

Theory of resonance

Theory of Resonance

Definition:

- The Theory of Resonance is a concept in chemistry that explains the delocalization of electrons in molecules that cannot be adequately represented by a single Lewis structure.
- It was introduced to explain the actual observed stability and properties of certain molecules and ions, which cannot be accounted for by any one canonical (or contributing) structure alone.

Key Concepts:

Resonance Structures (Canonical Forms):

- These are individual Lewis structures that differ only in the position of electrons, not the atoms.
- All resonance structures must:
 - Have the same positions of atoms (no change in the skeletal structure).
 - Differ only in the arrangement of π (pi) electrons or lone pairs.
 - Obey the rules of valid Lewis structures.
 - Have the same number of electrons and total charge.

Resonance Hybrid:

- The actual structure of the molecule is not any one resonance structure but a resonance hybrid, which is a weighted average of all valid resonance structures.
- The hybrid is more stable than any individual canonical form.
- Electrons are delocalized over the molecule, meaning they are not fixed between two atoms but spread over several atoms or bonds.

Conditions for Resonance:

- Presence of delocalizable electrons, such as lone pairs or π -bonds.
- Atoms involved must be coplanar or nearly coplanar, so that p orbitals can overlap effectively.
- Multiple valid Lewis structures must exist.

Examples of Resonance:

Example 1: Benzene (C_6H_6)

- Two resonance structures with alternating single and double bonds.

- Real structure: All C–C bond lengths are equal ($\sim 1.39 \text{ \AA}$), indicating delocalized electrons across the ring.

Example 2: Carbonate ion (CO_3^{2-})

- Three equivalent resonance structures with the negative charge and double bond delocalized among the three oxygen atoms.
- Real structure: All C–O bonds are equivalent and intermediate in length between a single and double bond.

Resonance Energy:

- The extra stability due to delocalization is called resonance energy.
- It is the difference in energy between the resonance hybrid and the most stable contributing structure.
- Higher resonance energy implies greater stability of the molecule or ion.

Importance of Resonance:

- Explains the stability of certain molecules and ions.
- Explains bond lengths and energies that cannot be predicted by simple Lewis structures.
- Helps understand reactivity, acidity/basicity, and other chemical properties.

Resonance in Alkenes

Overview

- In alkenes, the carbon-carbon double bond consists of one sigma (σ) bond and one pi (π) bond. The π -electrons are more loosely held and are available for delocalization under certain conditions.
- Although simple alkenes like ethene (C_2H_4) do not exhibit resonance, conjugated alkenes (i.e., compounds where double bonds are separated by a single bond) do show resonance.

Conjugation and Resonance

- Conjugation means alternating double and single bonds, which allows p-orbitals to overlap across multiple atoms.
- In such systems, the π -electrons become delocalized over the conjugated region, and resonance structures can be drawn.

Examples

1. 1,3-Butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$):

- Has two double bonds separated by a single bond.
- The π -electrons are delocalized over all four carbon atoms.

- Resonance structures can be drawn showing shifting of π -electrons:



2. Allyl Carbocation ($\text{CH}_2=\text{CH}-\text{CH}_2^+$):

- Has resonance between:



- The positive charge is delocalized over two carbon atoms (C1 and C3).
- This delocalization stabilizes the carbocation.

3. Allyl Anion ($\text{CH}_2=\text{CH}-\text{CH}_2^-$):

- Resonance between:



- The negative charge is delocalized similarly.

Importance of Resonance in Alkenes

- **Stability:** Resonance in conjugated alkenes increases their stability compared to isolated double bonds.
- **Reactivity:** Resonance affects the chemical behavior, particularly in electrophilic addition reactions.
- **Spectral Properties:** The delocalization of π -electrons affects UV-Visible absorption (used in spectroscopy).

Benzene as a Resonating Alkene

- Benzene (C_6H_6) is a special case: a cyclic conjugated alkene.
- Resonance structures show alternating double and single bonds, but the actual molecule has equal bond lengths and is aromatic, with 6 π -electrons delocalized over the ring.

Hyperconjugation

Definition

- Hyperconjugation is the delocalization of sigma (σ) electrons, typically from C–H or C–C sigma bonds, into adjacent empty or partially filled p-orbitals or π -systems.
- It is often described as an extension of resonance, though it involves σ -electrons instead of π -electrons.

Mechanism of Hyperconjugation

- It involves the overlap of a filled σ -orbital (usually C–H or C–C bond) with an adjacent empty p-orbital, π -antibonding orbital*, or positive charge (like in carbocations).
- This leads to delocalization of electrons, which stabilizes the molecule or ion.

Examples of Hyperconjugation

1. Carbocations:

- **Example:** Tertiary carbocations are more stable than secondary or primary due to more hyperconjugative structures.
- In CH_3^+ , no hyperconjugation possible.
- In $(\text{CH}_3)_3\text{C}^+$, the methyl groups have C–H bonds that donate electron density via hyperconjugation.

2. Alkenes:

- Alkyl groups attached to a double bond stabilize the alkene through hyperconjugation.
- **Example:** Propene ($\text{CH}_3\text{--CH=CH}_2$) shows hyperconjugation of C–H σ -electrons of methyl group with the adjacent π -bond.

3. Free Radicals:

- Similar to carbocations, free radicals (like $\text{CH}_3\bullet$) are stabilized by hyperconjugation.

Significance of Hyperconjugation

- Stabilization of carbocations, free radicals, and alkenes.
- Explains the order of stability:
 - Carbocations: $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$
 - Alkenes: Tetra-substituted > Tri-substituted > Di-substituted > Mono-substituted
- Contributes to the planarity and bond length shortening in certain compounds.
- Affects reaction mechanisms, especially in E1 and SN1 reactions.

Difference Between Resonance and Hyperconjugation

Feature	Resonance	Hyperconjugation
Electrons involved	π -electrons or lone pairs	σ -electrons (C–H or C–C)
Type of orbital overlap	π to π or lone pair to π	σ to p or σ to π^*
Need for conjugation	Yes (π -system or lone pair)	Yes (σ -bond adjacent to vacant/ π orbital)
Structures formed	Canonical forms	Not drawn explicitly but implied
Involves charges?	Often	Often

Allyl Radical as a Resonance Hybrid

What is an Allyl Radical?

- The allyl radical is a type of organic free radical with the formula $\text{CH}_2=\text{CH--CH}_2\bullet$.

- It consists of:
 - A carbon-carbon double bond ($C=C$)
 - An adjacent carbon-centered radical ($\bullet$)
- The unpaired electron resides on the sp^3 -hybridized carbon next to the double bond.
- This radical is an example of a conjugated system, where a p-orbital containing the unpaired electron can overlap with the π -system of the adjacent double bond.

Resonance Structures of Allyl Radical

- Because of this conjugation, the unpaired electron can be **delocalized** over multiple atoms through resonance.

There are two major resonance structures for the allyl radical:

1. Structure A:

- $CH_2=CH-CH_2\bullet$
- Double bond between C1 and C2
- Radical on C3

2. Structure B:

- $\bullet CH_2-CH=CH_2$
- Double bond between C2 and C3
- Radical on C1

- These resonance structures indicate that the unpaired electron is not localized on a single carbon atom but is shared (delocalized) between the terminal carbon atoms (C1 and C3).

Resonance Hybrid

- The actual structure is a resonance hybrid of these two canonical forms.
- In this hybrid:
 - The unpaired electron is delocalized between C1 and C3.
 - C2 (the middle carbon) is part of both π -bonds in different structures.
 - The bond orders between C1–C2 and C2–C3 are intermediate (between single and double).
- The delocalization stabilizes the allyl radical significantly compared to a localized radical.

Stability

- The delocalization of the unpaired electron results in resonance stabilization, which makes the allyl radical more stable than non-conjugated alkyl radicals.
- The greater the extent of delocalization, the greater the stability.



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