3.8 Resonance and Formal Charge Revisited

Skills to Develop

- To understand the concept of resonance.

Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding a single polyatomic species including fractional bonds and fractional charges. Resonance structure are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integer number of covalent bonds. When drawing resonance structures, you are allowed to move only lone pairs of electrons and pi bonds. You cannot move any atoms, and you cannot make any new sigma bonds or remove any existing sigma bonds.

Sometimes one Lewis Structure is not Enough

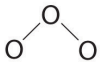
Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

Ozone (O_3)

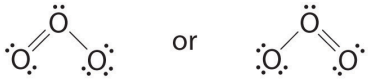
First we calculate the number of bonds needed

1. (3 O atoms) x (8) = 24 valence electrons needed
2. (3 O atoms) x (6) = 18 valence electrons present.
3. 24 - 18 = 6 electrons short, thus 6 electrons must be shared
4. 6 shared electrons/ 2 electrons per bond = 3 bonds
5. Connect the three atoms with one single bond. A three-membered ring is not impossible, but not very likely.

   We know that ozone has a V-shaped structure from the information given above, so one O atom is central:

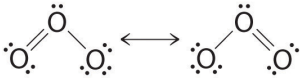


6. There is still one more bond to add. You could place that bond on either side, and then add the remaining 12 electrons as lone pairs, with 3 pairs on the singly-bonded O atom, 2 pairs on the doubly-bonded O atom, and one pair on the central O atom giving the following structures:



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

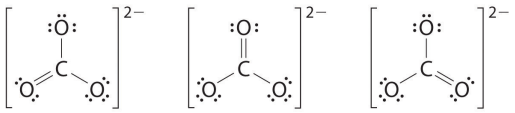
The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

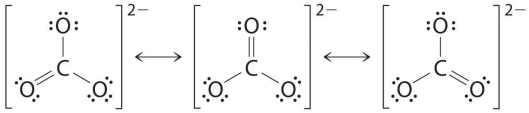
First we calculate the number of bonds needed

1. (3 O atoms) x (8) + (1 C atom) x (8) = 32 valence electrons needed
2. (3 O atoms) x (6) + (1 C atom) x (4) + 2 = 24 valence electrons present.
3. 32 - 24 = 8 electrons short, thus 8 electrons must be shared
4. 8 shared electrons/ 2 electrons per bond = 4 bonds
5. The C atom is the least electronegative element, so it is in the center. Connect the three O atoms to the C atom with one single bond per O atom.

6. There is still one more bond to add. You can place that bond as a pi bond to any one of the O atoms, and then add the remaining 16 electrons as lone pairs, with 3 pairs on the singly-bonded O atoms, and 2 pairs on the doubly-bonded O atom, giving the following three structures:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



The actual structure is an average of these three resonance structures.

Example 1: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

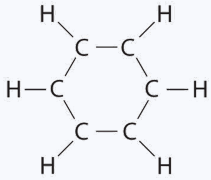
Strategy:

A. Calculate the number of bonds needed for the molecule
B. Draw the resonance structures for benzene.

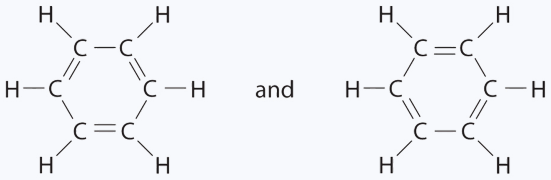
Solution:

1. (6 C atoms) x (8) + (6 H atoms) x (2) = 60 valence electrons needed
2. (6 C atoms) x (4) + (6 H atoms) x (1) = 30 valence electrons present.
3. 60 - 30 = 30 electrons short, thus 30 electrons must be shared
4. 30 shared electrons/ 2 electrons per bond = 15 bonds

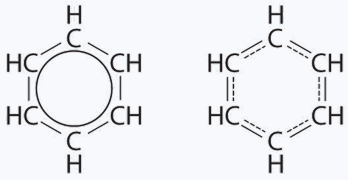
5. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



This structure has 12 bonds, so there are still 3 bonds to add. The only option is to place a pi bond between every other C atom. But there are 2 ways to do this**:**



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:

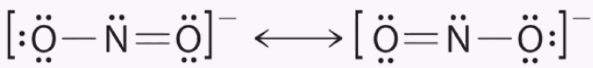


Benzene

Exercise 1: Nitrate Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example 1. Once would expect the double bonds to be shorter than the single bonds, but if once overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

Resonance structures is mechanism that allows us to use all of possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

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