Chemistry 334

Principles of Resonance

Many chemical species can be represented quite accurately by a single Lewis structure. Other chemical species cannot be represented so simply. The real system must be visualized as a hybrid of a multiple number of Lewis structures, called resonance structures, or canonical forms. This situation is depicted by chemists by the following shorthand:

$$\mathbf{A} \longleftrightarrow \mathbf{B} \longleftrightarrow \mathbf{C} \longleftrightarrow \mathbf{D}$$

Structures A, B, C and D are canonical forms that contribute to the overall resonance hybrid. If one knows the wave function, ψ_i, for each canonical form, one can express the wave function, Ψ, of the resonance hybrid as the sum of the (appropriately weighted) individual canonical forms' wave functions:

$$\Psi = \Sigma c_i\psi_i = c_a\psi_a + c_b\psi_b + c_c\psi_c + c_d\psi_d$$

ψ_i = wave function of canonical form_i

c_i = coefficient of the wave function of canonical form_i

A number of general principles govern the resonance stabilization of chemical species:

1. All canonical forms must be proper Lewis structures.
2. The positions of the nuclei remain constant from one canonical form to another.
   Only the electrons move.
3. All atoms involved in the resonance lie in or near to a single plane, to allow for maximum p-orbital overlap. This constraint is not required of atoms that are not involved in the electron delocalization.
4. All canonical forms must possess the same number of unpaired electrons.

5. If one can draw a greater number of reasonable canonical forms, the overall hybrid is more stable.
6. Resonance stabilization is significant when the relative energies of the individual canonical forms are approximately the same. Conversely, if a system can be represented, for example, by only two canonical forms, one of which is much higher in energy than the other one, resonance essentially does not exist.
7. As mentioned above, the actual molecule is a hybrid of all these canonical forms. It is not a rapidly interconverting mixture of different compounds.
8. Each canonical form contributes to the overall hybrid, the more "stable" one(s) contributing more. (N.B. Each canonical form is a hypothetical species which, of course, cannot be isolated! Why?)
   a. Stability is increased with a greater number of covalent bonds.
   b. Stability is decreased with an increased charge separation.
   c. Multiply charged species (e.g. 2^+, 2^-, etc.) contribute very little to the overall hybrid. This is particularly true for species with two like charges on adjacent atoms!
   d. Negative charges are preferred on electronegative atoms, and conversely for positive charges.
   e. Structures with distorted bond angles or bond lengths contribute little to the overall hybrid.
9. In general, although not always, the resonance hybrid is more stable than any of the canonical forms. This is a consequence of electron delocalization. The amount of stabilization is called the resonance energy of the system.