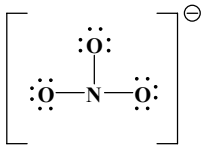
Organic Chemistry Web Review III

Resonance

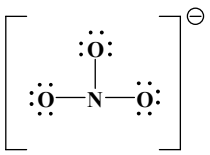
When the Lewis Model Start to Get Into Trouble

Let's Look at the Nitrate Ion, NO_3^{1-}

- There are 24 electrons to place
- Once we connect the atoms, we place the 18 additional electrons on the oxygen atoms
- This leaves nitrogen deficient in electrons with only 6

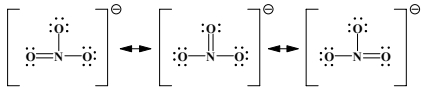


The Next Step Is to Use Unshared Pairs to Make a Double Bond



Which Unshared Pair? Does It Matter?

It Doesn't Really Matter Which You Use Because:



- They are all equivalent
- The structures formed would be identical
- The structure formed doesn't really describe nitrate very well anyway
- The real nitrate is probably a "blend" of all three possible structures

Here is What Is Wrong with This Lewis Structure

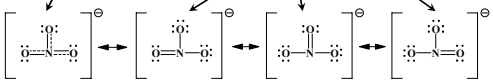
- All bonds in nitrate are the same length, not two long and one short bond (All 1.33X longer than a single bond)
- All bonds are the same strength, not one stronger and two weaker (All 1.33X stronger than a single bond)
- The nitrate ion is much more stable than one would calculate base upon this structure

What Is Happening Here is Resonance

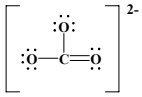
Anytime You Have to Make a Similar Choice as to Which Electrons You Should Use to Make the Needed Double Bond, You Will Have Resonance

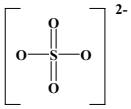
The Actual Molecule Will Be More Like a "Blend" of the Multiple Possible Structures

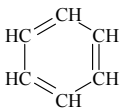
We The Actual Structure the Resonance Hybrid and the Individual Structures Resonance Forms



Some Species With Resonance







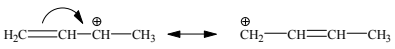
Rules For Writing Resonance Structures

Resonance is something that we deal with frequently in organic chemistry. For this reason it is important that you understand how to determine and write the resonance forms of a given molecule

Resonance Structures Exist ONLY on Paper

Although We Cannot Use Drawings on Paper to Adequately Represent Molecules With Resonance, Drawing Resonance Forms Allows to Make Predictions and Helps Us Understand the Reactivity of Organic Chemical Compounds

In Writing Resonance Structures We Are Only Allowed to Move Electrons



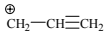
We Can Never Change the Connectivity of the Atoms of the Compound

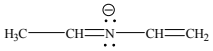
When Moving Electrons:

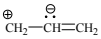
- The electron(s) moved must remain in association with at least one of the atoms with which it (they) was associated with before the move
- For 2-electron moves, you essentially make a double bond from an unshared pair, an unshared pair from a double bond, or move the position of a double bond

All of the Structures Must Be Proper Lewis Structures

The structures below are NOT proper Lewis Structures. Why?





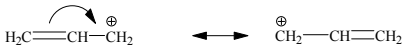


The Energy of a Molecule or Ion That Has Resonance Is Always Lower Than Might Be Predicted

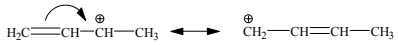
The measured energy of a sulfate ion is lower than would be calculated by a consideration of the atoms and bonds in the ion. This is because the ion has Energy of Resonance Stabilization.

Equivalent Resonance Structures Contribute Equally to the Overall Structure

The ion below can be "thought of" as existing equally in one of the two resonance forms shown, spending half of the time in one form and half in the other. Remember, only on paper.



Non-equivalent Forms Do Not Contribute Equally to the Final Structure



You will learn later that the structure on the left is more stable than the structure on the right. We can imagine the ion spending a greater percentage of time as the structure on the left.

The More Resonance Forms You Can Write For a Given Molecule, the More Stable the Molecule

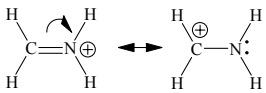
2 resonance forms

1 resonance form

(hydrogen atoms not shown)

The first ion is more stable than the second as we can draw more resonance forms.

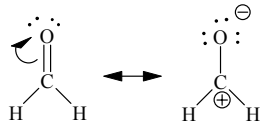
The More Covalent Bonds a Structure Has the More Stable It Is



More Stable

Less Stable

Resonance forms in which atoms have less than an octet of electrons contribute less to the final structure that forms where all atoms have an octet



The structure on the right is also less stable because it has charge separation

Summary of Rules for Resonance

- Resonance structures exist only on paper
- In writing resonance structures we are only allowed to move electrons
- All of the structures we write must be "proper" Lewis structures
- The energy of a molecule or ion that has resonance is always lower than might be predicted

Summary of Rules for Resonance, Continued

- Equivalent resonance structures contribute equally to the overall structure
- Non-equivalent forms do not contribute equally to the final structure
- The more resonance forms you can write for a given molecule, the more stable the molecule
- The more covalent bonds a structure has, the more stable it is

Summary of Rules for Resonance, Continued

- Resonance forms in which atoms have less than an octet of electrons contribute less to the final structure that forms where all atoms have an octet
- Charge separation decreases stability

End Review III