# The Study of Chemical Reactions

**Mechanism:**
The complete, step by step description of exactly which bonds are broken, formed, and in which order.

**Thermodynamics:**
The study of the energy changes that accompany chemical and physical transformations. It allows the comparison of the stability of reactants and products, and enables the prediction of the position of equilibrium.

**Kinetics:**
The study of reaction rates, determining which products are formed fastest. It can also allow the prediction of how a reaction rate will change under different conditions.

Recall the chlorination of Methane:
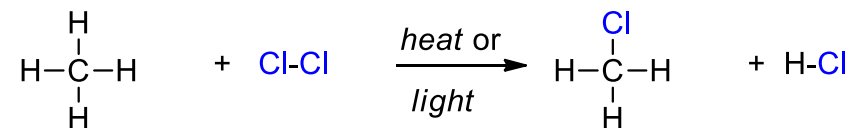


A study of the reaction revealed the following observations:
1) Chlorination did not occur at room temperature or in the dark (heat or light is required to *initiate* the reaction)
2) The most effective initiation is blue light. A chlorine molecule is known to absorb light of that wavelength. (The light is *activating* the chlorine molecule)
3) The light-initiated reaction has a high quantum yield. i.e. one photon gives more than one molecule of product. (The reaction is probably a *Chain process*).

The Free Radical Chain Reaction
Free radical chain reactions comprise of three different steps:
    Initiation
    Propagation
    Termination

The initiation step (This is where the *reactive intermediate* is generated).
Chlorine molecules absorb blue light, whereas methane does not, so it is safe to presume it is the chlorine molecule that is being *activated*, and doing the *initiating*.

Blue light contains the correct energy to split a chlorine molecule into two chlorine atoms (58kcal/mol).

$$:\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{Cl}}: \quad + \quad photon\ (h\nu) \quad \longrightarrow \quad :\overset{..}{\underset{..}{Cl}}\cdot \quad + \quad \cdot\overset{..}{\underset{..}{Cl}}:$$

(Remember: *fish hook* arrows are the movement of *one* electron).

This is the generation of a **reactive intermediate**: a short lived, highly reactive species that is never present in large concentrations due to its reactive nature.

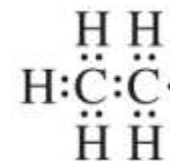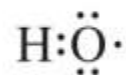Each chlorine atom has 7 valence electrons: 3 are paired, one is unpaired.

The unpaired electron is termed the **odd electron** or **radical electron**.

Species with unpaired electrons are called **free radicals**.

Normally radicals are electron deficient and strongly electrophilic.

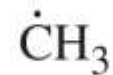## Common Radicals in Organic Chemistry

*Lewis structures*

$:\overset{..}{\underset{..}{Cl}}\cdot$    $:\overset{..}{\underset{..}{Br}}\cdot$    $H:\overset{..}{\underset{..}{O}}\cdot$    $H:\overset{H}{\underset{H}{\overset{..}{C}}}\cdot$    $H:\overset{H}{\underset{H}{\overset{..}{C}}}:\overset{H}{\underset{H}{\overset{..}{C}}}\cdot$

*Written*

$Cl\cdot$              $Br\cdot$              $HO\cdot$              $\dot{C}H_3$              $CH_3\dot{C}H_2$
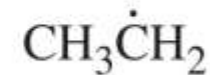
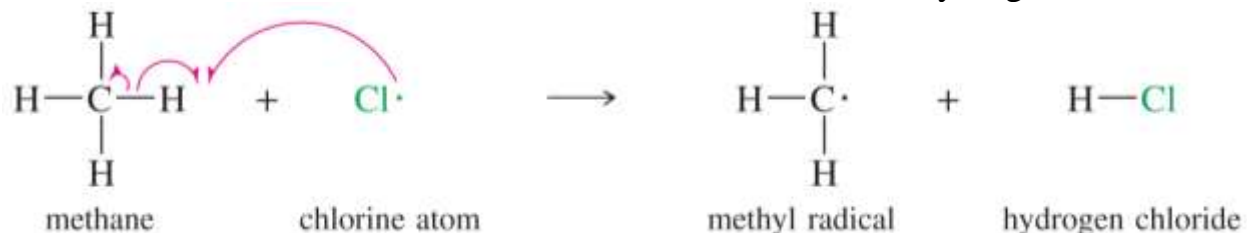chlorine atom      bromine atom      hydroxyl radical      methyl radical      ethyl radical

## Propagation Steps

The reactive chlorine atom collides with a methane molecule, and abstracts a hydrogen atom.



| methane | chlorine atom | methyl radical | hydrogen chloride |

One of the C-H bond electrons stays on the C atom.

The first propagation step is the **reaction** of the reactive intermediate.

The radical reacts, and generates another radical. (Molecule and radical → molecule and radical).

The reactive intermediate thus produced (methyl radical) reacts in the second propagation step.



| methyl radical | chlorine molecule | chloromethane | chlorine atom |

In addition to the generation of the product (chloromethane), another chlorine radical is produced.

This can then react with another molecule of methane to give HCl and a methyl radical, which in turn reacts with another molecule of chlorine to give chloromethane and a chlorine radical, which can react...
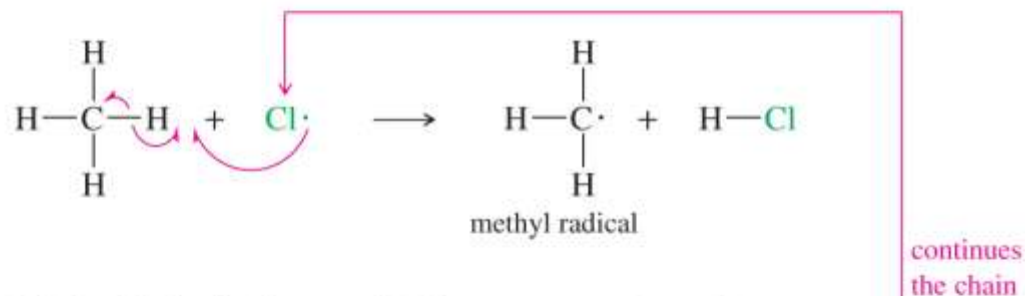
## Summary

*Initiation: Radicals are formed.*
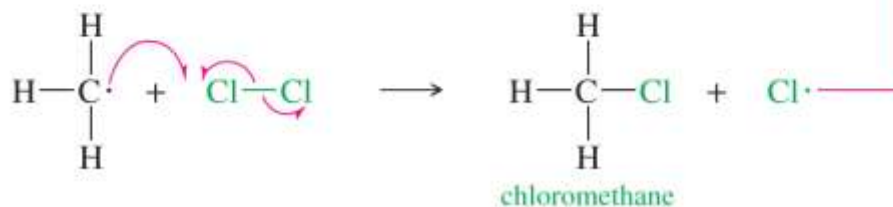Light supplies the energy to split a chlorine molecule.

$$Cl-Cl \; + \; h\nu \text{ (light)} \longrightarrow 2\,Cl\cdot$$
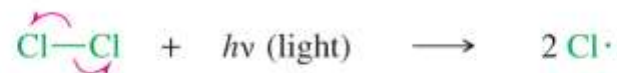
*Propagation: A radical reacts to generate another radical.*
**Step 1:** A chlorine radical abstracts a hydrogen to generate an alkyl radical.

methyl radical

continues the chain

**Step 2:** The alkyl radical reacts with $Cl_2$ to generate the product and a chlorine radical.



chloromethane

© 2013 Pearson Education, Inc.

A chain reaction will continue in such a fashion until either all the methane is used up, or the radicals are consumed in another way (termination steps).

## Termination steps

If a radical undergoes a reaction which *does not* generate another radical, then the chain reaction slows and stops.

Therefore side reactions which consume radicals are detrimental to chain reactions. These side reactions are called *Termination Reactions*.

## Possible Termination Steps
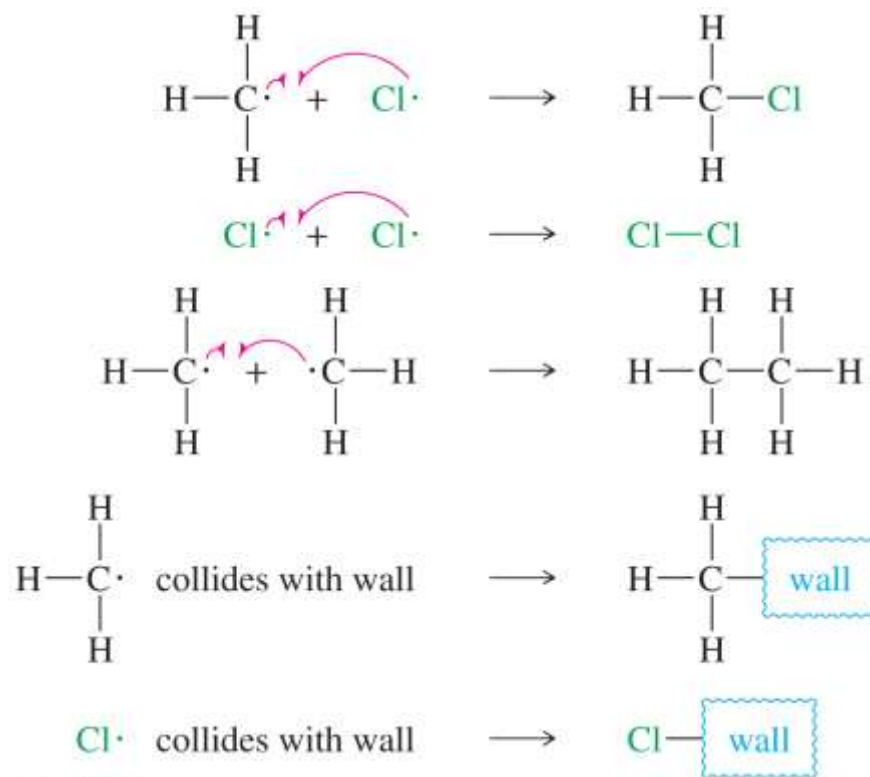


Since the termination steps usually involve the combination of two free radicals (which are always in low concentration) these are *less likely* than the collisions of radicals and atoms (i.e. desired reactions).

Equilibrium Constants and Free Energy

Free radical chain was the **mechanism**. Now let us consider the *Thermodynamics*…

Equilibrium Constant, $K_{eq}$

$$aA + bB \rightleftharpoons cC + dD$$

$$K_{eq} = \frac{[products]}{[reactants]} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

© 2013 Pearson Education, Inc.

$K_{eq}$ gives the **position** of equilibrium, that is whether the products or reactants are *more stable*, and therefore energetically *favored*.

If $K_{eq} > 1$ the reaction is favored left to right.

If $K_{eq} < 1$ the reverse reaction is favored.

For the chlorination of methane, $K_{eq} = 1.1 \times 10^{19}$

$$K_{eq} = \frac{[CH_3Cl]\,[HCl]}{[CH_4]\,[Cl_2]} = 1.1 \times 10^{19}$$

When $K_{eq}$ is so large, the remaining amounts of reactants are close to zero at equilibrium. The reaction is said to *go to completion*.

From the equilibrium constant it is possible to calculate the Gibbs Free Energy change (ΔG) that accompanies the reaction.

**ΔG = (free energy of products) – (free energy of reactants)**

A reaction is energetically favored when the product energy levels are less than those of the reactants. (A ball rolls downhill).

Most commonly this is expressed in terms of the standard Gibbs free energy, ΔG°.

The ° symbol denotes standard, and designates the reaction involving the reactants and products in their standard states. ( i.e. pure substances in their most stable states at 25°C and 1 atm pressure).

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

© 2013 Pearson Education, Inc.

Or

$$ \Delta G^\circ = -RT(\ln K_{eq}) = -2.303RT(\log_{10} K_{eq}) $$

© 2013 Pearson Education, Inc.

Where      R = gas constant 1.987 cal/kelvin-mol
           T = Absolute Temperature, K
           e = 2.718

The equation shows that $K_{eq} > 1$  (favorable reaction) ΔG is –ve, and Energy is released.

## Enthalpy and Entropy

There are two factors that combine to give the free energy change for a reaction: Enthalpy (H) and Entropy (S).

$$\Delta G° = \Delta H° - T\Delta S°$$

$\Delta H°$ = change in enthalpy = (enthalpy of prods) – (enthalpy of reactants)

$\Delta S°$ = change in entropy = (entropy of prods) – (entropy of reactants)

(Typically the $\Delta H$ term >> $T\Delta S$ term)

## Enthalpy

The change in enthalpy is the heat evolved or consumed in a reaction, normally in kcal/mol.

Reactions tend to favor products with *stronger bonds* (i.e. lower enthalpy).

$\Delta H$ is –ve, exothermic reaction, heat is evolved, stronger bonds are formed.

$\Delta H$ is +ve, endothermic reaction, heat is consumed, weaker bonds are formed.

A –ve $\Delta H$ is a favorable contribution to the free energy change.
A +ve $\Delta H$ is an unfavorable contribution to the free energy change.

The $\Delta H°$ for chlorination of methane is –25kcal/mol.  (Very exothermic)

<u>Entropy</u>
Entropy is often described as randomness, or freedom to move, or disorder.

Reactions tend to favor products with *greater* entropy.

Note the *sign* of the entropy contribution to ΔG:

A +ve ΔS term makes a favorable contribution to the free energy.

For the chlorination of methane, $\Delta S° = 2.9$ entropy units (eu)

So    $-T\Delta S° = -298K \times 2.9 = -0.86$kcal/mol

Remember $\Delta H° = -25$kcal, (much larger)

So    $\Delta G° = -25 - 0.86 = -26$kcal/mol.

(Often ΔG is approximated to be equal to ΔH).


In kJ…

$$\Delta G° = \Delta H° - T\Delta S° = -105.1 \text{ kJ/mol} - 3.61 \text{ kJ/mol}$$
$$= -108.7 \text{ kJ/mol} \ (-25.9 \text{ kcal/mol})$$

© 2013 Pearson Education, Inc.
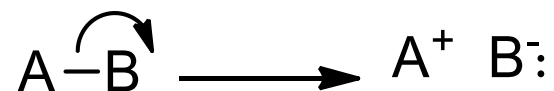
Bond Dissociation Energies (BDE's)
By use of BDE's, predictions can be made concerning the *endo-* or *exothermicity* of a given reaction.

The BDE is the amount of energy required to break a bond *homolytically*.
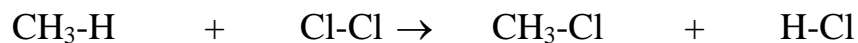
Homolytic Cleavage (gives free radicals)

$$A-B \longrightarrow A\cdot \qquad B\cdot \qquad \Delta H^o = BDE$$

Heterolytic (Ionic) Cleavage (gives ions)

$$A-B \longrightarrow A^+ \quad B\bar{:}$$

Energy is released when bonds are formed, energy is consumed to break bonds.

| Bond | BDE / kcal/mol |
|------|----------------|
| Cl-Cl | 58 |
| $CH_3$-H | 104 |
| $CH_3CH_2$-H | 98 |
| $(CH_3)_2$CH-H | 95 |
| $(CH_3)_3$C-H | 91 |
| H-Cl | 103 |
| $CH_3$-Cl | 84 |

These values allow the prediction of $\Delta H°$ for the chlorination of methane.

$CH_3$-H    +    Cl-Cl →    $CH_3$-Cl    +    H-Cl

$$\Delta H° = \Sigma(\text{BDE of bonds broken}) - \Sigma(\text{BDE of bonds formed})$$

© 2013 Pearson Education, Inc.

| Bonds Broken: | | | Bonds Formed: | |
|---------------|---|---|---------------|---|
| $CH_3$-H | +104kcal | | $CH_3$-Cl | -84kcal |
| Cl-Cl | +58kcal | | H-Cl | -103kcal |
| Total = | 162kcal | | | -187kcal |

$\Delta H°$  = 162 - 187
      = -25kcal/mol

An *exothermic* reaction.

(This also applies to the individual propagation steps, and gives the same answer).

Kinetics and the Rate Equation

The study of reaction rates is called **kinetics**.

The rate of a reaction is just as important as the position of equilibrium.

(Just because a reaction has a favorable $\Delta G°$, does not mean the reaction will spontaneously go).

The rate of a reaction is how fast the products appear and how slow the reactants disappear. These can be obtained experimentally by monitoring the concentrations of either the products or reactants with respect to time.

Reaction rates depend on the concentrations of reactants since at **higher** concentrations, collisions between reactants (leading to a reaction) are **more** likely.

The **rate equation** (rate law) relates the *concentrations* of the reactants to the rate of reaction.

Consider:    $A + B \rightarrow C + D$

The rate is proportional to the concentrations of A and B raised to some power (a and b).
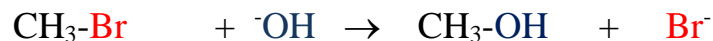
$$rate = k_r[A]^a[B]^b$$

Where $k_r$ is a rate constant, and a and b have to be determined *experimentally*.

Values a and b are usually whole numbers, and are called the **order** of the reaction.

(a+b) is the overall order of a reaction.

Consider the following reaction:

$$CH_3\text{-}Br \quad + \quad {}^-OH \quad \rightarrow \quad CH_3\text{-}OH \quad + \quad Br^-$$

Experiments show that doubling the concentration of bromomethane, doubles the rate of reaction. Also doubling the [⁻OH] doubles the rate.

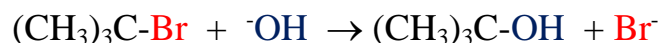Therefore the rate is proportional to both $[CH_3Br]$ and $[{}^-OH]$, and the rate equation would read:

$$\text{Rate} = k_r\,[CH_3Br]\,[{}^-OH]$$

The rate is said to be first order w.r.t. bromomethane, and first order w.r.t. hydroxide ion.

The reaction is second order overall.

However, similar reactions can have **different** kinetic orders.

$$(CH_3)_3C\text{-}Br \; + \; {}^-OH \; \rightarrow (CH_3)_3C\text{-}OH \; + Br^-$$

For this reaction, doubling the [t-butylbromide] doubles the rate, but doubling [⁻OH] has **no effect** on the rate.

$$\text{Rate} = k_r\,[(CH_3)_3C\text{-}Br]$$

First order w.r.t. t-butylbromide, but zeroth order w.r.t. hydroxide ion.

The order has to be obtained **experimentally**.

Activation Energy ($E_a$) and Temperature Dependence of Rates
The Arrhenius equation relates the rate constant ($k_r$) to temperature.

$$k_r = Ae^{-E_a/RT}$$

where

$A$ = a constant (the "frequency factor")
$E_a$ = activation energy
$R$ = the gas constant, 8.314 J/kelvin-mole (1.987 cal/kelvin-mole)
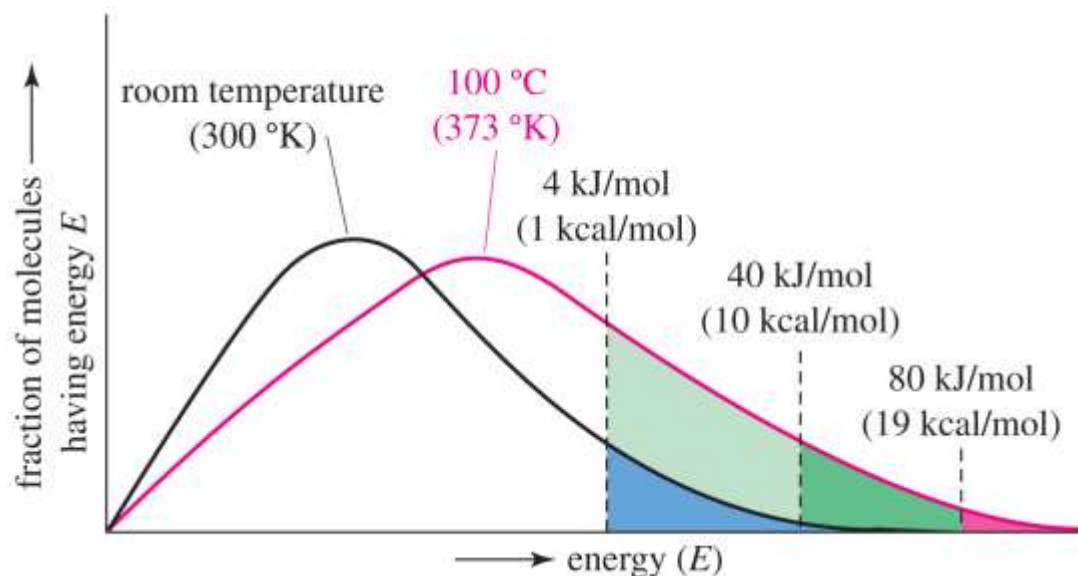$T$ = the absolute temperature

© 2013 Pearson Education, Inc.

The activation energy is the *minimum* kinetic energy required for a molecule to overcome the repulsions from another molecule's electron clouds for a collision to occur.

The exponential term is the fraction of those collisions that have sufficient $E_a$ to react.

The pre-exponential frequency factor deals with the frequency of the collisions and the fraction that have the necessary **orientation** for reaction to occur.

The Arrhenius equation implies that the rate of a reaction depends on how many molecules have at least $E_a$ amount of kinetic energy (k.e.).

room temperature (300 °K)

100 °C (373 °K)

4 kJ/mol (1 kcal/mol)

40 kJ/mol (10 kcal/mol)

80 kJ/mol (19 kcal/mol)

fraction of molecules having energy $E$

energy ($E$)

The area under the curve to the right of the dotted lines is the number of molecules that have enough energy to overcome such a barrier.

© 2013 Pearson Education, Inc.

At higher temperatures, more molecules have enough energy to result in reaction, and thus the reaction rate increases.

Variation of Relative Rate with Temperature    for    $k_{rel} = e^{-Ea/RT}/10^{-9}$

| $E_a$ (kcal/mol) | 27°C (300K) | 310K | 373K |
|---|---|---|---|
| 5 | 240,000 | 320,000 | 1,200,000 |
| 10 | 58 | 99 | 1,500 |
| 15 | 0.014 | 0.031 | 1.9 |
| 20 | 0.0000033 | 0.0000098 | 0.0023 |

Obviously the rate increases with higher temperatures.

This applies to not only the desired reaction, but also to side reactions too. Most organic reactions have an optimum temperature where the products are formed at a reasonable rate, relative to the side products.

Transition States

The *activation energy* $E_a$ is the energy difference between the reactants and the transition state, which is the highest energy state in a collision that leads to a reaction.

$E_a$ is essentially the barrier that must be overcome for the reaction to take place.

The transition state is the arrangement of atoms which is the transition between reactants and products, and in this arrangement the molecule can either return to reactants or go on to products.

The transition state **cannot** be isolated. It is unstable, and is only a *transient arrangement* on the pathway from one intermediate to another.

The transition state (T.S.) is represented by ‡, and is often drawn in brackets to highlight its transient nature.

Free energy of the transition state is $\Delta G^{\ddagger}$

Transition states have *high* energies since bonds must start to *break* before new bonds can form.
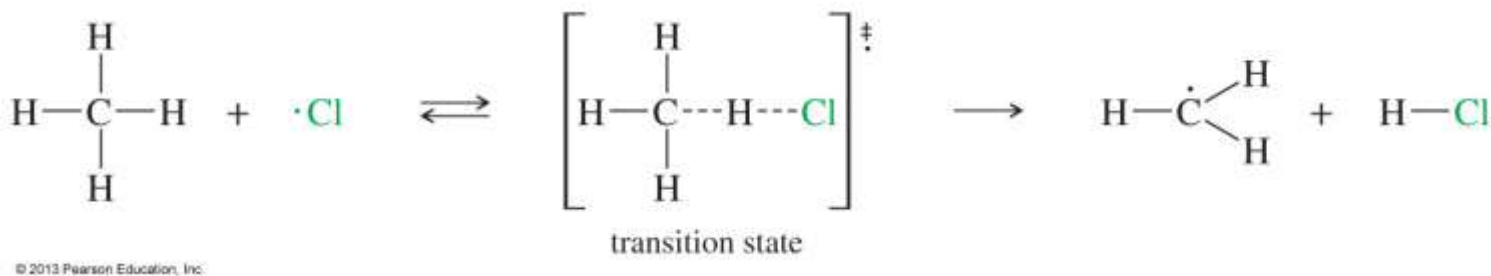

transition state

In the chlorination of methane, the transition state has the C-H bond partially broken, and the H-Cl bond partially formed.

Reaction Energy Profiles
These help to explain the concepts of $E_a$ and T.S.

The vertical axis is the *total potential energy*, and the horizontal axis is the *reaction co-ordinate*, which symbolizes the *progress* of the reaction, with reactants on the left and products on the right.
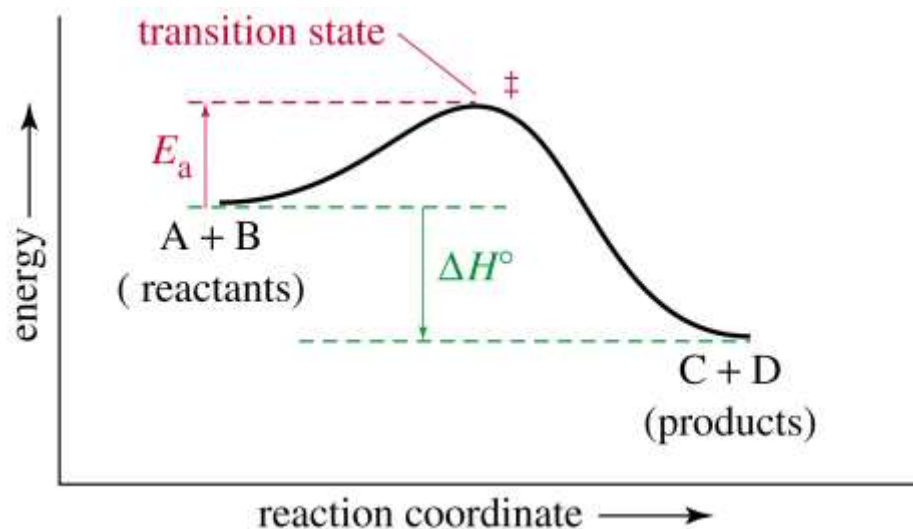


The T.S. is the highest point on the graph, and the $E_a$ is the difference between the energy of the reactants and the T.S.
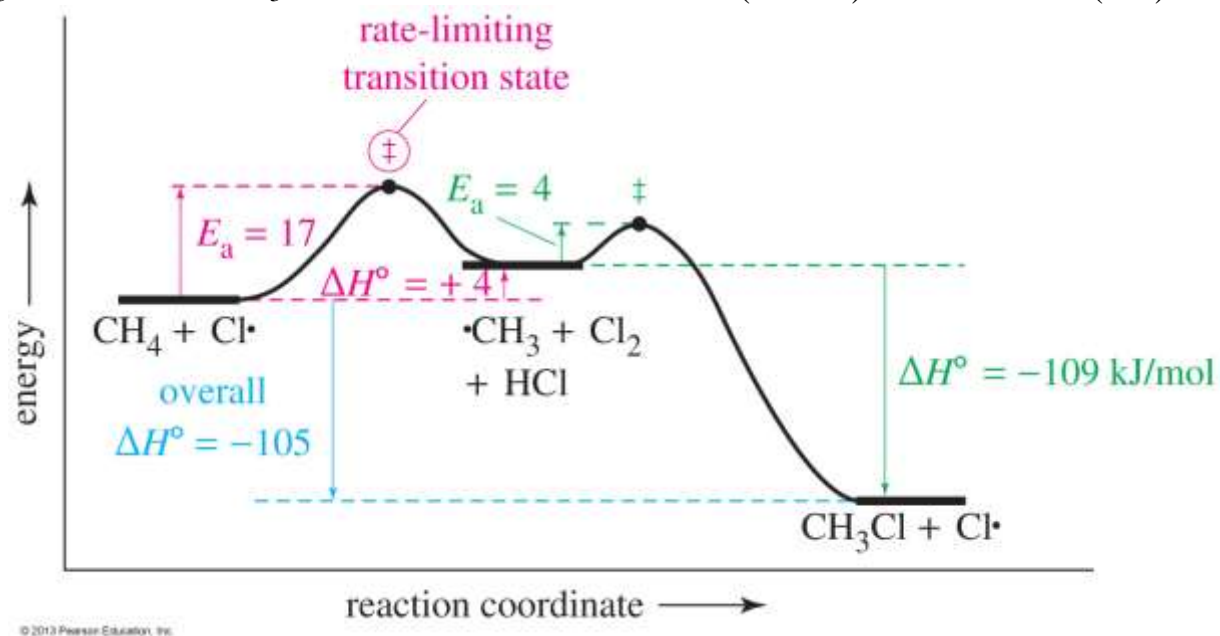
$\Delta H^\circ$ is the difference between the energy of the reactants and the products.

A catalyst works by lowering (changing) the $E_a$ so that more molecules can react at a certain temperature - it does not **alter** the energies of reactants or products.

## Rates of Multistep Reactions

In reality most organic reactions are *not* single step processes.

Consider the chlorination of methane:

|  | $\Delta H°$ /mol | $E_a$ /mol |
|---|---|---|
| $CH_4 + Cl• \rightarrow CH_3• + H\text{-}Cl$ | +1kcal (+4kJ) | 4kcal (17kJ) |
| | | |
| $CH_3• + Cl\text{-}Cl \rightarrow CH_3\text{-}Cl + Cl•$ | -26kcal (-109kJ) | 1kcal (4kJ) |



Cl• and $CH_3•$ are reactive intermediates and energy low points.

T.S.'s are energy *maxima*.

Rate Determining Step (R.D.S.)

Each step in a multi step has its own reaction rate. However, there must only be one *overall* rate for a reaction, and this is controlled by the R.D.S.

Typically, the "bottleneck" occurs at the highest energy step in a multistep reaction, and it is this step that controls the rate of a reaction.

**The highest point in the energy profile is the T.S. with the highest energy, and this is normally the T.S. for the R.D.S.**

The *overall* rate of reaction is equal to the rate of the *slowest* step, since the subsequent intermediates react quicker than they are formed.

Halogenation of Higher Alkanes

Halogenation is a **substitution** reaction, where a hydrogen is replaced by a halogen. In methane, all the hydrogens are equivalent – but what happens when there are more hydrogens to choose from ?

Consider the chlorination of propane: there are two possible hydrogens which can be substituted by chlorine.



1° carbon    2° carbon

$CH_3-CH_2-CH_3$ + $Cl_2$ $\xrightarrow{hv, 25\,°C}$ $CH_2-CH_2-CH_3$ + $CH_3-CH-CH_3$

propane       1-chloropropane, 40%    2-chloropropane, 60%
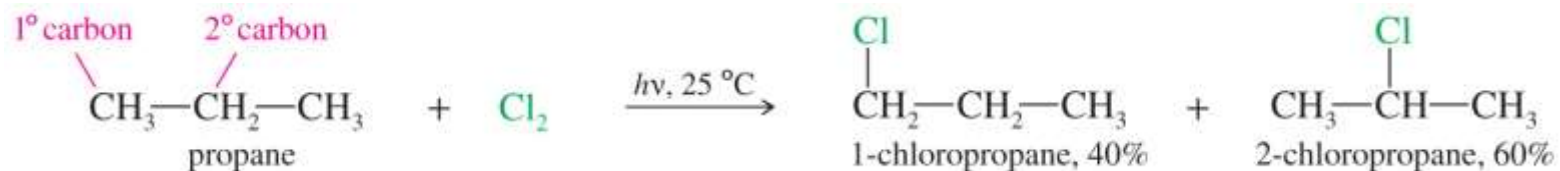
One product has the Cl on the primary carbon, the other is on the secondary carbon atom.

Note that there are 6 primary H's and only 2 secondary H's, yet still the major product is substituted on the secondary carbon.

Primary:     40% / 6 = 6.67% per H   (rel.1)
Secondary:  60% / 2 = 30% per H     (rel.4.5)

So the secondary H's are about 4.5 times *more reactive* than primary hydrogens.

To explain this selectivity we must look at the *mechanism* of the reaction:

*Initiation:* Splitting of the chlorine molecule

$$Cl_2 \;+\; h\nu \;\longrightarrow\; 2\,Cl\cdot$$

*First propagation step:* Abstraction (removal) of a primary or secondary hydrogen

$$CH_3-CH_2-CH_3 \;+\; Cl\cdot \;\longrightarrow\; \cdot CH_2-CH_2-CH_3 \;\;\text{or}\;\; CH_3-\dot{C}H-CH_3 \;+\; HCl$$

primary radical         secondary radical

*Second propagation step:* Reaction with chlorine to form the alkyl chloride

$$\cdot CH_2-CH_2-CH_3 \;+\; Cl_2 \;\longrightarrow\; Cl-CH_2-CH_2-CH_3 \;+\; Cl\cdot$$

primary radical         primary chloride
(1-chloropropane)

$$\text{or}\;\; CH_3-\dot{C}H-CH_3 \;+\; Cl_2 \;\longrightarrow\; CH_3-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_3 \;+\; Cl\cdot$$

secondary radical         secondary chloride
(2-chloropropane)
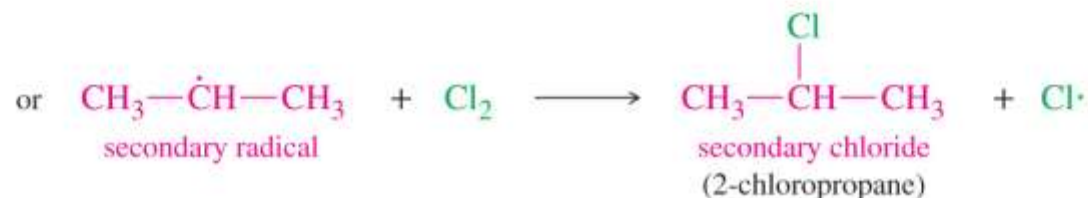
© 2013 Pearson Education, Inc.

When the Chlorine atom abstracts a hydrogen, it can either abstract a primary hydrogen (to give a primary radical) or secondary hydrogen (giving a secondary radical).

From the product ratios (40/60), the secondary radical would seem to be more stable.

<u>Free Radical Stabilities</u>
Consider the following BDE's:

<div align="right">BDE /kcal/mol (kJ/mol)</div>

$CH_4$  $\rightarrow$ H$\bullet$  +  $CH_3\bullet$  $\Delta H°$=104 (435)

$CH_3CH_2CH_3$  $\rightarrow$ H$\bullet$  + $CH_3CH_2CH_2\bullet$  $\Delta H°$=98 (410)

$CH_3CH_2CH_3$  $\rightarrow$ H$\bullet$  + $(CH_3)_2CH\bullet$  $\Delta H°$=95 (397)

$(CH_3)_3CH$  $\rightarrow$ H$\bullet$  + $(CH_3)_3C\bullet$  $\Delta H°$=91 (381)

Free radicals are *more stable* if they are *more highly substituted*.
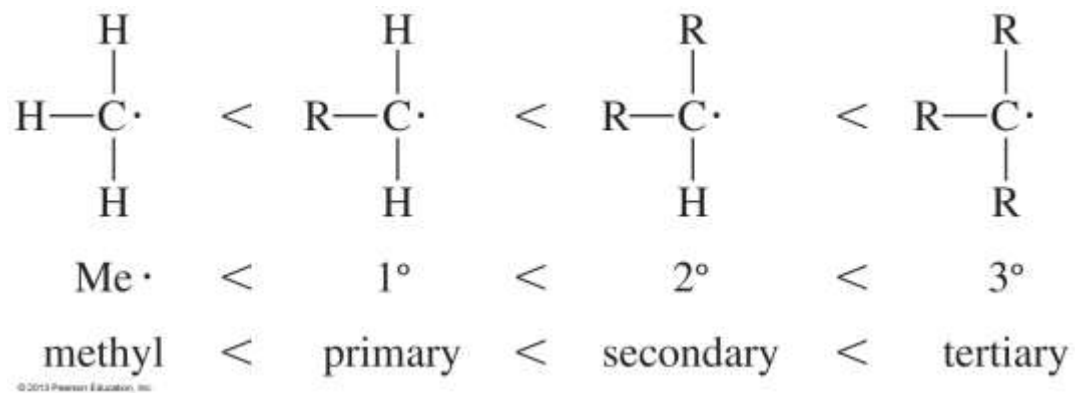
In the chlorination of propane, the secondary hydrogen is abstracted more often than the primary because the transition state leading to it is lower in energy.
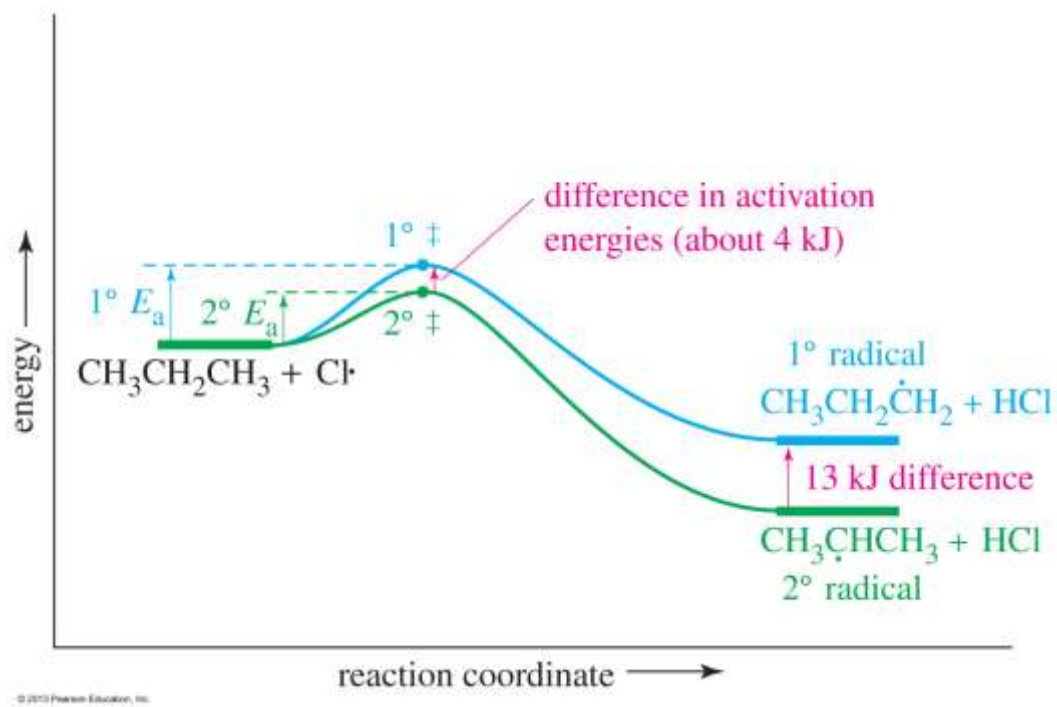


The activation energy for forming the secondary radical is *lower*, and it therefore forms *faster* than the primary radical.

## Bromination of Propane

For halogenation reactions:

$$F_2 > Cl_2 > Br_2 > I_2$$
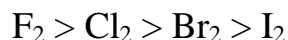
Typically fluorination is uncontrollable and very exothermic, whereas iodination is difficult and slow.

Bromination requires a higher temperature compared to chlorination.
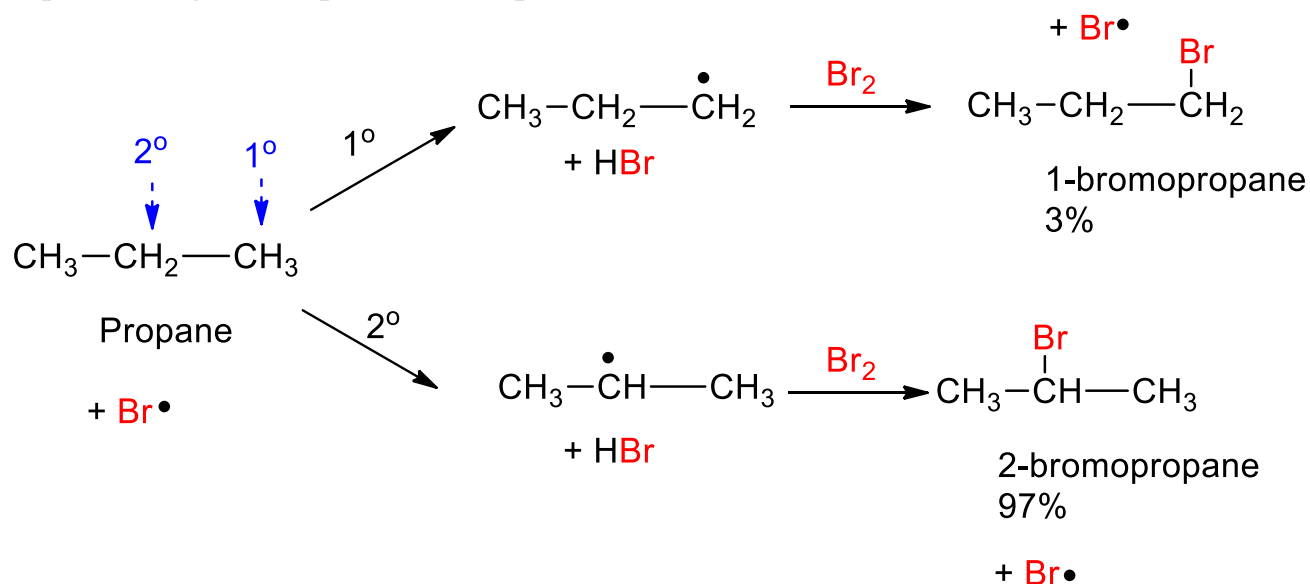


Relative reactivity:
1°      3% / 6 = 0.5% per H
2°      97% / 2 = 48.5% per H

The 2° H's are 97 times more reactive than 1° hydrogens. (Ratio for chlorination was 4.5 times more reactive).

Since the major product is favored by a larger amount, we say that bromination is more **selective** than chlorination.

Consider the BDE's for bromination:

$$CH_3CH_2\textcolor{red}{H_3} + \textcolor{blue}{Br\bullet} \rightarrow CH_3CH_2CH_2\bullet + \textcolor{red}{H}\text{-}\textcolor{blue}{Br}$$
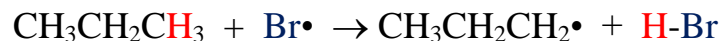
Energy required to break the $CH_2$-H bond                +98kcal/mol
Energy released in forming H-Br bond                -88kcal/mol
Total Energy for reaction at primary site                +10 kcal/mol (42kJ/mol)


$$(CH_3)_2C\textcolor{red}{H_2} + \textcolor{blue}{Br\bullet} \rightarrow (CH_3)_2CH\bullet + \textcolor{red}{H}\text{-}\textcolor{blue}{Br}$$
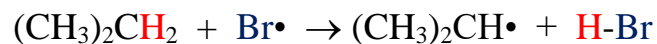
Energy required to break the CH-H bond                +95kcal/mol
Energy released in forming H-Br bond                -88kcal/mol
Total Energy for reaction at secondary site                +7 kcal/mol (29kJ/mol)

Note:
1) H-Br bond is weaker than H-Cl.
2) Hydrogen abstraction by a bromine atom is endothermic.

Compare bromination to chlorination:



(a) BROMINATION
endothermic
TS close to products
large difference in $E_a$

(b) CHLORINATION
exothermic
TS close to reactants
small difference in $E_a$
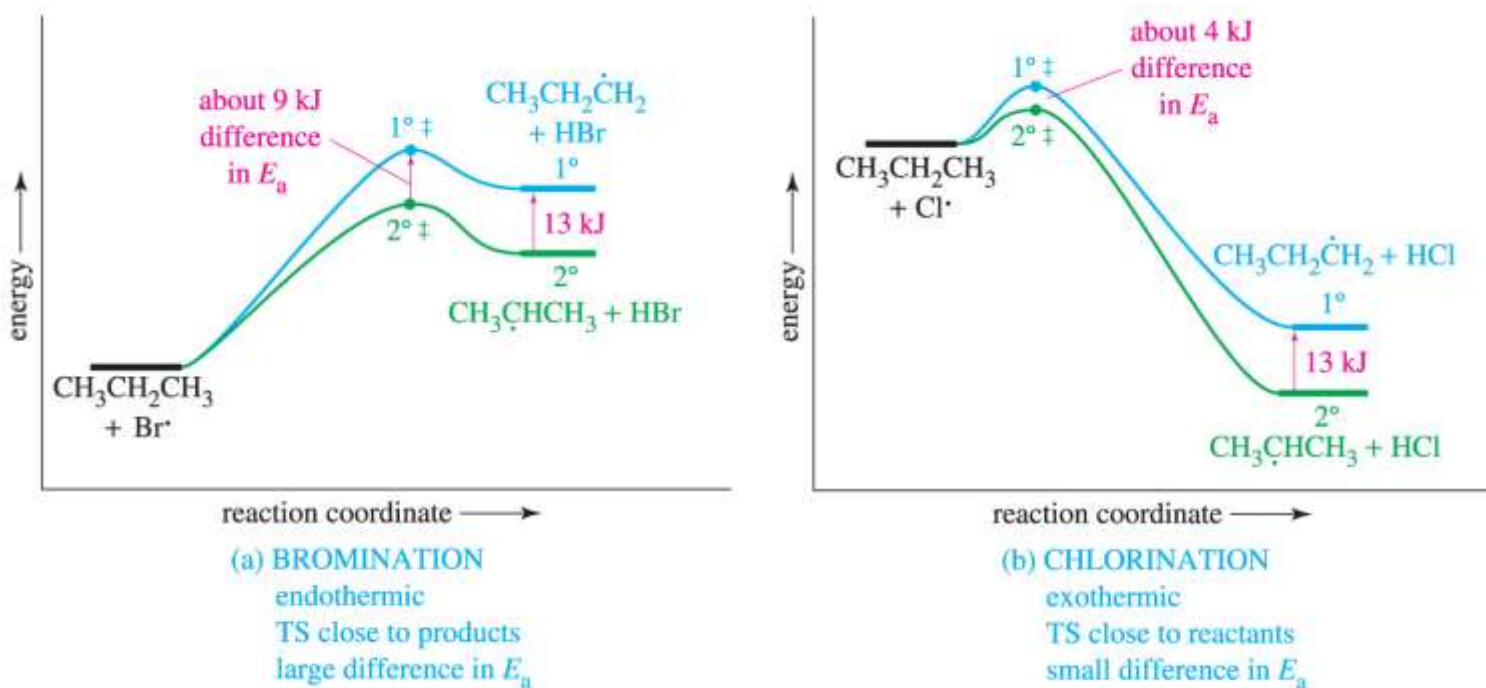
© 2013 Pearson Education, Inc.

The energy profile for bromination shows a much *larger difference in activation energies* for the abstraction of primary and secondary hydrogens, than for chlorination. This is why bromination is more selective.

(The $\Delta H°$ for the abstractions are similar to the chlorination values, it is the difference in the T.S. energies).

The Hammond Postulate

If we compare the energy profile diagrams for the chlorination and bromination of propane, we see 2 differences:
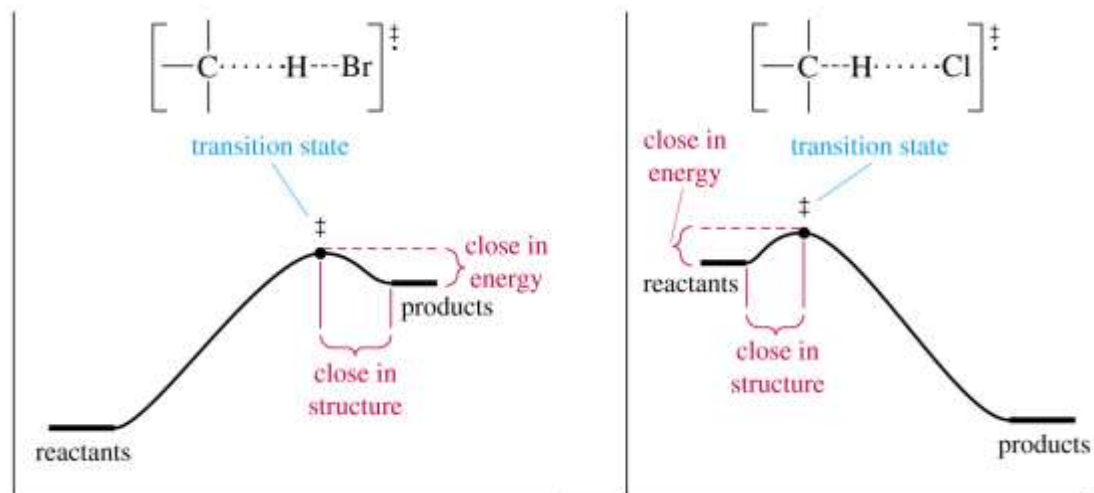


1) The hydrogen abstraction for bromine is *endothermic*, but *exothermic* for chlorine.
2) The T.S.'s forming for the 1° and 2° radicals for the endothermic bromination have a larger energy difference than those forming for the exothermic chlorination, despite the fact that the energy difference of the products is the same for both cases.

A general rule

In an endothermic reaction, the T.S. is closer to the products in energy and in structure. (Late TS)
In an exothermic reaction, the T.S. is closer to the reactants in energy and structure. (Early TS)

These are examples of the **Hammond Postulate**:
    *Related species that are similar in energy are also similar in structure.*

So here - the structure of a transition state resembles the structure of the closest stable species.

Reactive Intermediates
The free radicals we have studied are just one type of reactive intermediate (which are short lived species, never present in high concentrations, and react as quickly as they are formed).

Other examples:

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}+ \qquad H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\cdot \qquad H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\!:^{-} \qquad \overset{\displaystyle H}{\underset{\displaystyle H}{\phantom{}}}\!\!C\!:$$

carbocation     radical     carbanion     carbene
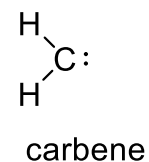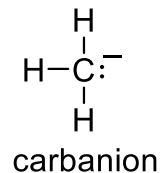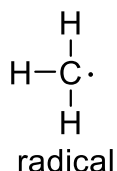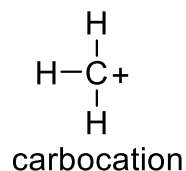
Carbocations (Carbonium ions)
These are species in which a carbon atom bears a +ve charge.



top view            side view
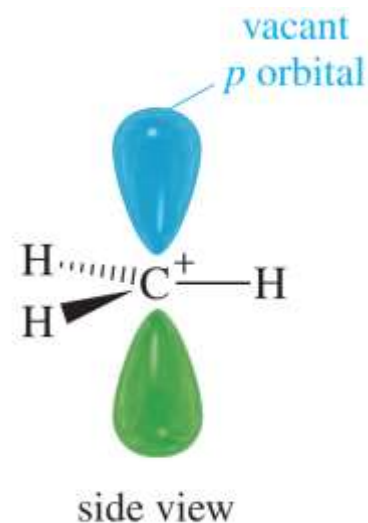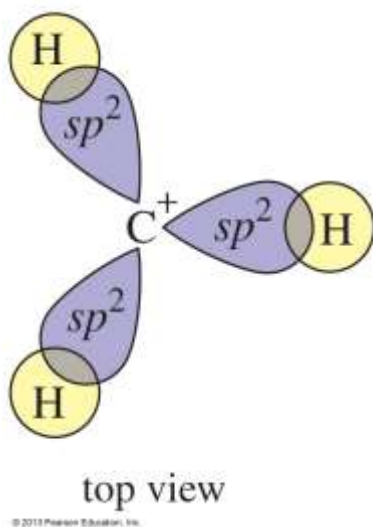
This carbon is bound to 3 atoms, and has no nonbonding electrons.

It is sp$^2$ hybridized, with a planar structure.

The vacant p orbital lies perpendicular to the plane of the other atoms.

The carbocation carbon only has 6 valence electrons, and the +ve charge attracts nucleophiles.

Thus a carbocation is very strong electrophile.

In the same way that radicals (another electron deficient moiety) are stabilized by alkyl substituents, carbocations are also stabilized by alkyl substituents.

This happens through 2 ways:
      1) Inductive effect
      2) Partial overlapping of filled orbitals with empty ones. (Hyperconjugation)

The inductive effect is a donation of electron density through the sigma bonds. The positively charged carbon draws electron density from the alkyl groups bound around it.
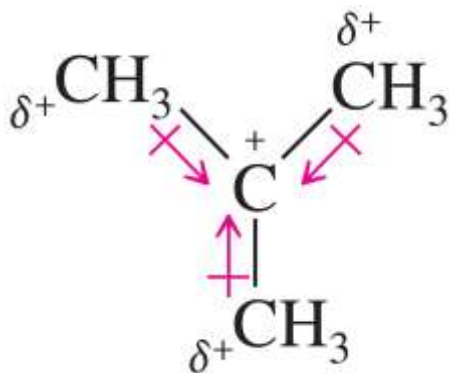
Alkyl substituents have filled sp$^3$ orbitals which can overlap with the empty p orbital, and this stabilizes the carbocation.
Even though the alkyl group rotates, one of the sigma bonds is always aligned for overlap into the vacant p orbital.

This is **hyperconjugation**.
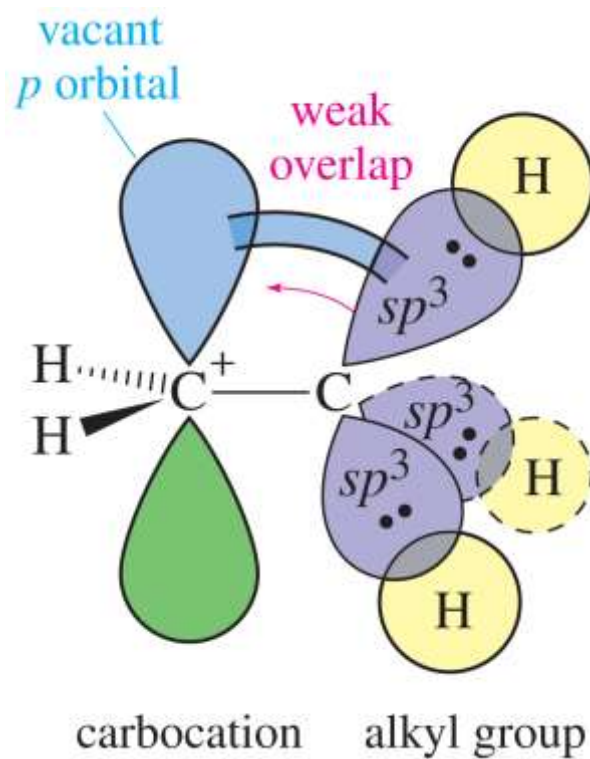
In general, more substituted carbocations are more stable.
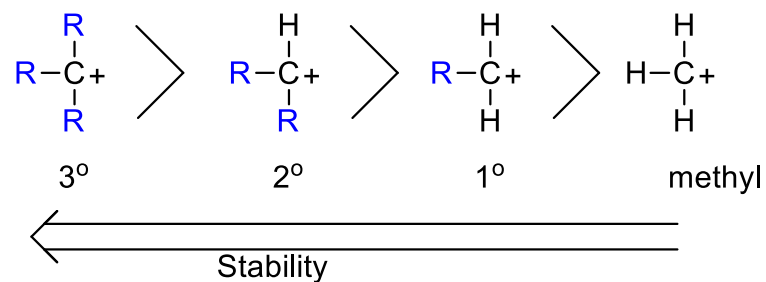


Unsaturated carbocations can also be stabilized by *resonance stabilization*. When a π bond is adjacent to an empty p orbital, the filled p orbital will overlap the empty p orbital. This gives a *delocalised* carbocation, which is resonance stabilized.
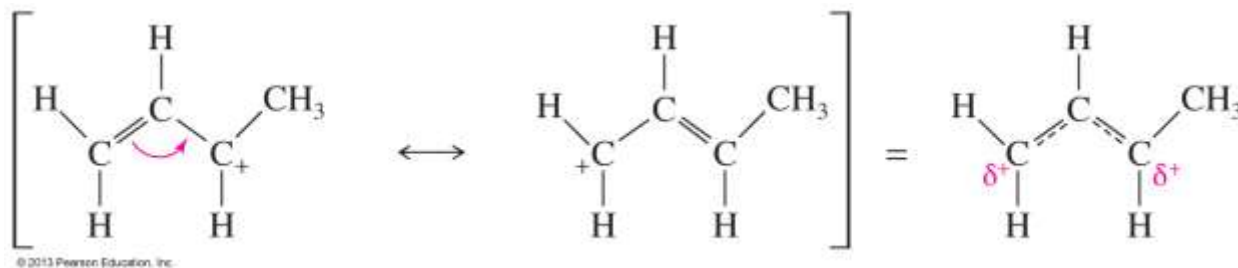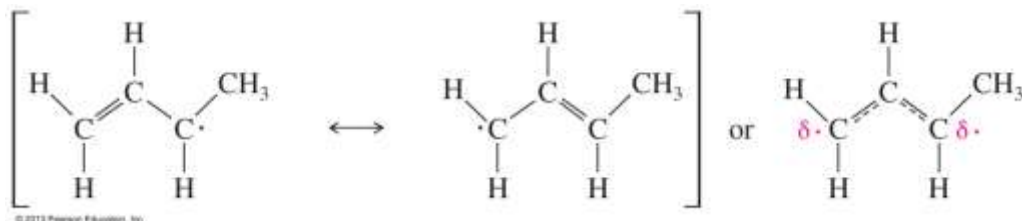
## Free Radicals

Like carbocations, radicals are $sp^2$ hybridized and planar. However the perpendicular p orbital is not empty – it contains an odd electron.



top view                                              side view
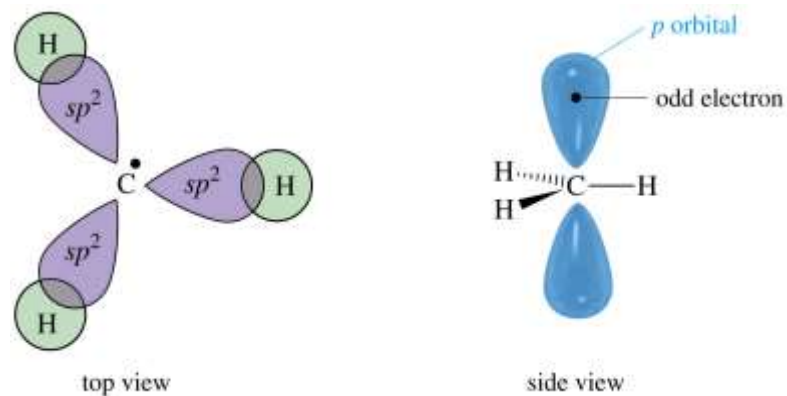
Radicals and carbocations are both electron deficient since they lack an octet. They show similar stability trends.
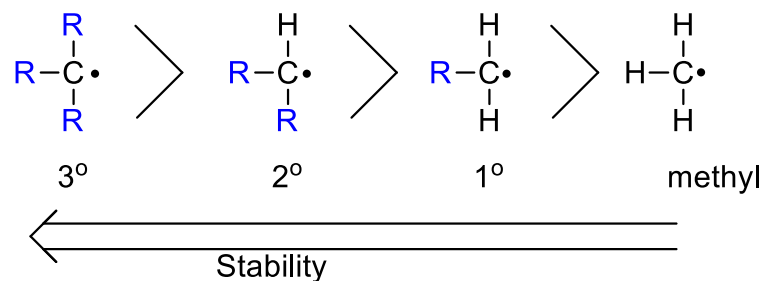


Unsaturated radicals can also be resonance stabilized.

Carbanions

Carbanions have a trivalent carbon that bears a *negative* charge.

The carbon is sp³ hybridized and tetrahedral. The carbon has 3 bond pairs and one lone pair (8 electrons).

The lone pair occupies one of the tetrahedral positions.

It is electron rich, and therefore nucleophilic.

The structure resembles an amine (isoelectronic structures)



methyl anion                    ammonia
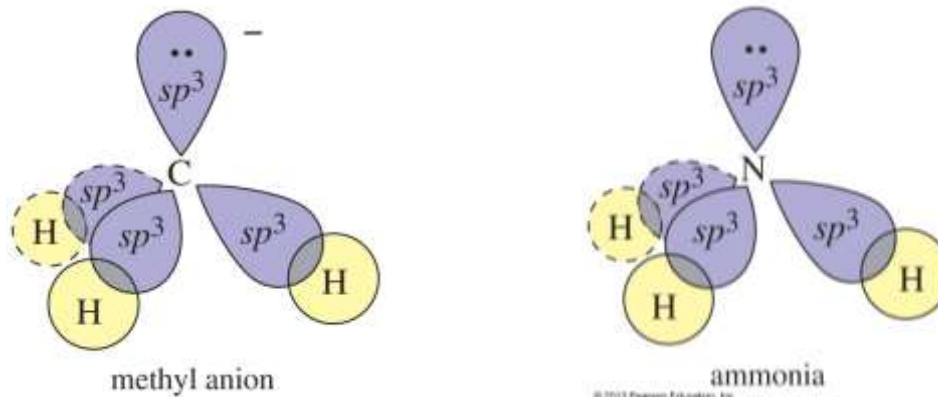
Like amines, carbanions are nucleophilic and basic, but the negative charge on C (versus N) makes carbanions more nucleophilic and more basic than amines.

Therefore carbanions are sufficiently basic to remove a proton from ammonia (normally a base).

$$CH_3^- + NH_3 \rightarrow CH_4 + NH_2^-$$
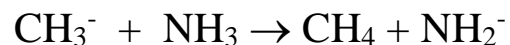
The stability order of carbanions reflects their high electron density.



| 3º | 2º | 1º | methyl |
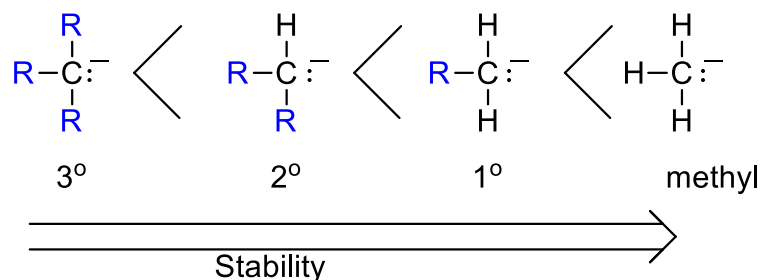
Stability

Notice the order is *reversed* from radicals and carbocations (electron deficient species).

Typically, carbanions are found bound to some stabilizing group or groups. They can be stabilized by either inductive effects or resonance.

For example, an adjacent carbonyl group will stabilize a carbanion by the overlap of the C=O double bond with the carbanion's lone pair.
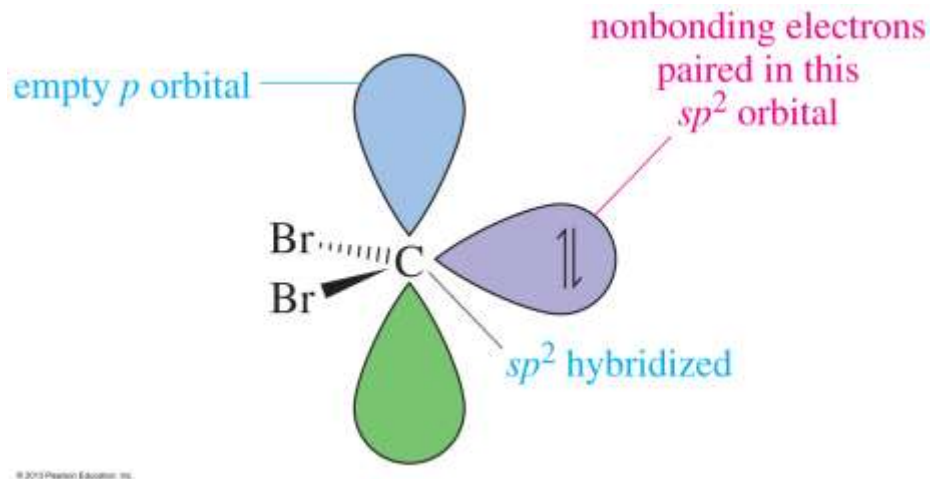
This *delocalizes* the –ve charge onto the *more electronegative* atom of oxygen.



resonance-stabilized carbanion
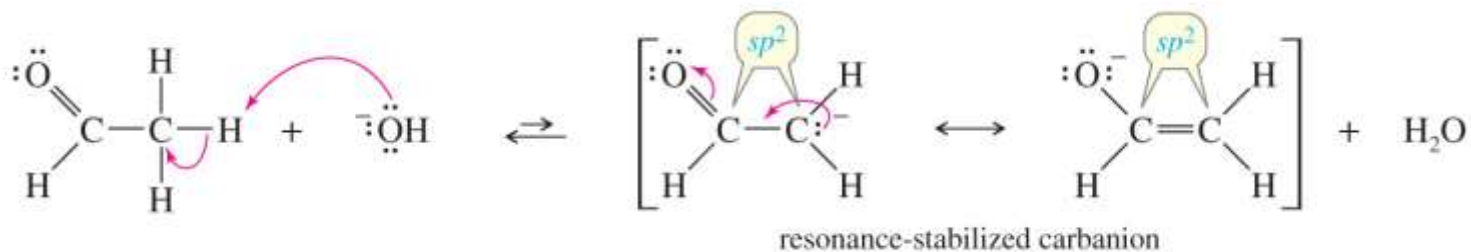
© 2013 Pearson Education, Inc.

Carbenes

These are *uncharged* reactive intermediates that contain a divalent carbon atom.



The carbon atom is sp² hybridized, with a trigonal geometry.

The lone pair occupies one of the sp² orbitals. There is a perpendicular vacant p orbital.

The fact that carbenes have a lone pair AND a vacant orbital means they display both nucleophilic and electrophilic properties.

A common route to carbenes is to generate carbanions adjacent to good leaving groups. (α elimination).
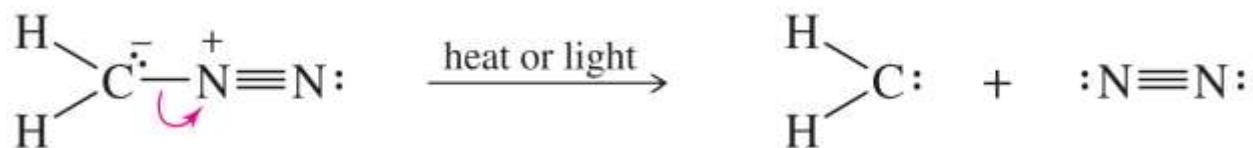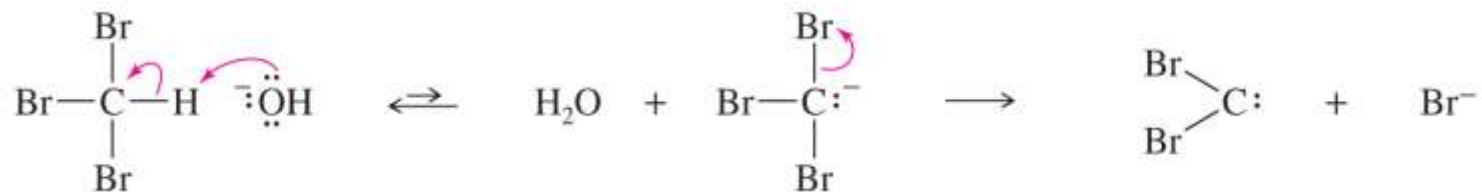


Carbenes can dimerise to give alkenes, and react to produce cyclopropanes.