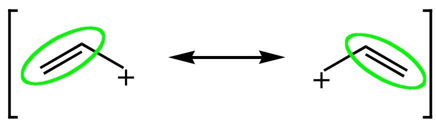
Resonance Structures

When to use them and what they mean

Resonance structures are needed when the line structure for a compound doesn't accurately portray the bonds present in the molecule. This most commonly occurs when the p orbital on a charged atom or radical overlaps with one or more pi bonds next to it, spreading the charge around and stabilizing the molecule.

Resonance structures are always shown in brackets, and have a double-headed arrow between them.

Resonance structures



Actual compound

the pi bond is actually spread over all three atoms

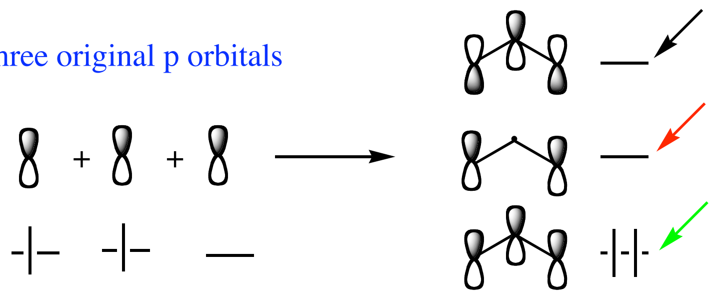
the + charge is shared by both of the atoms on the end

Resonance structures are an approximation of the actual molecular orbitals; the true characteristics of the compound are a blending of the individual resonance structures.

The true picture involves molecular orbitals in which pi bonds are spread over three or more atoms. As a result, pi bonds and lone electron pairs (and the resulting positive or negative charges) may also be spread over more than one atom.

three new pi orbitals

three original p orbitals



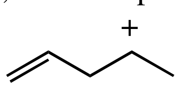
the top (antibonding) pi orbital is empty

the nonbonding pi orbital where the third electron should be is empty - the positive charge is on the two end atoms

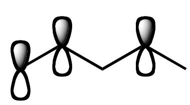
both electrons go to the lowest energy pi orbital which includes all three atoms

Since there is a positive charge, one electron has been lost.

Resonance structures may only occur when the p orbitals are next to each other. If there is an sp^3 atom in between, no overlap can happen.

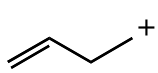


no resonance

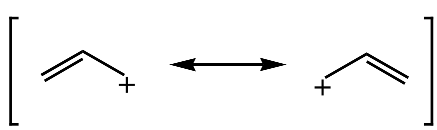


p orbitals can't overlap

Compounds with resonance structures are always more stable than similar compounds that don't have resonance structures.

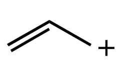


no resonance structures
less stable

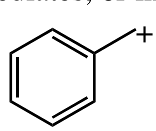


stabilized by resonance

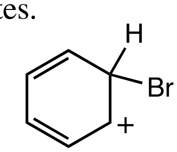
Resonance structures most often occur cations, radicals, and anions which are allylic or benzylic, in aromatic reaction intermediates, or in enolates.



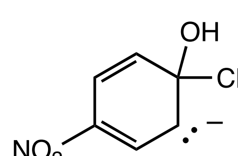
allylic
Ch 15



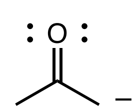
benzylic
Ch 16



electrophilic aromatic substitution
Ch 16



nucleophilic aromatic substitution
Ch 16

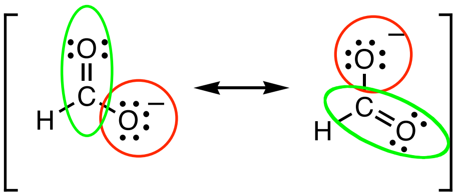


enolates
Ch 18

Equal, greater, or lesser resonance contributors

If all of the resonance structures are equal in energy, then they all contribute equally to the actual compound.

Resonance structures

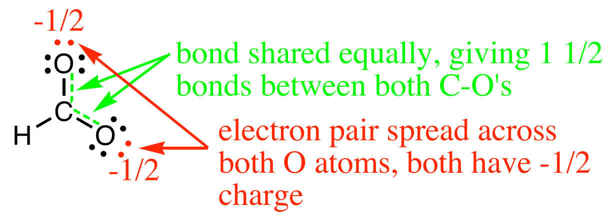


both have a C=O

both have a negatively charged O

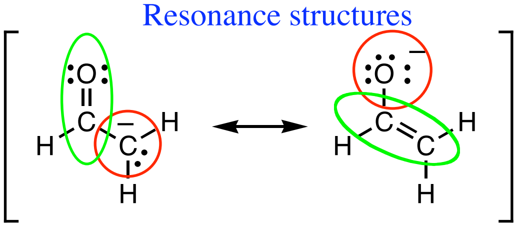
equal resonance contributors

Actual compound



If one or more of the structures are lower in energy (more stable), they will contribute more to the actual compound; that is to say, the actual compound will be more like them. These are called "greater resonance contributors". The structures which are higher in energy (less stable) will contribute less to the actual compound; it will be less like them. They are called "lesser resonance contributors".

Resonance structures



negatively charged O
more stable

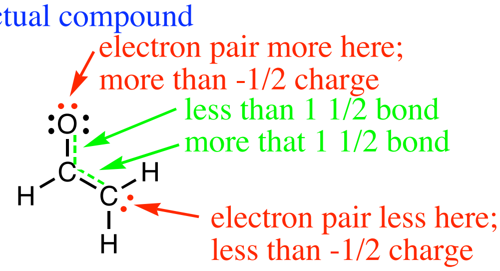
negatively charged C
less stable

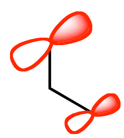
C=O about the same as C=C

lesser resonance contributor

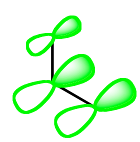
greater resonance contributor

Actual compound





pi bond with lone electron pair is larger on O

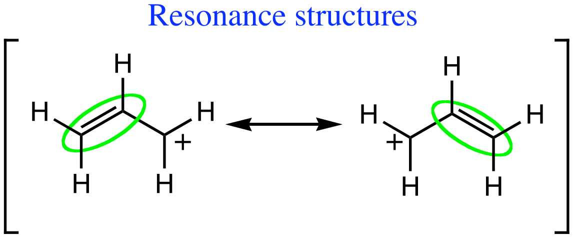


pi bond across all three is larger on the two C's

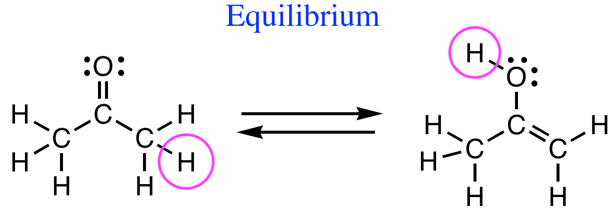
Difference between resonance and equilibrium

The compound represented by two or more resonance structures is not going back and forth between these structures; rather it is a blending of the structures. On the other hand, an equilibrium involves an actual change in the molecule; it is represented by two arrows in opposite directions, rather than a double-headed arrow, and has no brackets.

Resonance structures



Equilibrium



In an equilibrium, atoms change positions; in a set of resonance structures, only electrons appear to move (they are actually spread out). Atoms cannot occupy two places at once, while electrons are waves which can be spread over several nuclei.