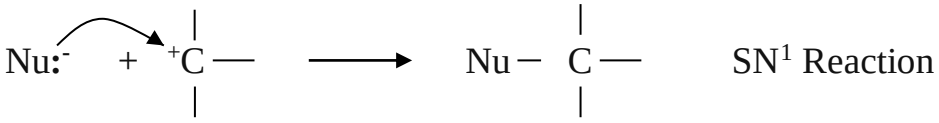
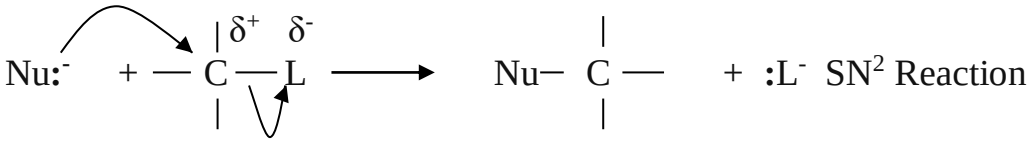
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Nucleophilicity

A nucleophile is a species which donates a pair of electrons to form a new covalent bond during the reaction.



Nucleophile Carbocation Substitution Product



Nucleophile Substrate molecule Substitution Product

In both these two reactions, a nucleophile is reacting with an electrophilic carbon atom forming a new Nu-C bond.

The term "nucleophilicity" represents the strength of a nucleophile i.e. the ease to which it donates the pair of electrons to an atom other than hydrogen (usually carbon). Thus, the stronger the base, more is its nucleophilicity.

When a species donates a pair of electrons to a hydrogen (more specifically, a proton, H^+) it is called as a base.

In general, basicity and nucleophilicity describe the same phenomenon, except basicity is concerned with the donation of lone pair of electrons to hydrogen while, nucleophilicity is concerned with the donation of lone pair of electrons all other atoms.

Nucleophilicity of a nucleophile is measured by comparing the rate of its reaction. The faster the reaction, the better or stronger is the nucleophile.

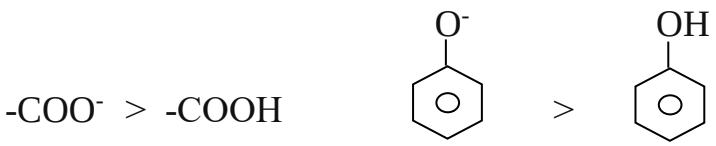
Factors deciding nucleophilicity of Nucleophiles

The nucleophilicity of nucleophiles is decided by following four factors-

1. Charge density-

Since nucleophiles are the species which donate a pair of electrons. The ability of nucleophiles to donate electron pair increases with increase of electron density on donor atom and therefore, their nucleophilicity increases. For example, the conjugate bases are the better nucleophile than their respective conjugate acids. For example,

$HO^- > H_2O$ $SH^- > H_2S$ $H_2N^- > NH_3$



2. Electronegativity

The ability of a species to donate the electron pair i.e. its nucleophilicity is inversely proportional to the electronegativity of donor atom and therefore, decreases with increase of the electronegativity of its donor atom. In fact, if the electronegativity of donor atom is more, the electron pair is more tightly held to the donor atom. Thus, the ability of a species to donate the electron pair i.e. its nucleophilicity is lesser. For example, the order of nucleophilicity of some important nucleophiles is as under-

$$H_3C^- > H_2N^- > HO^- > F^-$$

$$NH_3 > H_2O > HF$$

3. Solvent

Nucleophilicity is not a property inherent to a given species, but it is affected by the medium i.e. the solvent in which the reaction is being carried out.

A polar protic solvent such as water, alcohols, carboxylic acids etc. form hydrogen bond with the nucleophile resulting in the formation of a shell of solvent molecules around the nucleophile. It results in the decrease of reactivity and therefore, nucleophilicity of the nucleophile.

The ability of nucleophiles to form hydrogen bond with protic solvent goes on decreasing on moving down the group of periodic table and therefore, nucleophilicity goes on increasing. Thus, amongst halide ions, fluoride ion having highest tendency to form hydrogen bond has least nucleophilicity while, iodide ion having least tendency to form hydrogen bond has the highest nucleophilicity. This means that, the lone pairs of iodide ion is considerably more free than those of fluoride ion, resulting in its higher rate of reaction and greater nucleophilicity. Thus, the order of nucleophilicity of halide ions in protic solvents is as under-

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

Similarly, the order of nucleophilicity of HSe^-, HS^- and OH^- in protic solvents will be as under-

$$HSe^- > HS^- > OH^-$$

A polar aprotic solvent such as acetone, N,N-dimethyl formamide (DMF), Dimethyl sulphoxide (DMSO) etc. do not form hydrogen bond to nucleophiles and therefore, the nucleophiles have greater freedom of reaction in solution. Here, nucleophilicity of nucleophiles correlates well with their basicity. For example, in polar aprotic solvent, fluoride ion being the most unstable amongst the halide ions, reacts fastest with electrophiles and has the highest nucleophilicity while, iodide ion has least nucleophilicity.

- Here, we have not discussed the reaction in non polar solvents. In fact, in a nucleophilic reaction, we use such a solvent which actually dissolves the nucleophile. Most of the nucleophiles are either charged species or polar molecules and therefore, they don't dissolve in non-polar solvents.

4. Steric hindrance

Steric hindrance also plays an important role in deciding nucleophilicity of the nucleophiles. The bulkier a nucleophile is, the slower the rate of its reactions and therefore, the lower its nucleophilicity.

For example, the order of nucleophilicity of some important alkoxide ions (deprotonated alcohols) is as under-

CH_3O^- > $CH_3CH_2O^-$ > $(CH_3)_2CHO^-$ > $(CH_3)_3CO^-$

Here, methoxide ion is the strongest nucleophile, while, t-butoxide ion is the weakest nucleophile.

Apart from these four major factors, the nucleophilicity of nucleophiles also depends upon- the the nature of the electrophile, atoms with lone pairs adjacent to the nucleophile, the nature of the counter-ion i.e. positively charged species etc.

Competition Corner for IIT, AIIMS, NEET-

Q. Which of the following has the highest of nucleophilicity ?

(a) I^- (b) Br^- (c) Cl^- (d) F^-

Ans.- (a) I^-

Explanation- The term "nucleophilicity" represents the strength of a nucleophile i.e. the ease to which it donates its lone pair of electrons to an atom. Thus, the stronger the base, more is its nucleophilicity.

Here, I^- being the strongest Lewis base amongst the halide ions has the highest nucleophilicity while, F^- being the weakest Lewis base amongst the halide ions has the least nucleophilicity.

Thus, the order of nucleophilicity of different halide ions will be as under-

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

Q. Which of the following has the highest of nucleophilicity ?

(a) CH_3O^- (b) H_2N^-

(c) $(CH_3)_2CHO^-$ (d) $(CH_3)_3CO^-$

Ans.- (a) CH_3O^-

Explanation- Steric hindrance plays an important role in deciding nucleophilicity of the nucleophiles. Here, bulkier nucleophiles have slower rate of their reactions and therefore, they have relatively lower nucleophilicity.

Here, methoxide ion is the strongest nucleophile, while, t-butoxide ion being the bulkiest is the weakest nucleophile.

Thus, the order of nucleophilicity of these alkoxide ions (deprotonated alcohols) will be as under-

CH_3O^- > $CH_3CH_2O^-$ > $(CH_3)_2CHO^-$ > $(CH_3)_3CO^-$

Q. Which of the following has the highest of nucleophilicity ?

(a) H_3C^- (b) H_2N^-

(c) HO^- (d) F^-

Ans.- (a) H_3C^-

Explanation- The ability of a species to donate the electron pair i.e. its nucleophilicity is inversely proportional to the electronegativity of donor atom and therefore, decreases with increase of the electronegativity of its donor atom. If the electronegativity of donor atom is more, then electron pair is more tightly held to the donor atom. Hence, the ability of the species to donate its electron pair i.e. its nucleophilicity is lesser.

Here, H_3C^- contains the least electronegative donor atom and therefore, has the highest of nucleophilicity. Here, the order of nucleophilicity of the given nucleophiles will be as under-

H_3C^- > H_2N^- > HO^- > F^-

Q. Which of the following has the highest of nucleophilicity ?

(a) NH_3 (b) H_2O

(c) HF (d) PH_3

Ans.- (d) PH_3

Explanation- The ability of a species to donate the electron pair i.e. its nucleophilicity is inversely proportional to the electronegativity of donor atom and therefore, decreases with increase of the electronegativity of its donor atom. If the electronegativity of donor atom is more, then electron pair is more tightly held to the donor atom. Hence, the ability of the species to donate its electron pair i.e. its nucleophilicity is lesser.

Here, PH_3 contains the least electronegative donor atom and therefore, has the highest of nucleophilicity. Here, the order of nucleophilicity of the given nucleophiles will be as under-

$$PH_3 > NH_3 > H_2O > HF$$