

# [Types of substitution reactions biology essay](https://assignbuster.com/types-of-substitution-reactions-biology-essay/)

In a substitution reaction, a functional group in a particular chemical compound is replaced by another group . In organic chemistry, the electrophilic and nucleophilic substitution reactions are of main importance. Organic substitution reactions are classified into depending on whether the reagent that brings about the substitution is considered an electrophile or a nucleophile, whether a reactive intermediate involved in the reaction is a carbocation, a carbanion or a free radical or whether the substrate is aliphatic or aromatic. A reaction can be made faster or slower by taking into consideration the temperature and the solvent we are using. A good example of a substitution reaction is the photochemical chlorination of methane forming methyl chloride.

Nucleophilic substitution

What is a nucleophile

Nucleophilic substitution happens when the reagent is a nucleophile, which means the attacking species is a nucleus loving species . it is itself negatively charged or has a lone pair. Such species get attracted to positive or electron deficient carbon centres..

A nucleophile reacts with an aliphatic substrate in a nucleophilic aliphatic substitution reaction. These substitutions can be of two dofferent mechanisms: unimolecular nucleophilic substitution (SN1) and bimolecular nucleophilic substitution (SN2). The SN1 mechanism has two steps. In the first step, the leaving group leaves, forming a carbocation. In the second step, the nucleophilic species attacks the carbocation and forms a sigma bond. This mechanism can result in either inversion or retention of configuration. An SN2 reaction has just one step. The attack of the reagent and the expulsion of the leaving group occurs simultaneously. This mechanism always results in inversion of configuration.

When the substrate is an aromatic compound the reaction type is nucleophilic aromatic substitution.

Electrophilic substitutions

What is an electrophile

An electrophile is a electron loving species, it itself is positively charged and wants to stabilize itself by making a sigma bond with the electron rich carbon centre.

Electrophiles are involved in electrophilic substitution reactions and particularly in electrophilic aromatic substitutions.

SN1 REACTION

The SN1 reaction is a substitution reaction. “ SN means nucleophilic substitution and the “ 1” represents the fact that the rate-determining step is unimolecular . Carbocation intermediate is formed in this reaction . It is seen that tertiary carbocations are very stable due to + I effect and thus go for SN1 Reaction. With primary alkyl halides, the alternative SN2 reaction occurs. As primary Alkyl Halides mostly Form primary carbocation which is very unstable and thus have to go through SN2 Substitution reaction.

Mechanism

An example of a reaction taking place with an SN1 reaction mechanism is the hydrolysis of tert-butyl bromide with water forming tert-butyl alcohol:

This SN1 reaction takes place in three steps:

Formation of a tert-butyl carbocation by separation of a leaving group (a bromide anion) from the carbon atom: this step is slow and reversible.

Nucleophilic attack: the carbocation reacts with the nucleophile. If the nucleophile is a neutral molecule (i. e. a solvent) a third step is required to complete the reaction. When the solvent is water, the intermediate is an oxonium ion. This reaction step is fast.

Deprotonation: Removal of a proton on the protonated nucleophile by water acting as a base forming the alcohol and a hydronium ion. This reaction step is fast.

WHY THIS REACTION OCCURS

Bulky atoms(methyl, ethyl) surrounding the carbon atoms mostly allow SNI reaction. As the bulky alkyl halides are attached to the central carbon atom, it is both stabilized by hyperconjugation and +In ductive effect. The SN1 mechanism therefore dominates in reactions at tertiary alkyl centers and is further observed at secondary alkyl centers in the presence of weak nucleophiles.

SN2 REACTION

The SN2 reaction (also known as bimolecular nucleophilic substitution or as backside attack) is a type of nucleophilic substitution, where a lone pair from a nucleophile attacks an electron deficient electrophilic center and bonds to it, expelling another group called a leaving group. Thus the incoming group replaces the leaving group in one step. Since two reacting species are involved in the slow, rate-determining step of the reaction, this leads to the name bimolecular nucleophilic substitution, or SN2. Among inorganic chemists, the SN2 reaction is often known as the interchange mechanism.

REACTION MECHANISM

The reaction most often occurs at an aliphatic sp3 carbon center with an electronegative, stable leaving group attached to it – ‘ X’ – frequently a halide atom. The breaking of the C-X bond and the formation of the new C-Nu bond occur simultaneously to form a transition state in which the carbon under nucleophilic attack is pentacoordinate, and approximately sp2 hybridised. The nucleophile attacks the carbon at 180 to the leaving group, since this provides the best overlap between the nucleophile’s lone pair and the C-X s\* antibonding orbital. The leaving group is then pushed off the opposite side and the product is formed.

If the substrate under nucleophilic attack is chiral, this can lead, although not necessarily, to an inversion of stereochemistry, called the Walden inversion.

SN2 reaction of bromoethane with hydroxide ion. The products are ethanol and a bromide ion.

In an example of the SN2 reaction, the attack of OH- (the nucleophile) on a bromoethane (the electrophile) results in ethanol, with bromide ejected as the leaving group.

SN2 attack occurs if the backside route of attack is not sterically hindered by substituents on the substrate. Therefore this mechanism usually occurs at an unhindered primary carbon centre. If there is steric crowding on the substrate near the leaving group, such as at a tertiary carbon centre, the substitution will involve an SN1 rather than an SN2 mechanism, (an SN1 would also be more likely in this case because a sufficiently stable carbocation intermediary could be formed.)

In coordination chemistry, associative substitution proceeds via a similar mechanism as SN2.

FACTORS AFFECTING REACTION

1) The Basicity of the Leaving Group. By comparing the relative SN2 reaction rates of compounds with atoms in the same periodic group (the halides, for example), results show that the ability as a leaving group during an SN2 reaction depends on its basicity. In general, the weaker the basicity of a group, the greater its leaving ability. For example, the iodide ion is a very weak base and because it is so, it is the most reactive. Weak bases do not hold their electrons tightly, making it easier for their bonds to be broken. In contrast, the fluoride ion is a stronger base than the other halides and, therefore, the least reactive. In fact, the fluoride ion is such a strong base that compounds involving them essentially do not undergo SN2 reaction. Looking at the periodic table, relative basicity decreases down a group.

(Stronger Base) F- > Cl- > Br- > I- (Weaker Base)

2) The Size of the Nucleophile. How readily a compound attacks an electron-deficient atom also affects an SN2 reaction. As a rule, a negatively charged species (e. g. OH -) are better nucleophiles than neutral species (e. g. H2O, water). There is a direct relationship between basicity and nucleophilicity: stronger bases are better nucleophiles. Acidity, the ability of an atom to give up a proton (H+), is comparatively relative in molecules whose attacking atoms are approximately the same in size, the weakest going toward the left side of the periodic table. If hydrogen were attached to second-row elements of the periodic table, the resulting compounds would have the following relative acidities:

(Weaker Acid) NH3 < H2O < HF (Stronger Acid)

If each of these acids were to give up a hydrogen, the result would be its conjugate base, and the relative strengths will reverse. The stronger base now moves toward the left side of the periodic table.

(Stronger Base) -NH2 > HO- > F- (Weaker Base)

Elements increase in size down the periodic table. Although basicity decreases down the periodic table, nucleophilicity increases as size increases depending on the solvent used.

3) Solvent. If a reaction is carried out in a protic solvent, whose molecules have a hydrogen bonded to an oxygen or to a nitrogen, the larger atom is a better nucleophile in an SN2 reaction. In other words, the weaker base is the better nucleophile in a protic solvent. For example, the iodide ion is better than a fluoride ion as a nucleophile. However, if the reaction is carried out in an aprotic solvent, whose molecules do not have hydrogen bonded to an oxygen or to a nitrogen, then the stronger base is the better nucleophile. In this case, the fluoride ion is better than the iodide ion as a nucleophile.

4)

Sterics. Steric hindrance is any effect of a compound due to the size and/or arrangement of its

substituent groups. Steric effects affect nucleophilicity but does not affect base strength. A bulky nucleophile, such as a tert-butoxide ion with its specific arrangement of methyl groups, is a poorer nucleophile than an ethoxide ion with a straighter chain of carbons, even though tert-butoxide is a stronger base.