

## Reaction Intermediates and Reaction Energetics

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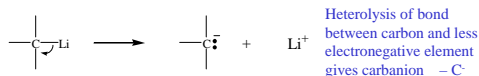
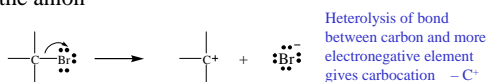
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### Intermediates of Heterolysis

- Heterolysis of neutral structures gives a cation and an anion  $\text{Atom1}-\text{Atom2} \longrightarrow \text{Atom1}^+ + \text{:Atom2}^-$
- Heterolysis will only occur at polar bonds and the **MORE ELECTRONEGATIVE** atom will become the anion




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### Reactant Types

- Cations (and in fact any other Lewis acid) react with electron sources and are therefore called ELECTROPHILES – electron loving
- Anions (and in fact any other Lewis base) react with Lewis acids (electron sinks) and are called NUCLEOPHILES – nucleus loving

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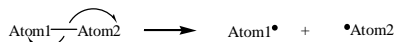
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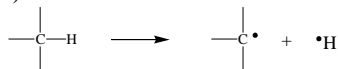
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## Intermediates of Homolysis

- Homolysis of neutral structures gives radicals



- Homolysis will only occur if sufficient energy (usually in the form of light or heat) is present to break a bond (and the WEAKEST bond usually breaks)



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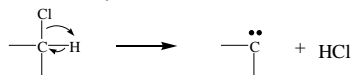
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## The 'Other' Intermediate

- Elimination of two groups from the same carbon (alpha-elimination) gives a carbene – a neutral carbon with only two bonds



- Carbenes are able to act as BOTH electrophiles (electron acceptors) and nucleophiles (electron donors)

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## Frequency of Occurance

- Heterolysis to give
  - Carbocations: You will see this throughout the course
  - Carbanions: You will see this less frequently
- Homolysis
  - Even less frequently
- Carbenes: Very rarely

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## Problem

- Draw the most likely intermediates formed by heterolysis of 2-chlorobutane

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## Carbocation Structure/Stability

- What hybridization and shape will a carbocation have?
- Substituents attached to the positively charged carbon atom influence the stability of the structure based on their release or withdrawal of electrons

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## Carbocation Stability

- Carbocations are inherently unstable due to
  - Incomplete octet for carbon
  - Positive charge
- However, some are not as bad as others
- Substituents that release electrons will stabilize carbocations by spreading the charge over a larger volume
- Substituents that withdraw electrons will destabilize carbocations by packing a greater charge onto the carbon

Repeat from notes on mass spectrometry

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## Electron Release/Withdrawal Mechanisms

- Induction
  - Induction involves the push and pull of electrons through sigma bonds
  - Example: bromine is more electronegative than carbon and will pull at the electrons in their sigma bond
- Resonance
  - Resonance involves the push and pull of electrons through a pi system

Repeat from notes on mass spectrometry

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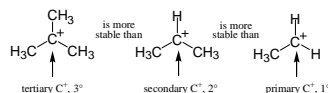
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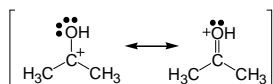
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## Electron Releasing Substituents

- Inductive only
  - Alkyl groups



- Resonance
  - Atoms with lone pairs
  - Alkenyl groups
  - Aromatic rings



Structure has 1/2 of positive charge on each atom, much more stable than having the entire charge on one atom

Repeat from notes on mass spectrometry

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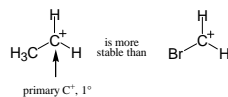
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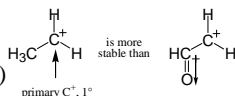
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## Electron Withdrawing Substituents

- Electronegative atoms  
(at least those more electronegative than O):  
Br, Cl, I, F



- Groups with positive  
(or partial positive charges)



Repeat from notes on mass spectrometry

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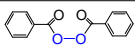
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## Homolytic Bond Strengths

(excerpted from Table 10.1)

Bond	DH° (kcal/mol)	Bond	DH° (kcal/mol)
H-H	435	Cl-Cl	243
CH <sub>3</sub> -H	435	Br-Br	192
CH <sub>3</sub> CH <sub>2</sub> -H	410	I-I	151
(CH <sub>3</sub> ) <sub>2</sub> CH-H	395		
(CH <sub>3</sub> ) <sub>3</sub> C-H	381	CH <sub>3</sub> -Br	293
		CH <sub>3</sub> CH <sub>2</sub> -Br	289
HO-OH	213	(CH <sub>3</sub> ) <sub>2</sub> CH-Br	285
(CH <sub>3</sub> ) <sub>3</sub> CO-OC(CH <sub>3</sub> ) <sub>3</sub>	157	(CH <sub>3</sub> ) <sub>3</sub> C-Br	264
	139		

Typical radical initiators – bonds can break if exposed to heat or visible light

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## Radical Structure/Stability

- Carbon radicals (like carbocations) are electron deficient due to their lack of an octet of valence electrons
- Carbon radicals are therefore stabilized by electron-releasing substituents (as we saw in the previous table) and destabilized by electron-withdrawing substituents
- What hybridization and shape will a neutral carbon radical have?

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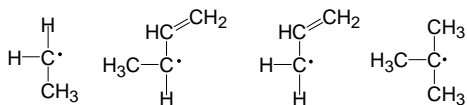
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## Problem

- Rank the following carbon radicals from most to least stable




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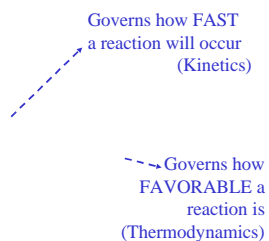
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## Reaction Energetics



See figure 6.2 in text

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## Transition State

The highest energy point on the lowest energy path from reactants to products

See figure 6.3 in text

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## Multistep Reactions

See figure 6.7 in text

- The slowest step in a multi-step reaction will determine the overall rate of the reaction (rate determining step)
- In the reaction above, what is the rate determining step? (1, 2 or 3)
- Can you propose a reason?

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## Rate Expressions

- Reaction rates are proportional to the concentrations of the reactants that have to collide in the rate determining step
  - On “Reaction Energetics” slide the rate is proportional to  $[X]$  and  $[Y-Z]$ 
    - Second order – rate depends on concentrations of two reactants
    - Bimolecular – two molecules involved in the slow step
  - On “Multistep Reactions” slide the rate is proportional only to  $[(CH_3)_3CCl]$ 
    - First order – rate depends on the concentration of one reactant
    - Unimolecular – one molecule involved in the slow step
- This is important because it is much easier to measure concentrations and rates than energies of transition states!

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## Problem

- Determine the order of a reaction for which the following data was collected.
- What molecules are reacting in the slow step?

Experiment	Initial $[CH_2=CH_2]$	Initial $[HCl]$	Initial Rate (mol/L•sec)
1	0.01	0.01	$3.2 \times 10^{-8}$
2	0.02	0.01	$6.4 \times 10^{-8}$
3	0.02	0.02	$12.8 \times 10^{-8}$

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