STUDY MATERIAL

VIVEKANANDA COLLEGE
THAKURPUKUR

NAAC ACCREDITED GRADE—'A'

Subject: Organic Chemistry

Topic: Resonance

Name of the Teacher: Yasin Nuree

Introduction

Chemists developed Lewis structures to understand qualitatively the structures of molecules, ions or radicals. For a great many molecules and ions, a single Lewis structure provides a truly accurate representation, but this is not sufficient for many other compounds. The carbonate ion is an example.

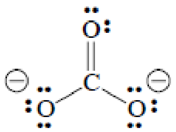

Fig 1.1

From the above structure, it is obvious that all oxygen atoms are not equivalent. Two of the oxygen atoms each bear a formal charge of –1, giving the ion a total charge of –2. The structure also implies that one carbon-oxygen bond is different from the other two. However, experimental evidence demonstrates that this structure is not in consistent with the above structure, and hence not an accurate representation of the molecule. Instead, the evidence shows that the ion has three identical C—O bonds, that each O—C—O angle measures 120^o, and that each of the three oxygen atoms bears the same amount of negative charge. So the problem was how to represent the molecules or ions or radicals, accurately. To solve this problem, theory of resonance was proposed by Linus Pauling.

Theory of Resonance

The theory of resonance was mainly developed by Pauling in 1930s. A molecule or ion or radical can be represented by more than one legitimate Lewis structures. The actual structure is considered to be properly weighted hybrid or average of all these Lewis representations. Each Lewis structure is called as canonical form or resonating structure or resonance contributor and the molecule is said to show resonance. According to the theory of resonance, there is no real existence of the canonical forms. The real molecule or ion is a resonance hybrid of the various contributing structures. The contributing structures are drawn by interconnecting them with double-headed (⟷) arrows. Do not confuse the double-headed arrow with the double arrow used to show chemical equilibrium (remember resonance structures are not in equilibrium with each other). Now we are going back to solve the anomalies in carbonate anion. The carbonate ion is represented as a resonance hybrid of three equivalent contributing structures shown below.

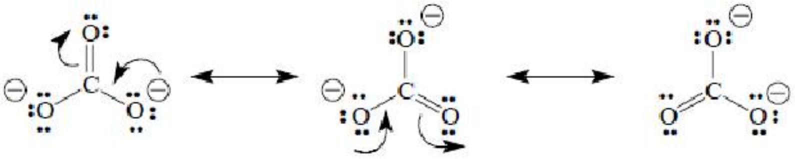

Fig 1.2

The three resonance contributors of the carbonate ion are equivalent. That is, they all have equal energy and contribute equally to the structure of the ion. A more accurate drawing of the carbonate ion shows the bonds using a combination of solid and dashed lines indicating that the bonds fall somewhere between single and double bonds (see Fig 1.3, *each oxygen bears 2/3 of a negative charge)*.

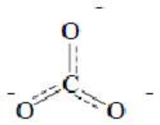

Fig 1.3

How to draw resonating structures

There are are certain rules for writing acceptable contributing structures. These are

1. Each canonical form must be a legitimate Lewis structure. For example, none of them may have a carbon with five bonds.
2. The relative positions and the geometrical arrangement of all nuclei must be the same in all contributing structures, to ensure that contributing structures differ only in the distribution of valence electrons.
3. All resonance contributors must have the same number of paired and unpaired electrons. Thus $^{\bullet}CH_2{-}CH{=}CH{-}CH_2{\bullet}$ is not a valid canonical form for butadiene.
4. All the atoms participating in resonance must lie in a plane or nearly. Coplanar arrangement of the participating atoms is required for overlap of the p-orbitals in parallel orientation.
5. The energy of the canonical forms must not differ widely.
6. Each canonical form contributes to the actual structure based upon their relative stability.

7. The energy of the actual molecule is lower than that of any canonical form, obviously. Therefore, delocalization is a stabilizing phenomenon.

Now we have to learn how to predict the relative contribution of each resonating structures towards the resonance hybrid.

Relative contribution of resonating structures

Not all structures contribute equally to a resonance hybrid. Each form contributes in proportion to its stability, the most stable form contributing most.

1. Equivalent canonical forms being energetically similar, contribute equally. For example, three canonical structures of carbonate ion are structurally and hence energetically equivalent, so their contributions to the resonance hybrid are also equivalent.
2. Structures with a greater number of covalent bonds contribute more than those with fewer covalent bonds. As for example: The structure on the left has eight covalent bonds and makes the greater contribution to the hybrid.

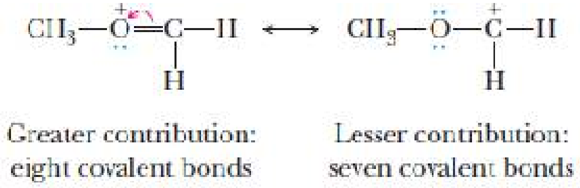

Fig 1.4

3. The aromatic structures contribute more over the non-aromatic structures among the canonical forms with same number of covalent bonds.
4. Among structures with equal number of covalent bonds, the neutral structure contributes more than the charge separated canonical form.
5. For charged structures, the (–)ve charge on more electronegative atom or (+)ve charge on less electronegative atom makes them greater contributors towards the actual hybrid.
6. Lastly, we have to consider the distance between the charges in the resonating structures. Proximity of the opposite charges makes the structure more stable, hence the greater contributor, over the structure with opposite charges at distal atoms. On the contrary, the close proximity of the like charges destabilizes the structure making it less

contributor to the hybrid.

Let us take an example to clarify the above points. The resonating structures of acrylate anion have been shown below.

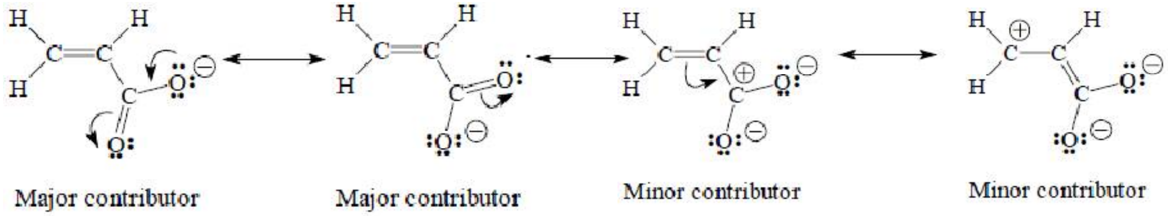

Fig 1.5

The first two resonance contributors have equal numbers of bonding and nonbonding electrons and equal numbers of charges. Thus, they are equivalent structures. The third and fourth structures have an increase in the number of charges giving them higher energy levels. They are minor contributors to the structure of this anion.

Resonance energy and resonance stabilization in different systems

Energy of the resonance hybrid is less than the theoretically calculated energy of the most stable or most contributing canonical form. Hence, resonance is a stabilizing phenomenon. Resonance stabilization can be measured using resonance energy which is defined as the the difference in energy between the theoretically calculated energy of the most stable canonical form and the experimentally determined energy of the true species or resonance hybrid.

However, to qualitatively predict the resonance stabilization in different molecules or ions or radicals the following rule may be useful.

1. Resonance energy of aromatic systems is always greater than the analogous nonaroamatic systems.
2. The system with equivalent resonating structures is more stable than the system with non-equivalent canonical forms.
3. Greater the number of legitimate canonical forms, greater will be the resonance energy of the hybrid and hence the stability of the actual structure will also be higher, in similar type of systems.

4. The system with extended conjugation will have greater resonance energy than cross-conjugated systems.

Steric inhibition of resonance

When resonance is reduced or prevented because the atoms are sterically forced out of planarity, the phenomenon is termed as the steric inhibition of resonance. The C-N bond lengths at *ortho*- and *para*- postions in picryl iodide are not equal. This phenomenon can be explained by the concept of the steric inhibition of resonance. The oxygens of the *p-nitro* group are in the plane of the ring and thus in resonance with it, so the *para*- C-N bond has partial double-bond character. On other hand, the oxygens of the *o-nitro* groups are forced out of the plane by the steric repulsion of large iodine atom, inhibiting the resonance.

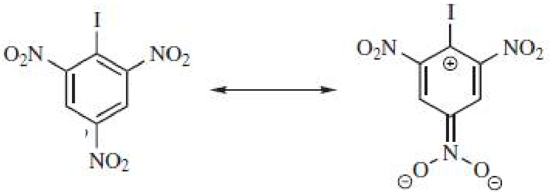

Fig 1.6 Picryl iodide

References and further reading

1. Gasteiger, Saller; *Angew. Chem. 97, 699*.
2. March, Jerry; *Advanced organic Chemistry, 4th Ed.*
3. Clayden, Jonathan; Warren, Stuart; Greeves,Nick; *Organic Chemistry, OUP*.
4. Mukherjee, R; Ghosh, D.C.; *Organic Chemistry, Structure*.