Objectives

After completing this section, you should be able to

1. describe how differences in electronegativity give rise to bond polarity.
2. arrange a given series of the elements most often encountered in organic chemistry (C, H, O, N, S, P and the halogens) in order of increasing or decreasing electronegativity, without referring to a table of electronegativities.
3. predict the partial positive and partial negative ends of a given bond formed between any two of the elements listed in Objective 2, above, without the use of a table of electronegativities or a periodic table.
4. predict the partial positive and partial negative ends of a given bond formed between any two elements not listed in Objective 2, above, using a periodic table.

Key Terms

Make certain that you can define, and use in context, the key terms below.

• electronegativity inductive effect
• polar covalent bond

Study Notes

Students often wonder why it is important to be able to tell whether a given bond is polar or not, and why they need to know which atoms carry a partial positive charge and which a partial negative charge. Consider the chloromethane (CH₃Cl) molecule. The carbon atom is shown as carrying a partial positive charge. Now, recall that opposite charges attract. Thus, it seems reasonable that the slightly positive carbon atom in chloromethane should be susceptible to attack by a negatively charged species, such as the hydroxide ion, OH⁻. This theory is borne out in practice: hydroxide ions react with chloromethane by attacking the slightly positive carbon atom in the latter. It is often possible to rationalize chemical reactions in this manner, and you will find the knowledge of bond polarity indispensable when you start to write reaction mechanisms.

**Note:** Because of the small difference in electronegativity between carbon and hydrogen, the C-H bond is normally assumed to be nonpolar.

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity** (represented by the Greek letter \( \chi \), pronounced “ky” as in “sky”), which is defined as the relative ability of an atom to attract electrons to itself in a chemical compound. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.
Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by the neighboring atoms in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The larger the electronegativity value, the greater the attraction.

Unfortunately there is no direct way of measuring electronegativity. Dipole-moment measurements tell us about the electrical behavior of all electron pairs in the molecule, not just the bonding pair in which we are interested. Also, the polarity of a bond depends on whether the bond is a single, double, or triple bond and on what the other atoms and electron pairs in a molecule are. Therefore the dipole moment cannot tell us quantitatively the difference between the electronegativities of two bonded atoms. Various attempts have been made over the years to derive a scale of electronegativities for the elements, none of which is entirely satisfactory. Nevertheless most of these attempts agree in large measure in telling us which elements are more electronegative than others. The best-known of these scales was devised by the Nobel prize-winning California chemist Linus Pauling (1901 to 1994) and is shown in the periodic table found below. In this scale a value of 4.0 is arbitrarily given to the most electronegative element, fluorine, and the other electronegativities are scaled relative to this value.
Electronegativities of the elements

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group (vertical)

Period (horizontal)

What if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. If the atoms are equally electronegative, then both atoms have the same tendency to attract the bonding pair of electrons, and so electrons will be found on average halfway between the two atoms.
To get a bond like this, A and B would usually have to be the same element, for example, H₂ or Cl₂ molecules. Note: It's important to realize that this is an average picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital. This sort of bond could be thought of as being a "pure" or non-polar covalent bond - where the bonding electrons are shared evenly between the two atoms.

What if B is slightly more electronegative than A?

If B is slightly more electronegative than A, then B will attract the bonding electron pair more than A.

\[ \delta^+ \quad \delta^- \]

That means that the B end of the bond will have a greater share of the electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. This unequal sharing of the bonding electrons is indicated in the diagram above using the symbols "\( \delta^+ \)" and "\( \delta^- \)". "\( \delta \)" (read as "delta") means "slightly", so "\( \delta^+ \)" means slightly positive, and "\( \delta^- \)" means slightly negative. Because the electrons are shared unequally, the bond between A and B is polarized, and the bond is called a polar covalent bond.

A polar covalent bond is a covalent bond in which there is a separation of charge between one end and the other - in other words one end is slightly positive and the other slightly negative. Examples include most covalent bonds, like the hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water.

\[ + \quad - \]

If B is a lot more electronegative than A, then the electron pair is dragged completely over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed. Because the electrons are no longer shared, the bond is an ionic bond rather than a covalent bond.

A "spectrum" of bonds

There is no clear-cut division between covalent and ionic bonds. In a pure non-polar covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. Sodium chloride is typically considered an ionic solid, but even here the sodium has not completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic. Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons has not moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do. A general rule in organic chemistry is if the bond is between metal and a non-metal atoms, then the bond should be considered ionic. Examples of this are the lithium - carbon bond in methyl lithium and the potassium - oxygen bond in potassium tert-butoxide,
Summary

- No electronegativity difference between two atoms leads to a non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

Exercises

1. Identify the positive and negative ends of each of the bonds shown below.

   four simple molecules

Answer:

   1. charges on four simple molecules

Questions

Q2.1.1

Rank the following from least polar to most polar using knowledge of electronegativity

CH₃CH₂-Li CH₃CH₂-K CH₃CH₂-F CH₃CH₂-OH
Solutions

S2.1.1

(least polar) OH < F < Li < K (most polar)

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