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MECHANISM OF ORGANIC REACTIONS UNDER THE EFFECT OF RADIOLYSIS

A Review Article

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ABSTRACT

The mechanism of interaction of radiation especially with organic material explains the ways of optimum utilization of nuclear energy and to avoid its harmful effects. Nowadays three principal mechanisms are adopted to interpret the formation of radiolytic products. These three principal mechanisms are: free radical mechanism, excited state mechanism and interaction with solvated electrons. The presence of atmospheric oxygen, impurities, scavengers, as well as type of solvent, type of radiation, dose and dose rate affect on the mechanism of the radiolytic reaction. The adopted mechanisms are supposed according to the experimental found free radicals and radiolytic products.

The review collected most adopted mechanisms for the most important organic compounds. Summarized mechanisms for radiolysis of hydrocarbons, alkyl halides, olefins, unsaturated and aromatic hydrocarbons, alcohols, organic acids are shown. Also the mechanism of radiolysis of aqueous solutions of some organic compounds is offered. Finally some important technological applications of radiation are offered.

KEY WORDS

Radiolysis, Mechanism of Radiolysis, Radiolysis of Organic Materials, Polymers, Dyes, Detoxification by Radiolysis, Treatment of Chlorinated Organic Compounds.

* Egyptian Armed Forces

1- INTRODUCTION

The fundamental studies in radiation chemistry aim to identify the various formed species during radiolysis, to understand the mechanism of their formation, to get the effect of absorbed dose and dose rate and to try to determine the intermediate and final stable end products [1].

The use of radiation, especially γ and beta to initiate chemical reactions, is important in polymerization, controlled degradation, cross-linking and graft-polymerization. Much of information and results have been gathered on an empirical basis and development of fundamental knowledge that can be used to expect the improvements in materials via the use of radiation energy [2].

The biological effects of radiation are very important for treatment, bacterial and pharmaceutical sterilization, sterilization of seeds and preservation of food [3,4].

2- PRINCIPAL MECHANISMS OF GENERATION OF RADICALS DURING RADIOLYSIS OF ORGANIC COMPOUNDS

The three principal radiolytic mechanisms to interpret the production of free radicals as well as radiolytic products are [1,5]:

Molecular excited mechanism, in which the excited molecules interact either with themselves or with other molecules to produce radicals and radiolytic products.

Free radical mechanism, in which the free radicals (formed due to deexcitation of the excited molecules) interact with solute, with the solvent molecules or with each others, or degradation occurs to produce radiolytic products.

Solvated electron mechanism, in which solvated electron interact with reducible centers such as carbonyl groups to reduce them to alcoholic groups or to react with positive molecules to produce excited ones, or to reduce higher oxidation state metal ion to lower one.

The three mechanisms participate simultaneously to produce radicals and radiolytic products and the predominant one depends on:

- The nature of solvent.
- The nature of solute.
- Presence or absence of oxygen.
- Absorbed dose and dose rate.
- Temperature and pH of solutions.

The nature of solvent depends on whether it is polar or not. Polar solvents facilitate the rapid formation and stabilization of solvated electrons that enable them to be more efficient for reduction such as in isopropyl alcohol.

The nature of solute affects on the direction of radiolytic mechanisms. If solute scavenge electrons, other mechanisms will be efficient for affecting on the solvent

and the scavenging solute will be reduced. If the solute S is keton, electrons can be scavenged, and free radicals may be scavenged also to produce radiolytic products [6].

Oxygen has an important role with $\cdot\text{H}$ to form $\cdot\text{O}_2\text{H}$ and this changes the nature of radiolytic reactions to produce different radiolytic products. The nature of $\cdot\text{H}$ is reduction whereas that of $\cdot\text{O}_2\text{H}$ is oxidation. The present solvated oxygen can scavenge easily the solvated electrons to form O_2^- which reacts with H^+ to form $\cdot\text{O}_2\text{H}$ which has higher oxidizing tendency instead of reducing by solvated electrons in case of absence of oxygen. As a result, different radiolytic products may be formed due to different actions of formed species in absence and presence of atmospheric oxygen [7].

The dose rate and absorbed dose affect on the radiation yields due to the rapidity of some reactions than others. For examples, the physical and physicochemical changes are more effective at high dose rates due to their short period of reaction, whereas the chemical stage reactions are effective at moderate and low dose rates. The variation of absorbed dose and dose rate interprets the difference of G-values obtained during radiolysis of the same medium [6].

The difference in the working conditions of pH and temperature affects on the radiolytic mechanisms and reactions. For example, at lower pH value, the H^+ acts as scavenger for electron to produce $\cdot\text{H}$ or facilitate the ability of oxygen molecule to scavenge electrons to produce H_2O_2 . The temperature has an important effect on the rate of radiolytic reactions like normal reactions. The raise of temperature increases the radiolytic yield due to raise of energy levels of solute and solvent, and as a result less energy will be required for production of ion pairs and other excited species [6,7].

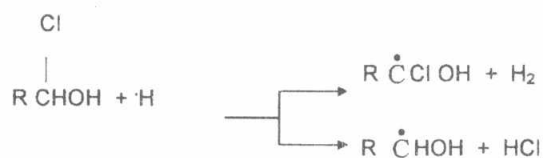
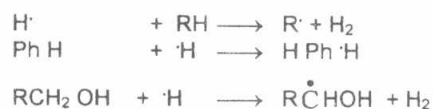
The homolysis of excited molecules forms free radicals that are very reactive. They have unpaired electron and enter in many reactions in irradiated medium. The free radicals may react with stable molecule M or another radical or ion forming intermediate or final products.

Sometimes, scavengers are added to react with some certain primary radical species. Some scavengers are specific for certain species (such as electrons). This can be utilized to measure the quantitative formation of these species. Other scavengers are less specific. At concentrations lower than 10^{-4} M, scavengers will react only with some diffusing species. Scavengers of concentrations of more than 10^{-4} M will react with all diffusing species formed. High concentrations (over 0.1 M) are used to scavenge the primary species and inhibit the intermediate reactions. Sometimes, certain scavengers are added to remove certain primary species to prevent some reactions and to let another to proceed. Sometimes in the excited molecules, the energy is absorbed at certain location, and the effect appears at another susceptible site [1,6].

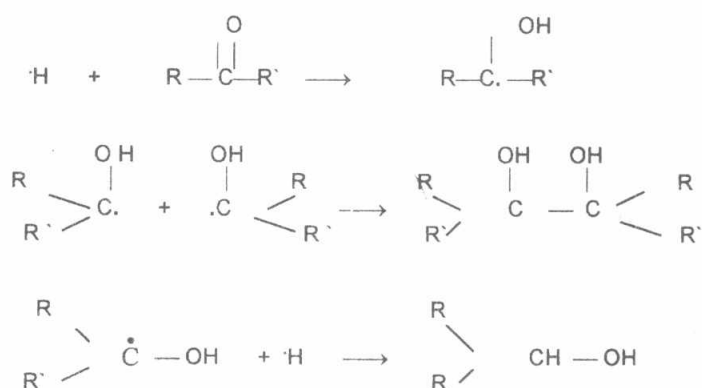
2.1- The Hydrogen Atoms

They are important reducing agents liberated during radiolysis of most solutions or hydrogen containing substances. They can liberate hydrogen molecules and radicals from organic compounds. Hydrogen radicals can be produced as a result of interaction of solvated electrons with H^+ in acidic solutions or directly from molecular species. In acidic solution, the hydrogen atoms predominate than solvated electrons. In existence of oxygen, they interact with it giving hydroperoxyl radical $\cdot O_2H$ and become high effective oxidizing agent [7].

The main reactions of hydrogen radicals with organic compounds are addition (on double bond or in a ring) or hydrogen abstraction from $-CH_2-$ groups of α positions to $-COOH$, $-OH$ and withdrawing groups. They also produce with carbonyl compounds the corresponding alcohols and pinacols as follows [6,7]:

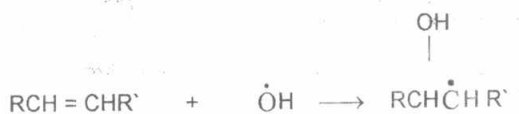


They also produce with carbonyl compounds the corresponding alcohols and pinacols



2.2- The Hydroxyl Radicals

They are important oxidizing species that are formed during radiolysis of water and alcohols. In the reaction medium, they may show charge transfer (with $^-\text{OH}, \text{X}^-$), hydrogen abstraction, addition or displacement as follows[1,6]:



2.3- Hydroperoxyl Radicals

They have been identified as primary species in the tracks of heavy particles in aerated solution as a result of attack of H^\cdot to O_2 to get $^\cdot\text{O}_2\text{H}$ or as a result of interaction of negatively ionized oxygen molecule (as a result of interaction of O_2 with electrons) with H^+ . They are considered as high oxidizing species [6].

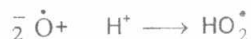
Hydroperoxyl radicals have been identified as primary species in the tracks of heavy particles in deaerated solution due to the following reaction :



In aerated solution, they are formed also as a result of attack of H^\cdot to O_2



or as a result of interaction of negatively ionized oxygen molecule (as a result of interaction of O_2 with electrons) with H^+

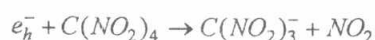


2.4- Solvated Electrons

They are the very active species that formed during radiolysis. They react as nucleophilic and their reductive property is very active and important. The main properties of free solvated electrons can be summarized as follows [6,8,9]:

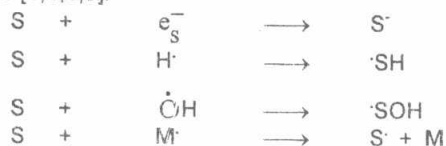
- If the solvent is pure water, the free solvated electrons have a broad optical absorption with maximum absorption at 720 mμ (nm). According to the type of solvent, they have absorption spectrum in UV, visible or IR.
- Solvated electrons react with oxidizing agents like sulfur, halogen, carbonyl (like ketones and aldehydes or nitro compounds).
- Solvated electrons have a period of life $> 10^{-6}$ s. They disappear according to the kinetic law of homogeneous ion system. Their mobility is lower than those of electrons of metal conductors and higher than negative ions.
- They have magnetic moment. Therefore they can be followed by Electronic Paramagnetic Resonance (EPR).

The solvated electrons can be converted to stable anion using tetra nitro methane as scavenger as follows [10]:



2.5- Solute Species

According to the type of solute, scavenging will be for certain radicals, electrons or excited species to produce solute species. Solute species may interact with solvent molecules or radicals to produce radiolytic final products. Some certain substances are more reactive towards radiation than others due to weakness of some bonds (like S - S), or due to high scavenging possibility of formed free radicals and electrons like urea, amines, and amino acids. These substances can be utilized to protect some biological systems against radiation damage or to determine quantitatively the formed radicals in order to utilize them for determination of absorbed dose [3,6,8,9].



$$-\frac{d[S]}{dt} = -\frac{d[R^\cdot]}{dt} = \frac{d[P]}{dt} = k_t[S][R^\cdot]$$

3- RADIOLYSIS OF ORGANIC COMPOUNDS

3.1- Radiolysis of Hydrocarbons

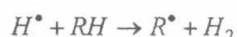
The mechanisms of radiolytic decomposition of organic compounds are not easy since the radiolytic products are too much to be analyzed. It can be expected that bonds of lower bond energy are broken before that of higher energy ones.

Radiolysis of hydrocarbons showed that C-H bond is broken easily than C-C. Radiolysis of organic compounds leads to formation of excited molecules, free radicals and ions that go through several reactions in the radiolytic medium. The excited molecules may induce reactions that give several radiolytic products, intermediate radicals or transfer energy to another molecules [6]. A simple mechanism can be represented as follows [10]:

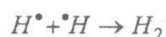
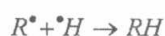
initiation :



propagation :



termination :



Another mechanisms during radiolysis of organic compounds exist like proton transfer, radical generation from excited molecules, hydrogen abstraction and fragmentation of branched alkanes. Alkyl and hydrogen radicals that produced from excited species cause further degradation. Steric effects decrease the rate of recombination.

In aqueous solutions, degradation is formed by hydroxyl radical at pH greater than 6 and by hydrogen radicals at lower pH [11,12]. The main effects of radiation on alkanes are: liberation of H₂, development of unsaturation, formation of dimers, production of fragments from C₁ to C_n and their combinations. Radicals will undergo dimerization, abstraction, and addition reactions. Electrons can be scavenged by nitrous oxide, sulfur hexafluoride, CO₂, or aromatic compounds. Also water or ammonia can scavenge protons. Positive ions and free radical are scavenged by nitric acid. Free radicals can be scavenged by iodine, O₂, DPPH [1,1 diphenyl 2 picryl hydrazyl]. Unsaturated produced positive ions and electrons can be scavenged by biphenyl and alkyl iodides. The presence and type of scavengers affect on the radiation yield. Mechanisms of ion molecules and ion molecule radicals interpret the formation of many radiolytic products [13,14].

Ter-butanol acts as ·OH scavenger in aqueous oxygenated system forming ter-butanol peroxy radical [15]. The halogenated hydrocarbons scavenge electrons and the produced HX scavenge electrons too [16,17]. Baicalin scavenge hydroxyethyl and peroxy radicals during radiolysis of aerated ethanol in presence of oxygen. Baicalin molecule could inhibit formation of one molecule of hydrogen peroxide and two molecules of acetaldehyde during radiolysis of ethanol [18]. Hydroxy-cinnamic

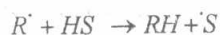
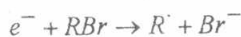
acid derivatives scavenge superoxide radical anion during radiolysis of organic acids [19].

3.2- Alkyl Halides

Usually their gas radiolytic products contain both halogens, HX and dimer as in case of dichloromethane [20]. Mechanism of reaction follows through excited state and free radical mechanisms. In aromatic halides, excess energy can be taken by the pi-electrons of benzene ring [21]. In radiolysis of chlorofluorocarbons, dechlorination was reported due to the effect of hydroxyl radicals [22]. Modern utilization of radiolysis of halogen compounds is to get rid of them as pollutants in industrial wastewater. Radiolysis with photolysis and using titanium oxide as catalyst proved good way for their detoxification specially that act as toxins and very difficult to be removed by classical chemical redox reactions. New attempts are directed to increase the radiation yield in their chain reactions [23]. More attempts are now made to utilize the spent reactor fuel as gamma radiation sources to decompose the halogenated hydrocarbons from wastewater [24].

Oxidative degradation of chlorinated organic compounds was proved due to surface adsorbed hydroxyl radicals on titanium oxide [25]. The presence of oxygen accelerates the chain reaction degradation and increases the effect of hydroxyl radical [26]. The main mechanisms are hole transfer for chlorinated radicals to cause electron transfer from the molecules as well as through free radical mechanisms [27,28]. The use of alcohol helps in degradation since hydroxyl radicals are formed radiolytically from them [29].

Electron attachment mechanism in halomethanes was proved [30]. In radiolysis of CH₃Br and CH₃CH₂Br (which can be represented by R-Br) as electron scavengers in tetrahydrofuran (HS). The yields of CH₄ and C₂H₆ were formed due to this mechanism:



Let G(P) is the radiation yield of CH₄ or C₂H₆, C is the concentration of CH₃Br or CH₃CH₂Br, G_{esc} is the yield of escaping spurs recombination, G_{gi} is the yield of geminated recombination and α is adjustable parameter depending on the efficiency of scaping, then:

$$G(P) = G_{esc} + G_{gi} \frac{(\alpha C)^{0.5}}{1 + (\alpha C)^{0.5}}$$

For low concentration of R-Br:

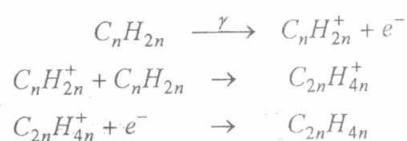
$$G(P) = G_{esc} + G_{gi} (\alpha C)^{0.5}$$

For low concentration of CH₃Br (1.51 × 10⁻⁴ to 0.13 mol. l⁻¹) G_{esc} = 0.338 ± 0.17, G_{gl} = 3.82 ± 0.24 and α = 19.8 ± 3.4 [31].

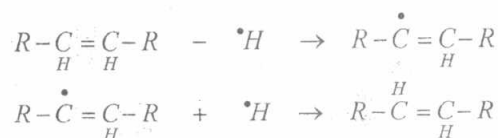
3.3- Unsaturated Hydrocarbons and Cyclic Compounds

They possess Π's orbital which differs significantly from σ-one of saturated hydrocarbons in having lower ionization potentials. The Π's orbital can add free radicals and ions. Presence of double bonds in molecule stabilizes the radical via resonance. Irradiation of liquid alkenes produces free ions of about the same yield as saturated hydrocarbons due to similar dielectric constants. The radiolysis of unsaturated hydrocarbons give products of multi-carbon atoms due to the ability of free radicals or cations to add to double bonds [12]. The main radicals detected during radiolysis of liquid alkenes are those from loss of a hydrogen atom from allyl positions and those corresponding to addition of hydrogen atoms at the double bond and the proposed mechanisms as follows [12]:

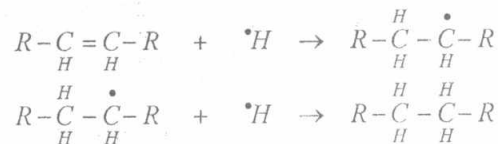
Polymer formation:



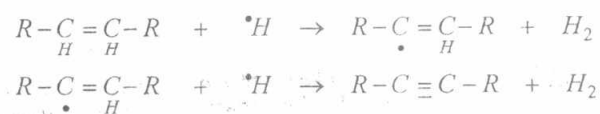
Cis-trans isomerization:



Addition on the double bond:



Formation of alkynes:



The radiolysis of cyclohexane may produce dimerization of cyclohexyl radicals. In substituted cyclohexane, the mechanism of production of radiolytic products was through excitation energy transfer [32]. Hydrogen gas was obtained as principal product due to radiolysis of liquid cyclohexane [33]. During radiolysis of cyclohexane in presence of oxygen, hydroperoxide radical with cyclohexane ones are produced [34,35].
In cyclohexane :

$$G(P) = G_{esc} [1 + (1.61 r_c^2 k C / D)^{0.6}]$$

Where r_c is Onsager escape radius, k is rate constant of scavenging of electron by solute, C is concentration of scavenger and D is the sum of diffusion coefficient of electron and counter ions.

Radiolysis of cyclopentane yields cyclopentene and bicyclopentyl radical [36]. Radiolysis of fluorohexane produces fluorine [37,38].

3.4-Aromatic Hydrocarbon

Due to conjugated electrons, aromatics resist irradiation. This resistivity is due to the ability of conjugated system to degrade excitation energy without localizing it on certain bond, and hence there is no scission. Thiophenol is the only aromatic that is reported to be sensitive to radiation due to ability of C—S bond to be ruptured [39]:

The aromatic ring scavenges radicals, electrons, and H_2 . During their γ -irradiation, polymer, as well as ethers are produced. The presence of different scavengers at different doses affects the degradation yield and its mechanism. Alkyl substitution increases the sensitivity to radiation and abstraction is less than addition [39]. The radiolysis of substituted benzenes in aqueous solution involves both direct electron transfer, addition and elimination reactions [40,41,42].

Addition of oxygen on ortho and para positions to hydroxyl group in cresols during radiolysis was investigated [43]. In radiolysis of vapor form with other compounds and water, substitution of groups takes place by hydrogen atom, hydroxyl radicals or other radicals depending on the nature of existing material and ratio of composition of vapor as follows [44]:

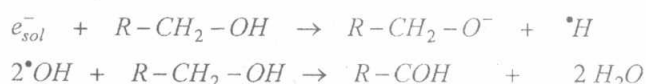


3.5- Alcohols

The properties of simple alcohols are intermediate between those of water, which contains only (O-H) bonds, and the saturated hydrocarbons, which contain only

(C-H) bonds. The simple alcohols have dielectric constants at ordinary temperature of 20 - 30, compared with 80 for water and 2 for hydrocarbons. Therefore, the results obtained during their radiolysis are between those found from the two [45].

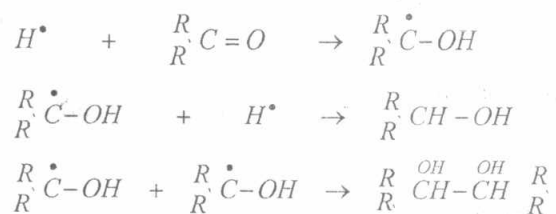
Aliphatic alcohols scavenge solvated electrons but not strongly as in water. Isobutanol scavenge hydroxyl radicals to form aldehyde [44]. Radiolysis of isopropyl alcohol can be utilized as a source of producing hydroxyl radicals for detoxification of halogenated waste [45]. The mechanism of radiolysis of methanol alikes that of glycerin. The principal mechanisms of interactions of solvated electrons and excited molecules in alcohols cooperate to form radiolytic products as follows[47,47]:



The existence of scavengers lessens the yield of radiolytic products [49,50].

3.6- Radiolysis of Ketones

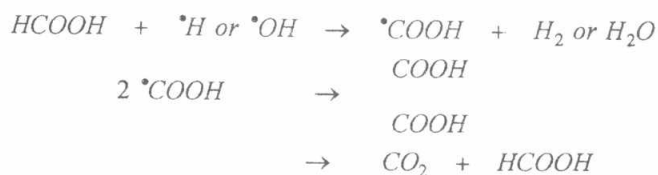
The radiochemical yields of main products during γ -radiolysis of furyl ketones in 2-propanol were studied. The yields of hydrogen and methane were lower than those obtained from 2-propanol only. Concerning the mechanism, electron capture and radical processes are probably the reason of formation of the alcohol and pinacols which are produced by radioreduction and dimerization respectively. Substitution products indicated radical processes as follows[51]:



3.7- Radiolysis of Organic Acids

The radiolysis of formic acid as an example is studied; since it is good scavenger for electrons hydrogen and hydroxyl radicals. The G value depends on pH ,

solution concentration, medium, dose and dose rate. Irradiation of carboxylic acids produce large quantities of H₂, CO₂ as follows:



The gas phase during their radiolysis contains CO₂ and light hydrocarbon. The formation of radiolytic products increases with temperature [52,53].

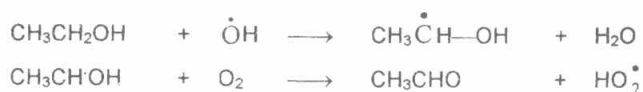
3.8- Radiolysis of Ethers

Ethers are attacked by hydroxyl radicals generated by radiation [54]. Most radiolytic mechanisms are based on experimental results, like rupture of C – O bond [55]. Also free radical mechanism for formation of radiolytic products was adopted due to degradation of C – O, C – H bonds. Beside radical interaction mechanism, both ionic and excitation mechanisms are operative [56].

3.9- Radiolysis of Some Organic Aqueous Solutions

Neutral aerated aqueous solution of ethanol gives acetaldehyde. In deaerated

solutions, CH₃·CHOH is formed from the reaction of ·H and ·OH with the molecule of alcohol. Two of the formed radicals give the corresponding pinacol. In acidic deaerated solution, acetaldehyde and pinacol are formed [57,58]. In neutral aerated aqueous solution of ethanol gives acetaldehyde as follows:



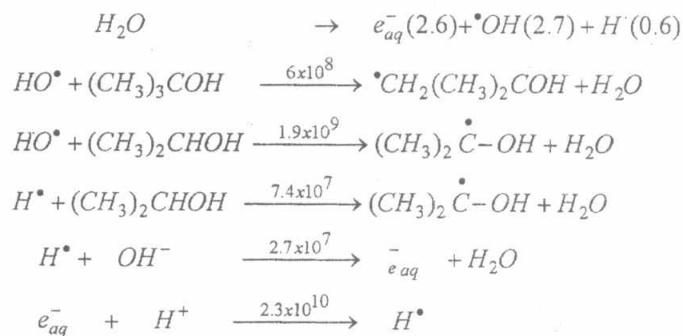
In deaerated solutions CH₃·CHOH is formed from the reaction of ·H and ·OH with the molecule of alcohol. Two of the formed radicals give the corresponding glycol:



In radiolysis of 0.25 M aqueous solution t-BuOH, $\cdot\text{OH}$ is scavenged with $k = 6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, whereas $\cdot\text{OH}$ and $\cdot\text{H}$ species react with 0.17 M t-PrOH with $k = 1.9 \times 10^9$ & $7.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ respectively. In alkaline medium e_{aq}^- is produced from reaction of $\cdot\text{H}$ with $\cdot\text{OH}$ ($k = 2.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$), whereas in acidic medium e_{aq}^- reacts with H^+ to give $\cdot\text{H}$ ($k = 2.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) as follows:

At pH 13, G of i-PrOH was independent of dose and equals 3.2 and G of t-PuOH equals 6.6 [59].

3.10- Radiolysis of Chlorinated Oils



Radiolysis of hydraulic and transformer oils was studied. The result of radiolysis was that dechlorination had occurred [60]. The same mechanism occurred in radiolysis of polychlorinated phenols in several oils. This dechlorination process by radiation can be utilized as an advanced way for dechlorination in waste treatment of toxic chlorinated compounds [59,60].

4- MECHANISM OF IRRADIATION OF POLYMER

The mechanisms of irradiation of polymers are deduced from changes in structure and properties of irradiated polymer, or from the properties of prepared polymers by irradiation. The analysis of effects of radiation was studied by Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR), Gas Chromatography (GC), Fourier Transformed Infrared (FTIR), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Dynamic Mechanical Analysis (DMA) [2]. In copolymerization by radiation, cationic and radical mechanisms were proved [61].

Both degradation during irradiation and graft polymerization in post irradiation occur through radical mechanism [62]. The dependence of scission as a function of LET was almost constant at low LET and decreased at high LET ion irradiation [63]. The scission chain reaction decreases with lowering temperature [64]. The scission does not take place immediately after absorption of radiation energy, but it is induced by the intramolecular radical conversion [65]. Some changes

may be attributed to trapping of negative charge on certain electronegative groups or benzene rings [66]. The mechanical properties of polymers are deteriorated by radiation and additional crosslinking beside degradation have occurred. Thermal annealing may be useful for recovery of mechanical properties [67]. The mechanism of free radical polymerization can be considered in terms of four elementary steps as follows[68]:

1-Formation of free radicals R^\bullet :

The rate of decomposition R_d is:



$$R_d = k_d [I]$$

Where k_d is radical formation rate constant ($l \cdot M^{-1} \cdot s^{-1}$) and $[I]$ is the concentration in $M.l^{-1}$.

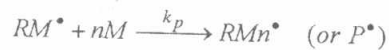
2-Addition of the first monomer molecule M with radical R^\bullet to initiate the chain reaction:



$$R_i = k_i [R^\bullet] [M]$$

Where k_i is chain initiation rate constant .

3-Propagation reaction to add monomers with propagation rate constant k_p and propagation rate R_p as follows:



$$R_p = \frac{d[P^\bullet]}{dt} = k_p [RM^\bullet] [nM]$$

Where $[nM]$ is the monomer concentration, $[P^\bullet]$ is the sum of concentration of all RM_n^\bullet .

4-Bimolecular termination reaction which can be represented by the termination rate constant k_t and rate of termination as follows:



$$R_t = -\frac{d[Y]}{dt} = k_t [P^\bullet]^2$$

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