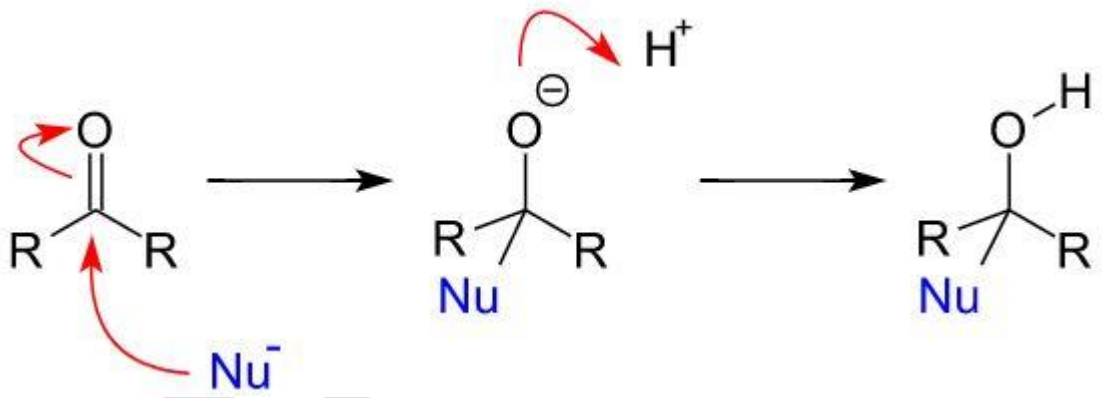
NUCLEOPHILIC ADDITION REACTION

Nucleophilic addition reaction is a chemical addition reaction in which a nucleophile forms a sigma bond with an electron-deficient species. These reactions are considered very important in organic chemistry since they enable the conversion of carbonyl groups into a variety of functional groups. Generally, nucleophilic addition reactions of carbonyl compounds can be broken down into the following three steps.

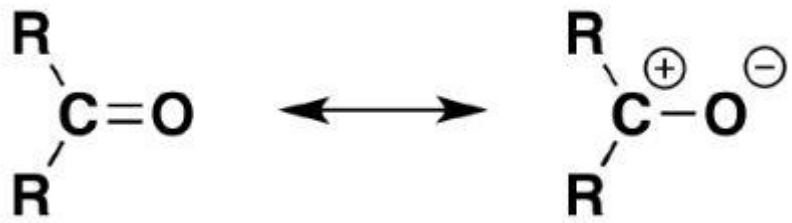
- The electrophilic carbonyl carbon forms a sigma bond with the nucleophile.
- The carbon-oxygen pi bond is now broken, forming an alkoxide intermediate (the bond pair of electrons are transferred to the oxygen atom).
- The subsequent protonation of the alkoxide yields the alcohol derivative.

The carbon-oxygen double bond is directly attacked by strong nucleophiles to give rise to the alkoxide. However, when weak nucleophiles are used, the carbonyl group must be activated with the help of an acid catalyst for the nucleophilic addition reaction to proceed.



The carbonyl group has a coplanar structure and its carbon is sp^2 hybridized. However, the attack of the nucleophile on the C=O group results in the breakage of the pi bond. The carbonyl carbon is now sp^3 hybridized and forms a sigma bond with the nucleophile.

In carbonyl compounds, the carbon-oxygen bond is polar. Owing to the relatively higher electro negativity of the oxygen atom, the electron density is higher near the oxygen atom. This leads to the generation of a partial negative charge on the oxygen atom and a partial positive charge on the carbon atom.



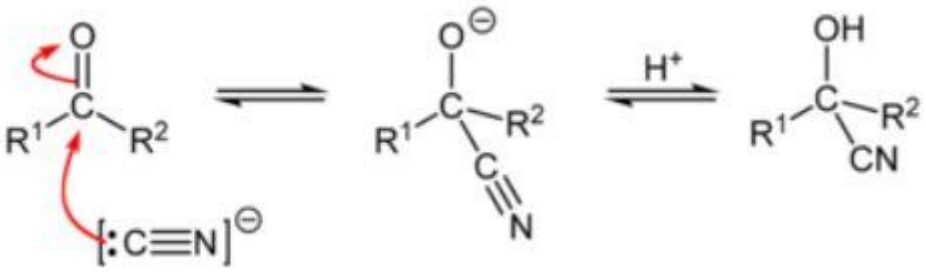
Since the carbonyl carbon holds a partial positive charge, it behaves as an electrophile. The partial negative charge on the oxygen atom can be stabilized via the introduction of an acidic group. The proton donated by the acid bonds with the carbonyl oxygen atom and neutralizes the negative charge.

Aldehydes are relatively more reactive towards nucleophilic addition reactions when compared to ketones. This is because the secondary carbocations formed by ketones are stabilized by the adjacent R groups. The primary carbocations formed by aldehydes are less stable than the secondary carbocations formed by ketones and are, therefore, more susceptible to nucleophilic attacks.

EXAMPLE:

1. **Reactions with Hydrogen Cyanide:**

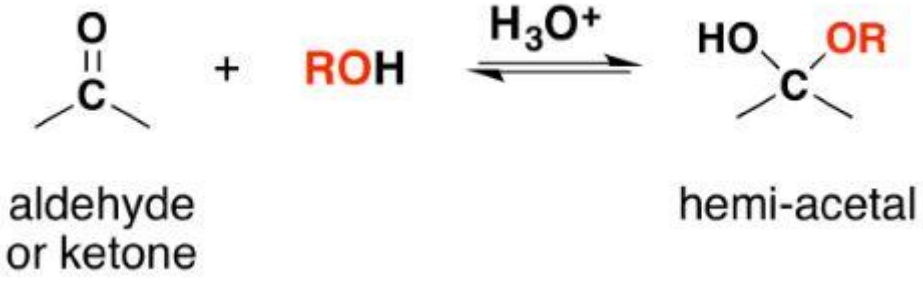
The nucleophilic addition reaction between hydrogen cyanide (HCN) and carbonyl compounds (generally aldehydes and ketones) results in the formation of cyanohydrins. Base catalysts are often used to increase the rate of the reaction. The cyanide anion (CN^-) acts as a powerful nucleophile and attacks the carbonyl carbon to form a new sigma bond



The polar nature of the C=O bond makes the carbonyl carbon electrophilic in nature. The cyanide anion executes a nucleophilic attack on the carbonyl carbon, resulting in the formation of an intermediate. This intermediate is now protonated to afford the cyanohydrin product.

2. **Nucleophilic Additions with Monohydric Alcohols**

Aldehydes and ketones undergo nucleophilic addition reactions with monohydric alcohols to yield hemiacetals. Upon further reaction with another molecule of the alcohol, an acetal is obtained. Since alcohols are weak nucleophiles, the reaction requires an acid catalyst for the activation of the carbonyl group towards nucleophilic attack.



Since the hemiacetals can undergo hydrolysis to yield the reactants (the alcohol and carbonyl compound), the water formed during the reaction must be removed. In this reaction, the carbonyl oxygen is protonated before the nucleophilic attack is carried out by the alcohol. The nucleophilic alcohol is now deprotonated to form the hemiacetal. This reaction can be repeated to obtain the acetal.

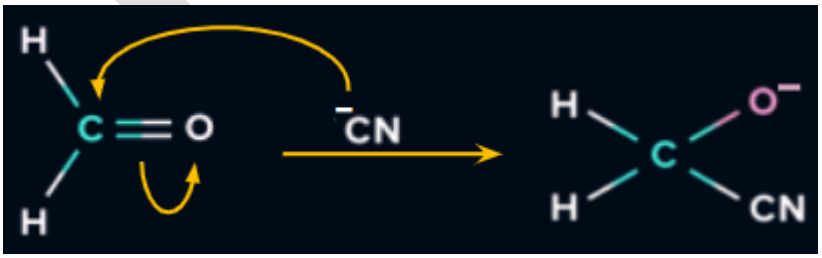
ELECTROMERIC EFFECT

The electromeric effect is also known as the E-effect. The electromeric effect can be defined as a temporary effect produced when a reagent attacks the multiple bonded compounds, causing a complete shift of pi electrons to either of the two atoms of the bond. This total transfer of the shared pair of electrons produces polarity.

This phenomenon is greatly observed in organic compounds that usually contain at least one double or triple bond in their structure.

As mentioned, it is a temporary effect, so once the reagent is removed, the polarized molecule goes back to its unpolarized state (original state). The reagent causing the electromeric effect can be an electrophile or a nucleophile.

Example:



Consider an aldehyde containing a carbonyl carbon; the carbon and oxygen atoms are held together by a double bond. When a negatively charged reagent attacks such a molecule, it causes a complete transfer of pi electrons from the carbon atom to the oxygen atom. This transfer of electrons towards oxygen and not carbon is because oxygen is more electronegative than carbon.

This complete shift causes the double bond to break, and the negatively charged reagent now forms a bond with the positively charged carbon atom.

This movement of electrons from one atom to another is called the electromeric effect.

Types of Electromeric Effects

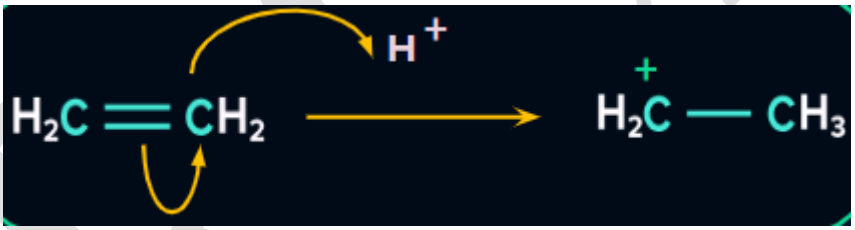
There are two main types of Electromeric effects based on the direction in which the electron transfer occurs.

1. +E effect
2. -E effect

+E Effect

The positive electromeric effect occurs when the shared electron pair is transferred towards the attacking reagent. The attacking reagent forms a bond with the atom that has received the shared pair of electrons. In this case, the reagent is positively charged and is seeking a negatively charged site.

This +E effect can be observed in the reaction involving the addition of acid to alkenes. A classic example portraying the positive electromeric effect is the protonation of ethene.



Here, π electrons of the multiple bonds are transferred to the atom to which the reagent gets attached.

-E Effect

A negative electromeric effect is observed when the shared pair of electrons is transferred away from the attacking reagent.

In simple terms, the nucleophilic reagent attacks the atom that has lost its shared pair of electrons and forms a bond with it. This phenomenon is greatly observed in reactions involving carbonyl carbon atoms like aldehydes and ketones.

For example: the reaction of an aldehyde with a cyanide ion.

Here, π electrons of the multiple bonds are transferred to the atom to which the reagent does not get attached.