

# Resonance

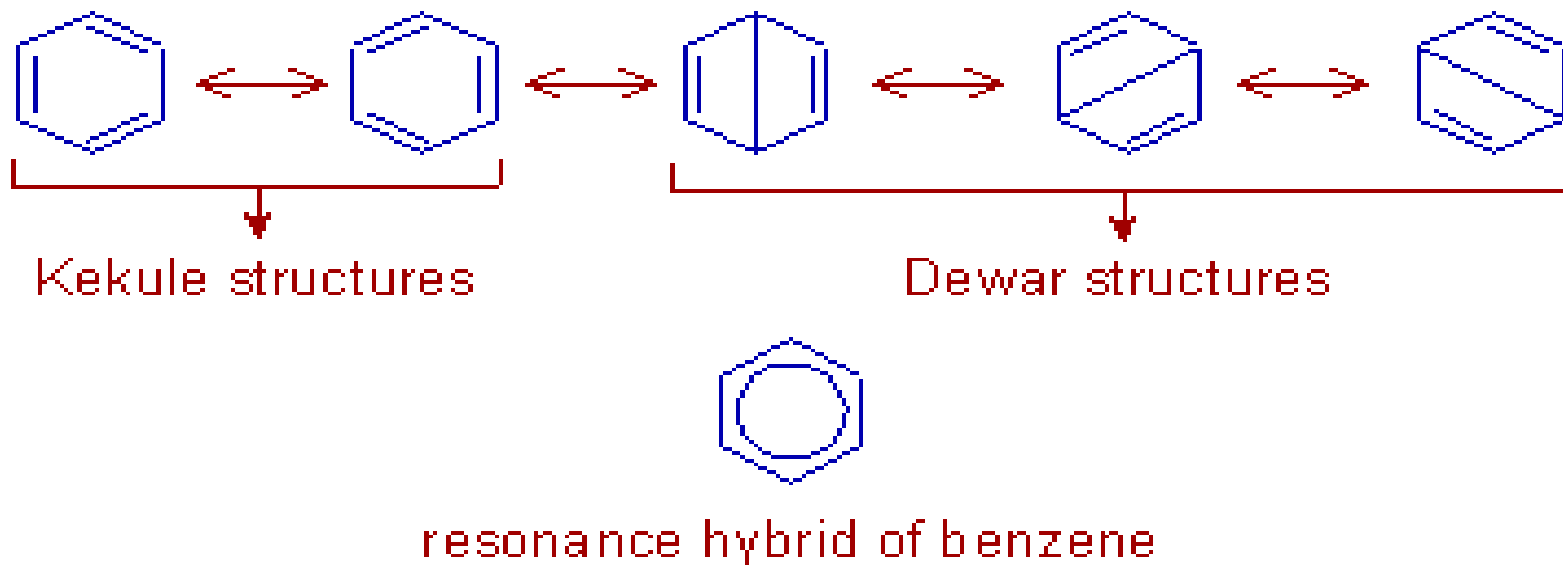
- Resonance structures are a way of understanding the positioning of electrons. This is a vital topic for chemists, as understanding where electrons are located within the molecule is the key to understanding the molecule's chemical behavior. You can't really say anything about chemical reactivity or chemical properties without knowing what parts of the molecule are electron-rich (containing a large density of electrons) and which are electron-poor

# RESONANCE

- **Defination.**
- When a compound can be represented by more than one Lewis structure and actual structure is hybrid of all structures, the compound is said to possess Resonance
- OR
- The representation of structure of a molecule as a weighted average of two or more hypothetical structures, which only differ by the arrangement of electrons but with same positions for atoms is referred to as resonance.

# EXAMPLES OF RESONANCE STRUCTURES

- The following resonance structures can be written for benzene which are hypothetically possible due to delocalization of  $\pi$  electrons. The Kekule structures have more weightage than Dewar structures.



The actual structure of benzene is thus shown to be the hybrid of these contributing structures. The bond order of every C-C bond is 1.5 and hence the every C-C bond length is reported to be same and equals to 1.39 Å, which is in between the bond length values of C-C single bond (1.54 Å) and C=C double bond (1.20 Å).

Due to resonance, benzene gets extra stability and does not undergo electrophilic addition reactions. However it shows electrophilic substitution reactions. This phenomenon is known as aromaticity.

# Features of resonance:

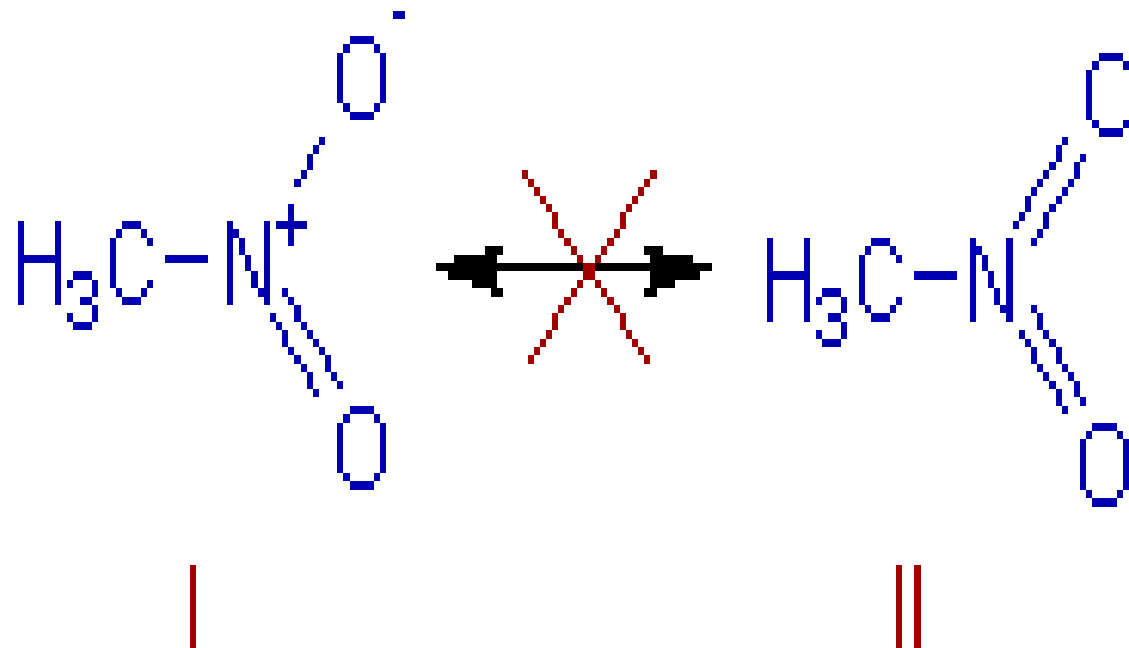
- \* The hypothetical structures with different arrangement of electrons but with identical positions for atoms are called resonance structures or canonical forms or contributing structures.
- \* The resonance structures are only imaginary and the actual structure of the molecule is considered as the hybrid of all the valid resonance structures.

# Features of resonance

- \* The resonance structures are formed (only on paper) due to delocalization of electrons and not by changing the positions of atoms.
- \* The delocalization of electrons is shown using curved arrows.
- \* The energy of resonance hybrid is always less than the energy of any of the contributing resonance structure.

# RULES OF RESONANCE

- The valid resonance structures must satisfy the following rules:
- \* They must be valid Lewis structures obeying octet rule.
- E.g. Carbon or Nitrogen with five bonds is not allowed.
- In the structure (II), the nitrogen atom violated the octet. It has 10 electrons around it.

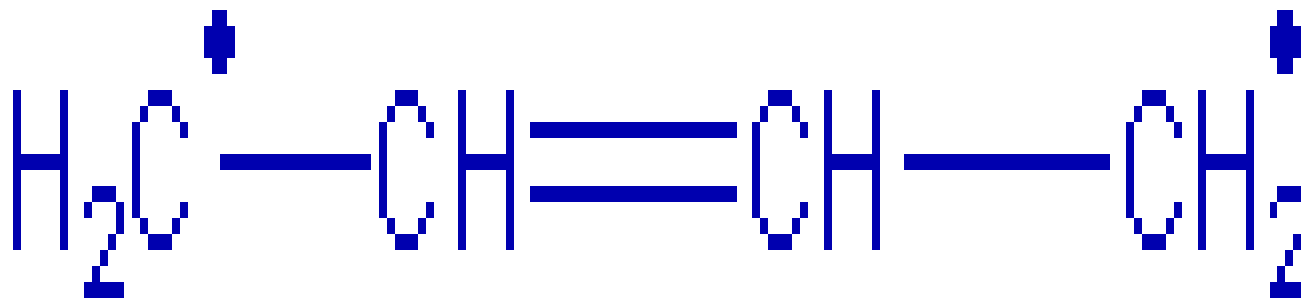


Not a valid structure  
since the valency of  
nitrogen is exceeded to 5

\* They should possess same number of electrons and equal net charge.

\* The number of unpaired electrons in them must be same.

E.g. Following structure for butadiene is not valid.



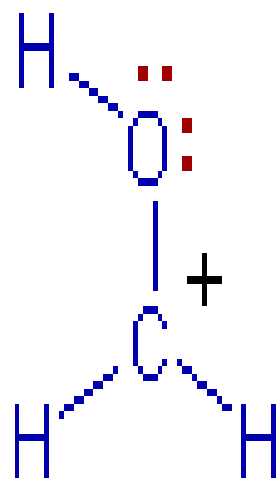
# STABILITY OF RESONANCE STRUCTURE

- \* The actual structure i.e., resonance hybrid of a molecule has lower energy than any of the contributing form and hence the resonance is a stabilizing phenomenon.
- \* Greater the number of contributing structures, greater is the stability of the resonance hybrid.
- \* All the structures do not contribute equally to the hybrid.
- \* Greater the stability of a resonance structure, larger is its contribution to the resonance hybrid.

\* The contributing structures that have atoms with full octets are more stable than the ones with open octets.

\* The contributing structure with more covalent bonds is more stable.

E.g. Among the following, the structure II is more stable since all the atoms have octet configuration and there are more covalent bonds.

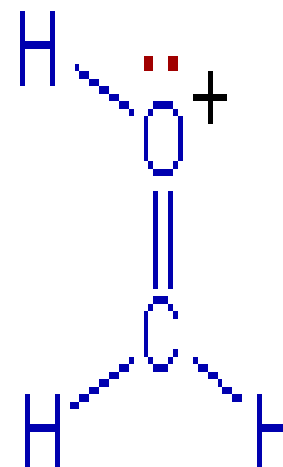


I

less stable

carbon with sextet

less number of covalent bonds



II

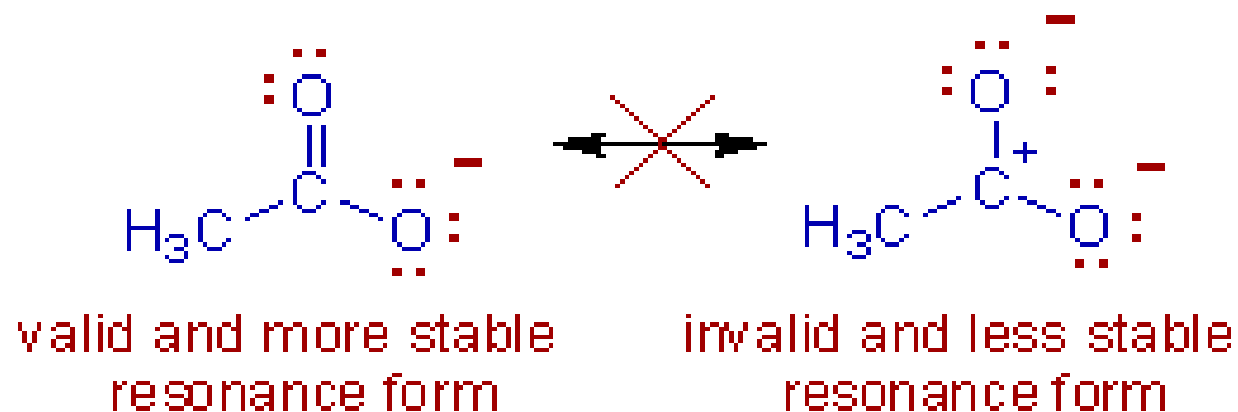
more stable

all atoms are with octet

more number of covalent bonds

# STABILITY

- \* Resonance structures with fewer charges are more stable than those with more charges.
- E.g. The second structure with two negative charges is not only less stable.



# RESONANCE EFFECT

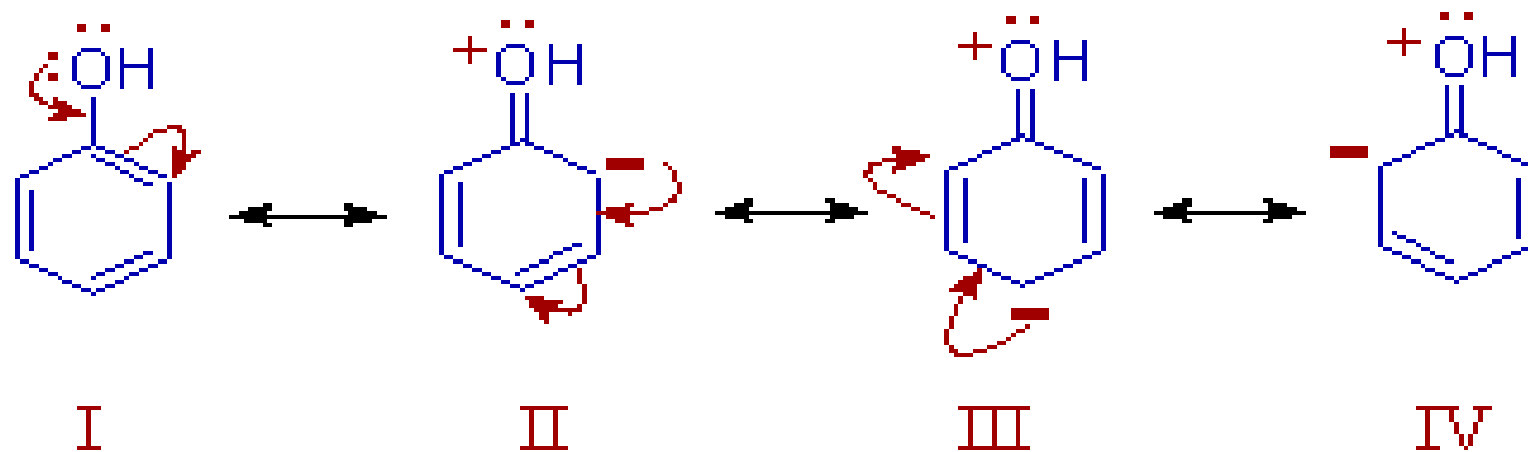
- The increase in electron density at one position with a corresponding decrease at another position is called resonance effect
- It is symbolized by M or R.
- Negative resonance or mesomeric effect (-M or -R)
- E.g. -NO<sub>2</sub>, Carbonyl group (C=O), -C≡N, -COOH, -SO<sub>3</sub>H etc.

Positive resonance or mesomeric effect (+M or +R): The groups show positive mesomeric effect when they release electrons to the rest of the molecule by delocalization. These groups are denoted by +M or +R. Due to this effect, the electron density on rest of the molecular entity is increased.

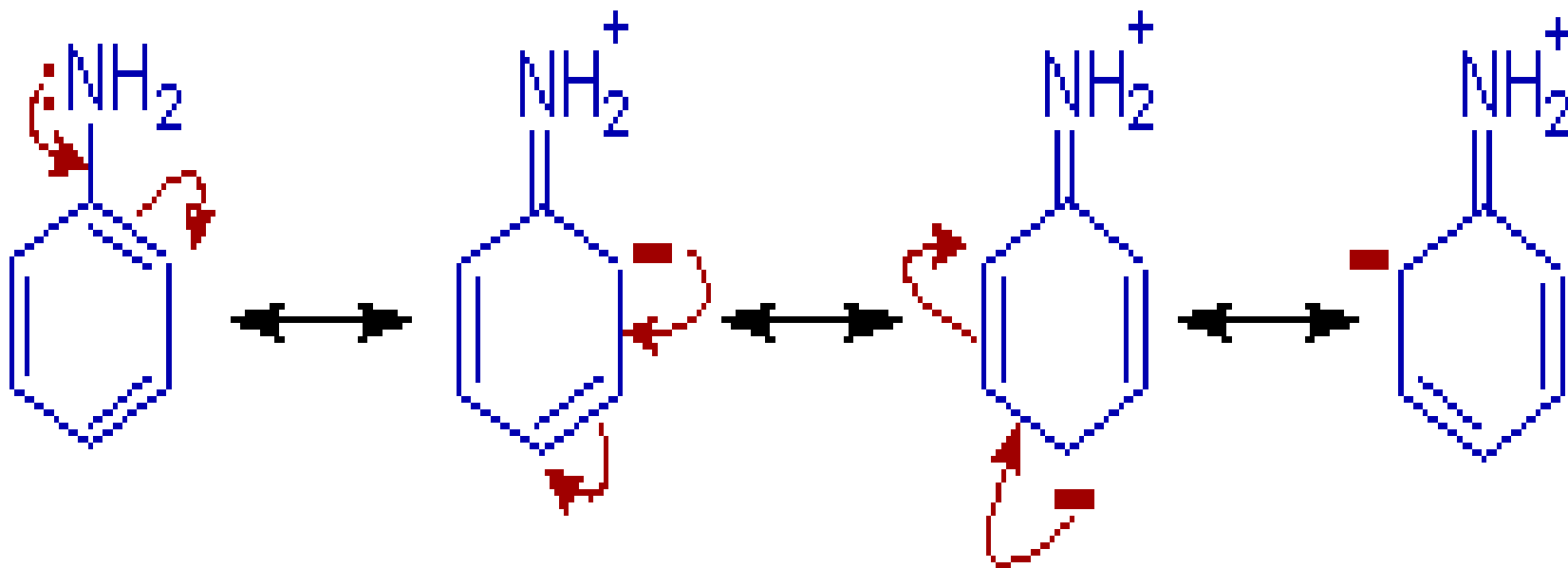
E.g. -OH, -OR, -SH, -SR, -NH<sub>2</sub>, -NR<sub>2</sub> etc.

# +M or +R EXAMPLES

- 1-In phenol, the -OH group shows +M effect due to delocalization of lone pair on oxygen atom towards the ring. Thus the electron density on benzene ring is increased particularly on ortho and para positions.

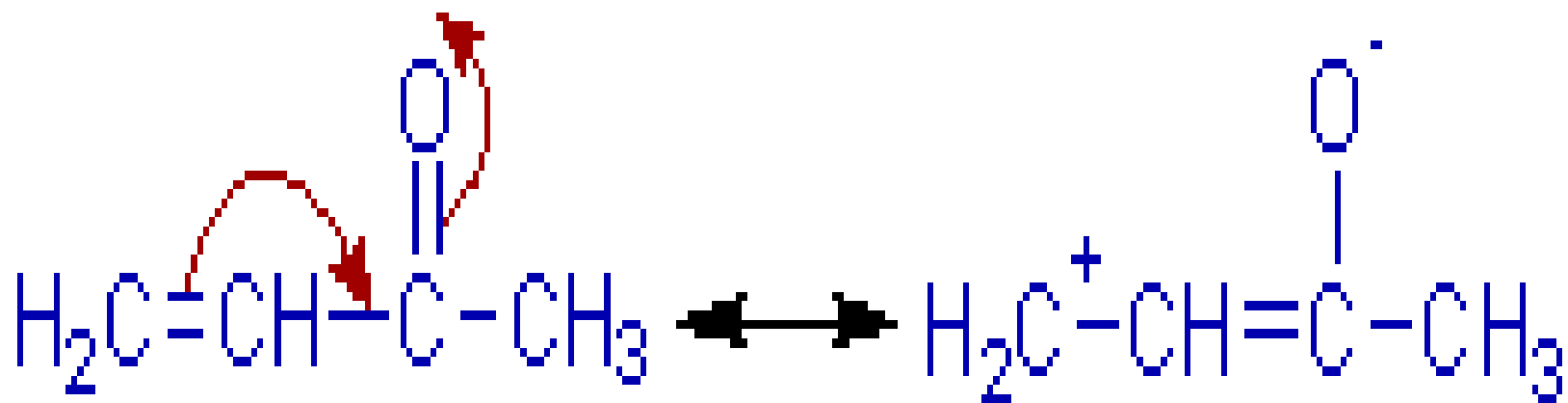


2-The  $\text{-NH}_2$  group in aniline also exhibits +R effect. It releases electrons towards benzene ring through delocalization. As a result, the electron density on benzene ring increases particularly at ortho and para positions. Thus aniline activates the ring towards electrophilic substitution.

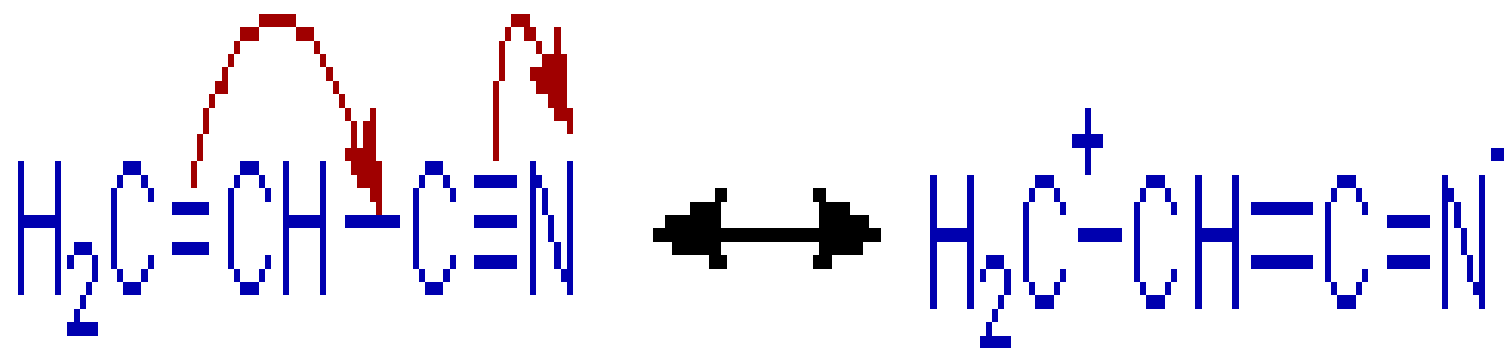


# -M or -R EXAMPLES

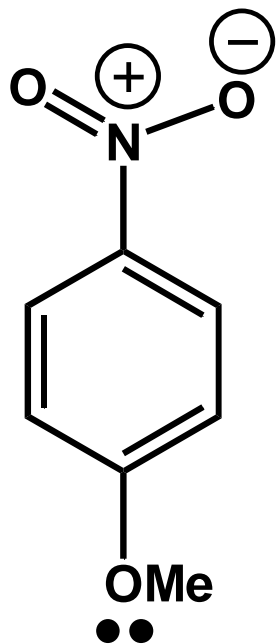
- 1) The negative resonance effect (-R or -M) of carbonyl group is shown below. It withdraws electrons by delocalization of  $\pi$  electrons and reduces the electron density particularly on 3rd carbon.



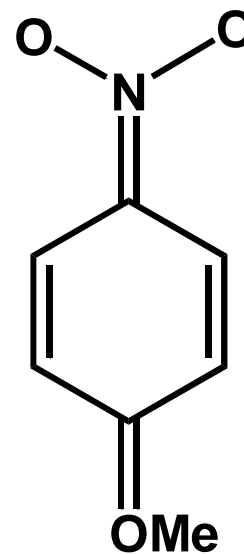
2) The negative mesomeric effect (-R or -M) shown by cyanide group in acrylonitrile is illustrated below. The electron density on third carbon decreases due to delocalization of  $\pi$  electrons towards cyanide group.



# Answer 1: Resonances



A



B



The 4-methoxybenzyl bromide **A** undergoes C-Br bond cleavage much more easily to generate the benzyl cation **B**, than does the C-Br bond in benzyl bromide in question 3. Identify **B** and then draw in the curly arrows that lead to the resonance structure **C**.

