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 (~1.39 Å), 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 ($CH_2=CH–CH=CH_2$):

- 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:

$$CH_2=CH–CH=CH_2 \leftrightarrow {}^-CH_2–CH=CH^+–CH_2^- \text{ (in ionic form under certain reactions)}$$

2. Allyl Carbocation ($CH_2=CH–CH_2^+$):

- Has resonance between:

$$CH_2=CH–CH_2^+ \leftrightarrow CH_2^+–CH=CH_2$$

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

3. Allyl Anion ($CH_2=CH–CH_2^-$):

- Resonance between:

$$CH_2=CH–CH_2^- \leftrightarrow {}^-CH_2–CH=CH_2$$

- 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 $(CH_3)_3C^+$, 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 (CH_3–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 CH_3•) are stabilized by hyperconjugation.

Significance of Hyperconjugation

- Stabilization of carbocations, free radicals, and alkenes.
- Explains the order of stability:
  - Carbocations: 3° > 2° > 1° > 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 CH_2=CH–CH_2•.

- It consists of:
  - A carbon-carbon double bond (C=C)
  - An adjacent carbon-centered radical (•)
- 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•
   - Double bond between C1 and C2
   - Radical on C3
2. **Structure B:**
   - •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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