

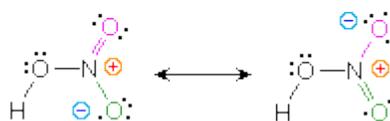
# Resonance

Kekulé structural formulas are essential tools for understanding organic chemistry. However, the structures of some compounds and ions cannot be represented by a single formula. For example, sulfur dioxide ( $\text{SO}_2$ ) and nitric acid ( $\text{HNO}_3$ ) may each be described by two equivalent formulas (equations 1 & 2). For clarity the two ambiguous bonds to oxygen are given different colors in these formulas.

1) sulfur dioxide

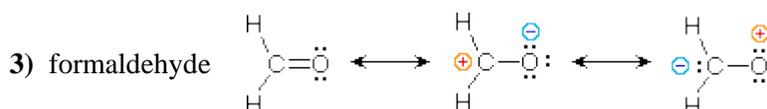


2) nitric acid



If only one formula for sulfur dioxide was correct and accurate, then the double bond to oxygen would be shorter and stronger than the single bond. Since experimental evidence indicates that this molecule is bent (bond angle  $120^\circ$ ) and has equal length sulfur : oxygen bonds ( $1.432 \text{ \AA}$ ), a single formula is inadequate, and the actual structure resembles an average of the two formulas. This averaging of electron distribution over two or more hypothetical contributing structures (canonical forms) to produce a hybrid electronic structure is called **resonance**. Likewise, the structure of nitric acid is best described as a **resonance hybrid** of two structures, **the double headed arrow being the unique symbol for resonance**.

The above examples represent one extreme in the application of resonance. Here, two structurally and energetically equivalent electronic structures for a stable compound can be written, but no single structure provides an accurate or even an adequate representation of the true molecule. In cases such as these, the electron delocalization described by resonance enhances the stability of the molecules, and compounds or ions composed of such molecules often show exceptional stability.



The electronic structures of most covalent compounds do not suffer the inadequacy noted above. Thus, completely satisfactory Kekulé formulas may be drawn for water ( $\text{H}_2\text{O}$ ), methane ( $\text{CH}_4$ ) and acetylene  $\text{C}_2\text{H}_2$ ). Nevertheless, the principles of resonance are very useful in rationalizing the chemical behavior of many such compounds. For example, the carbonyl group of formaldehyde (the carbon-oxygen double bond) reacts readily to give addition products. The course of these reactions can be explained by a small contribution of a dipolar resonance contributor, as shown in equation 3. Here, the first contributor (on the

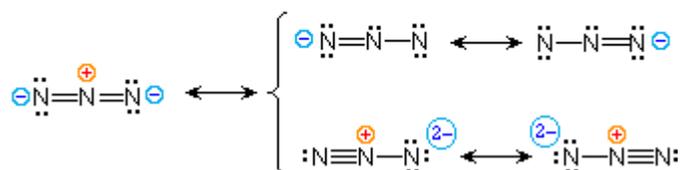
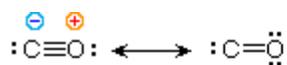
left) is clearly the best representation of this molecular unit, since there is no charge separation and both the carbon and oxygen atoms have achieved valence shell neon-like configurations by covalent electron sharing. If the double bond is broken heterolytically, formal charge pairs result, as shown in the other two structures. The preferred charge distribution will have the positive charge on the less electronegative atom (carbon) and the negative charge on the more electronegative atom (oxygen). Therefore the middle formula represents a more reasonable and stable structure than the one on the right. The application of resonance to this case requires a weighted averaging of these canonical structures. The double bonded structure is regarded as the major contributor, the middle structure a minor contributor and the right hand structure a non-contributor. Since the middle, charge-separated contributor has an electron deficient carbon atom, this explains the tendency of electron donors (nucleophiles) to bond at this site.

**The basic principles of the resonance method may now be summarized. For a given compound, a set of Lewis / Kekulé structures are written, keeping the relative positions of all the component atoms the same. These are the canonical forms to be considered, and all must have the same number of paired and unpaired electrons.** The following factors are important in evaluating the contribution each of these canonical structures makes to the actual molecule.

1. The number of covalent bonds in a structure. (The greater the bonding, the more important and stable the contributing structure.)
2. Formal charge separation. (Other factors aside, charge separation decreases the stability and importance of the contributing structure.)
3. Electronegativity of charge bearing atoms and charge density. (High charge density is destabilizing. Positive charge is best accommodated on atoms of low electronegativity, and negative charge on high electronegative atoms.)

**The stability of a resonance hybrid is always greater than the stability of any canonical contributor.** Consequently, if one canonical form has a much greater stability than all others, the hybrid will closely resemble it electronically and energetically. This is the case for the carbonyl group (eq.3). The left hand C=O structure has much greater total bonding than either charge-separated structure, so it describes this functional group rather well. On the other hand, if two or more canonical forms have identical low energy structures, the resonance hybrid will have exceptional stabilization and unique properties. This is the case for sulfur dioxide (eq.1) and nitric acid (eq.2).

- 4) carbon monoxide  
5) azide anion



To illustrate these principles we shall consider carbon monoxide (eq.4) and azide anion (eq.5). In each case the most stable canonical form is on the left. For carbon monoxide, the additional bonding is more important than charge separation. Furthermore, the double bonded structure has an electron deficient carbon atom (valence shell sextet). A similar destabilizing factor is present in the two azide canonical forms on the top row of the bracket (three bonds vs. four bonds in the left most structure). The bottom row pair of structures have four bonds, but are destabilized by the high charge density on a single nitrogen atom.

All the examples on this page demonstrate an important restriction that must be remembered when using resonance. **No atoms change their positions within the common structural framework. Only electrons are moved.**

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