

Chapter Four: The Study of Chemical Reactions

1,000's of organic reactions!

Classify according to similarities.

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I. Types of Reactions

- A. Addition
- B. Elimination
- C. Substitution
- D. Rearrangement

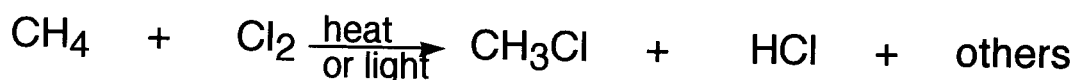
II. Types of Intermediates

- A. Radicals
- B. Carbocations
- C. Carbanions
- D. Carbenes

Tools for studying reactions:

1. Mechanism: the steps of bond breaking and bond forming that convert the reactants to the products
2. Thermodynamics: stability (energy) of the reactants vs stability (energy) of the products
3. Kinetics: reaction rates

Our practice reaction: Halogenation of Alkanes



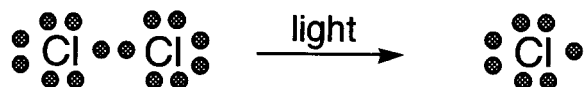
Observations:

1. Rxn. will not proceed in the dark at RT.
2. Rxn. begins if exposed to light (or if heated).
3. Blue light is most effective in beginning the reaction.
4. High quantum yield reaction - one photon produces many product molecules.
5. Reaction proceeds momentarily in the dark before stopping.

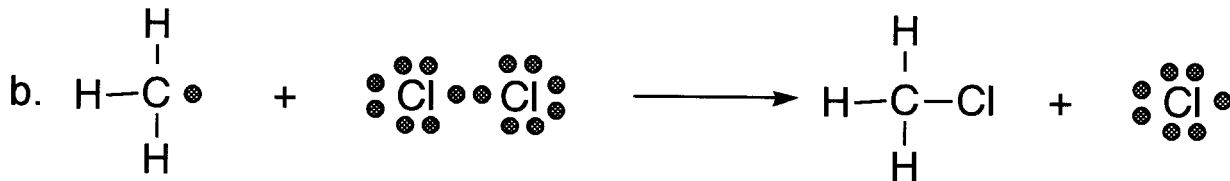
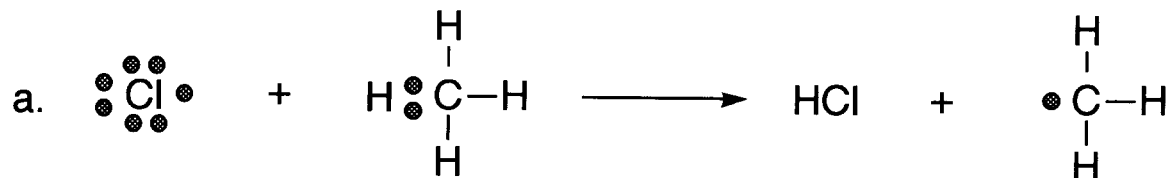
Our proposed mechanism must account for all of the above.

Mechanism of Free Radical Halogenation:

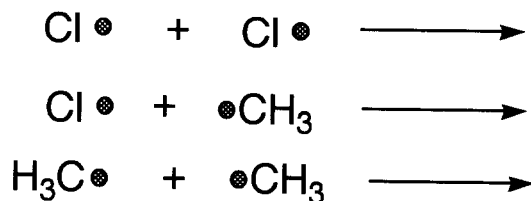
Step 1: Initiation



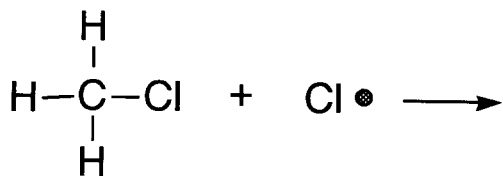
Step 2: Propagation



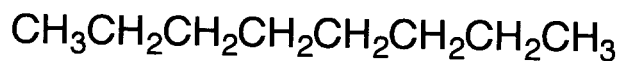
Step 3: Termination



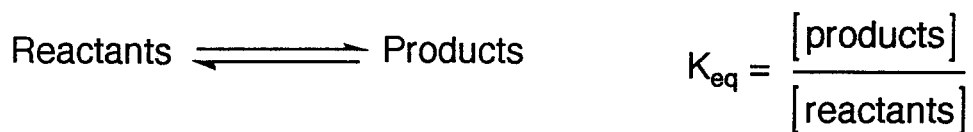
Reaction does not stop at monochlorination. The chlorine radical can abstract any hydrogen atom it collides with.



Product mixtures are a problem, especially when the starting alkane has more than one type of hydrogen.

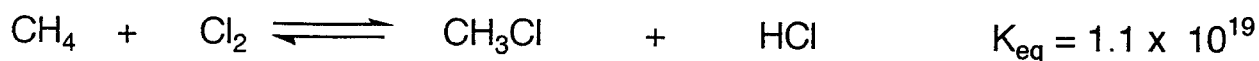


Thermodynamics: Equilibrium Constants and Free Energy (A Summary)



If K_{eq} is >1 , reaction proceeds to the RIGHT (more products than reactants at EQ).

If K_{eq} is large ($> 10^3$), reaction is considered to be "complete" (no reactants left).



What determines K_{eq} ? \Rightarrow Stability of the products vs Stability of the reactants



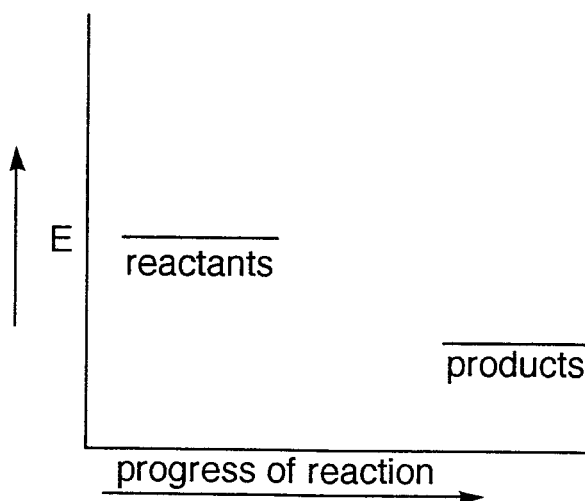
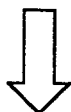
Energy of the products vs Energy of the reactants

Favorable \downarrow EQ

Energy of products $<$ Energy of reactants



Energy released



ΔG° - total energy change in a reaction

- related to K_{eq} by: $K_{eq} = e^{-\Delta G^\circ/RT}$ or $\Delta G^\circ = -RT(\ln K_{eq})$

$\Delta G^\circ =$ energy of the products - energy of the reactants

- ΔG°

+ ΔG°

Two factors contribute to ΔG° : Enthalpy (ΔH°) and Entropy (ΔS°)

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

Enthalpy - heat of reaction, heat evolved or absorbed in a reaction
- result of bond changes that occur in a reaction

$\Delta H^\circ =$ enthalpy of products - enthalpy of reactants

- ΔH°

+ ΔH°

Entropy - changes in the order of a system (disorder favored)

$\Delta S^\circ =$ entropy of products - entropy of reactants

- ΔS°

+ ΔS°

Summary:

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

favorable
unfavorable

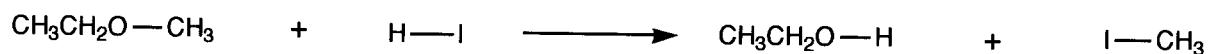
Bond Dissociation Energy: energy required to break a bond homolytically



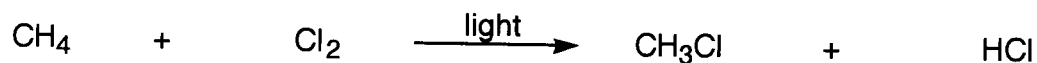
Energy is absorbed in bond breaking, so BDE is always positive (Table 4 - 2)

$$\Delta H^\circ = \text{BDE}_{\text{broken}} - \text{BDE}_{\text{formed}} \qquad \text{OR} \qquad \Delta H^\circ = \Delta H^\circ_{\text{broken}} + \Delta H^\circ_{\text{formed}}$$

Example:

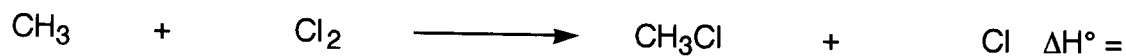
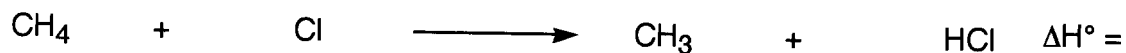


Apply to alkane halogenation:



$$\Delta H^\circ =$$

Consider mechanism: (propagation steps only)

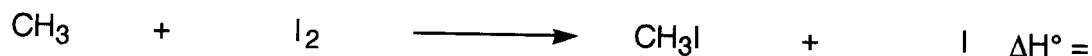
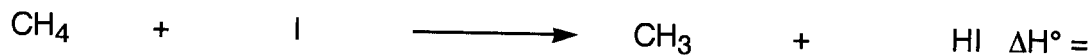


$$\Delta H^\circ_{\text{overall}} =$$

Is iodination of alkanes favorable?



$$\Delta H^\circ =$$



$$\Delta H^\circ_{\text{overall}} =$$

Kinetics and Rate Equation:

We cannot look at the reaction equation and predict the rate equation. The rate equation must be determined by experiment!

$$\text{rate} = k_r[A]^a[B]^b$$

$$k_r =$$

$$a \text{ and } b =$$

$$a + b =$$

Example: doubling the concentration of A doubles the reaction rate
doubling the concentration of B doubles the reaction rate

$$\text{rate} = K_r[A][B]$$

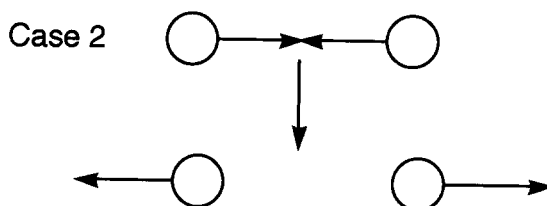
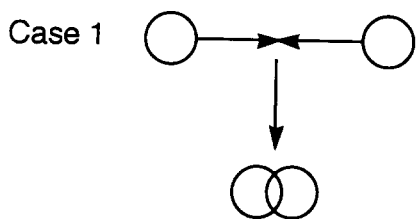
Example: doubling the concentration of A doubles the reaction rate
doubling the concentration of B does not affect the reaction rate

$$\text{rate} = K_r[A]$$

Reaction Rate, Activation Energy and Temperature Dependence

$$k_r = A e^{-E_a/RT}$$

Reactions occur because molecules are in motion (have KE) and they collide with each other. Not all collisions result in a reaction.



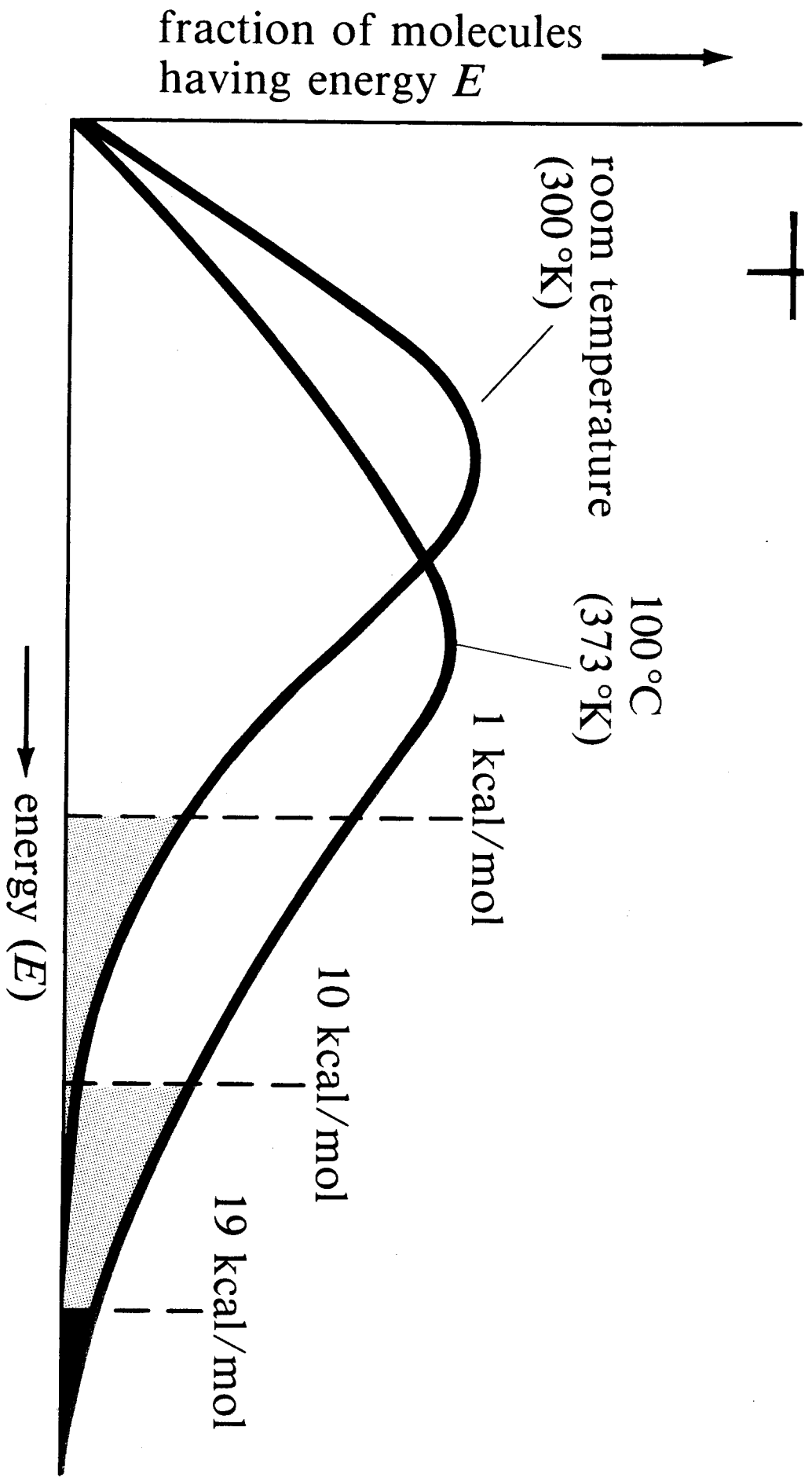
What determines case 1 vs case 2?

1. Orientation of the collision:

2. Activation energy:

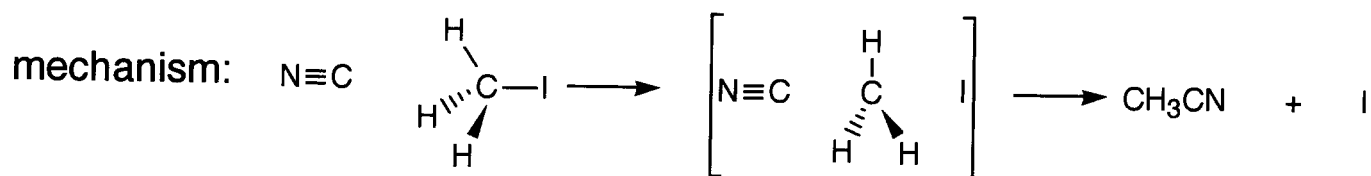
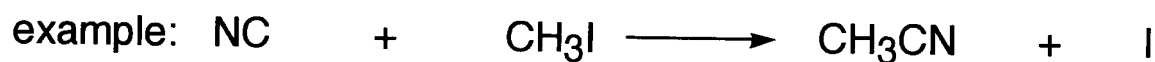
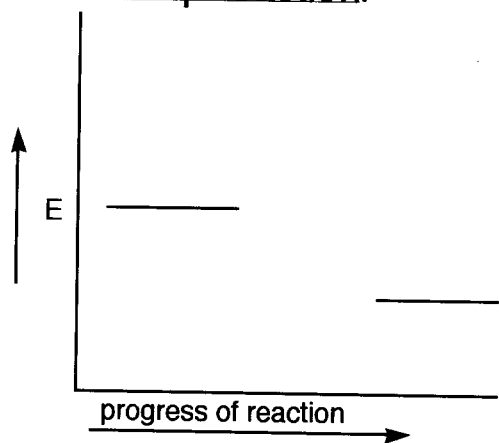
Temperature dependence:

MOLECULAR ENERGY DISTRIBUTIONS



Reaction Energy Diagrams/Transition States/Intermediates

A one-step reaction:



A two-step reaction:

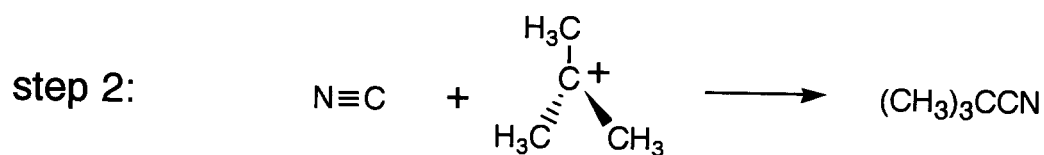
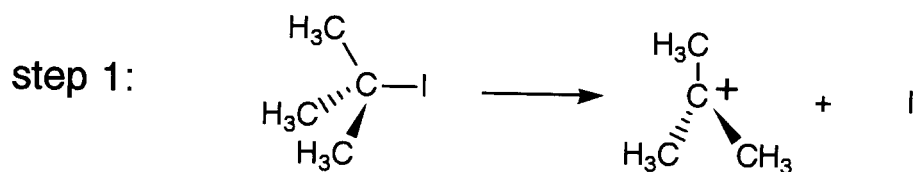
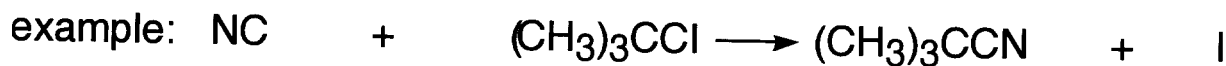
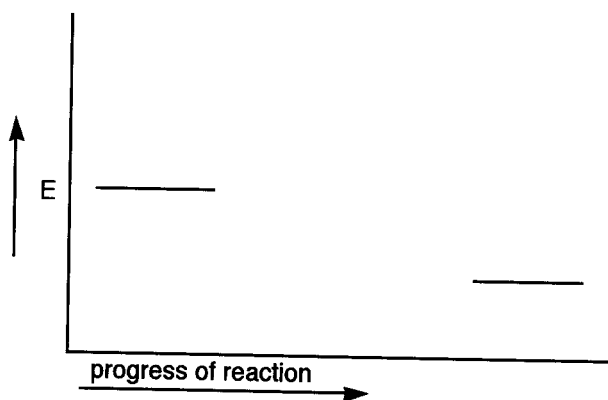
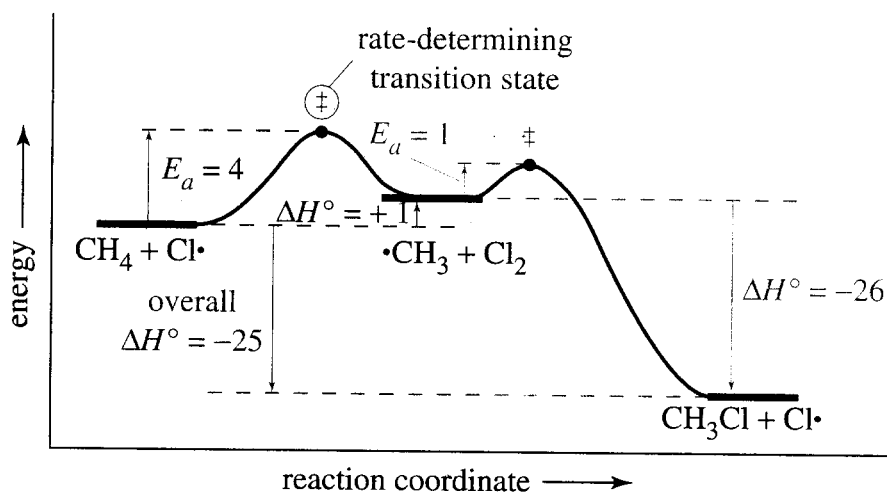
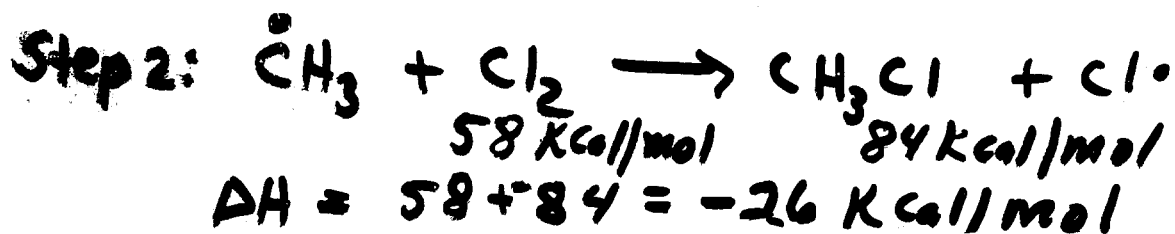
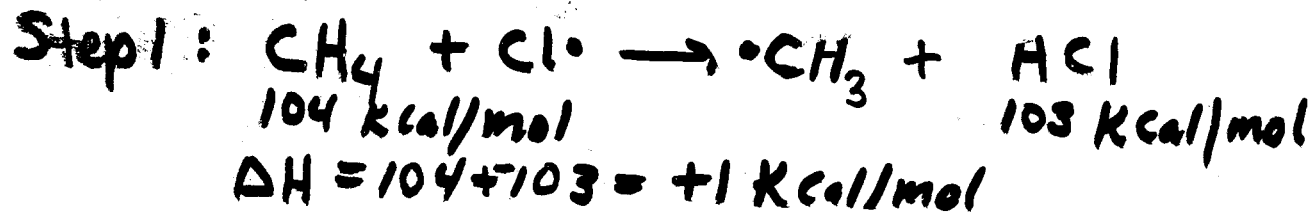


FIGURE 4-4 CHLORINATION OF METHANE



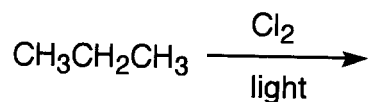
Propagation:



$$\Delta H_{\text{total}} = +1 \text{ kcal/mol} + -26 \text{ kcal/mol}$$

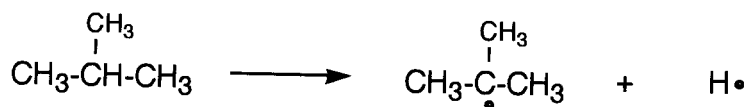
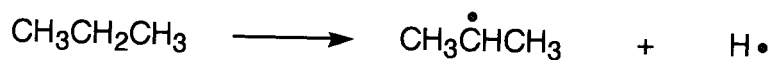
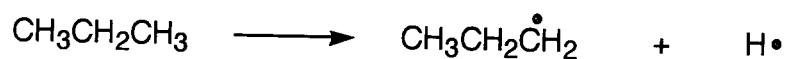
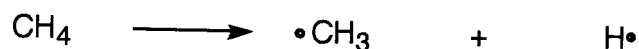
$$= \underline{\underline{-25 \text{ kcal/mol}}}$$

Halogenation of Larger Alkanes:

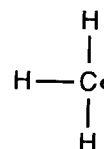
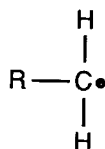
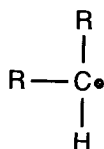
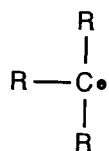


Consider Bond Dissociation Energies:

BDE

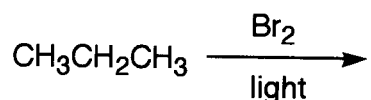
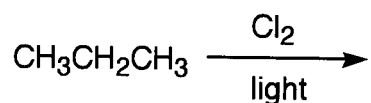


Stability of Radicals:



Alkyl groups stabilize an electron deficiency because alkyl groups are considered to be electron releasing. The more alkyl groups bonded to an electron deficient carbon, the more stable the species.

Structure of radical:

Reactivity VS Selectivity:

Simple explanation: Br • vs Cl •

more stable \longrightarrow

less stable \longrightarrow

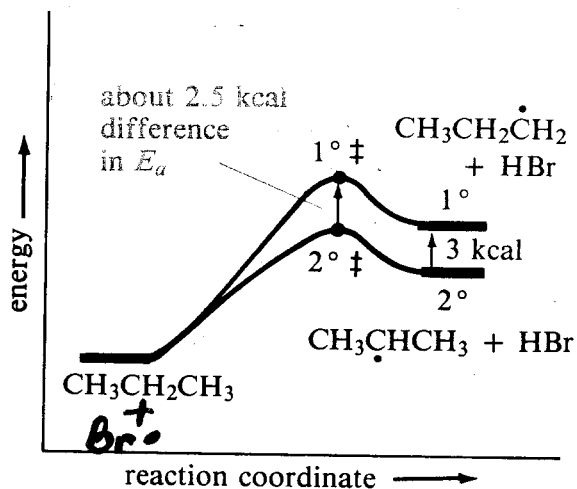
Complete explanation: see energy profiles on next page

Endothermic reaction: TS is closer to products in energy and structure

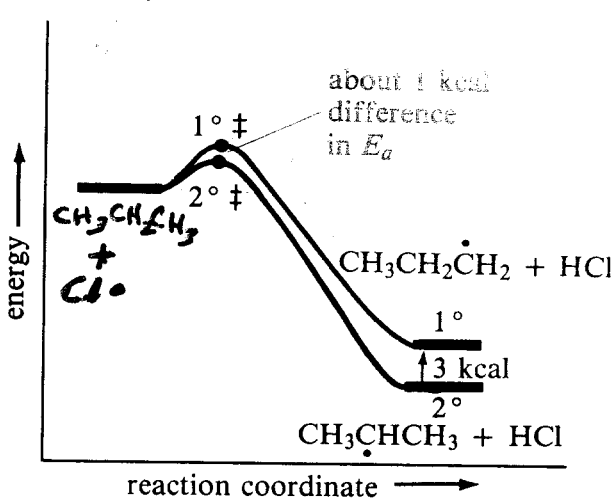
Exothermic reaction: TS is closer to reactants in energy and structure

Hammond Postulate: Related species (in a given reaction) that are closer in energy are also closer in structure. The structure of a transition state (TS) resembles the structure of the closest stable species.

COMPARISON of ENDOTHERMIC and EXOTHERMIC ACTIVATION ENERGIES



BROMINATION
endothermic
TS close to products
large difference in E_a



CHLORINATION
exothermic
TS close to reactants
small difference in E_a

Br•

$$\Delta H_{1^\circ} = +10 \text{ Kcal./mol}$$

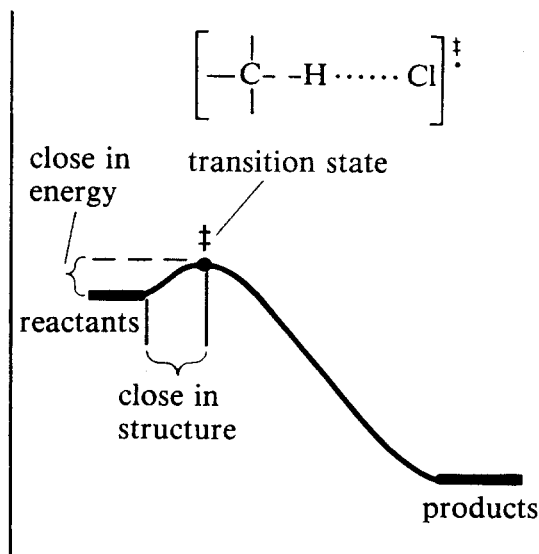
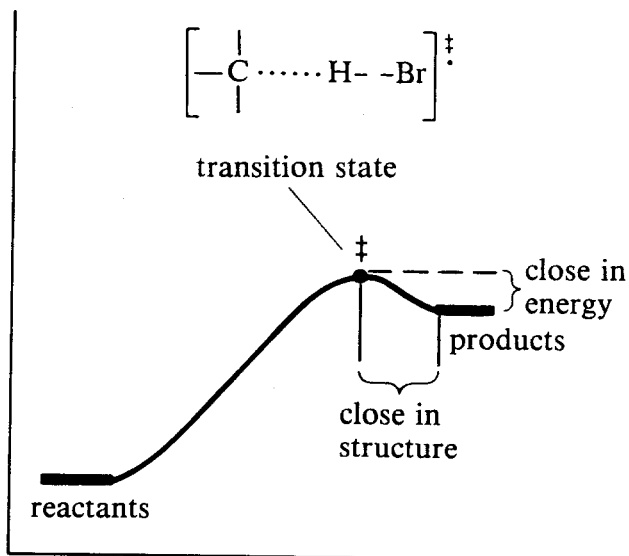
$$\Delta H_{2^\circ} = +7 \text{ Kcal./mol}$$

Cl•

$$\Delta H_{1^\circ} = -5 \text{ Kcal./mol}$$

$$\Delta H_{2^\circ} = -8 \text{ Kcal./mol}$$

COMPARISON of ENDOTHERMIC and EXOTHERMIC TRANSITION STATES

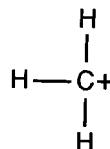
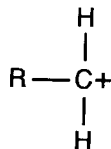
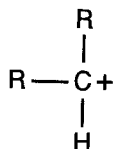
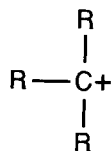


Other Reactive Intermediates:

- A. Radical (already discussed) - electron deficient carbon; uncharged
- B. Carbocation - also has electron deficient carbon, but with a positive charge
- a strong electrophile

Structure:

Stability of Carbocations:



Alkyl groups stabilize electron deficiencies in two ways:

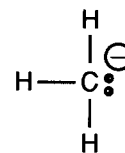
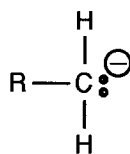
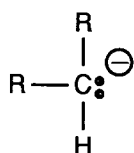
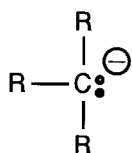
1. inductive effect - electron donation through sigma bonds - bonding pair of electrons is drawn closer to positive carbon
2. hyperconjugation - overlap of filled sp^3 orbital of adjacent alkyl group with empty p orbital of carbocation

3. resonance (when possible)

C. Carbanion - carbon has a lone pair of electrons and a negative charge
 - a strong nucleophile/strong base

Structure:

Stability of Carbanions:



electron donation -

electron withdrawal -

resonance -

D. Carbene - carbon has a lone pair of electrons and is uncharged
 - can serve as both an electrophile and a nucleophile

Examples:

methylene -

dichlorocarbene -

Structure: