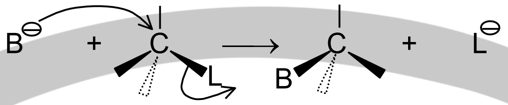
Nucleophilicity and basicity difference

A negatively charged species can function as nucleophile as well as like base but its nucleophilicity and basicity are different. Nucleophilicity of the species is the ability of the species to attack an electrophilic carbon while basicity is the ability of the species to remove H^+ from an acid. Let us have a species, B^-. Its function as a nucleophile is shown as



and its role as base is indicated as

$$B^{\ominus} + H\text{—}A \rightleftharpoons B\text{—}H + A^{\ominus}$$

The nucleophilicity is determined by the kinetics of the reaction, which is reflected by its rate constant (k) while basicity is determined by the equilibrium constant, which is reflected by its K_b.

The order of nucleophilicity of different species depends on the nature of solvent used.

For instance, let us take F^-, Cl^-, Br^- and I^- with their counter cation as Na^+ and see their nucleophilicity order in different solvents. There are four categories of solvents, namely non–polar (CCl_4), polar protic (H_2O), polar aprotic (CH_3SOCH_3) and weakly polar aprotic(CH_3COCH_3).

Polar solvents are able to dissociate the salts i.e. ion–pairs can be separated. On the other hand, non–polar and weakly polar solvents are unable to dissociate salts, so they exist as ion–pairs. The ion–pairing is strong when ions are small and have high charge density.

In non–polar and weakly polar aprotic solvents, all the salts will exist as ion–pairs. The ion–pairing will be strongest with the smallest anion (F^-) and weakest with the largest anion (I^-), thus the reactivity of X^- decreases with decreasing size. Thus, the nucleophilicity order of X^- in such solvents would be

$$I^- > Br^- > Cl^- > F^-$$

In polar protic solvents, hydrogen bonding or ion–dipole interaction diminishes the reactivity of the anion. Stronger the interaction, lesser is the reactivity of anion. F^- ion will form strong H–bond with polar protic solvent while weakest ion–dipole interaction will be with I^- ion. Thus, the nucleophilicity order of X^- in polar protic solvent would be $I^- > Br^- > Cl^- > F^-$.

Polar aprotic solvents have the ability to solvate only cations, thus anions are left free.

The reactivity of anions is then governed by their negative charge density (i.e. their basic character). Thus, the order of nucleophilicity of X^- in polar aprotic solvents would be

$F^- > Cl^- > Br^- > I^-$

On this basis, certain nucleophilicity orders are

(i) In polar protic solvents, $HS^- > HO^-$

(ii) In weakly polar aprotic solvents, $CsF > RbF > KF > NaF > LiF$

(iii) Bases are better nucleophiles than their conjugate acids. For example,

$OH^- > H_2O$ and $NH_2^- > NH_3$

(iv) In non–polar solvents, $^-CH_3 > {}^-NH_2 > {}^-OH > {}^-F$

(v) When nucleophilic and basic sites are same, nucleophilicity parallels basicity. For example,

$RO^- > HO^- > R - CO - O^-$

(vi) When the atom bonded to nucleophilic site also has an unshared pair of electrons, nucleophilicity of species increases. For example,

$HOO^- > HO^-$ and $H_2\ddot{N}{-}\ddot{N}H_2 > \ddot{N}H_3$

Edwards and Pearson gave following order of nucleophilicity for S_N2 reactions in protic solvents.

$RS^- > ArS^- > I^- > CN^- > OH^- > N_3^- > Br^- > ArO^- > Cl^-$ > pyridine > $AcO^- > H_2O$.