RADIATION STABILITY OF SOME CHEMICAL COMPOUNDS WITH POSSIBLE APPLICATION TO RADIATION DOSIMETRY

Thesis Submitted

By

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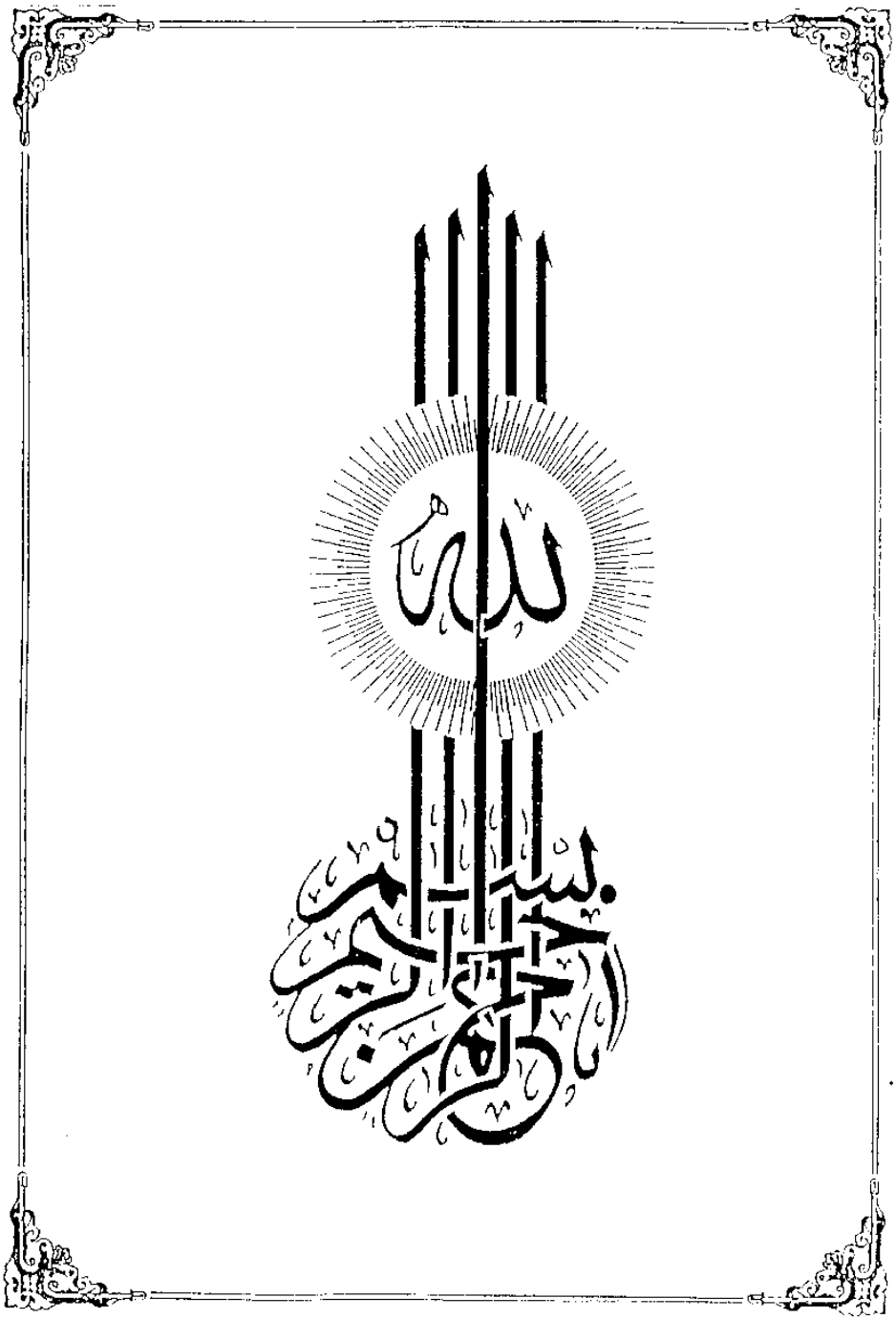

C O N T E N T S

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AIM OF THE WORK

The aim of this disertation on "Radiation stability of some chemical compounds with possible application to radiation dosimetry" is to elucidate the dosimetric characteristics of aqueous solutions of both Bromophenol Blue and Bromocresol Red, by studying the different factors affecting their radiolysis. Among these factors, are the pH of the solutions, the concentrations of the dyes, the presence of some organic additives as well as oxygen. The decoloration yield represented by G(-dye) (which is the radiolysis yield per 100 eV of absorbed energy is to be measured under different conditions. The color stability and the radiation response of the dyes under the different conditions are to be determined. In view of the obtained results, radiolysis mechanisms can be discussed. Specific bimolecular rate constants for reaction of the dyes with water radiolysis products can be estimated. Based on the experimental results and theoretical calculations assessment of the dosimetric characteristics of the different dye solutions can be deduced.

I. INTRODUCTION

1.1 Importance of Dosimetry in Radiation Processing

1.2 Radiolysis of Water and Aqueous Solutions.

1.3 Literature Survey on The Use of Dyes in Chemical Dosimetry.

Radiation chemistry may be defined as the study of the chemical effects produced in a system by the absorption of ionizing radiation. The last decades have seen a growing interest in radiation chemistry due to the great development and wide spreading of nuclear energy. Sources of radiation include, nuclear reactors, spent fuel rods, fission products, artificial isotopes, linear accelerators and radioactive cobalt. The controlled increase of nuclear energy and the accompanying release of nuclear radiation has focused a good deal of attention on the possible uses of such radiations in chemical industry. Radiation chemical processes possess several attractive features as compared to conventional processes. These features are well known to specialists and are covered in many text books[1-14] as well as many reviewing articles (15-24) and lead to a marked increase in the use of radiation in food sterilization, in the control of insects, in sprout inhibition, in sterilization of drugs, pharmaceuticals and medical supplies. The use of radiation in chemical synthesis has recently witnessed a great development manifested by: synthesis of gammexane, sulfochlorination of hydrocarbons, nitrogen fixation, polymerization of monomers, cross linking of polymers and graft and block copolymerization.

The effect of ionizing radiation on matter depends on the composition of matter and the amount of energy that is imparted to it by the radiation. The amount of absorbed radiation energy per unit mass is called the absorbed dose. A special dose unit is the rad which is defined as the deposition of 100 erg gm^{-1} of matter. The radiation yield is measured by the G-value which is the number of molecules, ions or radicals formed per 100 eV of absorbed radiation energy.

The development of all the above mentioned lines of radiation and process chemistry necessitates the presence of reliable dosimetric systems. The present work aims at studying the possibility of the use of aqueous solutions of some organic dyes in chemical dosimetry. The coming paragraphs outline relevant topics and include:

- The importance of dosimetry in radiation processing.
- The radiolysis of water and aqueous solutions.
- A literature survey on chemical dosimetry of dyes.

1.1 Importance of Dosimetry in Radiation Processing:

In the past sixty years, since Hugo Fricke[25-31] suggested that the oxidation of the ferrous ion induced by radiation could be used as a measure of the radiation dose, dozens of chemical systems and radiation-induced chemical reactions were examined from the point of view of absorbed dose measurements. Many of these systems were found to be applicable over the kilorad-to-megarad range.

The main purpose of dosimetry is to supply cheap and reliable quality control in radiation processing. Radiation processing is a rapidly growing industry involving beside the forementioned lines the improvement of polymers, paints and inks, elastomers, textiles and resins by ionizing radiation (electron beam, X-rays; gamma rays), either during production or by treatment of the finished product. Ionizing radiation is used to disinfest or prolong the shelf life of large volumes of food stuffs and sterilization of medical products and applicances.

In radiation processing accurate and reproducible radiation measurement (dosimetry) plays the key role.

Successful radiation processing depends greatly upon the ability of the processor to measure the absorbed dose delivered to the product, to determine the dose-distribution patterns in the product package and to control the radiation process once production begins. Therefore it is necessary that presonnel responsible for the operations of the plants have basic understanding of radiation engineering and dosimetry involved. In the last ten years Egypt introduced such a radiation technology and installed a Co-60 radiation facility located at the National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo. This unit has been already used for both sterilization of medical desposables and food preservation.

In measuring abosrbed dose over the range specified for industrial radiation processing (10^3-10^8 rads), a number of primary, secondary and tertiary dosemeters may be used,see the table[32-40]. Descriptions of these systems and how they are used in processing applications are adequately covered in literature. In the above mentioned list of measurement devices,there are several new promising systems and methods not widely used as yet but showing particular promise for future applications.

(32-40)

VARIOUS DOSIMETRY SYSTEMS FOR RADIATION PROCESSING

PRIMARY

Calorimeters

Ionization chambers

Ethanol-chlorobenzene sol.

Ferrous sulfate sol.

(Fricke or "super" Fricke)

Ferrous-cupric sulfate sol.

Cerric sulfate sol.

Gas evolution (water)

Hydrated electron

(NaOH and EtOH in water)

Aqueous ferrocyanide sol.

Aqueous potassium thiocyanate

Aqueous benzene

Oxalic acid sol.

Sodium formate sol.

Holographic interferometry

(refractometry)

SECONDARY (MISCELLANEOUS)

Biological systems

Semiconductors

(Silicon p-n junction)

Polymers

(measurements of changes in viscosity, ESR spectra, pressure, conductivity, size, mass, melting point, solubility

Various solutions

(potentiometry, oscillometric analysis)

SECONDARY (OPTICAL)

Plastics:

Cellulosics

Polycarbonate

Polyethylene

Polyethylene terephthalate

Polymethyl methacrylate

Polyvinyl halides

Dyed plastics:

Cellulosics

Polyamides (Nylon)

Polymethyl methacrylate (Perspex)

Polystyrene

Polyhalostyrenes

Polyvinyl halides

Other vinyl plastics and acrylics

Dyed solutions

Glucose sucrose, maltose etc.

(Optical rotation or bioluminescence)

Solid state systems

Crystalline systems

(therro-or photoluminescence)

Glasses

Photographic emulsions

TERTIARY

pH indicators

(hologenated hydrocarbons)

Radiochromic papers

1.2 Radiolysis of Water and Aqueous Solutions:

Water is the most important single solvent in which the physical and chemical processes that can occur are of broad importance in so many areas of natural sciences. As a result, the rates and equilibria of chemical reactions in aqueous solution have been the subject of countless investigations of almost every conceivable chemical system of substances soluble in water. The coming paragraph gives details of the interaction of water radiolysis products with some common materials. The short lived products of water for low linear energy transfer radiation LET radiation (Co^{60} gamma rays, x-rays, and electron with energies of about 30 KeV and above) are

$$H_2O \rightsquigarrow e^-_{aq} , H \quad \text{and} \quad OH$$

In the presence of oxygen, hydrated electrons and hydrogen atoms are transfered to other short lived species namely O_2^- and HO_2 - O^- and O_2^- can be also produced from the equilibria

$$OH \rightleftharpoons H^+ + O^- \qquad P_k = 11.9^{(41)}$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad P_k = 4.88^{(42)}$$

It is evident that by control of pH and oxygen concentration in water, one can get e_{aq}, H, OH, HO_2, $\bar{O}_2$ and $\bar{O}$. All these species have been identified and their reactions with hundreds of inorganic and organic compounds have been measured[42]. Generally the rate constants of short lived species are measured by steady state and pulse techniques. Steady state techniques yield ratio of rate constants which are deduced from certain mechanisms. The latters are usually quite complexed and hence they lead to a measurable uncertainty in the measured rate constants. Pulse techniques are more favorable since they can be considered as direct measuring techniques and depend on either decay kinetics or product build up kinetics. Another technique for measurement of rate constants is competition kinetics and depends on the use of relative rate ratios for reactions. Several compilations of specific bimolecular rate constants were published, among which one can mention the "National Standard Reference Data series NSRDS published by the National Bureau of Standards in 1977[43].
Based on the above compilation a short review of the reactivity of each of e^{-}_{aq}, OH, $\bar{O}_2$ ------ will be given.

The hydrogen atom [44]:

H is the simplest chemical species, ionizing a simple electron, its reactivity with other chemical species is