Section 5: Observation 3: Compounds of Nitrogen, Oxygen, and the Halogens

Many compounds composed primarily of carbon and hydrogen also contain some oxygen or nitrogen, or one or more of the halogens. We thus seek to extend our understanding of bonding and stability by developing Lewis structures involving these atoms. Recall that a nitrogen atom has a valence of 3 and has five valence electrons. In our notation, we could draw a structure in which each of the five electrons appears separately in a ring, similar to what we drew for C. However, this would imply that a nitrogen atom would generally form five bonds to pair its five valence electrons. Since the valence is actually 3, our notation should reflect this. One possibility looks like this.

Note that this structure leaves three of the valence electrons "unpaired" and thus ready to join in a shared electron pair. The remaining two valence electrons are "paired," and this notation implies that they therefore are not generally available for sharing in a covalent bond. This notation is consistent with the available data, i.e. five valence electrons and a valence of 3. Pairing the two non-bonding electrons seems reasonable in analogy to the fact that electrons are paired in forming covalent bonds.

Analogous structures can be drawn for oxygen, as well as for fluorine and the other halogens, as shown here.

With this notation in hand, we can now analyze structures for molecules including nitrogen, oxygen, and the halogens. The hydrides are the easiest, shown here.

Note that the octet rule is clearly obeyed for oxygen, nitrogen, and the halogens.

At this point, it becomes very helpful to adopt one new convention: a pair of bonded electrons will now be more easily represented in our Lewis structures by a straight line, rather than two dots. Double bonds and triple bonds are represented by double and triple straight lines between atoms. We will continue to show non-bonded electron pairs explicitly.

As before, when analyzing Lewis structures for larger molecules, we must already know which atoms are bonded to which. For example, two very different compounds, ethanol and dimethyl ether, both have molecular formula

. In ethanol, the two carbon atoms are bonded together and the oxygen atom is attached to one of the two carbons; the hydrogens are arranged to complete the valences of the carbons and the oxygen shown here.

Ethers can be recognized in Lewis structures by the C-O-C arrangement. Note that, in both ethanol and dimethyl ether, the octet rule is obeyed for all carbon and oxygen atoms. Therefore, it is not usually possible to predict the structural formula of a molecule from Lewis structures. We must know the molecular structure prior to determining the Lewis structure.

Ethanol and dimethyl ether are examples of isomers, molecules with the same molecular formula but different structural formulae. In general, isomers have rather different chemical and physical properties arising from their differences in molecular structures.

A group of compounds called amines contain hydrogen, carbon, and nitrogen. The simplest amine is methyl amine, whose Lewis structure is here.

"Halogenated" hydrocarbons have been used extensively as refrigerants in air conditioning systems and refrigerators. These are the notorious "chlorofluorocarbons" or "CFCs" which have been implicated in the destruction of stratospheric ozone. Two of the more important CFCs include Freon 11, CFCl3, and Freon 114, C2F4Cl2, for which we can easily construct appropriate Lewis structures, shown here.

Finally, Lewis structures account for the stability of the diatomic form of the elemental halogens, F2, Cl2, Br2, and I2. T he single example of F2 is sufficient, shown here.

We can conclude from these examples that molecules containing oxygen, nitrogen, and the halogens are expected to be stable when these atoms all have octets of electrons in their valence shells. The Lewis structure of each molecule reveals this character

explicitly.

On the other hand, there are many examples of common molecules with apparently unusual valences, including: carbon dioxide CO_2

, in which the carbon is bonded to only two atoms and each oxygen is only bonded to one; formaldehyde H_2CO; and hydrogen cyanide HCN. Perhaps most conspicuously, we have yet to understand the bonding in two very important elemental diatomic molecules, O_2 and N_2

, each of which has fewer atoms than the valence of either atom.

We first analyze CO_2

, noting that the bond strength of one of the CO bonds in carbon dioxide is 532 kJ, which is significantly greater than the bond strength of the CO bond in ethanol, 358 kJ. By analogy to the comparison of bonds strengths in ethane to ethene, we can imagine that this difference in bond strengths results from double bonding in CO_2. Indeed, a Lewis structure of CO_2 in which only single electron pairs are shared (Figure) does not obey the octet rule, but one in which we pair and share the extra electrons reveals that double bonding permits the octet rule to be obeyed (Figure).

A comparison of bond lengths is consistent with our reasoning: the single CO bond in ethanol is 148 pm, whereas the double bond in CO_2

is 116.

Knowing that oxygen atoms can double-bond, we can easily account for the structure of formaldehyde. The strength of the CO bond in H_2CO is comparable to that in CO_2, consistent with the Lewis structure here.

What about nitrogen atoms? We can compare the strength of the CN bond in HCN, 880 kJ, to that in methyl amine, 290 kJ. This dramatic disparity again suggests the possibility of multiple bonding, and an appropriate Lewis structure for HCN is shown here.

We can conclude that oxygen and nitrogen atoms, like carbon atoms, are capable of multiple bonding. Furthermore, our observations of oxygen and nitrogen reinforce our earlier deduction that multiple bonds are stronger than single bonds, and their bond lengths are shorter.

As our final examples in this section, we consider molecules in which oxygen atoms are bonded to oxygen atoms. Oxygen-oxygen bonds appear primarily in two types of molecules. The first is simply the oxygen diatomic molecule, O_2

, and the second are the peroxides, typified by hydrogen peroxide, H_2O_2. In a comparison of bond energies, we find that the strength of the OO bond in O_2 is 499 kJ whereas the strength of the OO bond in H_2O_2 is 142 kJ. This is easily understood in a comparison of the Lewis structures of these molecules, showing that the peroxide bond is a single bond, whereas the O_2 bond is a double bond, shown here.

We conclude that an oxygen atom can satisfy its valence of 2 by forming two single bonds or by forming one double bond. In both cases, we can understand the stability of the resulting molecules by in terms of an octet of valence electrons.