भारतीय संस्कृति, शिक्षा और दर्शन

विभिन्न संकल्पनाएं

सम्पादक : डॉ. दिनेश चन्द्र शर्मा

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रचना -
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आवरण -
श्रीनिवास प्रिन्टोग्राफिक्स, अजमेर

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Free Radical

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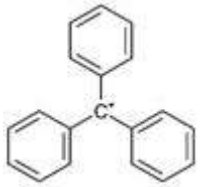
Principal: Free radicals may be defined as the species that contain one or more unpaired e-. They are generally less stable and react with another species within a few seconds.

Professor Gemberg are the one who firstly identify free radical in 1900. He defined triphenyl methyl radical. Property:-



* Having only one e- pair which make it highly unreactive and unstable.

* It's a e- deficient species.

* It's a neutral species.

* Hybridization- sp^3 and geometry- Flattened tetrahedral.

Formation of Free Radicals:-

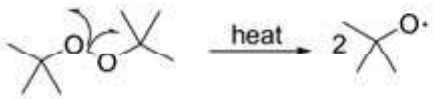
Three common methods are used to produce free radicals.

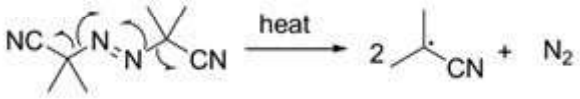
1. Thermal Generation:-

At moderate temperature, two types of compound dissociate to form free radicals:

i. Compounds containing weak internal bonds, such as dialkyl peroxide (D_{o-o} = 155kJ mol^{-1}), and

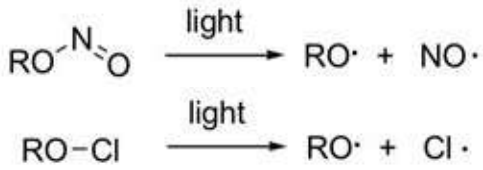
ii. Compounds that form strongly bonded products on dissociation, such as AIBN, which liberates N_2.





2. Photochemical Generation:-

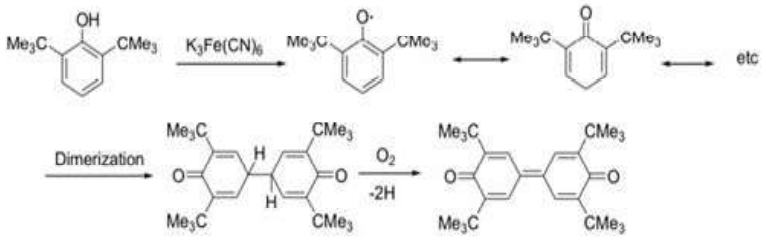
Light can split a compound if the wavelength of the light is greater than the energy of the bond to be split, and corresponds to the electronic excitation of the molecule. This process is suitable for the formation of alkoxy radicals from alkyl nitrites or hypochlorites.



3. Redox Generation:-

Covalent bonds can be broken by an electron transfer process, either by accepting an electron from a donor or donating an electron to an acceptor.

In the second group, the acceptor is usually a transition metal ion in a higher valence state.



Reactions of Free Radicals

Four types of reaction are possible with free radicals.

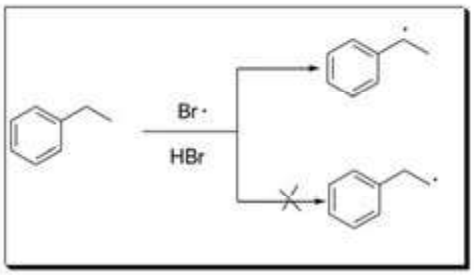
1. Abstraction

Free radicals react with saturated organic molecules by abstracting an atom from carbon. The selectivity of free radicals towards different types of C-H bonds is determined by bond dissociation energy and polar effects.

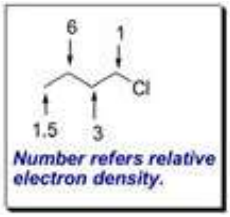
The rate of abstraction process increases as the bond dissociation energy decreases. For Example:

Bond:	$H-CH_3$	$H-CH_2Me$	$H-CHMe_2$	$H-CMe_3$
Bond Dissociation Energy ($KJmol^{-1}$)	426	401	385	372
Reactivity Order::	$H-CH_3$ <	$H-CH_2Me$ <	$H-CHMe_2$ <	$H-CMe_3$

Allylic and benzylic C-H bonds are weaker than those in saturated systems and exhibit greater reactivity and selectivity with free radicals.



Secondly, the polar effect is also active in radica reactions. For example, the relative reactivity of the C-H bonds towards the chlorine atom in butyl chloride is as follows:



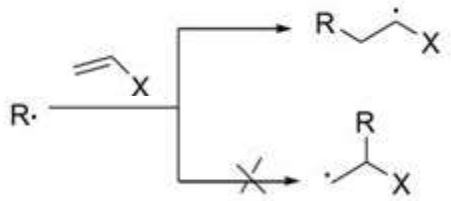
The chlorine atom is electronegative and reacts at C-H bonds with relatively high electron density.

In contrast, alkyl radicals, called nucleophilic radicals, react preferentially at C-H bonds when the electron density is low.

2. Addition

Free radicals add to carbon-carbon double bonds. This reaction is generally selective.

For ex, in CH_2=CHX, addition occurs only at the methyl group, regardless of the nature of X.



Alkynes also exhibit similar reactivity with free radicals.

3. Combination and Disproportionation:

Two free radicals may combine doubly or disproportionately.

$$2Br\cdot \longrightarrow Br_2$$
$$2CH_3\cdot \longrightarrow H_3C-CH_3$$
$$CH_4\cdot + Br\cdot \longrightarrow H_3C-Br$$
$$2Et\cdot \longrightarrow EtH + CH_2=CH_2$$

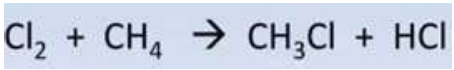
These reactions are generally rapid, and some have negligible activation energy.

Free Radical Substitution Reaction

* As we know that substitution reactions are those reactions in which as atom in a molecule is replaced by another atom or group of atoms. If free radicals are involved during substitution then it is knows as free radical substitution reaction.

* Generally, in free radical substitution, a carbon-hydrogen bond in alkenes is broken and then a new bond is formed with a new

bond. This reaction is called a free radical substitution reaction.



$$Cl_2 + CH_4 \rightarrow CH_3Cl + HCl$$

* In organic chemistry, a radicals-substitution reaction is a substitution reaction involving a free radical as a reactive intermediate.

* The reaction always involves at least two steps, and possibly a third step.

There are many examples of free radicals:

Hydroxylation of benzene by fenton's reagent is an example of free radical reactions.

Many oxidation and reduction reactions in organic chemistry involve free radical intermediates, for example the oxidation of aldehydes to carboxylic acids with chromic acid.

Coupling reactions can also be considered as radical substitution.

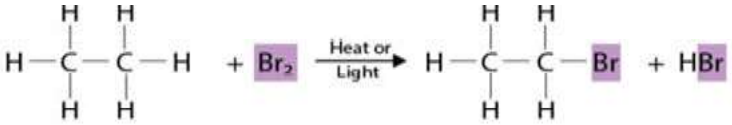
Some aromatic substitutions occur by radical-nucleophilic aromatic substitution.

Auto-oxidation is a process responsible for the degradation of pains and foods, as well as for the production of some laboratory hazards such as diethyl ether peroxide.

1-Halogenation of Alkanes with Br2

Halogenation of alkene with Br2 is an example of free radical substitution reaction.

The free radical halogenation reactions of aldehydes and cycloalkanes are substitution reactions in which the C-H bond is converted to a C-X bond (H is replaced by an X group).



* The symbol hv in this reaction is produced when we irradiate a mixture of ethane and Br2, in the form of gas or solvent, with ultraviolet(UV) or visible light.

* The symbol hv represents UV or visible light energy since the energy since the energy € of light is proportional to its frequency (v) (E=hv). We call this reaction a photochemical reaction because

it is initiated by light, but we will also see that many radical reactions that are not photochemical reaction).

* Although any of the molecular halogens F_2, Cl_2, Br_2 and I_2 will halogenate alkanes and cycloalkanes, Br_2 or Cl_2 are most commonly used. We will use bromination (X= Br) to represent alkanes.

The overall reaction of photochemical bromination of ethane involves several distinct steps. We will divide the first three of these steps into two categories, called initiation and transmission.

Initial Step- In Step 1, light energy breaks the Br-Br bond and forms two separate bromine atoms (Br).As we explained in the previous lecture, the "dot" (.) next to each Br represents one of the two electrons that originally formed the chemical bond between the two bromine atoms in Br-Br.

Propagation Step - Each Br formed in Step 1 has the ability to remove H from ethane.

Where Br removes an electron from the C-H bond along with an H ion.

H-Br is formed in step 2 and releases a reactive molecular fragment (CH_3-CH_2.) called the ethyl radical (CH_3CH_2).

Step 3 - CH_3-CH_2 radical. The ethyl radical (CH_3-CH_2) shown above is a neutral (uncharged) chemical species formed when Br removes (abstracts) a neutral H atom from a neutral ethane molecule.

* Its geometry can be planar or pyramidal (tetrahedral).

* If it is pyramidal, then the C atom is sp3 hybridized and the single unpaired electron is in the sp3 orbital.

* If it is coplanar, the C atom is sp2 hybridized and the single unpaired electron is in the 2p atomic orbital, which is perpendicular to the plane of the C-H and C-C bonds.

* Experimental results and calculations indicate that alkyl radicals generally prefer to be coplanar.

MECHANISM AT AROMATIC SUBSTRATE

* A type of substitution reaction in organic chemistry in which a nucleophilic substitution reaction occurs in an aromatic compound via an intermediary free radical species.

* This type of reaction was discovered by Bunnett and Kim in 1970 and the abbreviation SN1 means substitution radical-nucleophilic unimolecular.

* Let us explain this further by taking the example of the Sandmeyer reaction."

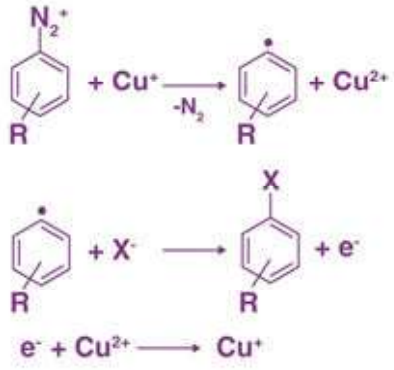
* ~ The Sandmeyer reaction is commonly used for the synthesis of aryl halides from aryl diazonium salts, using copper salts as reagents and catalysts.

* And this reaction follows a radical nucleophilic aromatic substitution.

* The Sandmeyer reaction is a chemical reaction used for the synthesis of aryl halides from aryl diazonium salts, using copper salts as reagents or catalysts.

* This is an example of radical-nucleophilic aromatic substitution, as it follows the same mechanism.

Simple reaction mechanism:



Neighbouring Group Participation (NGP)

* Neighboring group participation in organic chemistry is defined as a reaction in which neighboring groups are involved in the reaction mechanism.

* in which a lone pair of electrons in one atom or reaction center interacts with electrons present in a sigma bond or pi bond (in their neighbor)

* When NGP is activated, it is common for the reaction rate to increase. It is also possible that the stereochemistry of the reaction is unusual (or unexpected) compared to a normal reaction.

* Let us consider some examples involving ionic systems before discussing NGP in free radical reactions.

Neighboring Group Support in Free Radicals:

* We will now discuss the role of NGP in free radical reactions.

* Let us consider the example of a bromination reaction.

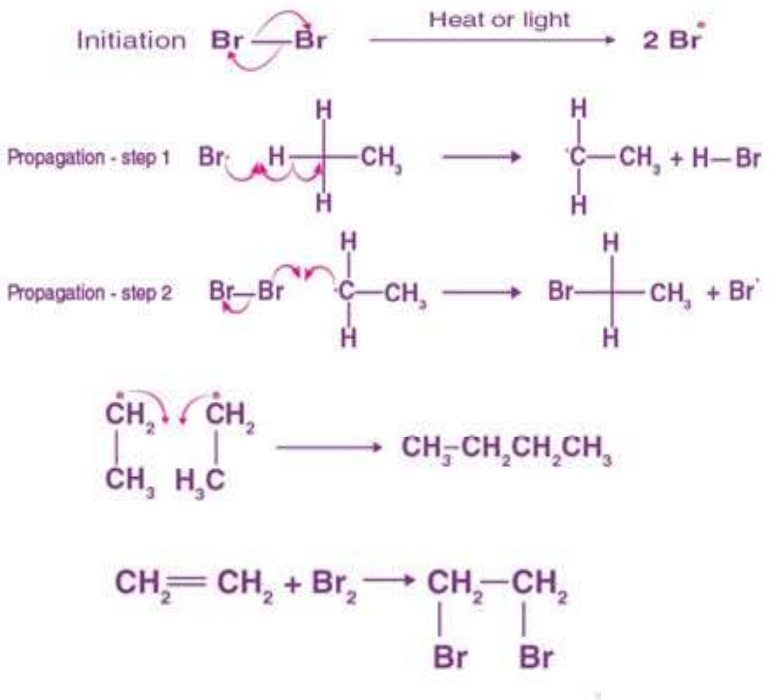
* If bromination occurs with the help of NGP, then the bromination of carbon chains containing bromine atoms occurs with high regional selectivity.

* Bromination of alkyl bromides resulted in 84 to 94% substitution of the carbon adjacent to the bromine already present

in the molecule.

* This is especially so because elements located near the -I group, such as bromine, should actually be neutralized by the electron-withdrawing effect of bromine.

* The unusual regional selectivity is explained by a mechanism in which the extraction of hydrogen is assisted by a neighboring bromine atom, as shown below:



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