶⟵ CH_3-CH_2-Br

$\Delta G^\circ = -44.8$ kJ/mol

$\Delta H^\circ = -84.1$ kJ/mol

$\Delta S^\circ = -0.132$ kJ/K·mol

$T = 298$ K

$\Delta H^\circ < 0$ favorable

$\Delta S^\circ > 0$

↳ ∴ any rx which has $\Delta G^\circ < 0$ should be favorable or spontaneous

Reaction Energy Diagrams:

Depict Energy changes during rxs

reaction progress or rx coordinate

transition state: represents highest-energy structure in rx coord.

difference btwn reactants + t.s is the activation energy $\Delta G^{\ddagger}$

larger $\Delta G^{\ddagger}$, slower rx

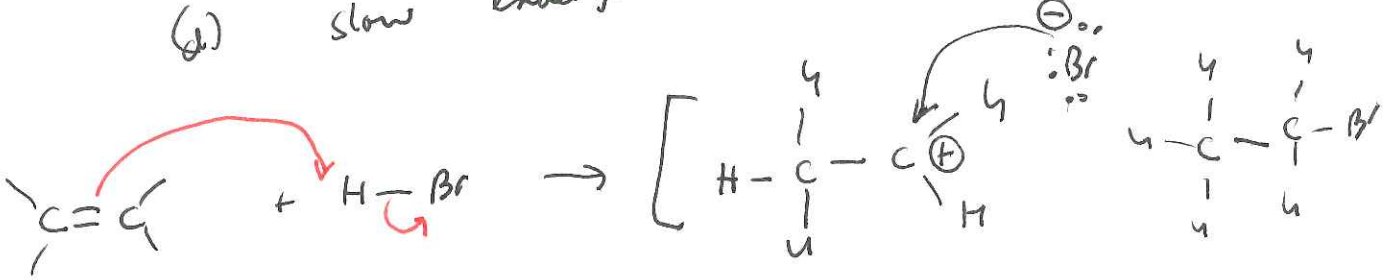
(overhead)

(a) fast exergonic

(b) slow exergonic

(c) fast endergonic

(d) slow endergonic



overall ΔG^{0} is energy diff btwn init. reactants + final products

(transient)

Carbocation rx intermediate

2nd transition state Br^{-} just starts to donate e⁻s and form C–Br bond