Notes on basics of organic reactions, reagents, types of reactions

By

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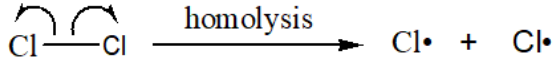
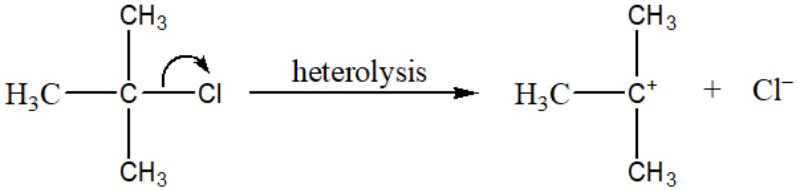
Homolytic and heterolytic bond cleavage

Homolytic bond cleavage is the breakage of a covalent bond which leads to the formation of molecular fragments each having one electron. In heterolytic bond cleavage, breaking of chemical bond occurs in such a way that leads to the formation of positively or negatively charged ions.





Formal charge = Number of valence electrons – (number of nonbonding electrons + ½ number of bonding electrons)

Formal charge is the difference between the number of valence electrons an atom has when it is not bonded to any other atoms and the number of electrons it actually owns when it is bonded.

Formal charge of oxygen in water = 6 – (4 + ½ x 4) = 0

Formal charge of oxygen in $^{-}$OH = 6 – (6 + ½ x 2) = –1

Formal charge of oxygen in H_3O^+ = 6 – (2 + ½ x 6) = +1

Types of reagents

Nucleophiles

An electron rich atom or molecule either negatively charged or an uncharged specie with unshared pair of electrons is called nucleophile.

Examples-

NO_2^-, N_3^-, $RCOO^-$, ^-CN, I^-, Br^-, Cl^-, OH^-, ^-OMe, H_2O, ROH, NH_3, RNH_2 etc.

The reactivity of a nucleophile is called nucleophilicity.

Nucleophilicity and basicity

A base shares its nonbonding electrons with a proton. Basicity is a measure of how well the base shares its electrons with proton. The stronger the base, the better it shares its electrons.

A nucleophile uses its nonbonding electrons to attack an electron deficient atom other than proton. Nucleophilicity is a measure of how readily the nucleophile is able to attack such an atom. Thus, a base forms new bond with a proton, whereas a nucleophile forms a new bond with an atom other than a proton.

When comparing molecules with same attacking atom, there is direct relationship between basicity and nucleophilicity. Stronger bases are better nucleophiles.

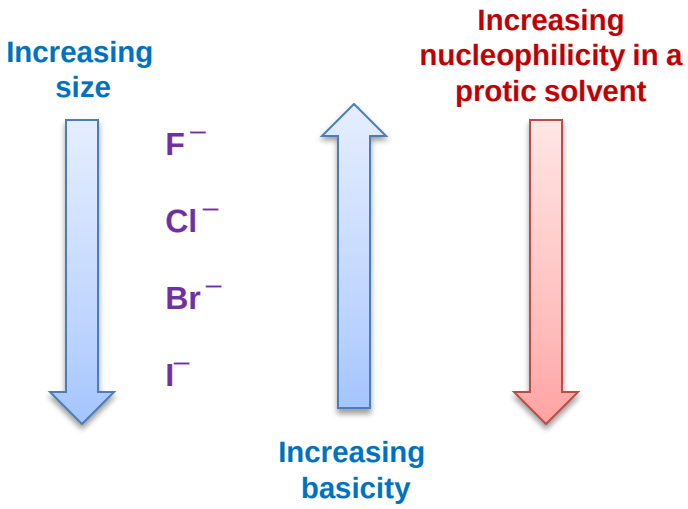
Stronger base, Better nucleophile		Weaker base, Poorer nucleophile
HO^-	>	H_2O
CH_3O^-	>	CH_3OH
$^-NH_2$	>	NH_3
$CH_3CH_2NH^-$	>	$CH_3CH_2NH_2$

When comparing molecules with attacking atoms of approximately the same size, the stronger bases are better nucleophiles.

$^{-}CH_3 > {}^{-}NH_2 > HO^{-} > F^{-}$

Increasing basicity and nucleophilicity

When comparing molecules with attacking atoms that are different in size, the direct relationship between basicity and nucleophilicity is maintained if the reaction occurs in a gas phase. If the reaction occurs in a solvent, the relationship between basicity and nucleophilicity depends on the solvent. If the solvent is protic, the relationship between basicity and nucleophilicity becomes inverted. In other words, as basicity decreases, nucleophilicity increases.



Electrophiles

An electron deficient atom or molecule is called an electrophile.

A few examples of electrophiles

H^+ $CH_3CH_2^+$ BH_3 $Br\cdot$ $RO\cdot$

These are electrophiles because they can accept a pair of electrons

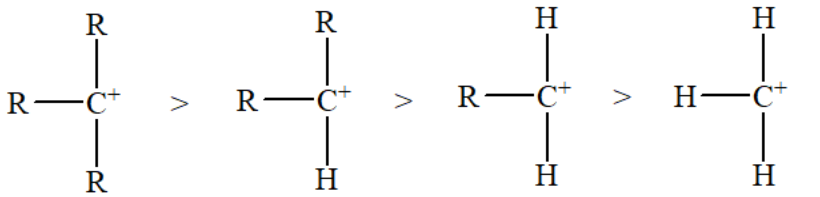
These are electrophiles because they are seeking an electron

Reaction intermediates

1. Carbocation 2. Carbanion 3. Free radical 4. Carbene

1. **Carbocation: A species containing a positively charged carbon atom is called carbocation. In other words, an organic species which has a carbon atom bearing only six electrons is called a carbocation.**

   The stability of a carbocation increases as the number of alkyl substituents bonded to the positively charged carbon atom increases, so tertiary carbocations are more stable than secondary carbocation, and secondary carbocations are more stable than primary carbocation.

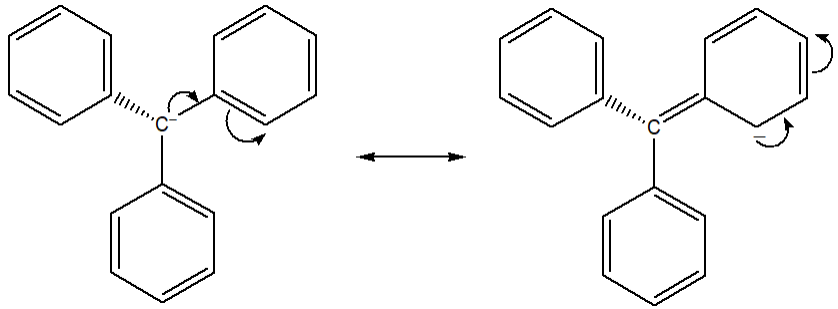


3° carbocation > 2° carbocation > 1° carbocation > methyl cation

Increasing stability

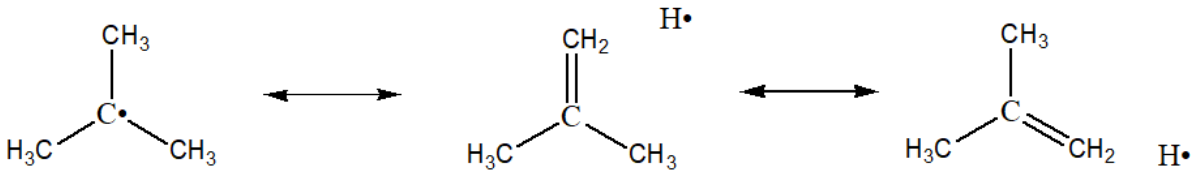
2. Carbanion: **Carbanions are anions of carbon, generated by the removal of one of the groups attached to a carbon atom without removing the bonding electrons.**

Carbanions are stabilized by the presence of electron withdrawing substituents attached to it or by delocalisation of the negative charge.



3. Free radicals: **Homolytic cleavage of covalent bond produces atoms which possess unpaired electrons. These neutral species are called radicals. They are extremely reactive yielding a variety of products depending on the experimental conditions.**

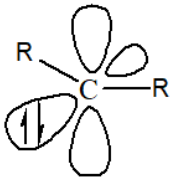
The stability of radicals increases in the order- primary< secondary< tertiary and also with the number of alkyl groups attached to the carbon atom carrying the unpaired electron. The carbon atom, carrying an unpaired electron has a half filled orbital that gives the radical its characteristic instability and hyperconjugative effect tends to stabilize it to some extent.



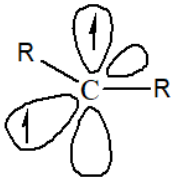
4. Carbene: **Carbenes are key intermediates in a wide variety of chemical and photochemical reactions. They are highly reactive and unstable, and have a lifetime less than one second. Carbenes can be defined as neutral, divalent carbon intermediates in which a carbon is covalently bonded to two atoms and has a lone pair of electrons and an empty orbital.**

The two nonbonded electrons of a carbene may be either unpaired or paired. When these are unpaired, the carbene is said to be in a triplet state; if they are paired, the carbene is said to be in a singlet state. In the singlet state, a carbon atom is presumed to have sp^2 hybridization. Two of the sp^2 hybrid orbitals are utilized in forming two covalent bonds whereas the third hybrid orbital contains the unshared pair of electrons. The remaining unhybridized p orbital remains vacant. Thus, a singlet carbene resembles a carbocation very closely.

On the other hand, triplet carbene have two unpaired electrons, one in sp^2 hybridized and p orbital.



Singlet carbene



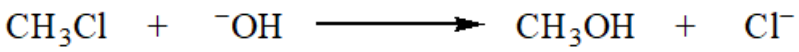
Triplet carbene

Both singlet and triplet carbenes have bent shape, bond angles are around 103 and 136º respectively.

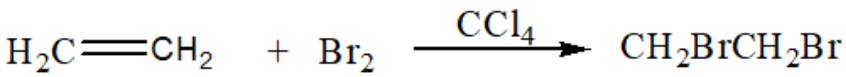
Types of organic reactions

1. Substitution reaction
2. Addition reaction
3. Elimination reaction
4. Rearrangement reaction

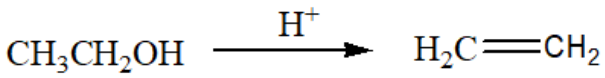
1. Substitution reaction: A substitution reaction is the one in which an atom or group in a molecule is replaced by another atom or group.



2. Addition reaction: An addition reaction is one in which two substances combine to form a single compound.



3. Elimination reaction: An elimination reaction involves removal of two atoms or groups from the same molecule.



4. Rearrangement reaction: A rearrangement reaction is one in which an atom or a group moves from one atom to another within the molecule.