# Organic Structures
# 4 - Resonance

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# Resonance - Introduction

Resonance is the movement of electrons over covalent bonds. It occurs only in molecules that have double bonds, lone pair of electrons, or ions. Here are some rules about resonance.

- Resonance structures occur only on paper, i.e. they cannot be isolated in the lab. (If they can be isolated then the molecules are in equilibrium – resonance structures cannot be isolated).
- All structures written for one compound are called contributing structures. One of them may contribute less or more to the overall stability of the molecule depending on its structure.
- A hybrid can be drawn of all the structures which shows the delocalization of all the electrons over all the carbons.
- The more contributing structures there are, the more stable the molecule is. This is due to delocalization of electrons over bonds.
- Resonance structures are shown by using curved arrows, which shows movement of electrons (one or two depending on the type of arrow).

# Rules and Stability of Resonance Structures

**Rules for writing resonance structures**

1. Resonance structures are indicated by the use of double-headed arrows.
2. Only electrons are allowed to move between resonance structures.
3. All structures must be proper Lewis structures.

**Stability of Resonance Structures**

1. A resonance form with more covalent bonds is more important than one with less.
2. Resonance forms in which all atoms have a complete valence shell of electrons are more important.
3. Resonance structures with separation of charge have high energy and are less stable hence contribute less to the hybrid structure.
4. The energy of the actual molecule, the hybrid, is lower than the energy of any single contributing form.
5. The more stable the structure the greater its contribution to the structure of the real molecule.

All the above are explained in the next few slides with examples.

# Rules for Writing Resonance Structures - 1

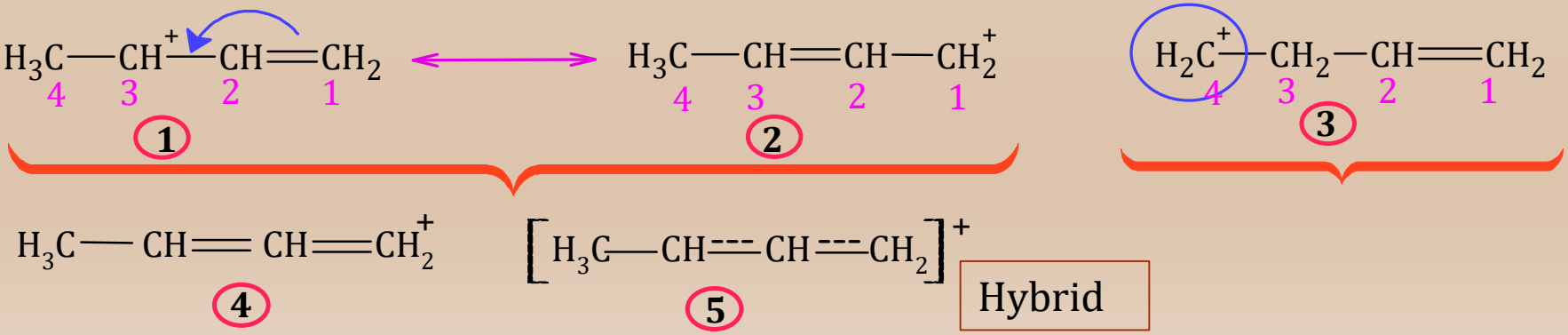
1) Resonance structures are indicated by the use of double-headed arrows.

2) Only electrons are allowed to move between resonance structures.

- Electrons in multiple bonds, nonbonding electrons or anions can be moved.
- Sigma bonds cannot be moved.
- In the **structures 1 and 2** below, the double bond (pi bond) is moved from between C1 and C2 to between 2 and 3. This creates a carbocation on C1. **Structure 3** is not a resonance structure of 1 and 2 because an atom (H) has moved from C4 to C3.

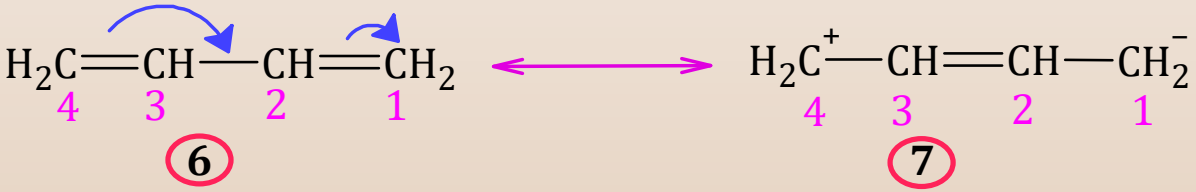
3) All structures must be proper Lewis structures but **structure 4** has 5 bonds.

- **Structure 5** is the hybrid where electrons are delocalized over the resonance bonds, shown as dash lines.

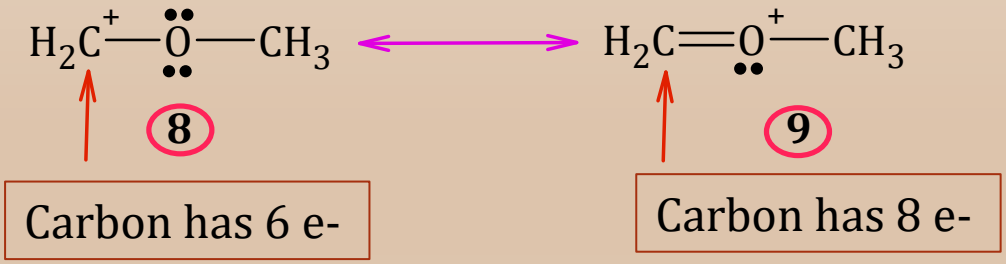


# Stability of Resonance Structures - 1

1) A resonance form with more covalent bonds is more important than one with less.
   - **Structure 6** is more stable than **7** and more important because it has more total covalent bonds.

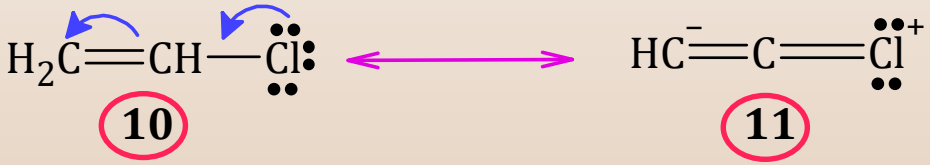



2) Resonance forms in which all atoms have a complete valence shell of electrons are more important.
   - **Structure 9** is more important than **8** because all atoms (except hydrogen) have complete octets.



# Stability of Resonance Structures - 2

3) Resonance structures with separation of charge have high energy and are less stable hence contribute less to the hybrid structure.
   - **Structure 11** is less important than **10** because it has charge separation.

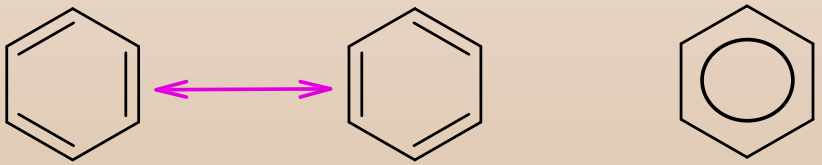



- Structures with negative charge on the more electronegative atoms are more stable.
- Those with positive charge on less electronegative atoms are also more stable.

# Stability of Resonance Structures - 3

5) The energy of the actual molecule, the hybrid, is lower than the energy of any single contributing form. Equivalent resonance forms make equal contributions to the structure of the real molecule.

- In the previous slide structures 1 and 2 are similar.
- Structures with equivalent resonance forms tend to be greatly stabilized.
- Example: The two resonance forms of benzene, shown below contribute equally and greatly stabilize it.



Resonance structures Hybrid representation

- Unequal resonance structures contribute based on their relative stabilities.

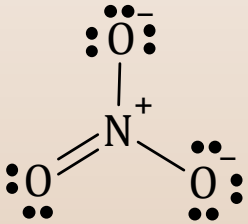
6) More stable resonance forms contribute more to the structure of the real molecule.

## Solved Example: Writing resonance structures

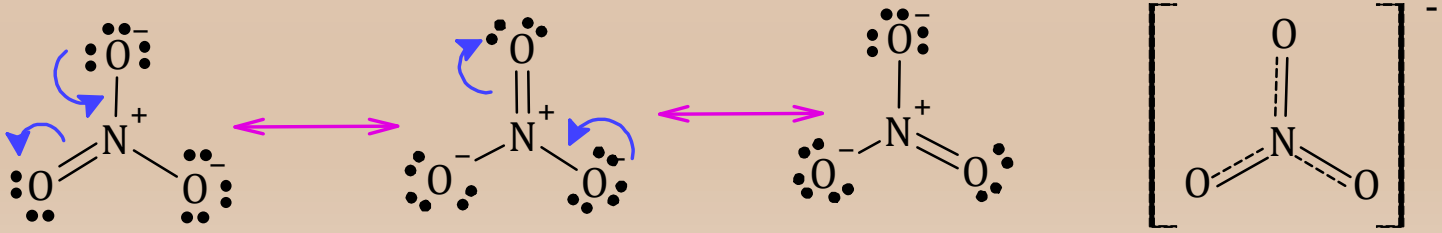
Write the resonance structures for nitrate ion.

**ANSWER**

- The nitrate ion is known to have all three nitrogen-oxygen bond lengths the same and the negative charge spread over all three atoms equally.



- Resonance theory can be used to produce three equivalent resonance forms.
  - Curved arrows show the movement of electrons between forms.
  - When these forms are hybridized (averaged) the true structure of the nitrate ion is obtained.



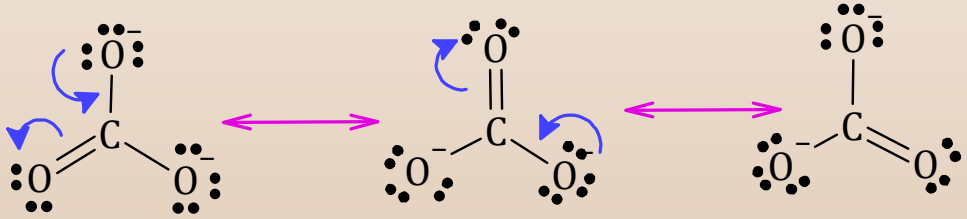
**Solved Example: Writing resonance structures**

Write the resonance structure of carbonate ion and ion of acetone $CH_3COCH_2^-$.

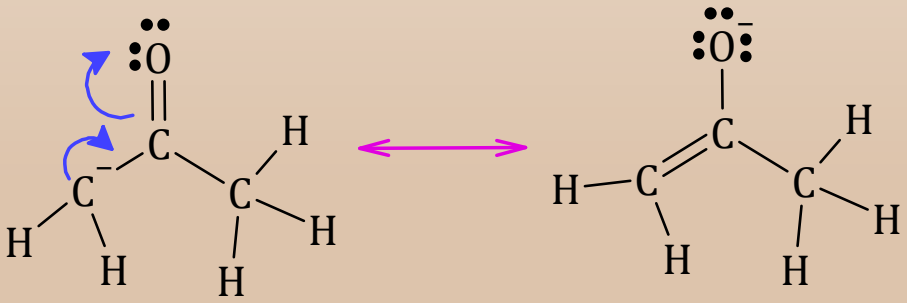
**ANSWER**

For both structures, write the Lewis structure first and see if there are any double bonds or lone pair of electrons to move.

- Carbonate Ion:

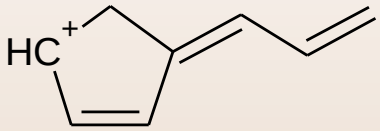


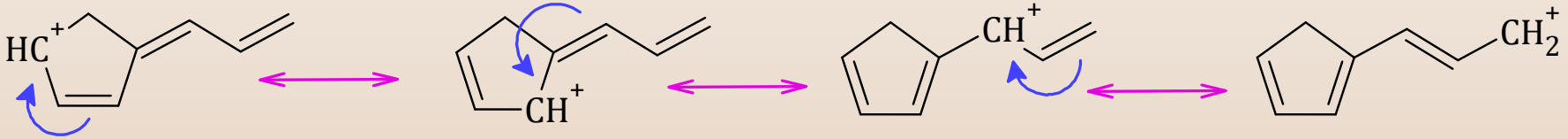
- Acetone



# Organic Molecules and Resonance

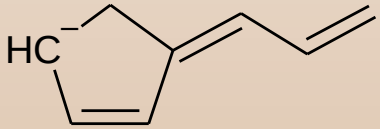
**Cation**

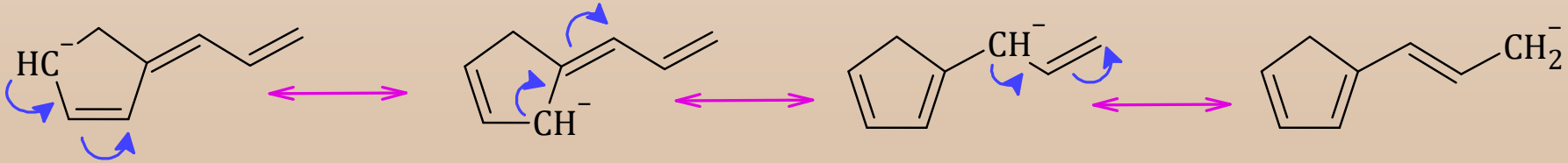



*Note that electrons are moving towards the cation as that is the positive center.*

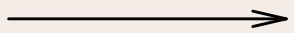
**Anion**




*Note that electrons are moving from the anion towards a carbon atom.*

# Arrows in Organic Chemistry



Synthesis

Equilibrium

Resonance

Retrosynthesis (going backward)

Transfer of two electrons

Transfer of one electron

# Key Words/Concepts

- Writing resonance structures by moving electrons in the correct direction.
- Learning the rules of resonance.
- Learning different arrows.