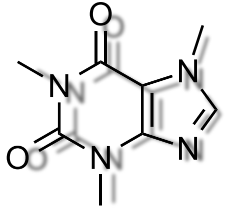


Chemistry 2500

Chapter 5

Organic Reaction Mechanism

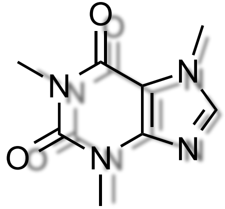
(sections 5.1-5.10)

Organic Reaction Mechanisms

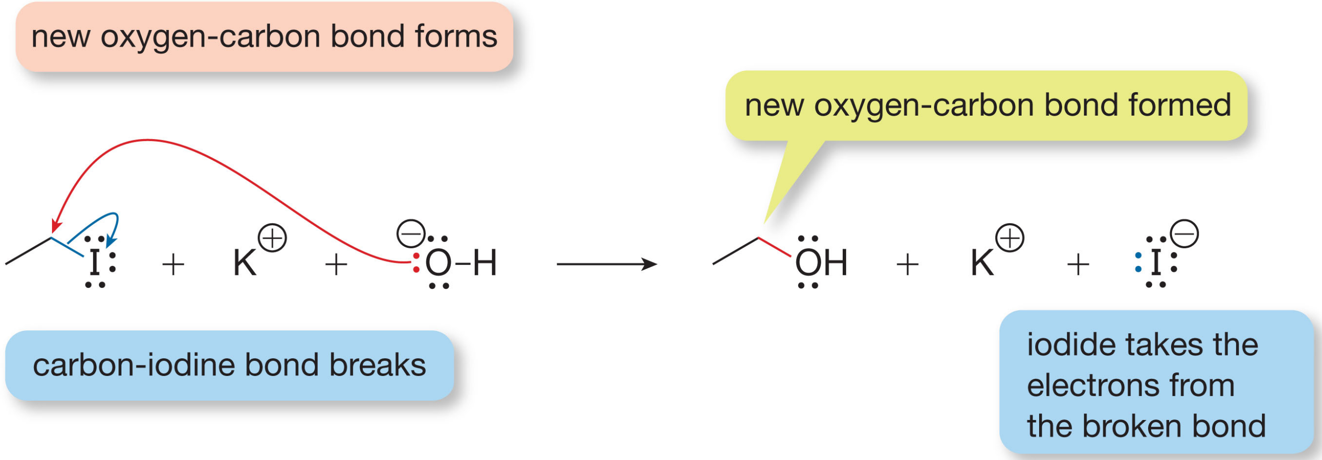
- In reactions, bonds are broken in the reagent molecules, and new bonds are formed between other atoms to make product molecules.
- Since bonds are pairs of electrons, understanding the movement of electrons is key to understanding chemical reactivity.
- Reaction equations tell you only what happens; what is reacting and what is formed.

Reaction equation – the 'What'?

Organic Reaction Mechanisms

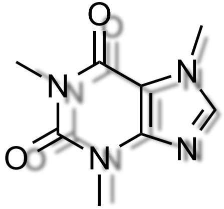


- ***Reaction mechanisms*** tell you how the reaction happens; how the reactants are converted to products.
- Reaction mechanisms are drawn using the ***curved arrow notation***, which depicts the movement of ***valence electrons*** during a reaction.



Reaction mechanism – the 'What and How'?

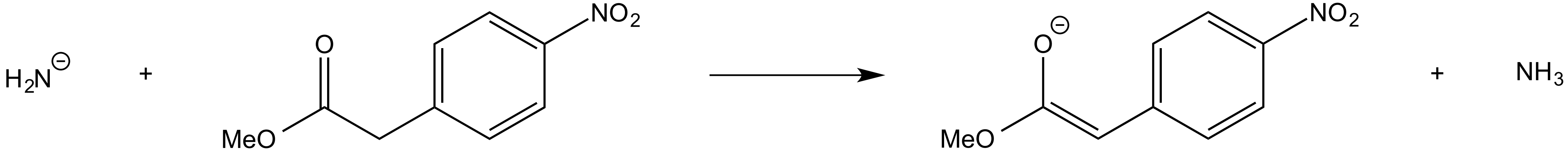
Organic Reaction Mechanisms



- Use the following points as a guide when using curved arrows:
  - Note that electron flows occur at or near ***functional groups:***
    - π bonds
    - heteroatoms
    - formal charges
    - unpaired electrons
  - ***Use arrows to show bond formation***
  - ***Use arrows to show bond breaking***
  - Use arrows to keep track of formal charges.

Reaction Mechanisms – Drawing Conventions

- Lone pairs are added if they are acting as an electron source and at all participating functional groups.
- Hydrogen atoms are typically omitted in line drawings; however, when they are directly involved in a reaction mechanism, they need to be explicitly shown.



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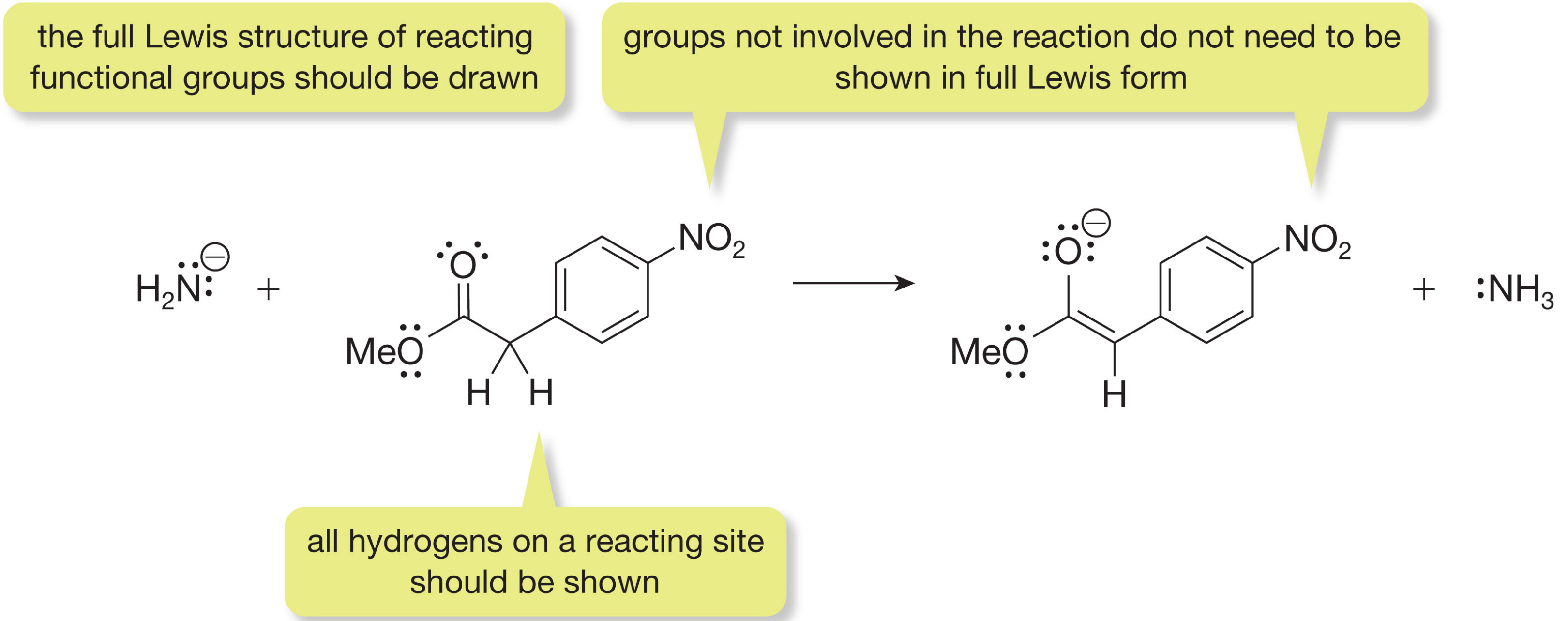
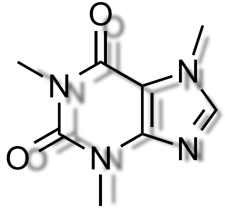
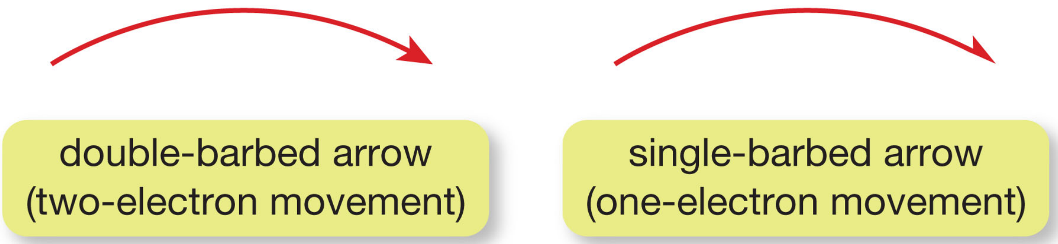


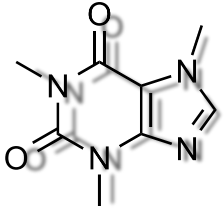
Curved Arrows – Bond Formation



- In reaction mechanisms, curved arrows are used to show the movement of electrons:
    - Arrows start at a source of electrons (a bond, lone pair, or unpaired electron)
    - Arrows end at an electropositive site (an area of electron deficiency)
    - The arrowheads point in the direction of electron travel
    - A double-barb arrowhead depicts the movement of an electron pair
    - A single-barb arrowhead depicts the movement of one electron

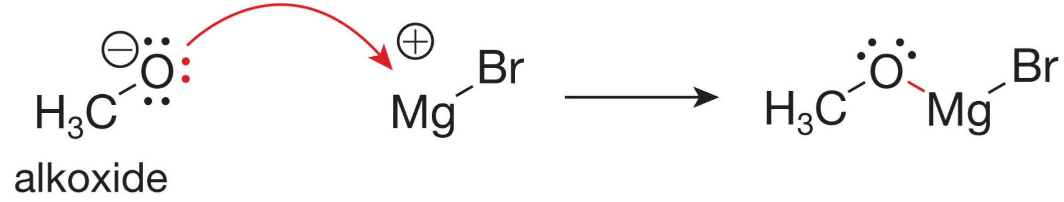


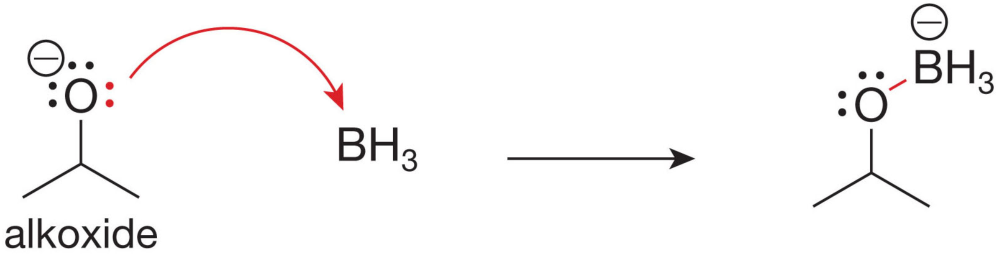
- Curved arrows show the movement of electrons, NOT the movement of atoms.

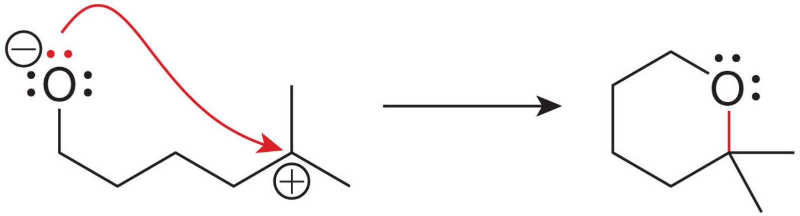


Curved Arrows – Bond Formation

- Ultimately, curved arrows (mechanistic arrows) show which bonds are being formed and which are being broken.
- Electron count and charge must always be conserved.

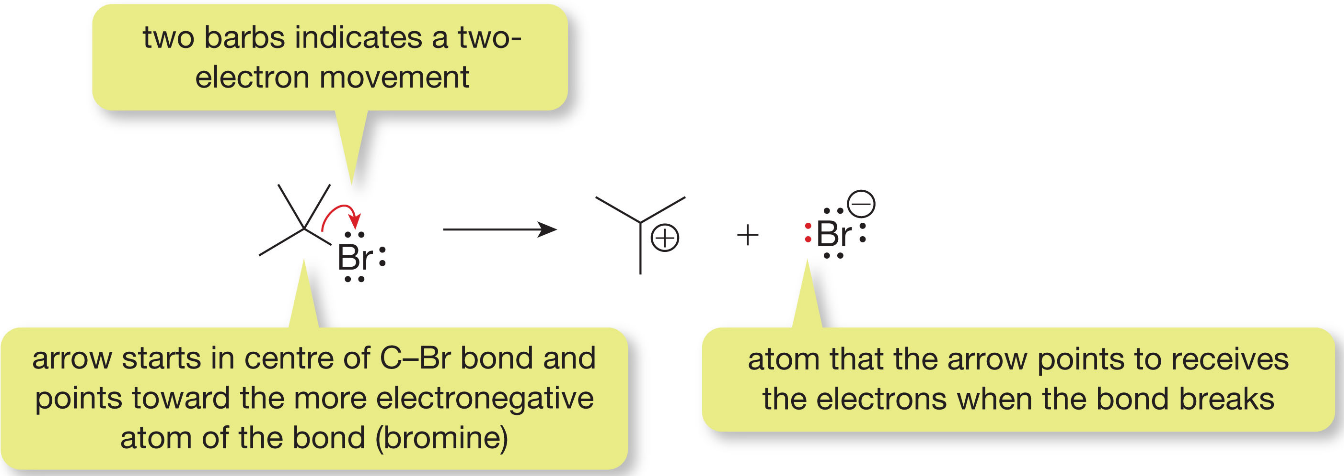
a) 

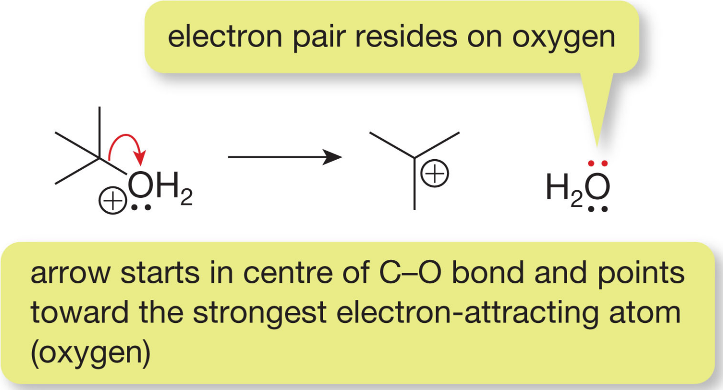
b) 

c) 

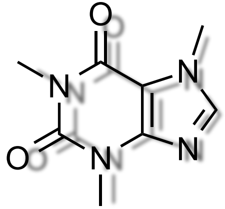
Curved Arrows – Bond Breaking

- When electron flow causes a bond to break, the curved arrow starts at the ***centre of the bond*** and points to the atom that will receive the electrons from the bond.
- Electron count and charge must always be conserved.

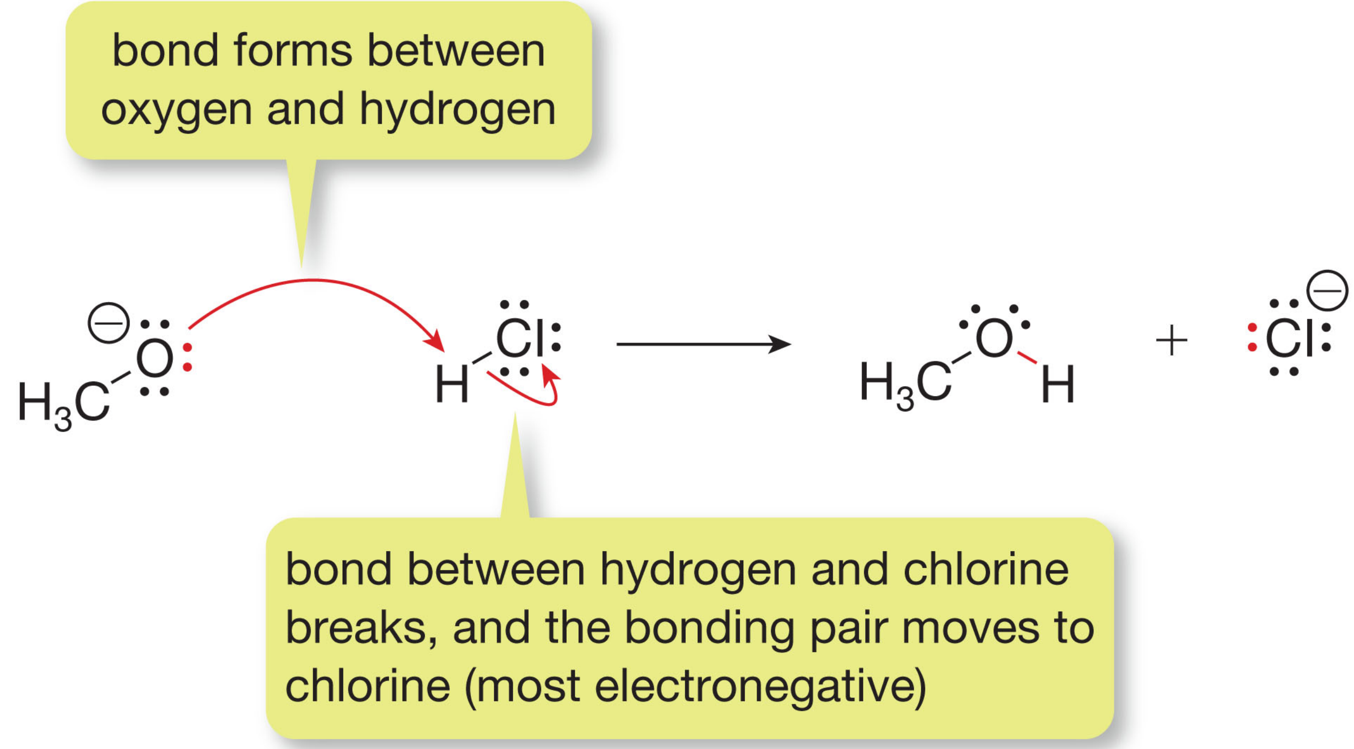




Curved Arrows – Bond Forming/Breaking



- Reactions mechanisms often involve the simultaneous formation and breaking of bonds.
- Electron count and charge must always be conserved.



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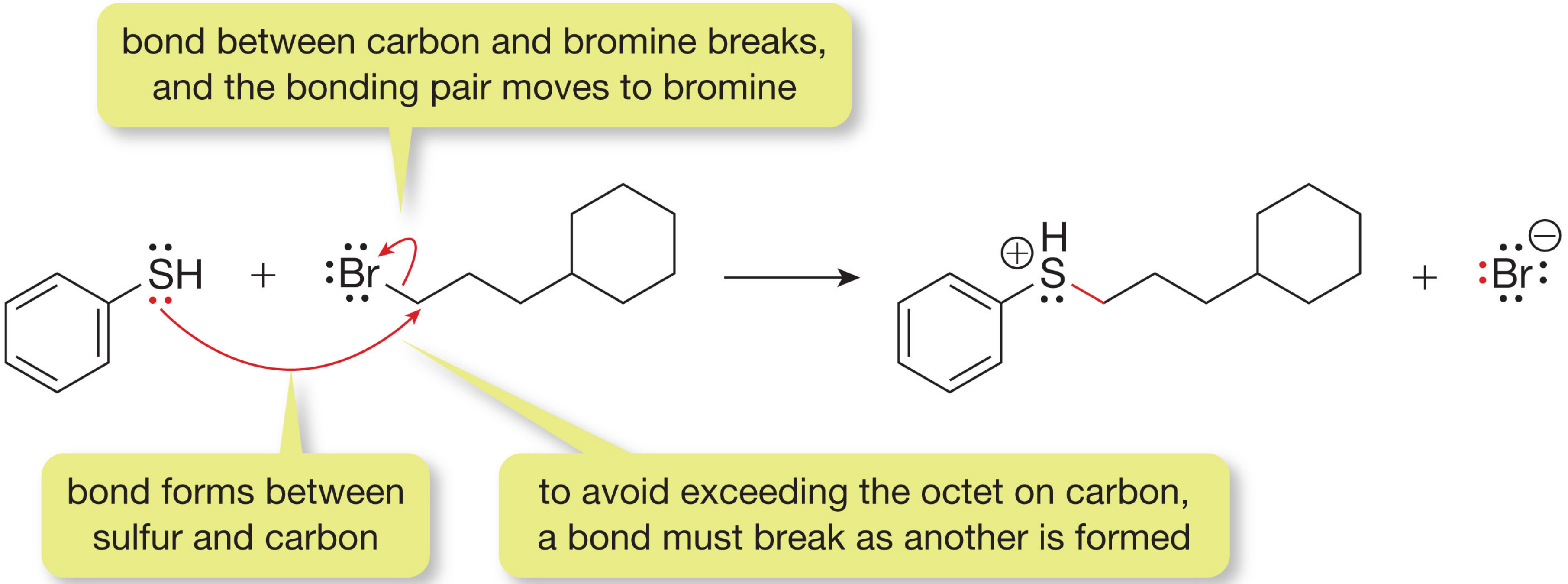
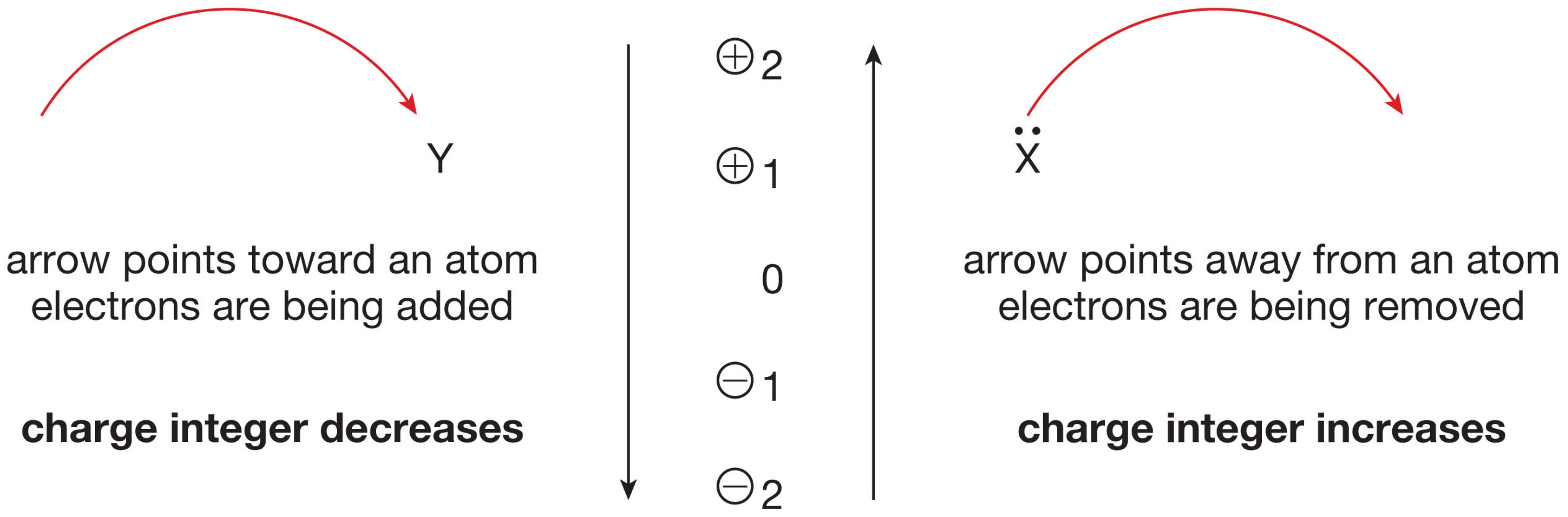


Curved Arrows and Formal Charges

- Because mechanistic arrows show electron movement, they also show how formal charges change during reactions.
- The flow of a ***pair*** of electrons can change the formal charge by one unit.



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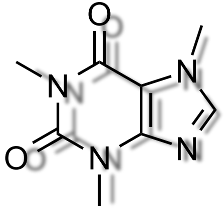

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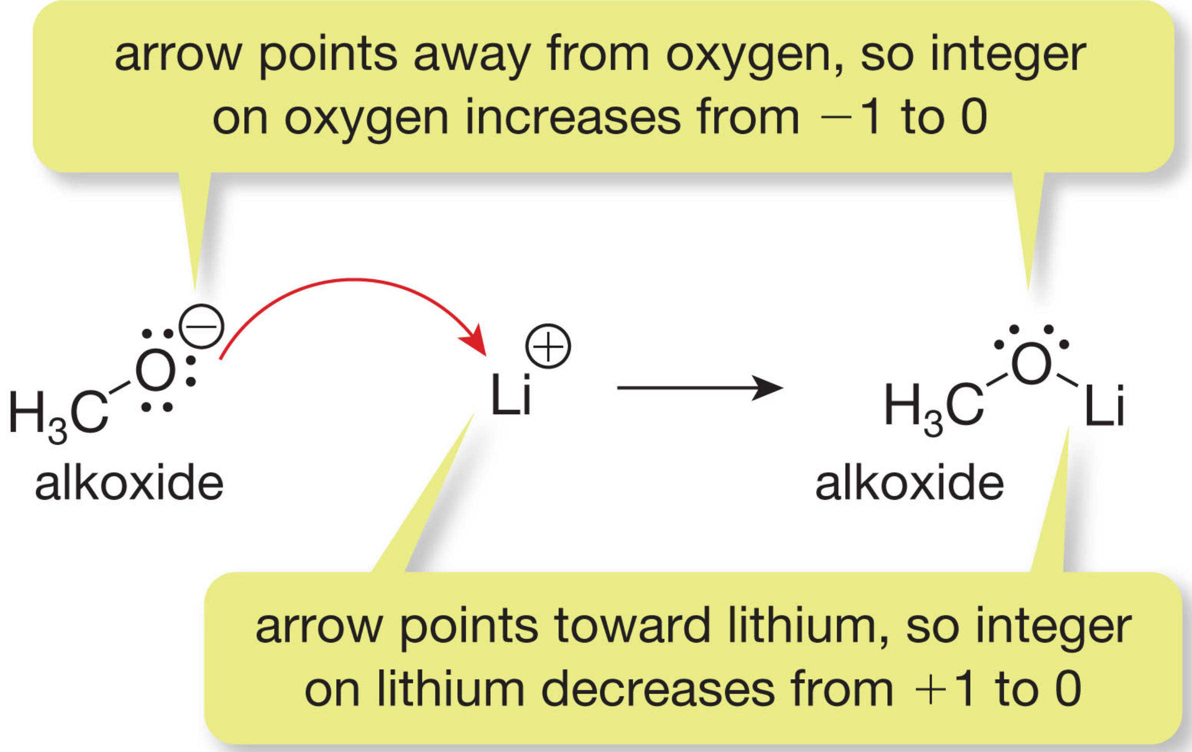

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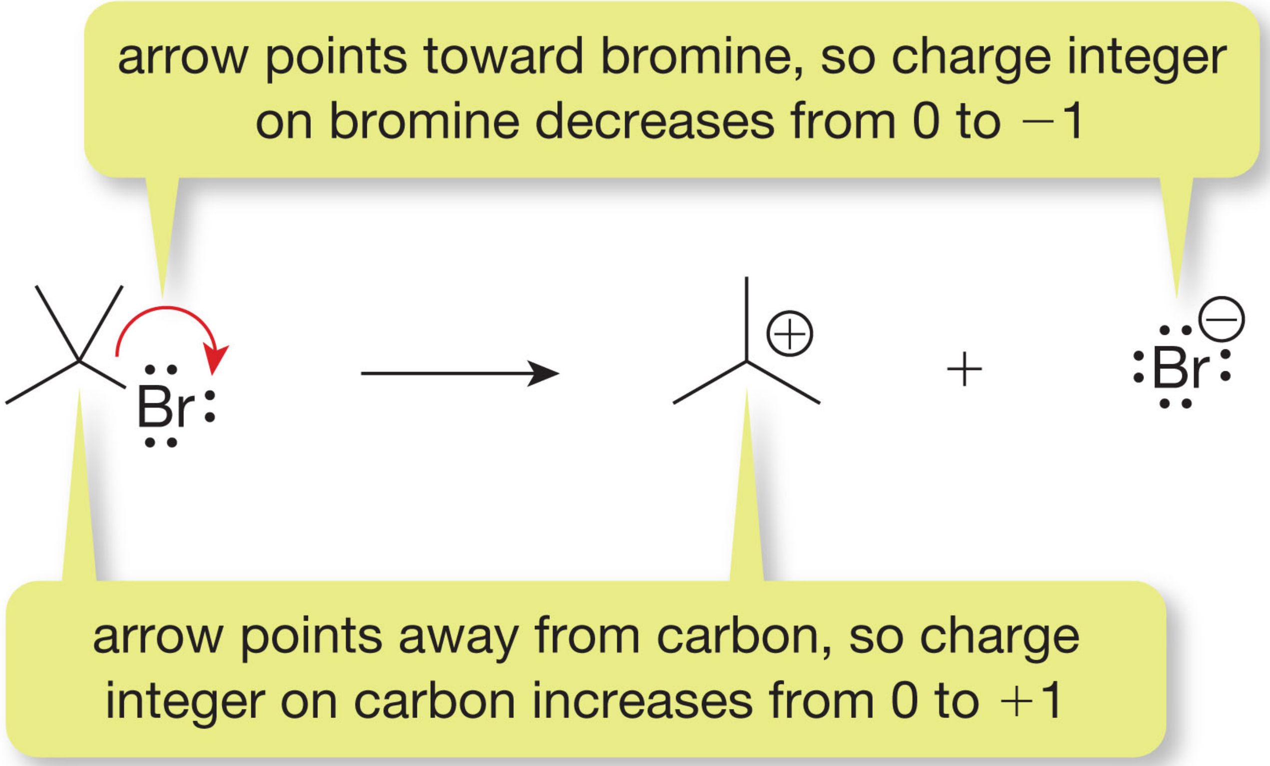

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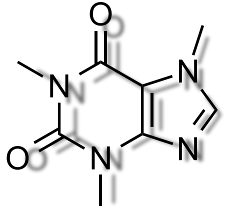

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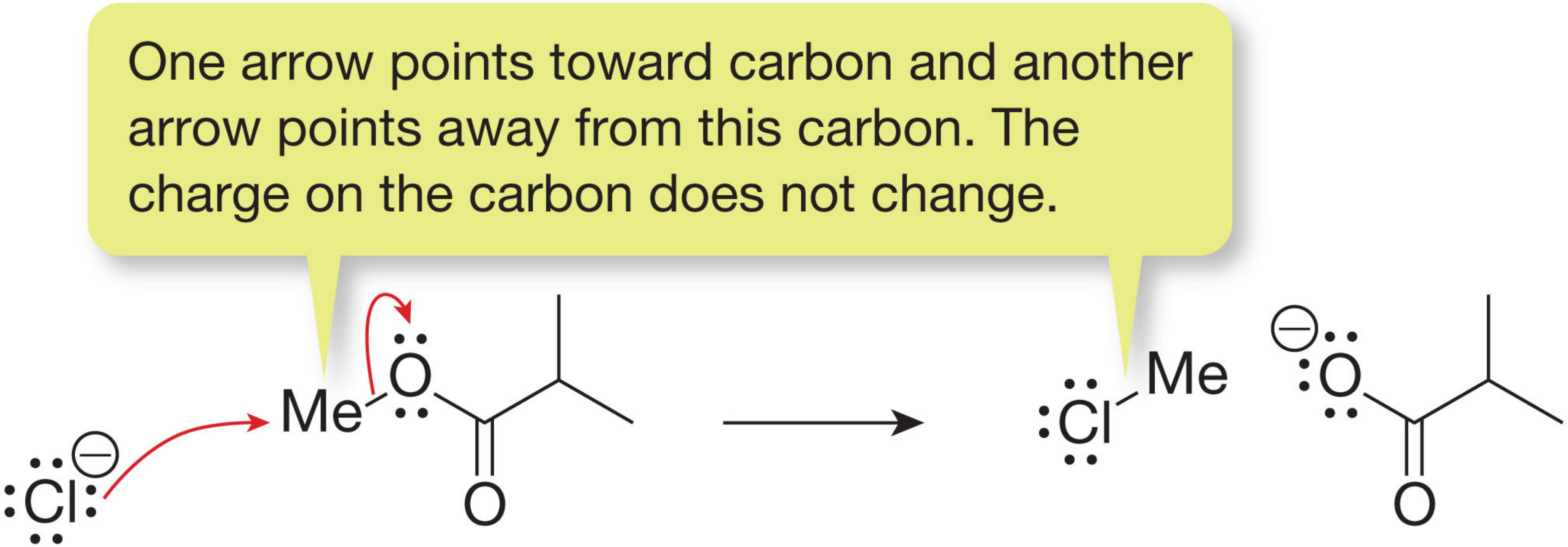
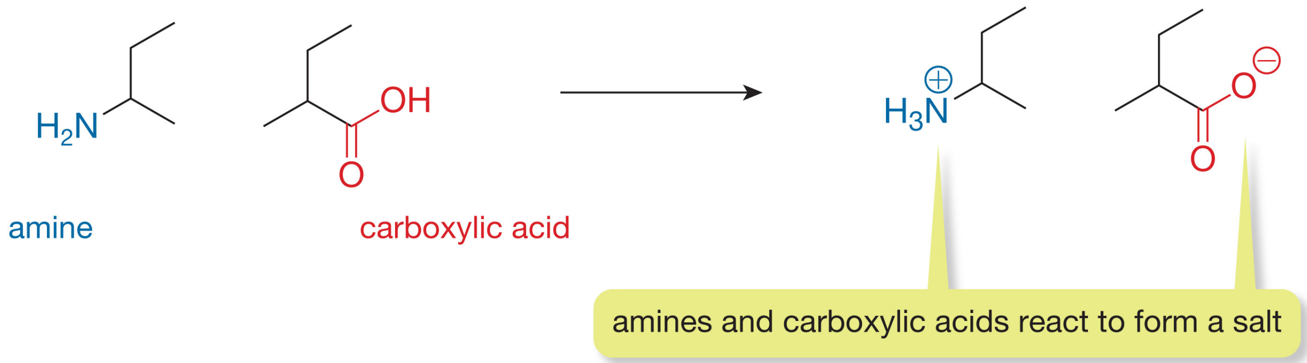
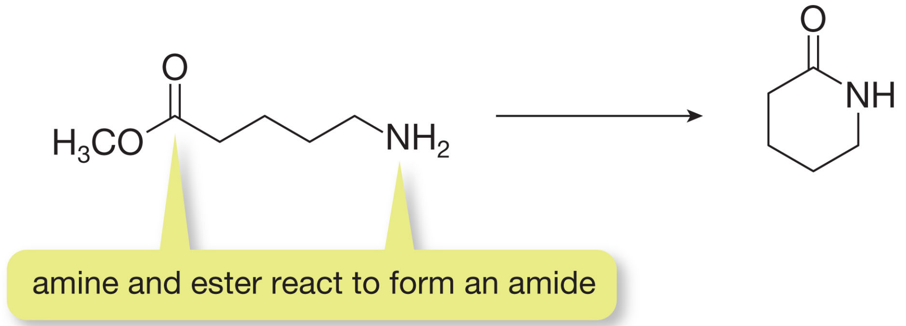


Intramolecular Reactions

- Reactions that occur between separate molecules are called ***intermolecular reactions***.
- Reactions that occur within a molecule are called ***intramolecular reactions***



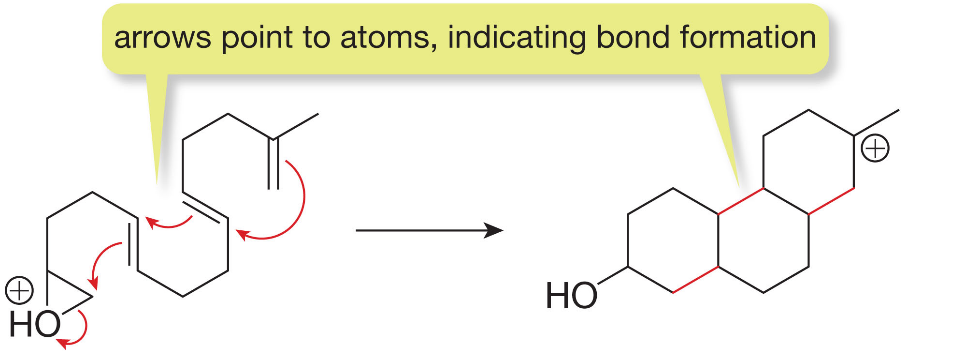
intermolecular

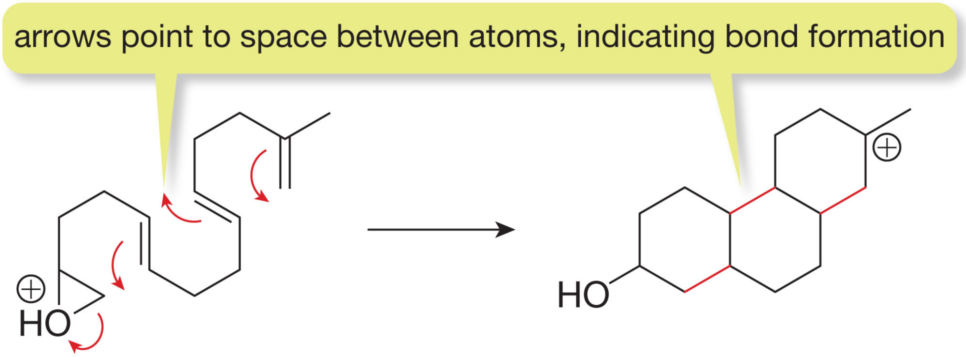


intramolecular

Intramolecular Reactions - π Bond Electrons

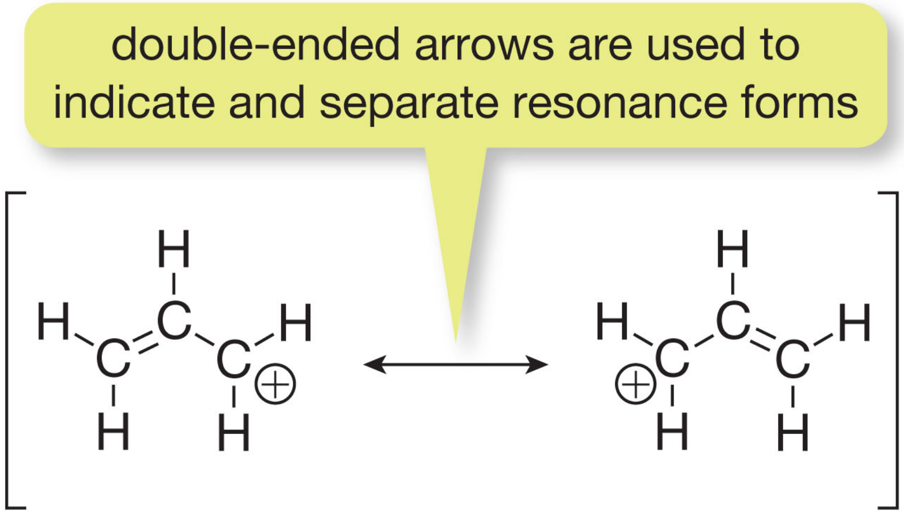
- There are 2 different conventions used when showing curved arrows for the flow of π electrons:
  - Show bond formation with an arrow that points to the *space between atoms*
  - Show bond formation with an arrow that points toward an atom



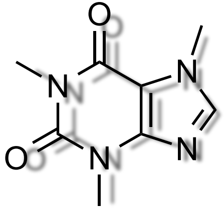


Constructing Resonance Forms

- Recall:
  - that resonance structures are used to describe the delocalization of π electrons in a molecule
  - that molecule does NOT flip-flop between resonance structures.
  - that the actual structure of the molecule is a weighted average of all resonance structures.
  - that resonance structures are separated by double-headed arrows



Constructing Resonance Forms

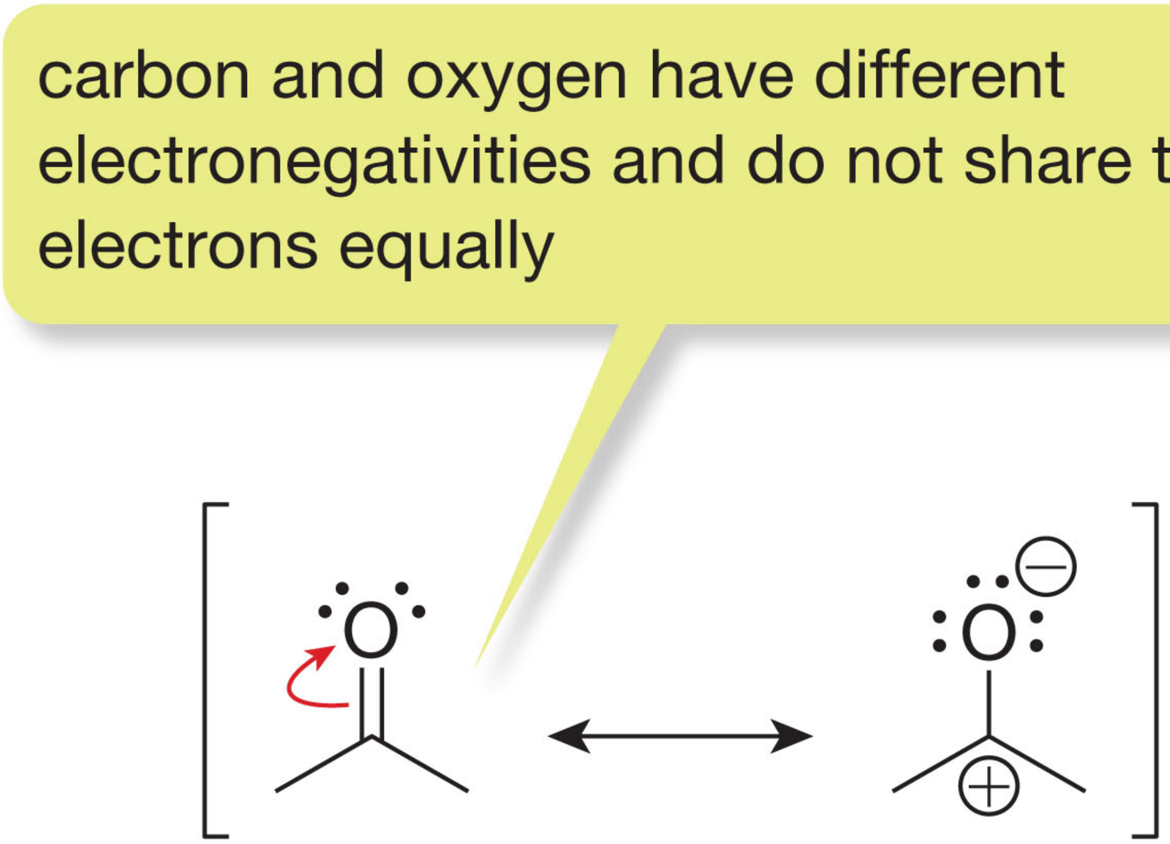


- For resonance to occur, at least one of the following structural features must be present in the molecule:

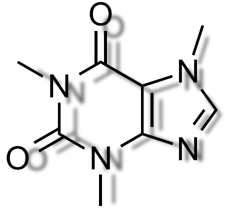
1. A π bond made up of atoms of different electronegativities
2. A π bond directly beside at least one of the following features:
   - paired or unpaired electrons
   - atoms with incomplete octets
   - other π bonds
   - charged atoms lacking octets or carrying lone pairs
3. An atom with an incomplete octet adjacent to an atom with a pair of non-bonding electrons

Constructing Resonance Forms

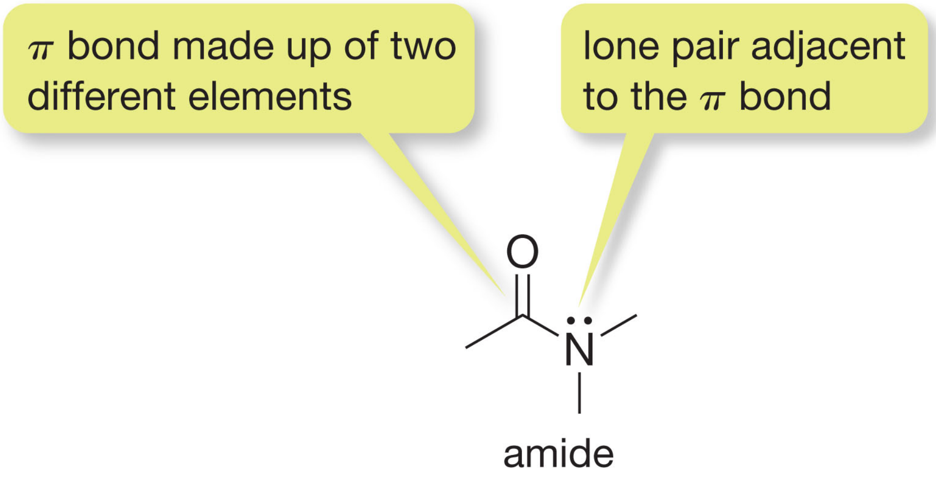
1. A π bond made up of atoms of different electronegativities

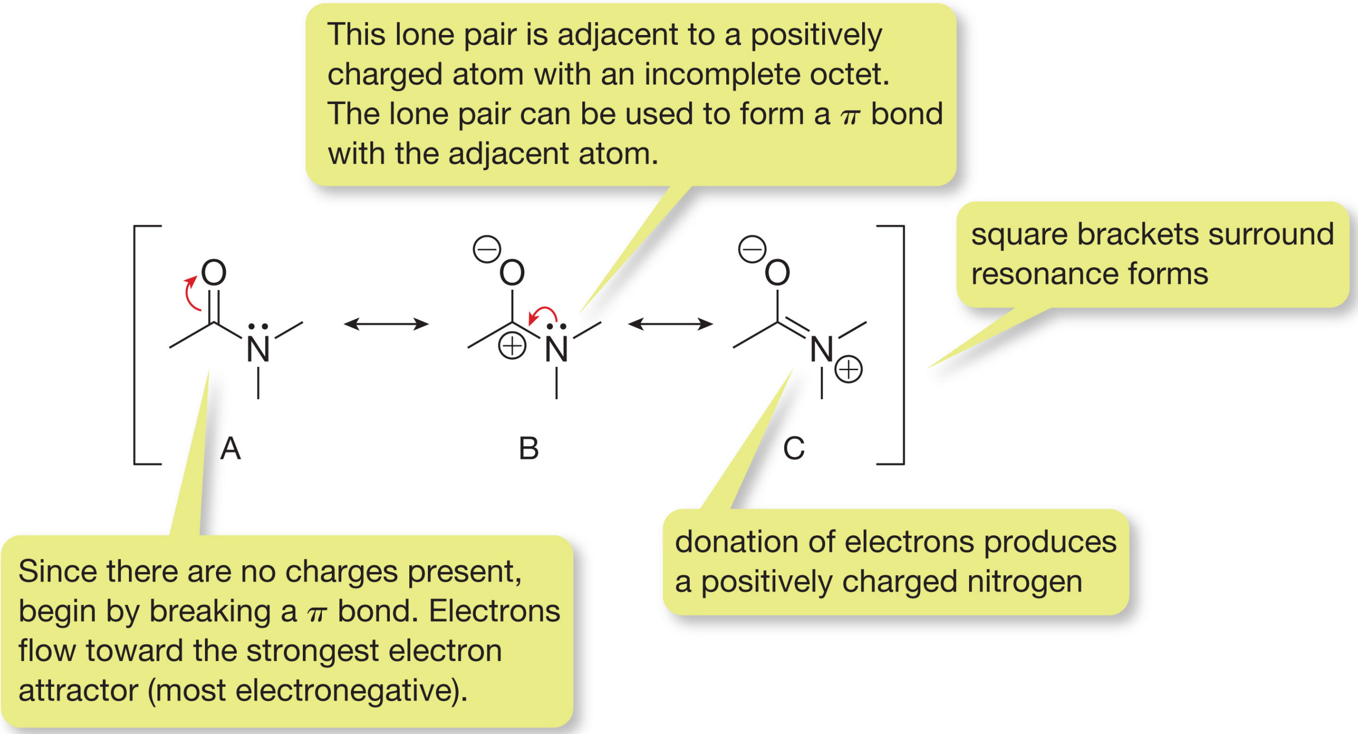


Constructing Resonance Forms



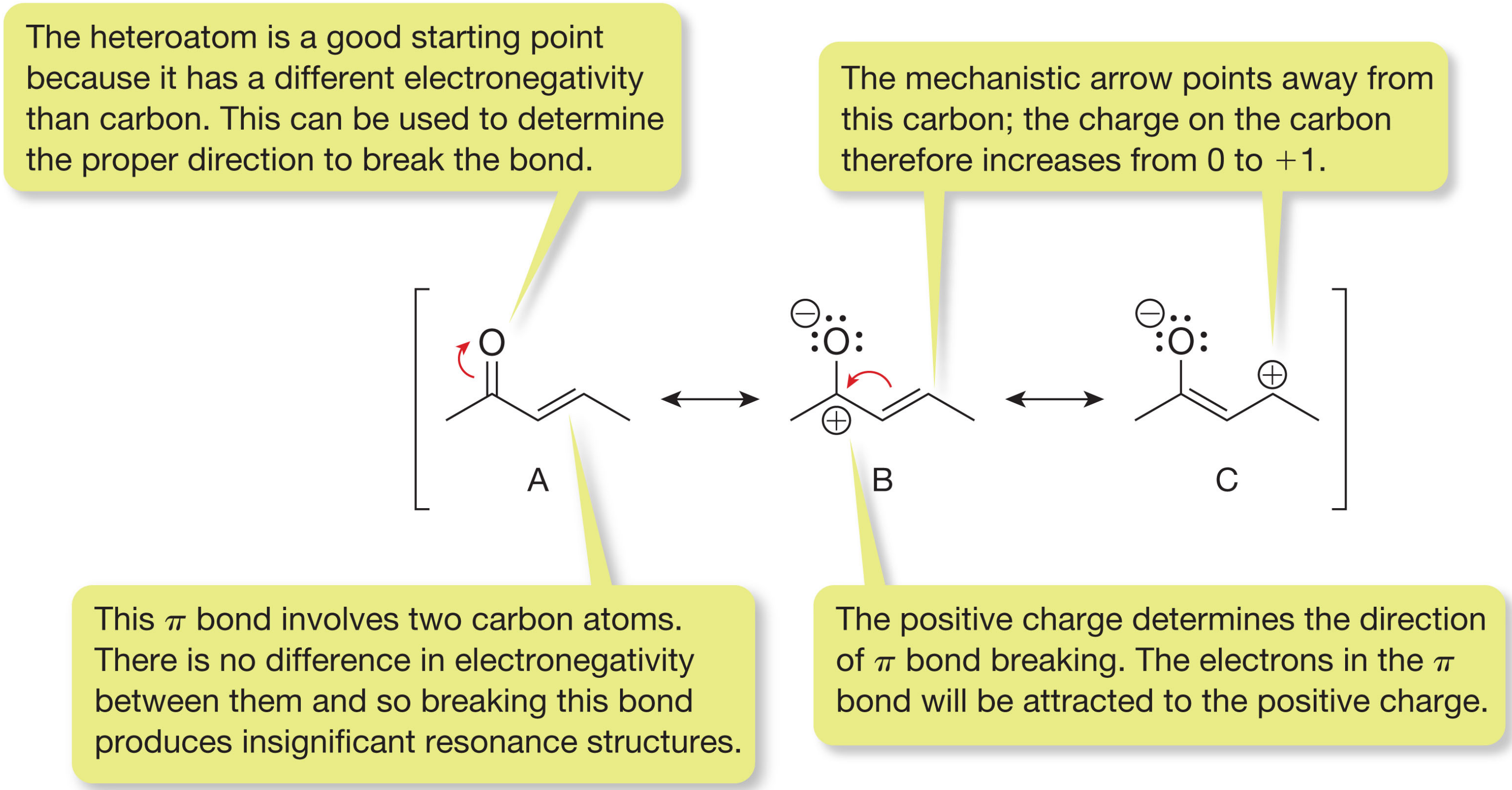
2. A π bond directly beside at least one of the following features:
   - paired or unpaired electrons





Constructing Resonance Forms

2. A π bond directly beside at least one of the following features:
   - other π bonds
   - charged atoms lacking octets or carrying lone pairs



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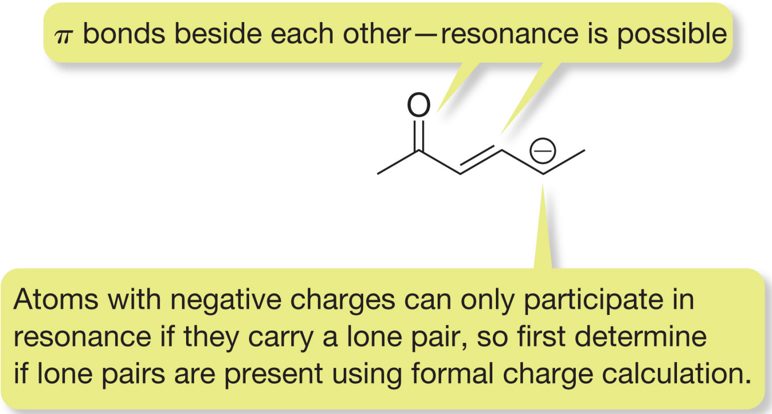
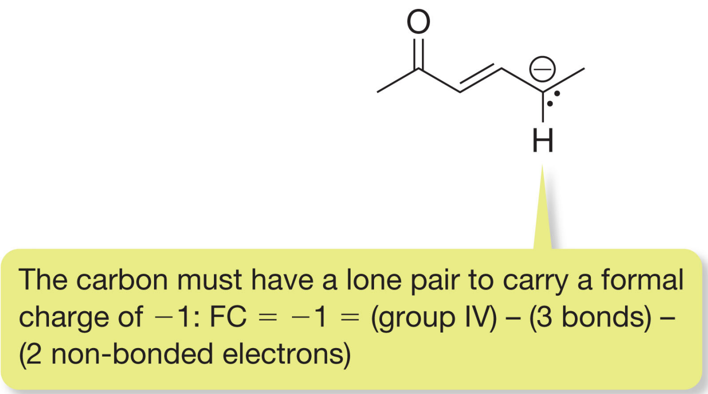
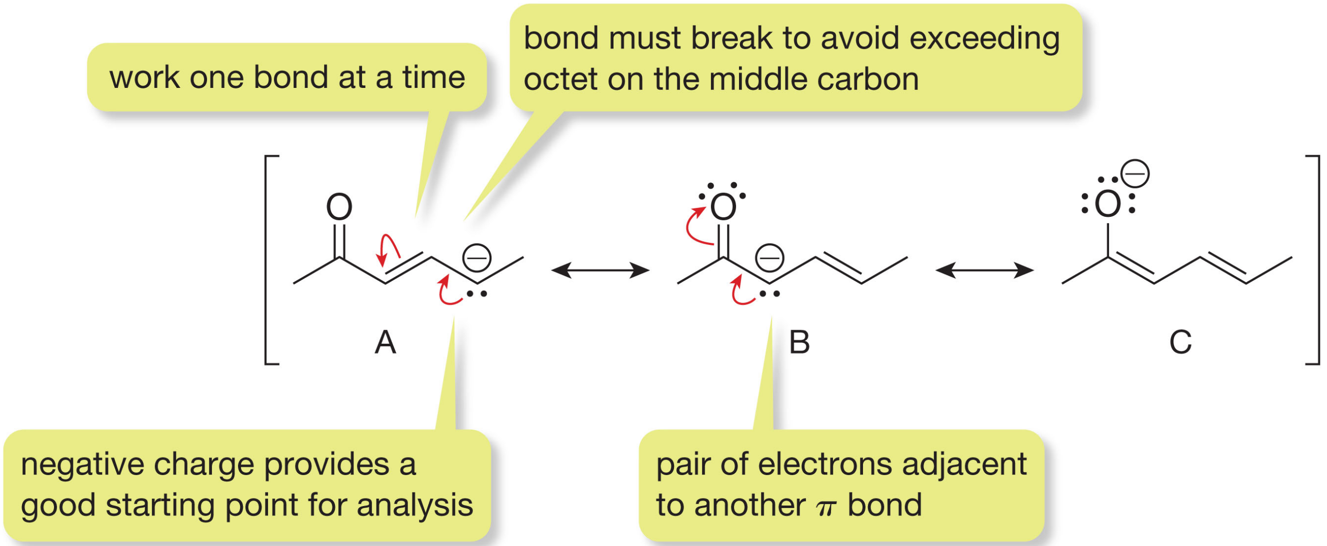
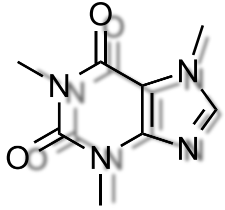






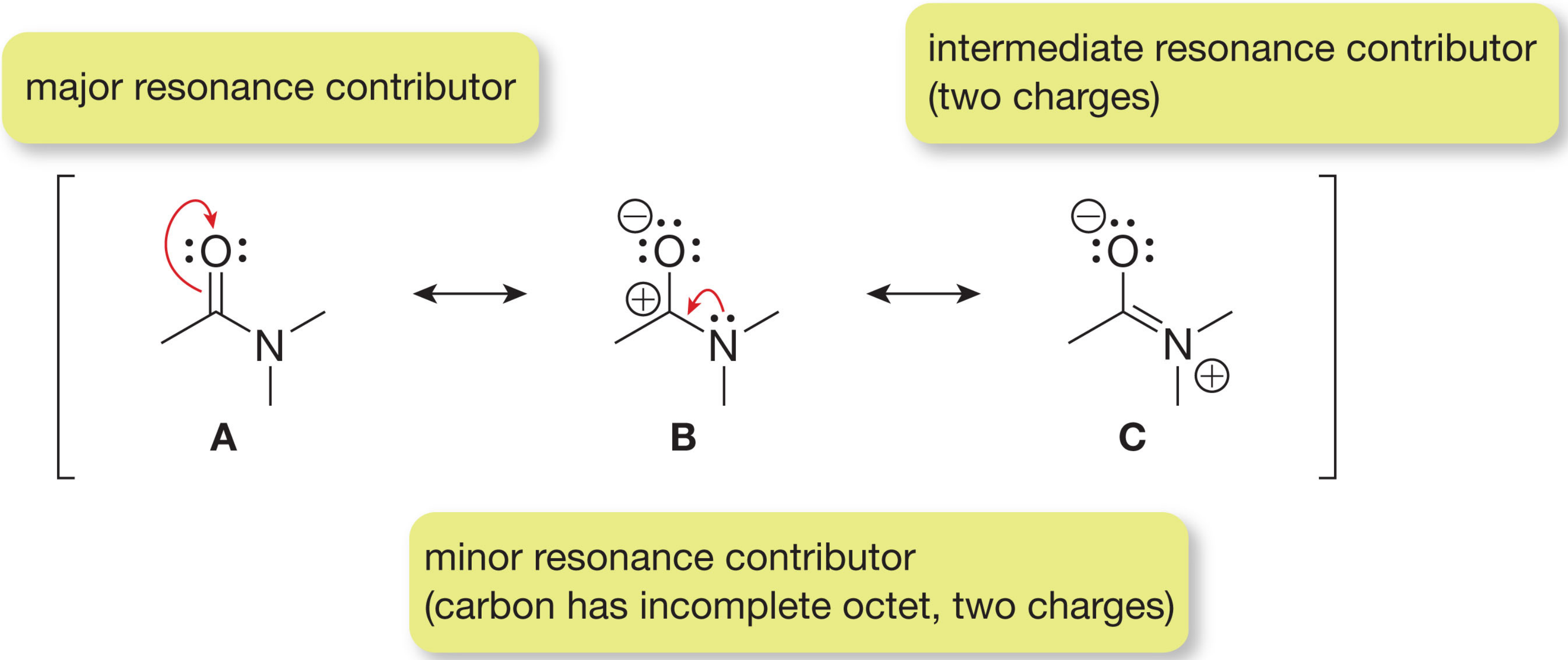
Evaluating Resonance Forms



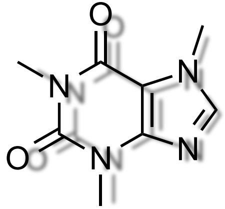
- It is important to understand that not all resonance forms are equal.
- Resonance structures with favorable electron distribution make a larger contribution to the overall structure than those with less favorable electron distribution.
- Use the following guidelines (***listed in order of importance***) to assess the quality of individual resonance forms:
  1. the most atoms with full octets
  2. the fewest number of formal charges
  3. (-) formal charges located on the most electronegative atoms and (+) formal charges located on the most electropositive atoms
  4. like charges separated as far as possible, opposite charges as close as possible

Evaluating Resonance Forms

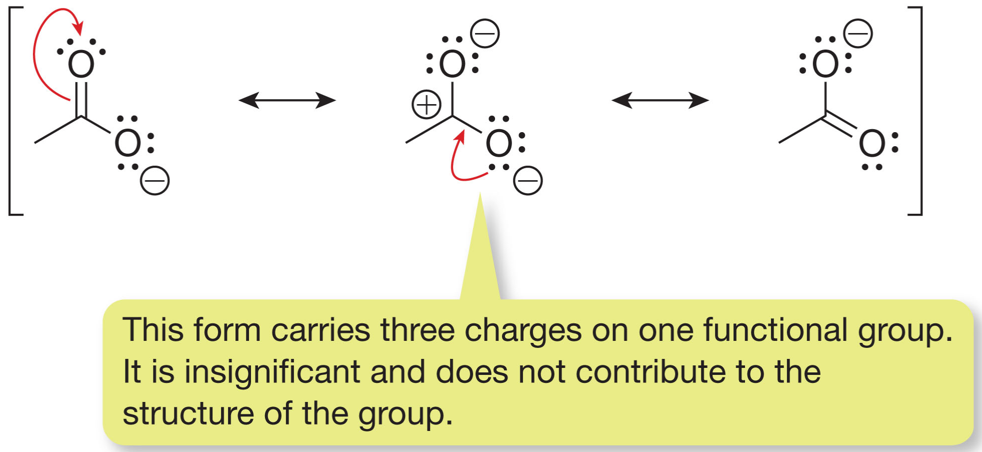
- Functional groups are normally represented by the ‘best’ resonance form.
- The relative quality of resonance forms also provide a guide to the most likely site of reactivity in a given functional group.

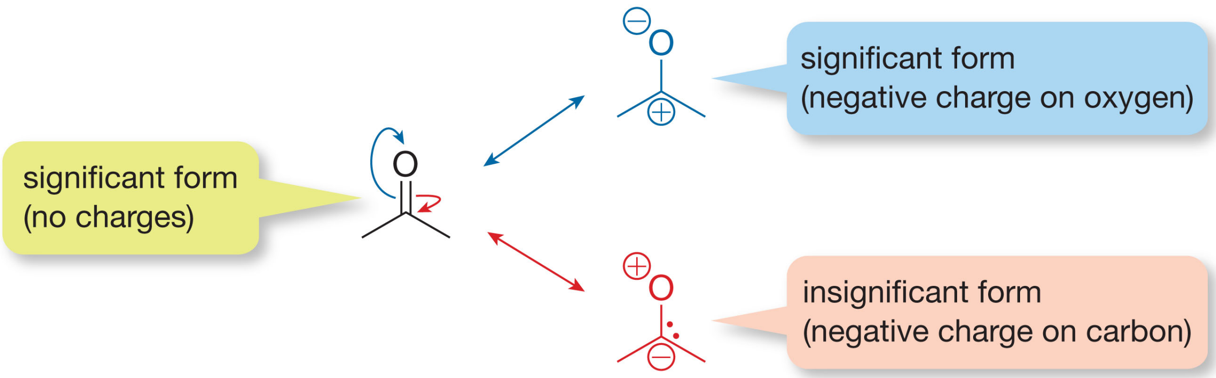


Insignificant Resonance Forms



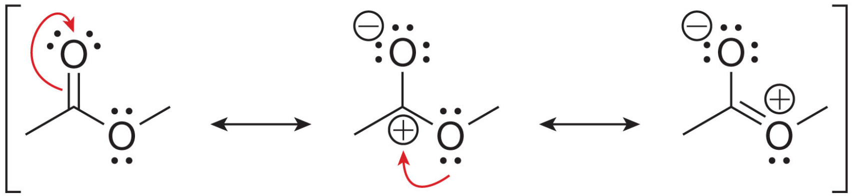
- Insignificant resonance forms occur when:
  - a functional group carries more than 2 formal charges
  - π bonds flow in the wrong direction
  - 2nd row elements have more than 8 electrons!

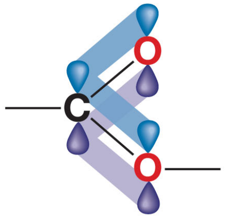




Resonance and Orbital Structure

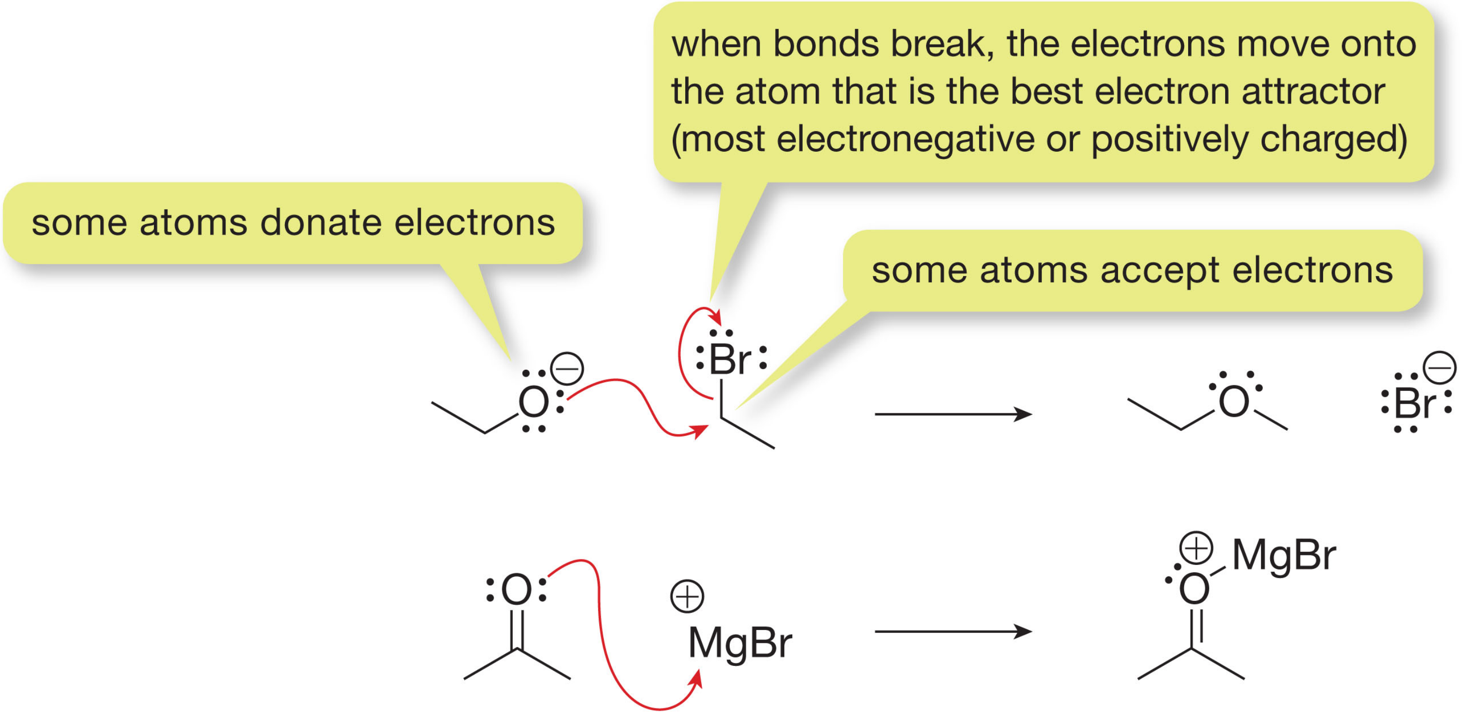
- Recall that the actual structure of the molecule undergoing resonance is a ***blend of all the resonance forms at the same time***.
- The electrons involved in resonance form a single orbital structure in which each atom participating in resonance contributes one orbital.
- The result is a network of orbitals that describes a region of space in which the resonating electrons may be found.





Patterns in Mechanism

- Reaction mechanisms are systematic and follow patterns.
- In reaction mechanisms, electrons flow from atoms with high electrons density (lone pairs or bond, often with – or δ- charge) to atoms of low electron density (lacking octet or +/δ+ charged).



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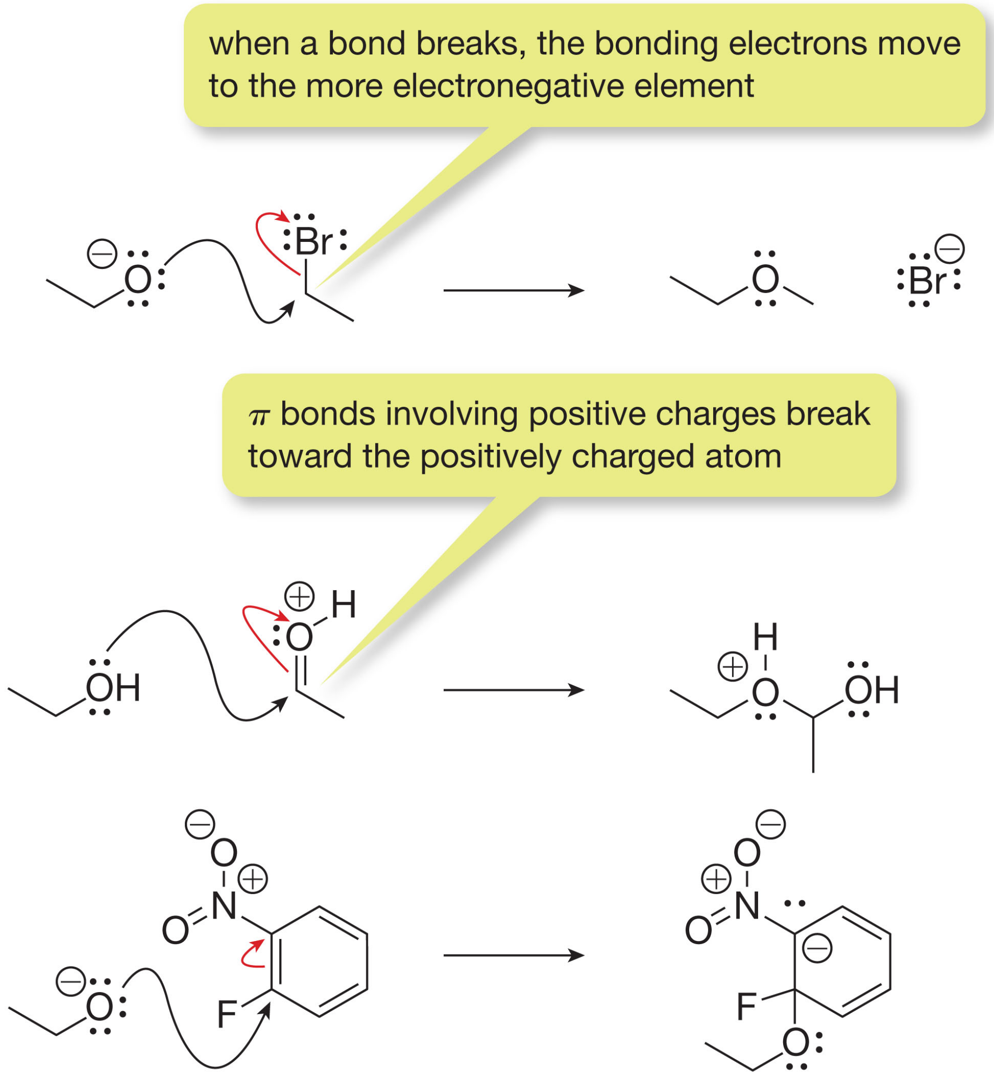

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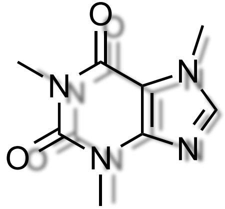

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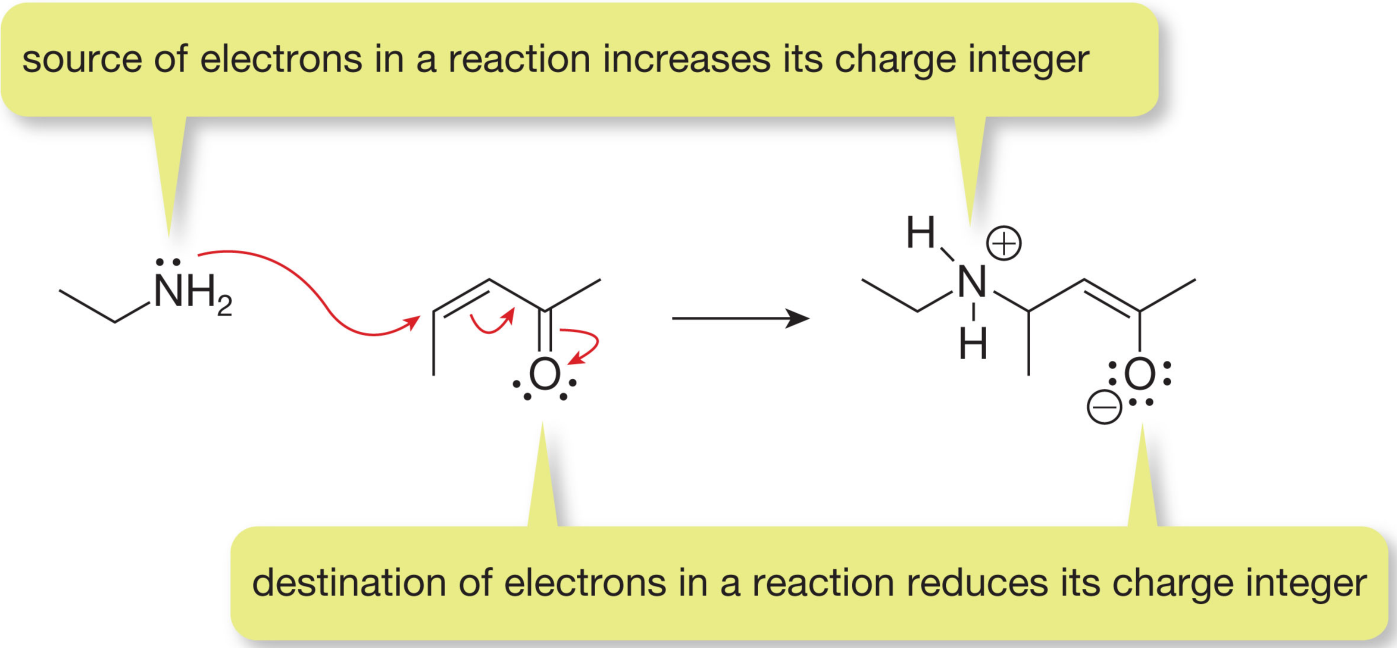
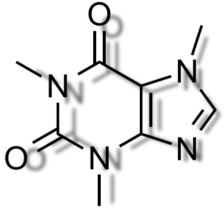


Patterns in Resonance



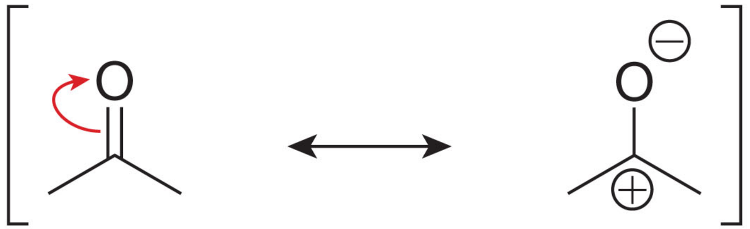
- ***Important – Organic molecules are greatly stabilized by the delocalization (i.e. resonance) of π electrons***.

- Resonance structures are systematic and follow patterns:
  1. π bond to lone pair
  2. lone pair to π bond
  3. π bond to π bond

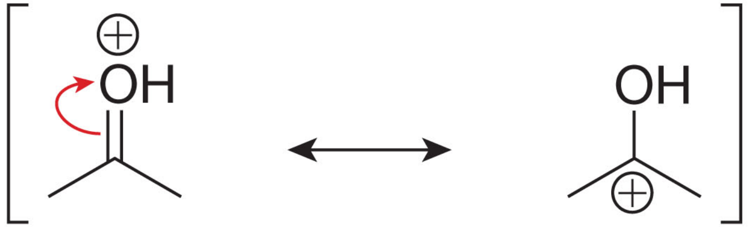
Patterns in Resonance

- Isolated double bonds:

isolated double bonds:



resonance is possible if the atoms are different types
resonance is not possible if the atoms are the same

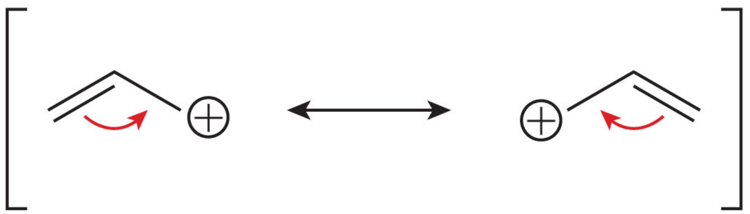


positive charge on an sp^2 atom will lead to resonance

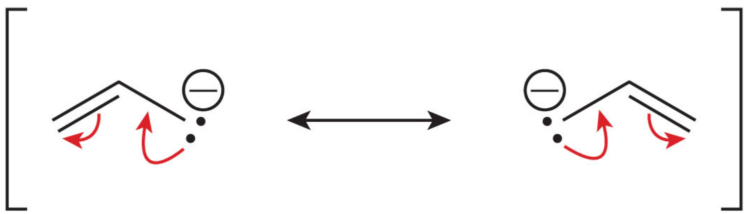
Patterns in Resonance

- Double bonds beside charges and non-bonding electrons:

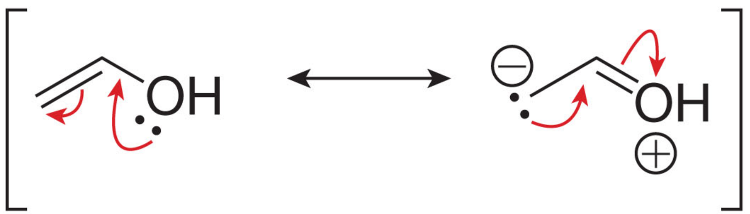
double bonds beside charges and non-bonded electrons



positive charge lacking octet adjacent to a π bond will lead to resonace



negative charge with lone pair adjacent to a π bond will lead to resonace

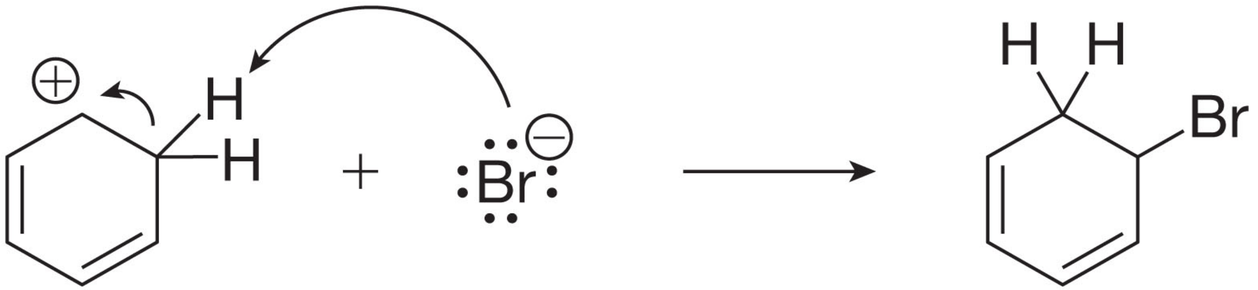


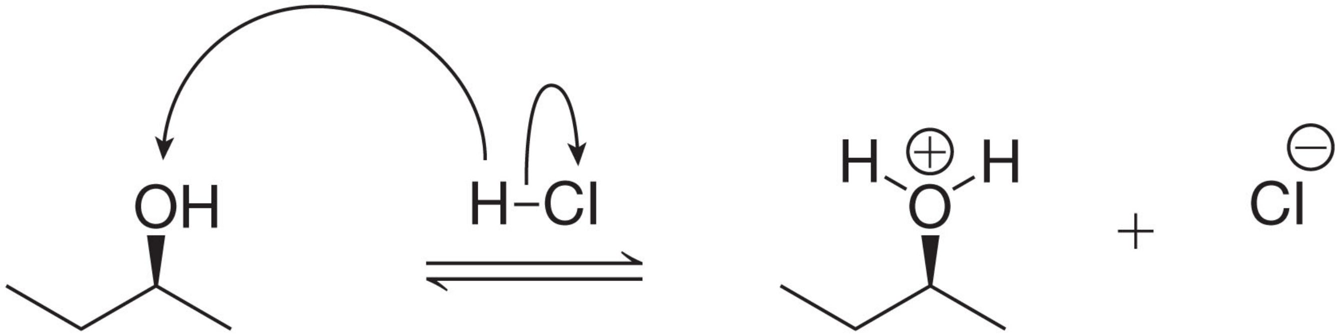
lone pair adjacent to a π bond will lead to resonace

Mechanisms – Practice

- Identify the error in each of the following mechanisms. Redraw each mechanism to give the products shown:

5.4

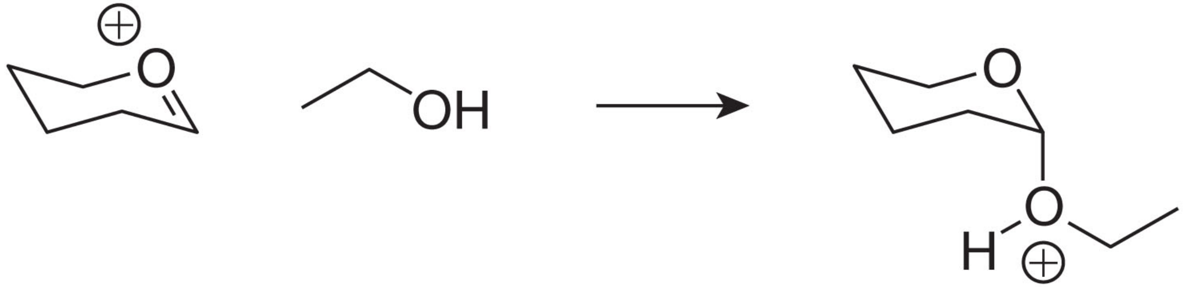
a) 

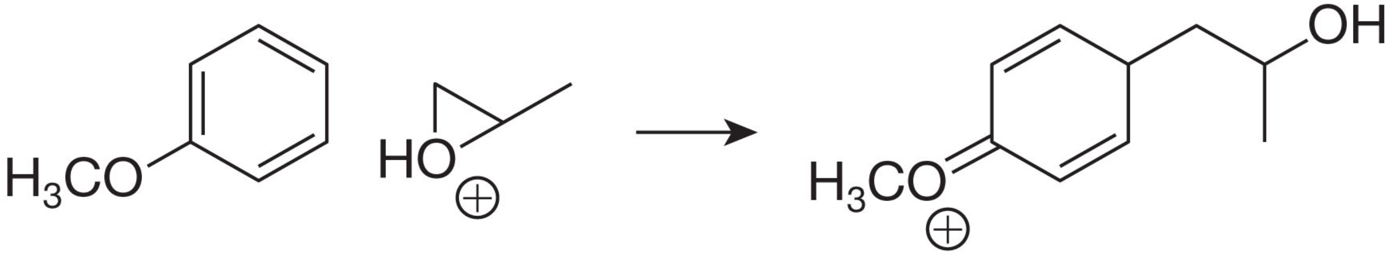
c) 

Mechanisms – Practice

- Add curved arrows to explain the formation of each product:

5.18

a) 

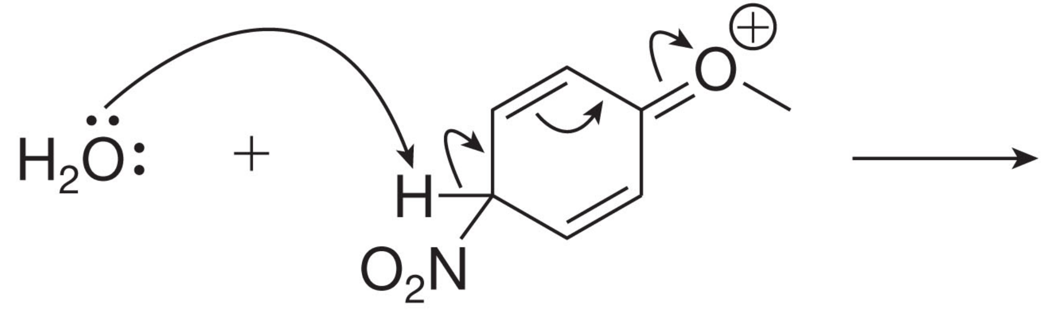
d) 

Mechanisms – Practice

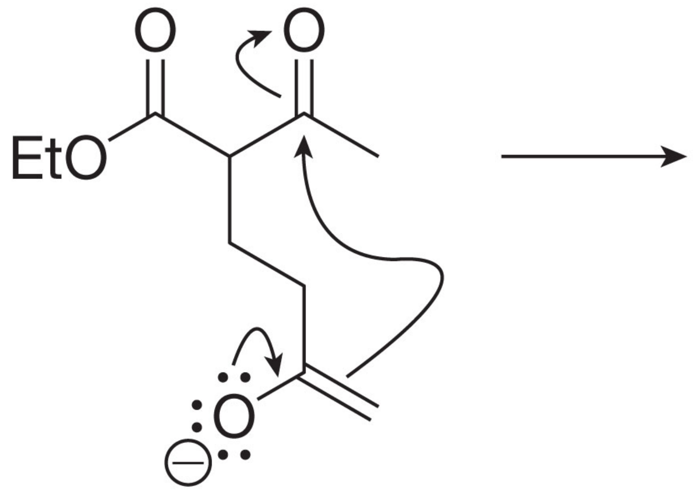
- Draw the products of the following reactions, including any formal charges:

5.21

b)



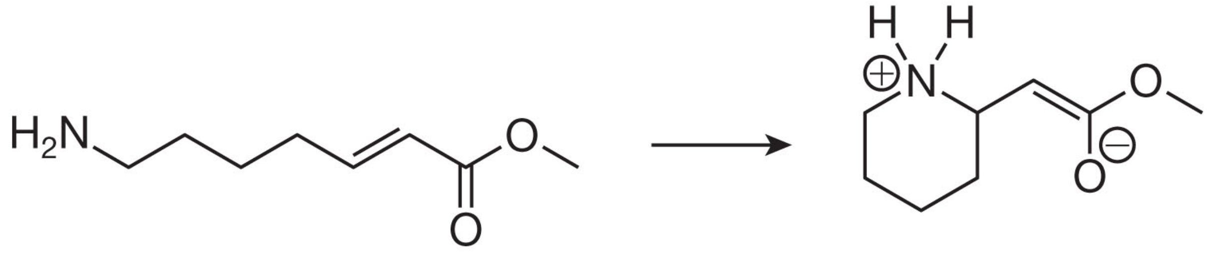
e)



Mechanisms – Practice

- For each of the following reactions, add mechanistic arrows to show the flow of electrons. Where appropriate, include lone pairs, as well as any missing formal charges:

5.22

i) 

5.23

d)