

5.3: POLAR REACTIONS- THE DANCE OF THE NUCLEOPHILE AND ELECTROPHILE

Learning Objective

- identify nucleophiles and electrophiles in polar reactions
- relate bond polarity to chemical reactivity

NUCLEOPHILES AND ELECTROPHILES

The reactants of polar reactions are often called the "nucleophile" and "electrophile". These terms are related to Lewis acid-base notation, so it can be helpful to apply and transfer the knowledge and wisdom gained from this definition of acid-base chemistry.

- Electrophile (Lewis Acid): An electron deficient atom, ion or molecule that has an affinity for an electron pair, and will bond to a base or nucleophile
- Nucleophile (Lewis Base): An atom, ion or molecule that has an electron pair that may be donated in bonding to an electrophile

Nucleophile

Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates. More specifically in laboratory reactions, halide and azide (N_3^-) anions are commonly seen acting as nucleophiles.

Enolate ions are the most common carbon nucleophiles in biochemical reactions, while the cyanide ion (CN^-) is just one example of a carbon nucleophile commonly used in the laboratory. Hydrocarbons carbons with pi bonds can also be nucleophiles. Reactions with carbon nucleophiles will be dealt with in later chapters In this chapter, we will concentrate on non-carbon nucleophiles.

When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and bases can be nucleophiles*. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

Neutral Nucleophiles: H_2O , NH_3 , RNH_2 , R_2NH , R_3N , ROH , RCO_2H , RSH , PR_3 , $R_2C=CR_2$, and alkynes

Charged Nucleophiles: RO^- , H_2N^- , RNH^- , R_2N^- , HS^- , RSe^- , Cl^- , Br^- , I^- , F^- , CN^- , N_3^- , OH^- , and RCO_2^-

ELECTROPHILES

In the vast majority of polar reactions, the electrophilic atom is a carbon atom bonded to an electronegative atom, usually oxygen, nitrogen, sulfur, or a halogen. The concept of electrophilicity is relatively simple: an electron-poor atom with partial positive charge is an attractive target an electron-rich nucleophile. Electrophiles can be challenging to recognize because their partial positive charge is hidden in polar bonds and/or resonance. Alkyl halides and carbonyl groups are useful electrophiles for synthetic organic chemistry.

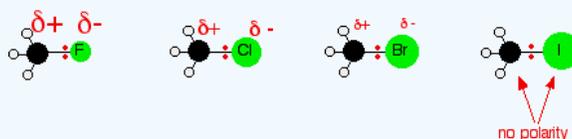
Electrophilicity of Alkyl Halides

With respect to electronegativity, halogens are more electronegative than carbons. This results in a carbon-halogen bond that is polarized. As shown in the image below, carbon atom has a partial positive charge, while the halogen has a partial negative charge.

The Polar C-X Bond



Alkyl halides are useful electrophiles for synthetic organic chemistry. Of the four halogens, fluorine is the most electronegative and iodine the least. That means that the electron pair in the carbon-fluorine bond will be dragged most towards the halogen end. Looking at the methyl halides as simple examples:



The following image shows the relative electronegativity of the halogens. Notice, as we move up the periodic table from iodine to fluorine, electronegativity increases.

Electronegativity I < Br < Cl < F

The following image shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length C-F < C-Cl < C-Br < C-I

Bond strength C-I < C-Br < C-Cl < C-F

Molecular size F < Cl < Br < I

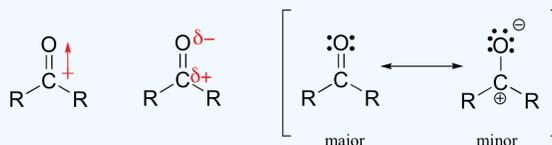
You might have thought that either of these would be more effective in the case of the carbon-fluorine bond with the quite large amounts of positive and negative charge already present. But that's not so - quite the opposite is true! The thing that governs the reactivity is the strength of the bonds which have to be broken. It is difficult to break a carbon-fluorine bond, but easy to break a carbon-iodine one. The relative electrophilicity of alkyl halides is summarized below.

Relative Electrophilicity R-I > R-Br > R-Cl > R-F

It is easier to break the weaker C-I bond.

ELECTROPHILICITY OF THE CARBONYL GROUP

The carbon atom of the carbonyl group (C=O) is electrophilic because the carbon-oxygen double bond is polar and one of the resonance contributors is ionized with a full positive charge on the carbonyl carbon. Oxygen is more electronegative than carbon, so electron density is higher on the oxygen side of the bond and lower on the carbon side. Both of these factors combine to increase the electrophilicity of carbonyl groups. Carbonyl chemistry is studied in greater detail in the second semester of organic chemistry.



Exercise

1. Recognizing organic compounds as nucleophiles or electrophiles is an important first step in recognizing and learning patterns of chemical reactivity. Classify the following compounds as nucleophiles or electrophiles.

- methoxide (CH₃O⁻)
- formaldehyde (CH₂O)
- bromocyclopentane
- water
- sodium cyanide
- methanamine (CH₃NH₂)

Answer

- charged nucleophile
- electrophile (Carbonyl carbon has partial positive charge.)
- electrophile (Alkyl halides are always electrophiles - one reason they are an o-chem student's best friend.)
- neutral nucleophile
- charge nucleophile (Don't let the cation distract us from the CN⁻)
- neutral nucleophile (The lone pair electrons on the nitrogen are nucleophilic in the same way they are Lewis bases (electron donators).

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- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

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