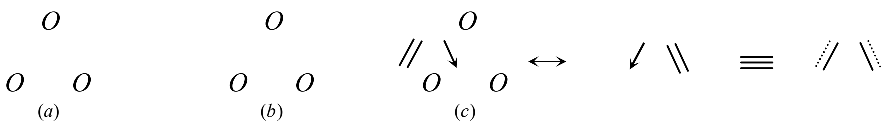
Resonance.

The phenomenon of resonance was put forward by Heisenberg to explain the properties of certain molecules.

In case of certain molecules, a single Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecule. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.

To illustrate this, consider a molecule of ozone O_3. Its structure can be written as



It may be noted that the resonating structures have no real existence. Such structures are only theoretical. In fact, the actual molecule has no pictorial representation. The resonating structures are only a convenient way of picturing molecule to account for its properties.

As a resonance hybrid of above two structures (a) and (b). For simplicity, ozone may be represented by structure (c), which shows the resonance hybrid having equal bonds between single and double.

Resonance is shown by benzene, toluene, O3, allenes (>C = C = C<), CO, CO2, CO_3^-, SO3, NO, NO2 while it is not shown by H2O2, H2O, NH3, CH4, SiO2.

(1) Conditions for writing resonance structures

The resonance contributing structures :

(i) Should have same atomic positions.

(ii) Should have same number of bond pairs and lone pairs.

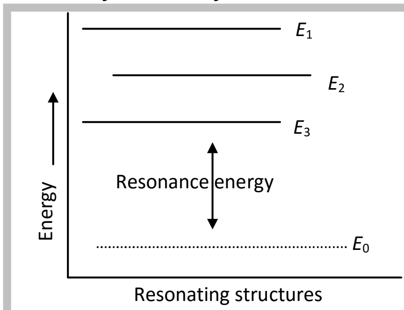
(iii) Should have nearly same energy.

(iv) Should be so written such that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom.

(v) The like charges should not reside on adjacent atoms. But unlike charges should not greatly separated.

(2) Characteristics of resonance

(i) The contributing structures (canonical forms) do not have any real existence. They are only imaginary. Only the resonance hybrid has the real existence.



Concept of resonance energy. Energies E_1, E_2 and E_3 for three structures and E_0 is the

(ii) As a result of resonance, the bond lengths of single and double bond in a molecule become equal e.g. O–O bond lengths in ozone or C–O bond lengths in CO_3^{2-} ion.

(iii) The resonance hybrid has lower energy and hence greater stability than any of the contributing structures.

(iv) Greater is the resonance energy, greater is the stability of the molecule.

(v) Greater is the number of canonical forms especially with nearly same energy, greater is the stability of the molecule.

(3) Resonance energy

It is the difference between the energy of resonance hybrid and that of the most stable of the resonating structures (having least energy). Thus,

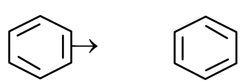
Resonance energy = Energy of resonance hybrid – Energy of the most stable of resonating structure.

(4) Bond order calculation

In the case of molecules or ions having resonance, the bond order changes and is calculated as follows:

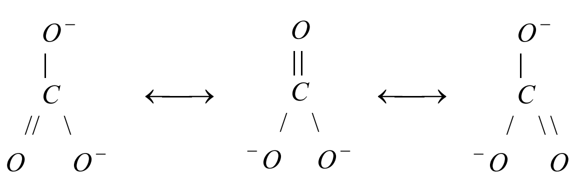
$$\text{Bond order} = \frac{\text{Total no. of bonds between two atoms in all the structures}}{\text{Total no. of resonating structures}}$$

e.g., (i) In benzene



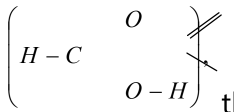
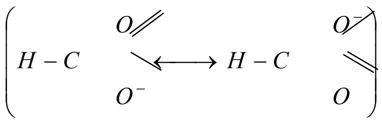
$$\text{Bond order} = \frac{\text{double bond} + \text{single bond}}{2} = \frac{2+1}{2} = 1.5$$

(ii) In carbonate ion



$$\text{Bond order} = \frac{2+1+1}{3} = 1.33$$

Important Tips

- Resonance structure (canonical form) must be planar.
- In case of formic acid  the two $C-O$ bond lengths are different but in formate ion  the two $C-O$ bond lengths are equal due to resonance.
- In resonance hybrid, the bond lengths are different from those in the contributing structure.
- Resonance arises due to delocalisation of π electrons. Resonating structures have different electronic arrangements.
- The resonating structures do not have real existence.
- Resonance energy = [Experimental heat of formation]–[Calculated heat of formation of most stable canonical form].
- Three contributing structure of CO_2 molecule are – $O=C=O \leftrightarrow \overset{+}{O}\equiv C-\overset{-}{O} \leftrightarrow \overset{-}{O}-C\equiv \overset{+}{O}$
- Resonance structure of carbon monoxide is $:C=\ddot{\underset{..}{O}} \leftrightarrow :C\overset{\leftarrow}{=}O:$
- Resonance energy of benzene is $152.0\ kJ/mol$.