STUDIES OF THE PHOTOCHEMICAL KINETICS OF METHYLENE BLUE WITH REDUCTANTS

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BY

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Dedicated To

My

Loving parents
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ZAHIDA KHALID
موجودہ تختیات مسلسل تیار کیے جانے میں موجودہ سب کی کمی کے بارے کی نامی (Methylene blue) نمی میں موجودہ تختیات کا استعمال کیا گیا ہے۔

تختیات کا مواد میں موجود (phenyl urea) اور (allyl urea) (Urea) اور (allyl thiourea) کو فیوریا اور (thiourea) کو فیوریا (Urea) مواد کے طور پر استعمال کیا گیا ہے۔ کیونکہ کانوں میں تختیات گیا کے معاون اور نظریہ طاقت کے

مشترکہ ابتدائی مقامات اور نظریہ نصب تختیات کے معاملے میں، اور نظریہ بہت معاون کے

تیار کے حسب میں۔ حال کے حساب میں فیوریا اور معاون کے مواد میں پہلا گیا ہے۔

شاہعہ پریزی کے لیے خاص منظری ترتیب کا استعمال خاص ہے۔ کی نظریہ تختیات کا ناصراء میں

ہے۔

ابتدائی طور پر مثبت گلیم میں بیج (Methylene blue) کی ضرورت ہے۔

تیزابنات (H_2O) پھر تیزابنات کی موجودی اور موجودی میں کتنی تیزابنات معلوم کردی گئی تھی کے کتنی تیزابنات موجودہ کی استعمال کی جا گئی۔ تیزابنات کی مقدار (Hammet)

ہے۔

ہے۔ ہے 4.06 سے 7.59 ہے۔

تیزابنات کی مقدار (quantum yield) کے حساب میں تیزابنات کی مقدار

کم کی گئی اور پھر بحال۔ اگر کتنی تیزابنات بحال ہو گئی ہیں کتنی ہے۔ کتنی مقدار کی مقدار پر نظریہ کی

دقت میں سب ہے۔ اسے سلسلہ سے تختیات میں تختیات اور نظریہ طاقت کے

ہے۔
پیشینہ: مقامدار پر میگیور دوامات افراد اعزاز نجی کے، نظر کے، تمادی، اور فیلڈ اور (Light intensity) کا سیٹ ہ دلء ہے۔ نویں شدت کی ہوتی ہے۔

وہی کا نظر ثانی ملا ہے کہ موجودہ بقیے مواد سے حاصل ہوئے دیاں ہوئے سے بیج دوائی مولی کی ہے۔ عمل میں نازکی سماج اور بکارا تعلیم کی میکانیک کے بات دوائی سے۔ ہمیشہ تعلیم کے میکانیک کی مہمگا ہے۔ مولا تعلیم کی میکانیک کا موزیک نقلی۔ ہمیشہ بیج دوائی سے بات دوائی مولی کی میکانیک کی سماجی استعمال لا ہے۔ بیج دوائی سے بات دوائی مولی کی میکانیک کے مختلف دوائی مولی کی شرح ہے۔ بیج دوائی مولی کی میکانیک کے مختلف دوائی مولی سے بیج ہوئی کے ساتھ کی ہے۔

پیشینہ شرح تعلیم کا کام یافتہ کے ساتھ کی ہے اور ایک تعلیم ہے۔

حراست چنیوں کی بہت سے بہت بہت بہت اور آرتھینس (Arrhenius) اور آرتھینس (Eyring) میں مساوات کی کوار ملتی، اور ایک میکانیک کی سمجھ کر۔

E_a (کے) کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجھ کی سمجhek
ABSTRACT

The present investigation reveals the study of photochemical reduction of methylene blue by some organic reductants. For this purpose urea, allylurea, phenylurea, thiourea and allylthiourea were chosen as suitable reducing materials, because their homologues and benzene ring substituted derivatives are well characterized and are prepared easily in a fairly good crystalline state. The reduction was carried out in 50% v/v aqueous 2-propanol. The photochemical reactions were characterized by using special optical arrangements for the irradiation of deaerated test solutions.

As a starting point, the photoreduction of methylene blue was carried out in presence of various reducing agents at different acidities. Acidities of the solutions were determined by Hammett acidity function (H0). The best selected acidities range found to be from 4.06 to 7.59. The quantum yield calculated at various acidities, decreases as the acidity values increases.

The quantum yield of the reaction varies directly with the increase in the concentration of the reductants and temperatures. Moreover, it was found that quantum yield for the reaction was independent of the concentration of the methylene blue. The results and experimental findings obtained were also interpreted in terms of comparative reaction mechanism associated with reported work, in terms of structure and concentration of
reducing agents. Ratios of the rate constants were calculated by using various relations in proposed mechanism. However tests were also put forwarded to verify the values of the rate constants of various steps. From the present investigation it has become more certain that the quantum yield is essentially controlled by two equilibria.

i. The triplet state of methylene blue with the proton and the protonated triplet state of methylene blue.

\[ \text{MBH}_T^+ + \text{H}^+ \rightleftharpoons \text{MBH}_{2T}^{++} \]

ii. The protonated triplet state of methylene blue with reductants, and associated complex of methylene blue.

\[ \text{MBH}_{2T}^{++} + \text{AH}_2 \rightleftharpoons \text{MBH}_{2T}^{++} \cdot \text{AH}_2 \]

Since the quantum yield is directly proportional to the rate constant and varies with temperature, Arrhenius and Eyring relationships were used to calculate activation parameters such as energy of activation \( (E_a) \), free energy change of activation \( (\Delta G^*) \), enthalpy change \( (\Delta H^*) \) and entropy change \( (\Delta S^*) \) of activation.
CHAPTER I

INTRODUCTION
1.1 INTRODUCTION TO PHOTOCHEMISTRY

Photochemistry is concerned with reactions, which are initiated by electronically excited molecules generated by absorption of suitable radiations in visible or near ultraviolet region. Since the absorption of light produces excited states of atoms and molecules, photochemistry is really the study of the chemistry of excited states. Electromagnetic radiation in the visible and ultraviolet region is generally required to produce chemical reactions because changes in electronic energy levels are required. More recently absorption of many infrared photons from a high-intensity laser can also cause similar chemical reaction.

An electronically excited state of molecule has a different electron distribution and nuclear configuration than the ground state. An electronically excited state of a molecule may be converted spontaneously into more possible products than the ground state because of the additional energy it has.

The activation of a photochemical reaction is quite different, and more selective, than the activation of an ordinary (thermal) reaction. Ordinary thermal reactions acquire their activation energy through random and successive collisions between molecules while photochemical reactions receive their activation energy by absorption of photons of light by molecules.
1.2 IMPORTANCE OF PHOTOCHEMISTRY

Photochemistry is concerned with reactions which are initiated by electronically excited molecules. Such molecules are produced by the absorption of suitable radiation in the visible and near ultraviolet region of the spectrum. Photochemistry is basic to the world we live in. With sun as the central figure, the origin of life itself must have been a photochemical act. In the primitive earth conditions radiation from the sun was the only source of energy. Simple gaseous molecules like methane, ammonia and carbon dioxide must have reacted photochemically to synthesize complex organic molecules like proteins and nucleic acids. Through the ages, nature has perfected her machinery for the utilization of solar radiant energy for all photobiological phenomena and providing food for the propagation of life itself. Photobiology, the photochemistry of biological reactions, is a rapidly developing subject and helps the understanding of phenomena like photosynthesis, phototaxis, photoperiodism, photodynamic action, vision and mutagenic effects of light.

The relevance of photochemistry also lies in its varied applications in science and technology. Synthetic organic photochemistry has provided methods for the manufacture of many chemicals which could not be produced by dark reactions. Moreover, greater efficiency and selectivity of these methods have an added advantage.
Some examples of industrially visible photochemical synthesis may mentioned here:

i. Synthesis of vitamin D₂ from ergosterol isolated from certain yeasts.

ii. Synthesis of cubanes which are antiviral agents.

iii. Industrial synthesis of caprolactam, the monomer of Nylon 6.

iv. Manufacture of cleaning solvents, insecticides and halogenated aromatics (used as synthetic intermediates) by photochlorination, and production of hydrogen peroxide in industry as an antiseptic and as a fuel because its decomposition releases a great amount of energy.¹,²

v. Synthesis of antioxidants by photosulphonation, photoinitiated polymerization and photopolymerization are used in photography, lithoprinting and manufacture of printed circuits for the electronic industry.

The light absorbed by dyes used for colouring the fabric initiates oxidative chain reactions in cellulose fibres. This causes the tendering of cotton. Similar depolymerizing action is observed in plastic materials. Researches are going on to find suitable colourless chemicals which when added to dyed materials or plastics will take over the excited energy and divert it to nondestructive pathway. These are known as energy degraders or photostabilizers e.g., O-hydroxybenzophenones.
The photophysical phenomena of fluorescence and phosphorescence have found varied applications in fluorescent tube lights. X-rays and TV screen as luminescent dials for watches, as optical brighteners in white dress materials, as paints in advertisement hoarding which show enhanced brilliancy by utilizing fluorescence, for detection of cracks in metal work, for tracing the course of river through caves, as microanalytical reagents and so on.

Certain chemicals change their colour, that is, their absorption characteristics, when exposed to suitable radiations and reverse when the irradiation source is removed. These are known as photochromic materials. A well known example is the spiropyrans, used in photochromic sunglasses.

Another revolutionary applications of electronically excited molecular system is in Laser technology. Lasers are intense sources of monochromatic and coherent radiations. Lasers have provided powerful tools for the study of diverse phenomena ranging from moonquakes to pico second processes of non-radiative decay of excitational energy in molecules. The intense and powerful beam of coherent radiations capable of concentration to a tiny point used for eye surgery, cutting metals, boring diamonds, as military range finders and detectors and many such applications. The advent of tunable dye lasers has increased the possibility of their application in science and technology.
A further impetus to the study of photochemical reactions has been provided by the energy crisis. This has initiated researchers into the conversion and storage of solar energy, processes which plants carry out so efficiently. Solar energy provides a readily available source of energy, especially in those countries which lie between the tropics of cancers and capricorn. In these areas, the daily incident energy per square kilometre is equivalent to 3000 tonnes of coal. If suitable photochemical reactions are discovered and devices for proper utilization of this abundant source of energy perfected, half of the world's energy problem might be solved. Solar batteries working as the principle of photogalvanic effects is one such device. The fundamental study of excited states of molecules is by exciting itself. The short lived energy states with nano and pico-seconds reactions kinetics have led to the proper understanding of chemical reactions, modes of energy transfer and the intricate structure of matter. Flash photolysis and pulsed laser photolysis are newer tools for the study of higher energy states. Now it is possible to excite individual vibronic levels or isotopically substituted compounds by using appropriate beams from tunable dye lasers.

Photochemical processes are also the basis of undesirable effects, such as degradation of polymers and the formation of smog, and of leisure activities, such as photography. Without photochemical processes the world be simply a warm, sterile, rock.
Photocatalysis has opened many avenues of further researches as far as its applications part is concerned. The photocatalysis has emerged as a probable solution to some of the problems like energy crisis, environmental pollution, wastewater treatment etc. Semiconductor particulate system can provide a low cost and convenient way of treating several undesirable chemicals. The principle of such a treatment lies in initiating an oxidation or reduction process at the semiconductor surface. For example, $\text{H}_2\text{S}$, which is a by-product in the coal and petroleum industry, can be oxidized to sulphur at CdS semiconductor surface. A quantum yield of 50% has been reported for the reaction between sulphids anion and photogenerated valence band holes in CdS suspensions. Similarly, photocatalytic transformation of $\text{CN}$ to $\text{SCN}$ has been carried out in presence of rhodium-loaded CdS particulate system. Photocatalysis can be used to eliminate pollutants from the environment. Chloral hydrate is a toxic compound, which is used for the synthesis of insecticides. Tanaka et al. reported the photocatalytic degradation of chloral hydrate in aqueous semiconductor suspension via the formation of OH radicals and utilizing these OH radicals for oxidizing chloral hydrate:

$$\text{CCl}_3\text{CH(OH)}_2 + 4 \text{ OH} \rightarrow 2 \text{ CO}_2 + 3 \text{ Cl}^- + 3 \text{ H}^+ + 2 \text{ H}_2\text{O}$$

Photocatalysis has been used for the degradation of pesticides like atrazine and also as a bactericide for spectroci. Nehara et al. made use
of irradiated titania semiconductor photocatalyst slurries in aqueous media for photooxidative degradation of the pesticides permethrin.

It has been shown by Domenech et al.\textsuperscript{8} that in presence of ZnO, Hg\textsubscript{111} can be photocatalytically eliminated from aqueous solutions. Muneer et al.\textsuperscript{9} investigated the photocatalytic degradation of an industrial pollutant like methyl vinyl ketone in aqueous solution using suspended TiO\textsubscript{2} and TiO\textsubscript{2}-immobilized on glass surface. The two oxidizing species OH and O\textsubscript{2} are the primary species utilized in photocatalytic degradation process. These oxidation reactions resulted in the depletion of O\textsubscript{2} and methyl vinyl ketone and in the formation of CO\textsubscript{2} and other semioxidized products in solution.

Herrmann et al.\textsuperscript{10} reported heterogeneous photocatalysis as an emerging technology for waste water treatment. It may also prove useful in recovery of some transition metals from industrial effluents. Das et al.\textsuperscript{11} observed photocatalytic degradation of waste water pollutants involving TiO\textsubscript{2} mediated oxidation of some polynuclear aromatic hydrocarbons. Recently Osawa and Sunakari\textsuperscript{12} reported photodegradation of polyurethane and polyvinyl chloride. Ahmed and Attia\textsuperscript{13} used certain aerogel materials for photocatalytic detoxification of cyanide in waste waters. Recently, Osunda and Osunala et al.\textsuperscript{14} have investigated photoreduction of manganese oxides in sea water. The photocatalysis can also prove to be useful in recovery of some costly metals from aqueous solutions, even if present in trace. Photocatalytic deposition of silver on TiO\textsubscript{2} powder was reported by Herrmann et al.\textsuperscript{10}
It has been advocated and predicted that hydrogen will be fuel of future and any newer method for efficient photocatalytic production of \( \text{H}_2 \) will be a well-come addition in solving the existing problem of energy crisis. The field of heterogenous photocatalysis has already grown out of its, infancy and has now emerged as a major field of research. The recent developments of ultrafine semiconductor particles have added some newer dimensions.\(^{15-20}\) The ability of such semiconductors to carry out redox processes with great efficiency and selectivity than in the homogenous solutions has made them more important in the conversion and storage of solar energy, in the mineralization of chemical pollutants and also for the treatment of some dreadful diseases. The use of dye molecules as light collectors in a solar cells (dye sensitized solar cells or D.S.S. cell) has been successfully used by Hagfeldt.\(^{16}\)

1.3 CLASSIFICATION AND DESIGNATIONS OF DYSES

The most authoritative compilation covering the constitutions, manufactures, and other coloring data is the publication of Color Index, which is edited jointly by the Society of Dyers and Colorists. In the color index a dual classification system is employed to group dyes according to area of usage and chemical constitution. Because of ease of synthesis of azo, disazo, and polyazodyes, and their wide range of applications, azo dyes comprise the largest chemical class in numbers, monetary value, and tonnage produced.
Thiazine Dyes

The presence of a thiazine ring in Cl sulfur Blue 9 was conclusively proved. The thiazine ring is the fundamental chromophore that accounts for the high color value of both the sulfur dye and methylene blue [61-73-4]. The dye CI Basic blue 9 was first reported in 1876. This is a basic dye:

\[
\text{[CH}_3\text{]}_2\text{N} \quad \text{N} \quad \text{NR}_{\text{CH}_3}\text{Cl}^-
\]

Methylene blue

Methylene blue has been widely used as a titration indicator, and for the evaluation of photophysical phenomena. The spectral properties of dye are also discussed by Koizumi et al. Thiazine is not important in dyes as such, but it is a part of some reactive dyes.

Synthesis: The method of synthesis for methylene blue described in reference is still the stepwise method of choice for thiazine dyes. N,N-Dimethyl-p-phenylene diamine [99-98-9], C₈H₁₂N₂, reacts with sodium thiosulphate [7772-98-7] to form the thiosulfonic acid which condenses with N,N-dimethylaniline [121-69-7], C₈H₁₁N, in the presence of sodium dichromate [10588-01-9], then with copper sulfate [18939-61-2] and sodium dichromate it gives out the methylene blue.
(ii) **Azo Dyes**

The term azo dyes is applied to those synthetic organic colorants that are characterized by the presence of the chromophoric and azo group (-N=N-). This divalent group is attached to sp² hybridized carbon atoms. On one side, to an aromatic or heterocyclic nucleus, on the other it may be linked to an unsaturated molecule of the carbocyclic, heterocyclic or aliphatic type. No natural dye contains this chromophore. Commerically, the azo dyes are the largest and most versatile class of organic dye stuffs.
Synthetic dyes are derived in whole or in part from cyclic intermediates. Approximately two-thirds of the dyes consumed in the United States are used by the textile industry to dye natural and synthetic fibers or fabrics, about one-sixth is used for coloring paper, and the rest is used chiefly in the production of organic pigments and in the dyeing of leather and plastics.

Dyes are sold as pastes, powders, and liquids, concentration varies from 6 to 100%. The concentrations, form, and purity of a dye is determined largely by the use for which it is intended.

1.4 APPLICATION OF DYES

Aromatic azo compounds which are also known as direct dyes, despite of their poor wet fastness properties, still represent an important class of dye for use on cellulose fibre because of their ease of applications and low cost.

Adsorption and adsorption processes are important fields of study in chemistry.\textsuperscript{26,27} They form the basis for understanding phenomena such a heterogeneous catalysis.\textsuperscript{26} Chromatographic analysis, dyeing of textiles,\textsuperscript{28} and clarification of various effluents.\textsuperscript{26}

The dyeing of cotton with direct dyes depends on the chemical nature of dye and auxiliaries used. The substantivity of dyes depends on the structure of dye molecule and the residual valency forces.
The dyeing of cotton with dyes also depends on the diffusion of dye in the pores of cellulose.\(^{26}\) Activated carbon finds particular applications in the clarifications of effluents, including the removal of coloring matter from various types of solution and elimination of organic substances from treated potable water and waste water. Adsorption of methylene blue, a cationic organic dye stuff commonly used for tracer studies in water research, on activated carbon.\(^{27}\)

Ecological and toxicological association\(^{28}\) of dye stuff manufacturing industry have been identified and assessed the risk to health caused by colorants and their intermediate. More than 4000 dyes have been analysed and showed acute toxicity values and the most toxic ones are cationic classes. In 1970's the major dye stuff manufacturers agreed to phase out the manufacture of benzidine derivative dyes and pigments.

Ascorbic acid was determined which was used in the preparation of vitamins by titration with \(\text{K}_3\text{Fe(CN)}_6\) in \(\text{H}_2\text{SO}_4\), \(\text{H}_3\text{PO}_4\), or \(\text{HCl}\) using ferroin triphenylmethane or thiazine dyes (methylene blue) as indicators.\(^{29}\)
CHAPTER - 2

LITERATURE SURVEY
2.0 LITERATURE SURVEY

2.1 INTRODUCTION

Methylene blue (MB⁺) is a water soluble cation dye molecule that has been widely studied since its synthesis in 1876.²⁵,³⁰ It was easily reduced by various reducing agents³¹ to the colourless hydrogenated molecule, leucomethylene blue which can be oxidized back to the blue colour. Earlier investigations of the electrochemistry, acid-base chemistry, and dimerization of MB⁺ are readily available in the literature.³²-³⁴ More recently MB⁺ and its one and two-electron reduced forms have been studied as important species in the MB⁺/HS⁻/O₂, oscillating reaction system.³⁵

Methylene blue exists in various states and every state has its own physical and chemical properties.³⁶-⁴³ The literature survey covers all of these properties. It deals with the reaction of methylene blue with organic and inorganic reductants. It gives information about different states of methylene blue, its reactivity and the mechanism of photochemical reactions of the dye. The literature survey also deals with the effect of inhibitors on photochemical reaction, mechanism of electron transfer reactions, the quenching of fluorescence of the dye and photolysis processes by laser and flash photolysis. The aims and objects of the present work are also given.
2.2 VARIABLE STATES OF METHYLENE BLUE

The most stable form of methylene blue is 3,7-bis-dimethylamino phenothiazine-5-iium chloride with following structure: The singly protonated form MB⁺ exists at pH > 4.0.⁴⁶

(Singly protonated form of methylene blue)

This structure is in agreement with the structure of the thiazone dye given by Faure,⁴⁷ Kikuchi⁴⁸ and Fischer.⁴⁹

The biprotonated form of methylene blue exists mostly in dilute acidic solution having structure as given below:

(Doubly protonated form of methylene blue)
Triply protonated form of methylene blue also exists in strong concentrated acidic solution.

\[
\text{H}_3\text{C}-\text{N}^+\text{H} \quad \text{H} \quad \text{N}^+\text{CH}_3
\]
\[
\text{CH}_3 \quad \text{N}^+\text{CH}_3
\]

(Triply protonated form of methylene blue)

In highly basic solution (pH ≥ 13), a brownish orange basic dye is formed which has structure as given below:

\[
\text{H}_3\text{C}-\text{N} \quad \text{H} \quad \text{N}-\text{CH}_3
\]
\[
\text{CH}_3 \quad \text{N}-\text{CH}_3
\]

(Basic form of methylene blue)

The photo-reduction of methylene blue results in the formation of Leucodye MBH$_2^{40,41}$ through the photo-reduction of intermediate MBH.$^{42}$ The complete photo-reduction after Kayser et al.$^{43}$ can be shown by the following mechanism.
2.3 ABSORPTION STUDIES OF METHYLENE BLUE

The absorption studies of methylene blue were carried out by several workers. Danziger et al.\textsuperscript{44-46} reported the molar extinction co-efficient ($\varepsilon$) in aqueous alkaline solution as 9000 mol\textsuperscript{-1}.dm\textsuperscript{3}.cm\textsuperscript{-1} at $\lambda_{\text{max}}$=420 nm and 18000 mol\textsuperscript{-1}.dm\textsuperscript{3}.cm\textsuperscript{-1} at $\lambda_{\text{max}}$=840 nm.\textsuperscript{37} Faure et al.\textsuperscript{37} found molar extinction co-efficient as 24000 mol\textsuperscript{-1}.dm\textsuperscript{3}.cm\textsuperscript{-1} at $\lambda_{\text{max}}$=850 nm in ethanol, while in methanol\textsuperscript{43} it was determined as 22500 mol\textsuperscript{-1}.dm\textsuperscript{3}.cm\textsuperscript{-1} at $\lambda_{\text{max}}$=420 nm.

Wildes et al.\textsuperscript{47}, reported that at 370 nm the molar extinction co-efficient of the triplet-triplet (T-T) absorption of methylene blue is 7000 mol\textsuperscript{-1}.dm\textsuperscript{3}. cm\textsuperscript{-1} in 1x10\textsuperscript{-2} N aqueous sulphuric acid and 14000 mol\textsuperscript{-1}.dm\textsuperscript{3}.cm\textsuperscript{-1} in 0.1 N sulphuric in 50% V/V aqueous methyl cyanide. Ohno et al.\textsuperscript{48} reported $\varepsilon_{\text{max}}$ = 7700 mol\textsuperscript{-1}.dm\textsuperscript{3}.cm\textsuperscript{-1} in water solution and 15300 in 50%
V/V aqueous methyl cyanide solution. The principal spectral features reported by Ohno et al.\textsuperscript{48}, are summarized in following Table-1.

**TABLE - 1**

*Values of molar extinction coefficient of methylene blue in various solvents.*\textsuperscript{48}

<table>
<thead>
<tr>
<th>Medium</th>
<th>T-T Absorption</th>
<th>S-S Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\varepsilon_{\text{max}}$ (mol(^{-1}).dm(^3).cm(^{-1}))</td>
</tr>
<tr>
<td>1.0x10(^{-2}) N aq H(_2)SO(_4)</td>
<td>690</td>
<td>14,500</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>12,500</td>
</tr>
<tr>
<td>1.0x10(^{-2}) N H(_2)SO(_4) in</td>
<td>703</td>
<td>18,700</td>
</tr>
<tr>
<td>30% V/V aq. ethanol</td>
<td>680</td>
<td>19,000</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>13,200</td>
</tr>
<tr>
<td>1.0x10(^{-2}) N HCl in</td>
<td>670-710</td>
<td>\geq 16,200</td>
</tr>
<tr>
<td>50% V/V aq. CH(_3)CN solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>15,300</td>
</tr>
<tr>
<td>pH=8.2 borate buffer in 30% V/V</td>
<td>840</td>
<td>20,000</td>
</tr>
<tr>
<td>aq. ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>9,000</td>
</tr>
</tbody>
</table>
Muller et al.\textsuperscript{49} reported the value of extinction coefficient in phosphate buffer i.e. $\varepsilon_{665} = 81600 \text{ mol}^{-1}\text{.dm}^3\text{.cm}^{-1}$, while Atherton et al.\textsuperscript{50} reported $\varepsilon_{665} = 82000 \text{ mol}^{-1}\text{.dm}^3\text{.cm}^{-1}$.

Solar et al.\textsuperscript{51}, reported the molar extinction co-efficient ($\varepsilon$) of the protonated forms of methylene blue, semiquinone (S) at different absorption bands, summarized in the Table-2.

\textbf{TABLE – 2}

\textbf{Spectral features of semiquinone at different pH values.}

<table>
<thead>
<tr>
<th>Absorption bands of semiquinone (S)</th>
<th>$\text{MBH}^{++}$ $\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{pH}=1.0}$, (\varepsilon) (mol(^{-1}).dm(^3).cm(^{-1}))</th>
<th>$\text{MBH}^{+}$ $\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{pH}=4.0}$, (\varepsilon) (mol(^{-1}).dm(^3).cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>880</td>
<td>1190</td>
<td>880</td>
<td>2350</td>
</tr>
<tr>
<td>2nd</td>
<td>380</td>
<td>900</td>
<td>395</td>
<td>910</td>
</tr>
<tr>
<td>3rd</td>
<td>290</td>
<td>3750</td>
<td>290</td>
<td>3800</td>
</tr>
</tbody>
</table>

The values of molar extinction co-efficient of $10^{-5}$ mol.dm\(^{-3}\) solution of methylene blue at different wave-lengths and pH given by several investigators are summarized in Table-3.
**TABLE - 3**

Variation in spectral features of methylene blue with pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>1st Band</th>
<th>2nd Band</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{\text{max}}) (nm)</td>
<td>(\varepsilon_{\text{max}}) (mol(^{-1}).dm(^3).cm(^{-1}))</td>
<td>(\lambda_{\text{max}}) ((\sigma)m)</td>
</tr>
<tr>
<td>0.65</td>
<td>880</td>
<td>1270</td>
<td>375</td>
</tr>
<tr>
<td>2.00</td>
<td>Orange red</td>
<td>8800</td>
<td>380</td>
</tr>
<tr>
<td>2.10</td>
<td>665</td>
<td>74000</td>
<td>370</td>
</tr>
<tr>
<td>3.40</td>
<td>880</td>
<td>8800</td>
<td>410</td>
</tr>
<tr>
<td>6.00</td>
<td>880</td>
<td>3300</td>
<td>-</td>
</tr>
<tr>
<td>7.00</td>
<td>665</td>
<td>1700</td>
<td>-</td>
</tr>
<tr>
<td>8.20</td>
<td>840</td>
<td>35000</td>
<td>665</td>
</tr>
<tr>
<td>10.20</td>
<td></td>
<td>20000</td>
<td>500</td>
</tr>
<tr>
<td>7.00</td>
<td>656</td>
<td>53500</td>
<td>-</td>
</tr>
</tbody>
</table>
2.4 REDUCTION STATES OF METHYLENE BLUE

Hydrogen attack on methylene blue in photochemical processes causes radiation induced decolouration of the dye.\textsuperscript{52-54} Two processes take place, one reversible and other irreversible, the first one predominated in the presence of organic substances.\textsuperscript{36,55} In neutral solution of methylene blue, the solvated electron reacts with MBH\textsuperscript{+} (k=2.5x10\textsuperscript{10} mol.dm\textsuperscript{-3}.sec\textsuperscript{-1}) resulting the production of semiquinone\textsuperscript{36} (\lambda_{max}=420 nm; \varepsilon_{420}=1040 mol\textsuperscript{-1}.dm\textsuperscript{3}.cm\textsuperscript{-1}). This semiquinone dismutates to leucomethylene blue with a rate constant as 2k=3x10\textsuperscript{9} mol.dm\textsuperscript{-3}.sec\textsuperscript{-1} as reported by Solar et al.\textsuperscript{56}

2.5 PHOTOPHYSICS OF METHYLENE BLUE IN H\textsubscript{2}O

pK\textsubscript{a} values for the ground state, triplet excited state,\textsuperscript{57-59} and one electron reduced form of methylene blue,\textsuperscript{60} were found to be 0.0, 7.2 and 9.0 respectively. The ground state of methylene blue showed self association. The value of dimerization constant varies in different experimental conditions.\textsuperscript{49,61-65}

The ground state self associates,\textsuperscript{44,65} with an association constant of (4 \pm 1) \times 10\textsuperscript{3} mol.dm\textsuperscript{-3}, to form a nonfluorescent dimer.\textsuperscript{50,65} The monomer is weakly fluorescent (\phi = 0.20 \pm 0.005).\textsuperscript{59,62,66,67} The first excited singlet state is short lived T\textsubscript{1} = 345 \pm 10 pS. Intersystem crossing to the triplet manifold occurs with high efficiency (\phi = 0.58),\textsuperscript{68} the first excited triplet
state is relatively long-lived. In mildly alkaline (pH=9.0) solution the triplet life-time was 45 ± 4 µs. The triplet life-time was found to reduced in mild acidic (pH=4.2) solution, and dependent on the degree of protonation.\textsuperscript{59,66-69}

The excited triplet-energy state level of methylene blue depends on the extent of protonation. The reported values of excited triplet-energy\textsuperscript{69,70} for the monoprotonated and unprotonated triplets are 96 and 139 kJ mol\textsuperscript{-1}, respectively. The triplet energy in benzene/ethanol\textsuperscript{70} is 144 kJ mol\textsuperscript{-1}.

Gensch et al.\textsuperscript{59} determined the production of triplet states of methylene blue and rose bengal by laser-induced optoacoustic spectroscopy (LIOAS) at different temperatures. These triplet states were found to be accompanied by a structural volume change of -1.5 and 1 ml/mol, respectively. The contractions were reverted as the triplet decayed.

It was concluded that the volume changes mainly originated due to changes in the solvation sphere due to the entire process of ground state to triplet transition (for the contraction) and back to the ground state (for the expansion). The presence of oxygen had no major effect on the contraction and the expansion observed.\textsuperscript{70}

### 2.6 REDUCTION PROCESS OF THE DYE

The photochemical reduction of a dye has been described by several workers.\textsuperscript{71-75} The proposed scheme was described as follows:
Where \( D^+ \) is the dye cation in ground state and \( D^{**} \) is that in first electronically excited singlet state. \( D'^t \) is a second metastable excited state. \([R]\) is the concentration of electron donor and \( M \) is monomer of half reduced dye.

\( K_1 \) & \( K_2 \) are the rate constants for dissociation processes, \( k_r \) is the rate constant for reduction process, and \( k_d \) is the rate constant of semi reduced dye.

Another proposed mechanism was given by Lindqvist\(^76\) and followed by Imamura\(^71\) according to which first the triplet state \( D^t \) goes to ground state by \( D^t + D^t \rightarrow 2D \) process or by a monomolecular process, but as the ground state dye accumulates, the \( D^t + D \rightarrow 2D \) process begins to make greater contributions. It produces semiquinone and half oxidized state \( X \). The whole process can be summarized as follows:

\[
\begin{align*}
D^t & \xrightleftharpoons{k_1} D \\
D^t + D & \xrightarrow{k_2} 2D \\
D^t + D & \xrightarrow{k_3} X \\
X & \xrightarrow{k_4} \text{leucodye}
\end{align*}
\]

Where \( k_1 \rightarrow k_4 \) are the rate constants for different processes of the reduction of methylene blue.
The most general mechanism for a photochemical reduction of a dye is given as follows:

\[
\begin{align*}
\text{D} + \text{hv} & \quad \rightarrow \quad D_s & \quad 2.5.5 \\
D_s & \quad \rightarrow \quad D + \text{hv}_r & \quad \text{Fluorescence} & \quad 2.5.6 \\
D_s & \quad \rightarrow \quad D + Q \text{ (heat)} & \quad \text{Internal conversion} & \quad 2.5.7 \\
D_s & \quad \rightarrow \quad D_T & \quad \text{Transition to triplet state} & \quad 2.5.8 \\
D_T & \quad \rightarrow \quad D + \text{hv}_p & \quad \text{Phosphorescence} & \quad 2.5.9 \\
D_T + AH_2 & \quad \rightarrow \quad DH + AH & \quad \text{Formation of free radical} & \quad 2.5.10 \\
D_s + AH_2 & \quad \rightarrow \quad DH + AH & \quad \text{Formation of free radical} & \quad 2.5.11 \\
& & \text{(electron transfer)} & \\
2DH & \quad \rightarrow \quad DH_2 + D & \quad \text{Semiquinone formation} & \quad 2.5.12 \\
2AH & \quad \rightarrow \quad \text{Product} & \quad \text{Disappearance of free radical} & \quad 2.5.13
\end{align*}
\]

Where \( D \) = Ground state of dye
\( D_s \) = singlet state of dye
\( D_T \) = triplet state of dye
\( DH \) = semiquinone
\( DH_2 \) = leucodye
\( AH_2 \) = reducing agent

Spatial pattern formation in methylene blue reaction system was given by Waltz et al.\textsuperscript{77} under basic conditions.

Ross and Calvin\textsuperscript{78} showed that the reaction of methylene blue was endothermic one by 50 Kcal/mol at pH=1.0. Sommer et al.\textsuperscript{79} observed that the reaction of methylene blue involved two excited species in the
mechanism. They observed an apparently long lived species and postulated the following mechanism.

\[
\begin{align*}
\text{MB} & \xrightarrow{h\nu} \text{MB}^* \quad \text{Excited singlet state} \quad 2.5.14 \\
\text{MB}^* & \rightarrow \text{MB}^1 \quad \text{Excited triplet state} \quad 2.5.15 \\
\text{MB}^1 + \text{MB}^1 & \rightarrow \text{MB} + \text{MB}^* \quad 2.5.16 \\
\text{MB}^1 & \rightarrow \text{MB} \quad 2.5.17 \\
\text{MB}^* & \rightarrow \text{MB} \quad 2.5.18 \\
\text{MB} + \text{MB}^1 + \text{H}_2\text{O} & \rightarrow \text{S} \quad 2.5.19 \\
2\text{S} + \text{H}^+ & \rightarrow \text{LMB} + 3\text{MB} + \text{H}_2\text{O}_2 \quad 2.5.20 \\
\text{LMB} + \text{H}_2\text{O}_2 & \rightarrow \text{MB} + 2\text{H}_2\text{O} + \text{H}^+ \quad 2.5.21 \\
\end{align*}
\]

Where MB\(^*\) is the first excited state of singlet methylene blue, MB\(^1\) is the corresponding triplet state and S is hypothesized long-lived intermediate and LMB is the leucomethylene blue.

Obata,\(^{40,74}\) Snehalatha et al.\(^{75}\) and Usui et al.\(^{80}\) found that methylene blue in suitable buffer solutions, without any reducing agent added, is photo-reduced to leucodye by the visible light. According to them quantum yield of photo-reduction reaches as much as 10\(^{-3}\) in the phosphate buffer.

Usui and Koizumi\(^{80}\) attempted a kinetic treatment and found that in the borate buffer solution the reaction proceeds approximately as of first order with respect to the dye, while in the phosphate buffer solutions the reaction is a simple second order with respect to the dye. This was due to some differences between the reaction mechanisms of these two cases.
2.7 REDUCTION OF METHYLENE BLUE IN ABSENCE OF REDUCING AGENT

The photo-reduction of methylene blue and thionine in aqueous solution were studied by several workers.\textsuperscript{81–85} Sommer \textit{et al.}\textsuperscript{86} studied the photo-reduction of methylene blue and thionine in water and found that photo-reduction of methylene blue proceeds in red light with only water available as reducing agent. Reaction energy consideration requires two photons to reduce each methylene molecule. They \textit{proposed a two photon mechanism involving a long-lived dimer intermediate}. They also studied the influence of light intensity and methylene blue concentration on rate constants.

Usui \textit{et al.}\textsuperscript{87} found that photo-reduction of phenazine dye to leucophenol and indophenone does not occur without reducing agents, but is apparently specific for thiazine dyes such as methylene blue, methylene green, toluidine blue, thionine and new methylene blue. Usui\textsuperscript{88} studied the photo-reduction of methylene blue and thionine in ethanol. He found that as initial dye concentration was varied in the region $10^{-6}$ — $10^{-5}$ mol.dm$^{-3}$ for both methylene blue and thionine, the overall second order rate constant ($k$) decreased. A linear relationship between the values of quantum yield ($\phi$) and mole fraction of ethanol was obtained.
2.8 PHOTOCHEMICAL REDUCTION OF METHYLENE BLUE BY ORGANIC REDUCTANTS

Since earliest investigations\textsuperscript{89-98} of photochemical reductions, generally the organic reductants were used. These organic reductants were organic amines, phenylhydrazines, anethole, urea, thiourea and their derivatives, N-phenylglycine, nitriloacetic acid, ethylene diamine tetraacetic acid (EDTA), paraphenyldiamine (PPD) and mono, di, tri-methylamines.

Early workers\textsuperscript{30,89-98} in the development of photographic bleach out processes noted that thiazine dyes are photo-reduced readily in the presence of mild reducing agent such as allylthiourea, anethol, glyoxol, EDTA etc.

The reaction of thiazine dye with phenylhydrazine sulphate as reducing agent in aqueous solution was studied by Holst\textsuperscript{99-100} and Kostryukova.\textsuperscript{101} Merkel et al.\textsuperscript{102}, in their studies on the photochemistry of riboflavine noted that methylene blue is photo-reduced with EDTA. Oster\textsuperscript{103} investigated the role of EDTA as an electron donor in the photo-reduction of methylene blue. Some important qualitative and quantitative investigations were also made by several workers.\textsuperscript{41,104-15}

Photobleaching of methylene blue in the presence of various derivatives of N-phenylglycine were studied by Matsumoto.\textsuperscript{116} Nature of photo-reduction was investigated according to the structure and reactivity of reducing agents. Matsumoto\textsuperscript{116} also found the relationship between quantum yield
with intensity of light ($I_0$), and concentration of the reductants. The relationship was given in the form of following equation:

$$\frac{1}{\phi} = \frac{1}{\phi_a} + \frac{b}{[R]}$$  \hspace{1cm} 2.8.1

Where $[R]$ is the concentration reductant, $\phi_a$ is the quantum yield for an infinite concentration of the reductant. $\phi_a$ and $b$ are constants. A straight line plot between $1/[R]$ and $1/\phi$ was observed at constant value of acidity (pH=7.0).

Matsumoto\textsuperscript{116} determined the effect of pH on quantum yield of the photoreduction of methylene blue in the pH range 5.0–10.5. He also paid attention to the effect of buffer solutions and to a possible change in the ionic species of N-phenylglycine with the pH value. N-phenylglycine behaved as a monobasic acid of $pK_a$ 4.3 to base titration, so that it existed solely as univalent anion $C_6H_5NH.CH_2COO$ in this pH range. The life-time of methylene blue was found to be dependant on the pH values.\textsuperscript{117} The dependence of the life-time on pH is given in Table-4.

**TABLE – 4**

**Variation in the life time of dyes with pH.**

<table>
<thead>
<tr>
<th>System</th>
<th>Life-Time ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH=4.5</td>
</tr>
<tr>
<td>Thionine</td>
<td>8.5</td>
</tr>
<tr>
<td>Azur B</td>
<td>5.0</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>4.0</td>
</tr>
</tbody>
</table>
The kinetics of photosensitized reaction of methylene blue with pre-irradiated cyclohexanone and cyclopentanone were studied by Hassan et al.\textsuperscript{118} According to them the reaction followed 2\textsuperscript{nd} order kinetics and the rate of reaction was directly proportioned to the time of irradiation. The mechanistic possibilities were also suggested.

2.9 PHOTO-REDUCTIONS OF THIAZINE DYES

The semi reduced species produced during the reduction of dyes in aqueous solutions have been investigated.\textsuperscript{83,119-123} In the course of a general survey of the mechanism of thiazine dyes, photo-reduction in presence of EDTA was established,\textsuperscript{103} and it was concluded that the primary photochemical act in the case of thionine is the electron abstraction by the protonated triplet dye.\textsuperscript{37,124,125} The dismutation process of semi-thiazine dyes has been investigated by R. Bonneau et al.\textsuperscript{59} in aqueous solutions as a function of pH using paraphenylenediame as electron donor, it was found that the stable specie in neutral solution is the protonated semireduced dye. From the kinetic data it appeared that the rate of dismutation was nearly constant with increasing alkalinity of the solution.

The protonation rate constant for the lowest state of thionine has been measured as a function of temperature and hydrogen ion concentration using the flash photolysis.\textsuperscript{125,127}
The photo-reduction of thionine and methylene blue in aqueous solutions were studied by several workers.\textsuperscript{125-129} In aqueous solution, pulse radiolysis of thionine methylene blue and formation of $\xi_{as}$ from excited thionine and methylene blue were also studied by Solar \textit{et al.}\textsuperscript{130} and Fischer \textit{et al.}\textsuperscript{131} Sommer \textit{et al.}\textsuperscript{86} studied the photo-reduction of methylene blue and thionine by water. Coulombic effects have been investigated in photo-induced electron transfer reactions between phenothiazines and Viologenes.\textsuperscript{132} The effect of acidity and concentration of phenylglycine and thionine and the quantum yield of the photochemical reduction were studied by F. Uddin\textsuperscript{133} using methanol as nonaqueous medium. The quantum yield was found to be a function of reductant concentration, acidity, and temperature and independent of concentration of thionine.

Kosui \textit{et al.}\textsuperscript{134} and Bonneau\textsuperscript{135} observed the photoreduction of methylene blue with EDTA. They observed an unusual sigmoidal dependence on the EDTA concentration, where the maximum quantum yield at high concentration of EDTA (~ 0.1 mol dm\textsuperscript{-3}) exceeded to the value (0.156) provided from the equation representing the quantum yield in aqueous solution:

$$\phi = \frac{\phi_{st} k_r (\mu) [\text{EDTA}]}{k_d + k_s (\mu) [\text{EDTA}]} \quad 2.9.1$$

Where $\phi_{st}$ is intersystem crossing probability of methylene blue, $k_r (\mu)$ and $k_s (\mu)$ are the reactive and overall rate constants for the reaction between triplet MB with EDTA respectively and $k_d$ is rate constant for the product.
Kinetics of thiazine dyes on acrylic fiber was studied by Maria et al.\textsuperscript{136} The dyeing rates were determined at various temperatures for some cationic thiazine dyes on acrylic fibers. Diffusion and combination factors were obtained by a linear relationship between the reciprocal rate constant and the inverse of the dye bath concentration. The influence of electrolytes and retarders on dyeing kinetics was determined. Photoreduction of methylene blue via chemical quenching of triplet benzophenone was studied by Sindhu et al.\textsuperscript{137} The kinetics data fit into the integrated rate expression, which was 1/2 order with respect to the substrates. The dye does not show any aggregation, but complexation between ground state benzophenone and MB\textsuperscript{+} was observed. A mechanism and a $\phi$ rate expression were proposed. Mishra and Chansoria\textsuperscript{138} studied the oxidation of mercapto succinic acid by methylene blue in acidic medium. The reaction studied at various ionic strengths and hydrogen ion concentration. Reaction showed 1\textsuperscript{st} order kinetics with substrate and 2\textsuperscript{nd} order kinetics in methylene blue. The rate constant showed optimum value with respect to hydrogen ion concentration and the ionic strength of the reaction system. The stoichiometry of the reaction was 2 : 1 and the formation of disulfide and leucobase of methylene blue was confirmed spectrophotometrically. Activation parameters\textsuperscript{138} have been evaluated and possible reaction scheme has been proposed.
The photo-reduction of thiazine dyes by EDTA was investigated by flash photolysis.\textsuperscript{139} The reaction was found to occur according to a three step mechanism. The first being the formation of the dye triplet state in weak acid solutions followed by protonation. During the 2\textsuperscript{nd} step, the triplet state of the dye disappears through two competing processes. The 3\textsuperscript{rd} step leads to the Leucodye. It is shown that the overall quantum yield of photoreduction is governed by the second step and can be calculated from the ratio of the rate constants of the two elementary processes involved in this step. This ratio was measured over a wide pH range. The production of singlet oxygen by thiazine dye photosensitization,\textsuperscript{139} was found to be very sensitive to changes of pH in the range 5–9. For methylene blue in aerated solutions, the production of $^1\text{O}_2^*$ is approximately five times more efficient in basic than in acidic medium. This was shown to be related to the $pK'_s$ of the triplet dyes, by evaluating the yields of $^1\text{O}_2^*$ from the lifetimes and the quenching rate constants for the two ionic species of sensitizer triplets measured by laser flash photolysis. Moreover changes in the quenching rate constants of the thiazine triple states can be correlated with their triplet energies.

Photo-reduction of thiazine dyes by EDTA was also studied by Bonneau et al.\textsuperscript{139-140} The apparent reactivity of thiazine dyes in their triplet states has been studied in aqueous solutions in the pH range 4–8. The trianionic species of ethylenediamine tetra-acetic acid (EDTA) was used as electron donor. The pH dependence was found to be related to the change in the
degree of protonation of the triplet excited dye. The apparent reactivity and life-time of two differently protonated forms of thionine, azur B and methylene blue were determined by classical and dye-laser flash techniques.

Effect of addition of EDTA in phenothiazine and phenothiazine derivatives in presence of reducing agents were determined with visible light of 400–800 nm.\textsuperscript{141} Wave-length dependence and the optimum conditions for the photopotential induced in a thionine – Fe\textsuperscript{2+} system were studied. The photopotential decreases proportionally with the increasing amount of EDTA added to the thionine Fe\textsuperscript{2+} system. In case of methylene blue – iron (+2) system; the addition of a small amount of EDTA causes an increase in its photopotential. It reached its maximum when the molar ratio of EDTA/M.B.=3 when the molar ratio Fe\textsuperscript{2+}/M.B was 500, the photopotential of which was ~3.4 times as high as that without the addition of EDTA. Effect of other chelating agents of aminopoly carboxylic acid type was also studied.

2.10 ELECTROREDUCTION OF DYE BY COMPLEXES

Electroreduction of bismuth (III) and tellunium (IV) for chloride and tartarate solution of thiazine dyes were studied by Kirijak.\textsuperscript{142} The influence of thionine, Azur T and methylene blue on the electroreduction were also discussed.
The variation of the electronic spectra of basic dye methylene blue and neutral reducants with time was studied by Gessner et al. The interaction of dyes (methylene blue and neutral red) on Montmorillonite and Hectorite were reported. Some reactions of methylene blue (oxi form) excited by visible light were studied by Harmatz et al. Methylene blue causes oxidation of sodium ascorbate, ferrocytochrome C, and EDTA. All investigations were carried out spectrophotometrically at 25°C, in dilute and deaerated aqueous solution.

The electrochemical reduction of thionine and methylene blue in the presence of iron (Fe⁺³) was examined in terms of a catalytic current due to homogeneous chemical reaction between leucodyes and Fe⁺³.

The trace amount of manganese in water was determined by the use of methylene blue. Periodate in presence of acetate buffer decolorises methylene blue. The rate of decolorization depends on the concentration of Mn (II). The interaction of Cr (IV) and the thiazine dye (M.B) has been examined by Kamburova. A sensitive and selective method for the determination of microquantities of Cr (VI) in soils and alloys was suggested. The polarographic characteristics of Tellurium (IV) and basic dye were investigated at mercury electrode. It was found that the mechanism of the electrode process depended on the concentration of Te (IV).
The kinetics of thionine reduction by several Fe (II) chelates were studied by Tanaka et al.\textsuperscript{149} in presence of nitrogenated system at pH 7.0. Meanwhile, the oxidation of leucothionine (II) by Fe (II) chelate was also examined.

The physicochemical studies of some metal complexes such as vanadium (V), niobium (Nb) and tantalum (Ta) with dyes such as Erichrome cyanine-R and methylene blue have been studied by Awadallah et al.\textsuperscript{150} The complexation processes of metal with methylene blue were investigated by conductometric and spectrophotometric methods. The measurements were used to investigate stoichiometry, formation constants and thermodynamic parameters such as enthalpy change (ΔH\textsuperscript{\#}), free energy change (ΔG\textsuperscript{\#}) and entropy change (ΔS\textsuperscript{\#}) of the complexes. The effects of pH on absorption spectra of complexes, time and temperature on the stability of metal chelates were also studied.

The photoreduction of aqueous sodium and potassium carbonates was carried out in the presence of methylene blue solution (photocatalyst).\textsuperscript{151} The photocatalytic formation of formic acid and formaldehyde were also measured spectrophotometrically. The effect of variation of various parameters like pH, amount of photocatalyst (methylene blue) concentration of Na\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3}, light intensity etc. on the yield of photoproducts were also investigated. A tentative mechanism for this reduction has been proposed.
Pezza et al.\textsuperscript{152} studied the photogalvanic effect in the system containing basic dyes (such as thionine, safranine T and Acridine orange) and a reducing agent Fe\textsuperscript{2+}, EDTA, triethanolamine and allylthiourea. Photovoltages and photocurrents generated by photogalvanic cell were measured in presence of various reducing agents. The results suggested that the photogalvanic system containing aminoaliph, reducing agents yields higher values of photovoltages and photocurrent than those employing Fe\textsuperscript{2+} as reducing agent. The energetics and feasibility in their systems were also discussed.

Phenothiazine dyes were reduced by Fe\textsuperscript{2+} as a reductant in buffer medium\textsuperscript{153,154} (pH 3.7–4.7) in presence of Na\textsubscript{o}xalate of concentration ranging 0.06–0.12 mol dm\textsuperscript{–2}. The dyes reduced to their colourless leucobases in a 2e reduction with Fe\textsuperscript{2+}. The function of pH and oxalate ion in the reaction medium was also discussed. A more extensive study on the redox potential of Fe\textsubscript{[III]}/[II] iron couple in buffer medium was also reported by Raju et al.\textsuperscript{154}

Photocatalytic reduction of methylene blue by cadmium sulphide CdS monoparticles mediated in reverse micelles was studied by Zhang et al.\textsuperscript{155}

Photochemistry of aromatic halides have been actively investigated due to their role as an environmental pollutants or photolability, as a mean of their efficient conversion to less toxic substrates. Photolability enhanced in presence of electron transfer agents such as amines and dienes.\textsuperscript{156–158}
2.11 PULSE RADIOLYSIS LASER PHOTOLYSIS

Thiazine dyes (Thionine and methylene blue) have become important in recent years, especially as sensitizers in photogalvanic cells for photoelectrochemical utilization of solar energy.\textsuperscript{159-162} The short lived intermediate products from these dyes, their semiquinones, have been successfully investigated by flash photolysis in the presence of various electron donors like Fe\textsuperscript{2+}, allyl thiourea and diphenylamine etc. In these systems reductive quenching of the excited dye, predominantly occurs through the triplet state.\textsuperscript{46,163-181} The extent of reduction of the excited dye in such systems is dependent on several factors e.g. on the free enthalpy change involved and the oxidation potential of the electron donor,\textsuperscript{170,172,173} nature and the concentration of the counter ion, nature of solvent and pH of the solution.\textsuperscript{58,171} The improved pulse radiolysis technique\textsuperscript{179} with extended simulation computation has allowed better investigation in the ultra-violet absorption range of both thionine and methylene blue, where there is a strong super-imposition of several transients and where bleaching occurs. A third absorption band arises due to semiquinone formation has also been reported.\textsuperscript{179,180}

Pulse radiolysis of methylene blue and toluidine blue were carried out in poly vinyl alcohol by Jia \textit{et al.}\textsuperscript{181} The transient spectra obtained between 400 and 880 nm and are assigned to the semiquinone radical anions, decayed by a second order process. Furthermore methylene blue in poly vinyl alcohol films were bleached by \(\gamma\)-radiolysis and the change in
absorbance was found to be linear with the dose. Similarly the photoreduction of methylene blue by a ruby laser light has also been studied. The kinetic treatment and the measurement of the apparent activation energy showed that under the high intensity radiation, the excited triplet state of methylene blue plays a significant role in its photoreduction in the presence of p-chlorophenyl glycine. The apparent activation energy of the reduction of methylene blue is reduced from 7.4 to 2.8 kcal mol$^{-1}$ as the laser light energy increases from 23 to 530 mj. Kamat et al. have measured the electron transfer yields by monitoring semi reduced thionine, by the laser flash photolysis method. It was concluded that the rate constant for quenching and the rate constant for electron transfer depend upon various parameters such as nature of solvent, nature of anions present and the ionic strength of the media. Moreover, photogalvanic conversion in iron-thiazine cell was also discussed.

Dose response characteristics of poly vinyl alcohol (PVC) film in the presence of methylene blue or methyl orange were studied by Chung et al.

The role of MB$^*$ excited state in fast H-atom abstraction reaction has been investigated by pulse laser techniques. The most interesting part on such work is the spatial pattern formation in methylene blue reaction systems under basic conditions. The photo-reduction of methylene blue has been extensively studied by continuous irradiation and by
the flash photolysis\textsuperscript{190-197} at various temperatures. The quenching of triplet excited dye eosine Y and methylene blue by hydrogen peroxide has been studied by Gak \textit{et al.}\textsuperscript{190} by laser and steady state photolysis. The apparent activation energy of the reduction of methylene blue was obtained by varying the laser-light intensity.\textsuperscript{182,196} It was found that the photoreductions through both the lowest triplet state and the excited triplet state, equally contribute to the apparent activation energy. In this connection, the activation energy extrapolated to zero light intensity should correspond to the activation energy for the lowest triplet states. The activation energy was also found to be decreased with an increase in the dose intensity.\textsuperscript{182}

The quenching rate constants and the radical yields of the electron transfer reaction between triplet methylene blue and ferrocenes have been determined in acetonitrile by an emission absorption flash technique.\textsuperscript{194} The rate constants are found to be diffusion controlled and the radical yields, being much lower than unity that decreases strongly when the free enthalpy, $\Delta H^\circ$ and free energy $\Delta G^\circ$ (gained in the electron transfer process) become smaller.

The spectral as well as temporal characteristics of the transient absorptions produced by flash photolysis of solutions of methylene blue in ethanol were reported by Gerald \textit{et al.}\textsuperscript{195} A transient species with an absorption maximum at 380 nm and a life-time of 4 $\mu$S was observed in acid solutions. The rate constants for the reactions of this species with
oxygen and other quenchers were determined. This suggested that the transient species is a semireduced methylene blue free radical.\textsuperscript{195-199}

Laser flash photolysis\textsuperscript{200} (694.3 nm) of MB\textsuperscript{+} in alkaline water at a pH 8.2 and neutral acetonitrile system revealed, in addition to the formation of the triplet dye. This triplet dye has a small absorption band at 520 nm. It was assigned to semi-oxidized methylene blue (radical cation) MB\textsuperscript{+2} and it was concluded that the MB\textsuperscript{+2} formation is the result of an electron ejection process from the excited dye molecule.\textsuperscript{201} A radical cation, however can also be formed by electron transfer process from the singlet excited dye molecule. The electron ejection is observed when aqueous thionine or methylene blue is excited using light of wave-length 253.7 nm. The quantum yields $\phi$ ($\epsilon_{aq}$) for such excitation reactions are $5.5\times10^{-3}$ for protonated thionine (pH 7.0), $9.5\times10^{-3}$ for unprotonated thionine (pH $\geq$13.5) and $5\times10^{-3}$ for methylene blue (pH 7.0). Furthermore, the excited OH\textsubscript{aq} ions produced $\epsilon_{aq}$ with the value of quantum yield of 0.05. The pK$_{2}$ value of thionine was predetermined and was found to be 11.5±0.1 in accordance with the reported value. The reactivity of thiazine dye, methylene blue, thionine and Azur B in aqueous solutions in their triplet state was studied by Bonneau \textit{et al.}\textsuperscript{202} The apparent reactivity and life-time of two differently protonated forms of methylene blue, thionine and Azur B were studied using dye laser flash photolysis. In this regards rate constants for the electron abstraction in the triplet state of dyes were also determined.
The fluorescence quenching of both protonated and unprotonated forms of thionine and neutral red, by several electron donors has been studied by static fluorometry method.\(^{203}\) The difference between the pK\(_a\) of the singlet states and those corresponding to semireduced radicals were established. Photoreduction of thionine by reducing agent such as alyl thiourea was investigated by Steiner et al.\(^{204}\) using flash photolysis and continuous illumination technique. The quantum yield of photoreduction was increased by addition of azulene. During photolysis, (thionine-azulene system) thionine was reported to be converted into its photoreduced form i.e. leucothionine. Similarly azulene reacts with the basic form of the thionine triplet to produce the semithionine radicals and then reduces to leucothionine by the addition of alyl thiourea. In such cases the quantum yield was found to be considerably higher as compared to the thionine and allylthiourea systems.\(^{204}\)

Sindhu et al.\(^{205}\) Zhong et al.\(^{206}\) and Tanaka et al.\(^{207a}\), determined the quantum yield for the reduction of methylene blue by photolysis technique. They reported that the quantum yield for the reduction in absence of reductant was negligibly small and the triplet state of methylene blue has so long life-time as to be detected by flash photolysis technique.

Miyashita et al.\(^{112}\) reported that under high intensity of irradiation, the excited triplet state of methylene blue plays main role in the photoreduction.
2.12 ELECTRON TRANSFER REACTIONS

Fry et al.\textsuperscript{208}, studied the quenching rate of some triplet by ferrocene (F) with a conventional flash photolysis technique and presumed that quenching is due to formation of a short lived charge transfer complex because they could not observe any transient absorption attributable to the addition of ferrocene (F). Many other aromatic compounds were quenched by ferrocene at a diffusion controlled rate as reported by Fry et al.\textsuperscript{208}, Bhaumik et al.\textsuperscript{209} and Candall et al.\textsuperscript{210}

Kikuchi et al.\textsuperscript{211}, studied the quenching of the triplet state of methylene blue by ferrocene and paraphenylenediamine in ethanol by an emission-absorption flash technique.

Tamura et al.\textsuperscript{212-214}, determined the quenching rate constant and the radical yield of the electron transfer reaction between methylene blue and ferrocene in acetonitrile by an emission absorption flash photolysis. The rate constants were diffusion controlled, and the radical yield being much lower than unity that decreases strongly when the free enthalpy $\Delta H$ (gained in the electron process) became smaller.

Rylkov et al.\textsuperscript{215} and Chibisov et al.\textsuperscript{216} studied the kinetics and thermodynamics of electron transfer reaction of the dye with metal ions. The free energy for the self exchange reaction of metal ions as well as the quantum yield for the radical were evaluated. They also discussed the measuring of frequency factor transmission coefficient, spin statistical
factor and ion radical pair formation in relation to the electron transfer kinetics.

Lunak et al.\textsuperscript{217} and Nosak et al.\textsuperscript{218}, studied the kinetics of electron transfer reaction of the dye. They also studied the dependence of quantum yield on incident pulse width for reduction of adsorbed dye. They found that for colloidal TiO\textsubscript{2}, the difference in quantum yield was caused by adsorption of incident pulses.

Jockusch et al.\textsuperscript{219} studied the electron transfer between ketone triplets and organic dyes. In their studies cationic dyes such as phenosafranine, safranine T, thiopyronine, and methylene blue were found to be efficient quenchers for the triplet states of aromatic ketones. The triplets of benzophenone, xanthone, thioxanthone, benzil, and N-methylacridone were quenched by these dyes via energy transfer. The mechanism of triplet quenching was found to be solvent dependent. Electron transfer occurred in polar solvents like acetonitrile, and energy transfer was dominant reaction pathway in less polar solvents, such as dichloromethane.

The electron transfer in photochemical reactions of organic dyes with metal ions was studied by Chibisov et al.\textsuperscript{216} Hatsui et al.\textsuperscript{220} studied the photooxidation of quadricyclane (I). The mechanism of photooxidation was explained by a photoclectron transfer from quadricyclane (I) to the excited methylene blue molecule.
Photo-reduction of thionine by reducing agent such as allylthiourea was investigated by Steiner et al.\textsuperscript{204} using flash photolysis and continuous illumination technique.

2.13 PHOTOPOLYMERIZATION OF METHYLENE BLUE

Photopolymerization process was studied by Shepp \textit{et al.}\textsuperscript{221} and Chaberek \textit{et al.}\textsuperscript{222} They reported that for photopolymerization process the initiating radical is semimethylene blue. The basic reaction mechanism for methylene blue triethanolamine, methylene blue acrylamide, thionine-triethanolamine and thionine acrylamide systems are identical with that described for thionine nitrilotripropionamide acrylamide as given by Chaberek \textit{et al.}\textsuperscript{223} In these reactions the rate of polymerizations depends on concentration of the reductant as well as on the presence of available oxygen. The polymerization process decreases with the increase in oxygen level. Kinetic measurements of acrylamide polymerization in water ethylene glycol, their binary mixtures and a water-glycerol binary mixture were performed dilatometrically.\textsuperscript{224} The reaction was photo initiated by irradiation of methylene blue (D\textsuperscript{+} Cl\textsuperscript{-}) in the presence of triethanolamine as a reducing agent. The application of a moderate external magnetic field (B \leq 0.1T) led to increase the process of the polymerization in ethylene glycol or glycerol-containing solutions having δ=3.0-17.0%. The photo-reduction of D\textsuperscript{+} Cl\textsuperscript{-} in viscous homogenous polymer-containing solutions was studied by flash photolysis. The application of a magnetic field
resulted in the increase in the concentrations of transient free radicals, which initiates the process of polymerization. At B=0.19T, a significant field effect, i.e. two fold increase of semiquinone free radical DH*, was found. Magnetic field effects are described within the frame of the hyperfine coupling mechanism. Despite having high dynamic viscosities, Polyacrylamide solutions are characterized by low microviscosity and exhibit a relatively small magnetic field effect. Diffusion rates of low molecular weight compounds in polymeric solutions were also discussed in such studies. An electron transfer photosensitization system for polymerization is reported by Miaozen et al.\textsuperscript{225} in which methylene blue triphenyl alkyl borate is used. The spectral properties along with the photochemical behaviours and application for polymerization were studied kinetically. The photo-induced electron transfer of MBB in the tight ion pair state which predominantly exists in non-polar solutions, was found to be greater than that observed in the free solvated ion state in polar solvents.

The photochemical reduction of dye in a solid polymer solution under the influence of laser radiation was studied by Sizykh et al.\textsuperscript{226} A high triplet quantum yield and intersystem crossing (ISC) yield provides the proof of linear dependence of the dye photo-reduction rate and the intensity of laser used. Generation of functional images by photo-induced chemical transformation of organic dyes in polymer films has also been reported by Kim et al.\textsuperscript{227}
The photoinitiation mechanism and photo-degradation of methylene blue using solar light and TiO$_2$ as, semiconductor were investigated by Noguerai, Lakshmi et al. The extent of degradation was monitored at 660 nm following the rate of mineralization of methylene blue, the rate constant $k$ and the half life $t_{1/2}$ of methylene blue were also calculated. Recently photocatalytic degradation of xylidine ponceau and orange-G have been observed by Sharma et al. and photocatalytic bleaching of crystal violet by Rao et al.

Ascorbic acid was determined indirectly by Leon et al. Flow injection technique was used for the reduction of methylene blue at 666 nm. The carrier stream was 12.7 $\mu$g.ml$^{-1}$ methylene blue in phthalate-HCl buffer solution at pH 3.2. The reactor was irradiated with a 500 W halogen lamp to facilitate the development of the photochemical reaction. The system allowed determination of ascorbic acid in the range of 0.18–6.12 $\mu$g.ml$^{-1}$ with relative standard deviations of 2.09 and 0.31% for 1.97 and 4.92 $\mu$g.ml$^{-1}$. The proposed method was applied successfully to the determinations of ascorbic acid in vitamin C tablets.

### 2.14 PHOTOBLEACHING

Photochemical reactions were studied by many workers such as Imamura, Oster et al., Vonnach et al., Matsumoto and Obata. Tetsu et al. studied the remote bleaching of methylene blue by ultra violet irradiated TiO$_2$ in the gas phase.
Ahmed\textsuperscript{238} and Uddin\textsuperscript{239} reported that aqueous thionine, a member of thiazone dyes which did not give correct result due to unstability and dimerisation process.

A methylene blue sensitized photooxidation\textsuperscript{240} of (poly cis-14-butadiene) in $\text{C}_6\text{H}_6/\text{MeOH}$ occurs via a singlet O mechanism. Here a decrease in concentration of methylene blue and molecular weight of poly butadiene exhibited an induction period followed by increased rate. The results were consistent with sensitized photolysis of OOH groups which yield radical species leading to bleaching and chain scission.

2.15 AIM OF THE PRESENT WORK

The present work deals with the study of photochemical reduction of methylene blue by organic reductants such as urea, allylurea, phenylurea, thiourea and allylthiourea. The effect of various parameters such as acidity, temperature, concentration of the reductants as well as concentration of methylene blue on the quantum yield of the photochemical reduction was photometrically determined. Arrhenius Erying relations will be used to evaluate the thermodynamic parameters in 50\% propanol. A reaction mechanism will be proposed to understand the kinetics of the photoreduction process of methylene blue with reductants. It is also intended to workout the values of the rate constant of the different steps to understand more clearly about the mechanism proposed. The results will be interpreted in terms of reaction mechanism. Tests will be put forward to verify the mechanism.
CHAPTER - 3

EXPERIMENTAL
3.1 INTRODUCTION TO INSTRUMENTAL ASPECTS

The intensity of light passing through a reaction cell can be measured either in terms of absorption or transmittance (emission). The measurement of such radiation through test solutions contain five basic components:

Light source, Monochromator, Sample container, Radiation detector and Signal indicator

3.1.1 Radiation sources

A suitable source of radiation must have following characteristics.

1. It must generate a beam with sufficient power.
2. The source should provide continuous radiation in the region being studies.
3. The source should be stable.
4. The source must emit a measurable signal throughout the region.

Sources of visible Radiation

A tungsten lamp in an excellent source of visible and near infra-red light. A typical tungsten filament operates at a temperature near 3000K and produces useful radiation in the range 320-2500 nm.

This covers the entire visible region and parts of the infra-red and ultra-violet regions as well.
Sources of Ultra-violet Radiation

Hydrogen gas lamps and a deuterium lamp are the common sources used in ultra-violet region. In deuterium arc lamp an electric discharge causes D\textsubscript{2} to dissociate and emit ultra-violet light in the approximate range 200-400 nm.

Sources of Infra-red Radiation

Mid-infra-red radiation (4000-200 cm\textsuperscript{-1}) is commonly obtained from a silicon carbide rod called globar, heated to near 1500 k by passage of an electric current through the rod. The hot globar emits radiation with approximately the same spectrum as a blackbody at 1000 k.

Laser

Laser are important source of monochromatic radiation available principally in the visible and infra-red region. Laser light is typically plane polarized, with the electric field oscillating in one plane perpendicular to the direction of travel. Another characteristic of laser light is its co-herence. Which means that all light waves emerging from the laser oscillate in phase with each other. Helium-neon laser is a common source of red light with a wave length of 632.8 nm and an output power of 0.1-25 mW.
3.1.2 Liquid sample cells

Sample containers, i.e. cells or cuvettes must satisfy two main requirements.

1- The cells or cuvettes that hold the sample must be made of substances which are transparent in the spectral region of interest.

2- They must be reproducible in path lengths or be designed in such a way that their path lengths may be easily determined.

The most common cuvets for measuring visible and ultra-violet spectra are made of quartz, have a 1.00 cm path length. Glass cells are suitable for visible light measurements, but not for ultra-violet region (because they absorb the ultra-violet light). Quartz is transparent through the normally accessible and ultra-violet regions.

Cells for infra-red measurements on liquids are commonly constructed of NaCl, KBr or AgCl, which transmit infra-red radiation. Polyethylene is suitable for measurement in the 400-50 cm⁻¹ region.

Solid samples, in infra-red region are handled differently. If the sample is soluble it may be dissolved and handled as for a liquid. Powdered solids are handled by one of the two methods. In the first, the sample is dispersed in a liquid, generally liquid paraffin, by moistening the finally
ground powder with the dispersing liquid. In the second, the solid is homogeneously mixed with 50-200 times its weight of finally divided alkali halide usually KBr and pressed carefully into a pallet.

Wave-length Selection

Two methods are usually employed in the selection of wave-length.

1. The use of filters.

2. Dispersion by means of prism or diffraction grating.

A filter is a device which will transmit radiations of some wave-lengths. Both absorption and interference filters have been used. Absorption filters limit radiation by absorbing certain proportions of spectra and have effective band widths that vary 30-250 μμ. Most common types of absorption filters consist of coloured glass or a dye suspended in gelatin and sandwiched between glass plates.

An interference filter consists of a transparent calcium fluoride or magnesium fluoride solution that occupies the space between two semitransparent metallic films coated on the inside surface of two glass plates.
Figure A - Radiation Detectors
(a) Thermopile; (b) Photo cell
3.1.3 Monochromator

The monochromator is used to separate polychromatic radiation into a suitable monochromatic form. A monochromator is a device that resolves radiation into its component wave-lengths and permits the isolation of any desired portion of the spectrum from the remainder.

3.1.4 Detectors

The general property of a detector is the ability to produce an electric signal when it is struck by photons. The response of most detectors depends on the wave-lengths of incident photons.

Detectors may be of two types

Heat detectors: Such as thermocouple, thermistor, bolometer, thermopile etc. used over a wide range of wave-lengths but have relatively low sensitivity and slow response.

Photon detectors: Photomultiplier, barrier layer cell, Pbs cell, photographic plate etc. are well known photon detectors. In general photon detectors are faster and more sensitive.

Photon multipliers: Operate on the principle of photon amplification, a photon strikes a photo-cathode causing emission of electrons which are multiplied by stricking a series of anodes resulting in electron multiplication Figure A. The radiant energy, thus converted into electrical energy which can be easily measured.
**Photocell**: in which the radiant energy generates a current at the interface of a semi-conductor and a metal. Figure A(b) are used for the detection and measurement of radiation in the visible region.

**Phototube**: A phototube emits electrons from a photosensitive, negatively charged surface when struck by visible or ultra-violet light. The electrons flow through a vacuum to a positively charged collector whose current is essentially proportional to the radiation intensity.

**Signal Indicator**: An optical processor usually involves the galvanometer/ammeter, that have a linear scale which covers a range from 0-100 units when the sample container is placed in the beam. The indicator gives percent transmittance directly provided the detector responds linearly to changes in radiant power.

### 3.2 EXPERIMENTAL SETUP

According to the need of reaction, an special type apparatus was constructed to carry out the experiments of photochemical reactions. The reaction of methylene blue was carried out using 50% aqueous propanol as a solvent. The photo-reduction of methylene blue was accomplished through the interaction between the lowest triplet state of methylene blue and the reducing agents such as urea, allylurea, phenylurea, thiourea and allylthiourea at different values of acidities $H_0$ range (4-8).
Acidity (H₀) of the reacting solution were determined with the help of acridine, a fluorescent dye. The hydrogen ion activity was controlled by using acetate buffer. The wave length of 660 nm for methylene blue in 50% aqueous propanol was used for the irradiation of the reaction solution. The change in the intensity of light was measured with a photocell-galvanometer arrangement.

All experiments were carried out in an inert condition by purging the reaction solution with oxygen free dry nitrogen. The flushing process was carried out in darkness to protect the interaction of an unreported amount of light.

Since the temperature also plays an important role in reaction, the temperature of the reacting system was controlled by a thermostatic bath (Model Haake T 52) of variation ± 0.1°C with constant stirring with a magnetic stirrer. Homogeneous deoxygenated reaction solution was allowed to irradiate with monochromatic light using high pressure mercury lamp.

Absorption spectra were recorded with a Schimadzu UV-visible spectrophotometer 160 A. Solutions were adjusted to possess an absorbance of 0.1307 at 660 nm. The value of molar extinction coefficient was calculated as 6.53 x 10⁴ M⁻¹ cm⁻¹ at 660 nm.
3.2.1 Light Source

The light source for irradiation of reaction solution was a 250 watts, 3 pin; 200/250 volts prefocus high pressure mercury ME/D compact Mazda lamp (box type) code No. 2191-0521 manufactured by GEC lamps and lighting Ltd. The voltage was kept constant within 0.01 V by using a 250 watts constant voltage transformer manufactured by Hanovia. The complete circuit diagram is shown in Figure B.

3.2.2 Optical Bench Arrangement

A special optical bench was arranged according to the need of experiments. An apparatus for irradiation of deoxygenated reaction solutions with monochromatic light was designed as shown in Fig. A-4. The 250 watt high pressure mercury ME/D compact source Mazda box type G.E.C. lamp (code No. 2191-0521) was run on 220 volts Ac mains using the circuit shown in Fig. A-4. The light from arc was focused by a combination of two convex lenses $L_1$ and $L_2$ on to a small hole (O) 2 mm, in a metal plate. This helps to cut off the stray light; only light from the centres of the arc is used. $L_3$ represents a lens which was placed at its focal length from the hole in the metal plate, O, to obtain a parallel beam of light. Monochromatic yellow light was obtained by passing the beam through a Kodak wratten filter F. A plain reflecting glass R was used for reflection of a fraction of the filtered light on to a reference photocell $P_2$. This light was then passed through reaction cell Figure C. A magnetic
Figure C - Reaction cell
stirrer (M) was used to homogenize the reaction solutions. The photocell \( P_1 \) was used to detect the light after passing through the reaction cell. \( G_1 \) and \( G_2 \) were used to convert the light signal into electronic current measured in \( \mu \text{A} \) or microampere from photocell \( P_1 \) and \( P_2 \) respectively.

### 3.2.3 Light Filters

A Kodak wratten filter No. 15 was used in order to obtain light of wavelength 660 nm as suggested by Steiner et al.\textsuperscript{169,172} A filter box was constructed and in the middle of this box the Kodak wratten filter was arranged in such a way that maximum light was passing through the filter.

### 3.2.4 Reaction Cell

The double-walled reaction cell, as shown in Fig. C, was a modified form of the cell used by Getoff,\textsuperscript{162} Sawkar\textsuperscript{52} and Uddin.\textsuperscript{239} It was cylindrical glass tube, 7.0 cm in length, 2.5 cm in diameter with flanged ends. At the end of the reaction cell, two joints attached to the cell were connected to the thermostatic bath for the circulation of water in the outer part of the cell.

### 3.2.5 Thermostatic Bath

The temperature of the system was controlled by a thermostatic bath of type T-52, manufactured by Haake, Karlsruhe of Germany.
3.2.6 Stirring System

The solution in the reaction vessel was magnetically stirred with the aid of a small horseshoe magnet, placed on an electric motor.

3.2.7 Deoxygenation System

The nitrogen gas used during the work was manufactured by Pakistan Oxygen Ltd. And was 99.98% pure. This nitrogen was made dry and oxygen free by the method given by Feiser.\textsuperscript{241} According to this method, the nitrogen was passed through a series of different draschel bottles containing Feiser's saturated solution of lead acetate, approximately 0.1 M sodium hydroxide, silica gel and the solvent of the reaction respectively.

3.2.8 Purification of Nitrogen

Following procedure was adopted for the purification of nitrogen gas.

Preparation of Feiser solution

62.5 g sodium hydroxide in 500 ml distilled water, 7.5 g of sodium arthraquinone-2-sulphonate in 500 ml distilled water and 75 g sodium hydrosulphite (dithionite) in 500 ml of distilled water were dissolved together in deaerated hot water. The solution was transferred into the two draschel bottles as quickly as possible. The lead acetate and sodium hydroxide solutions were placed in two more draschel bottles separately in order to remove the traces of (i) hydrogen sulphide formed by the decomposition of dithionite and (ii) acidic vapours respectively. The traces
Figure D - Feiser's arrangement for removal of Nitrogen
of moisture were then removed by passing the gas through another drasche\el bottle containing silica gel. The loss of solvent during the flushing period was avoided by saturating the dry oxygen free nitrogen with the vapours of the solvent. The arrangement is shown in Figure D.

3.2.9 Materials and methods

Methylene blue and all reductants such as urea, thiourea, allylurea, allylthiourea, phenylurea used were G.R. Grade, E. Merck. Methylene blue\textsuperscript{119,139} and reductants used without further purification.

Solvent

The solvent used for all the experimental purposes was n-propanol of E. Merck (Extra pure).

Acridine orange base  [494-38-2] :

Acridine orange an indicator of (extra pure) E. Merck, having molecular weight as 265.36 and $\lambda_{\text{max}}$ as 493.5 nm was used without further purification.

Sodium acetate : Anhydrous (Extra pure) E. Merck was used.

Hydrochloric acid : (Extra pure) E. Merck was used.

Sodium hydroxide : (Extra pure) E. Merck was used.

Oxalic acid : Crystals of (Extra pure) E. Merck was used.

Feiser solution : All chemicals used in Feiser solution were of extra pure E. Merck.
3.2.10 *Preparation of stock solution*

(i) *Stock solution of Methylene blue* \([51-73-4]\):

\[
\text{(H}_3\text{C)}_2\text{N}^\text{+} \text{N}^\text{-} \text{Cl}^{-}
\]

4x10^{-5} mol.dm^{-3} solution of methylene blue was prepared in 50% aqueous 2-propanol with a lot of care. Required amount of methylene blue was used to make a smooth paste first with a small amount of solvent, making sure that all the particles are thoroughly wet out before preparing the final stock solution. The solution was viewed through the red light obtained from a red bulb. In order to confirm that whether the dye is completely dissolved or not. All the solutions of methylene blue in aqueous and non-aqueous medium were prepared and preserved in well stoppered polythene bottles to keep the dye stable.

(ii) *Stock solution of Reductants.*

a) Stock solution of Urea \((\text{NH}_2\text{CONH}_2)\) mol.wt.=61.05

0.01 mol.dm^{-3} solution of urea was prepared in 50% aqueous propanol.

b) Stock solution of Allylurea \((\text{H}_2\text{C}=\text{CHCH}_2\text{NHCONH}_2)\) mol.wt.=100.12

0.01 mol.dm^{-3} solution of allylurea was prepared in 50% aqueous propanol.

c) Stock solution of Phenylurea \((\text{C}_6\text{H}_5\text{NHCONH}_2)\) mol.wt.=136.15

0.01 mol.dm^{-3} solution of phenylurea was prepared in 50% aqueous propanol.
d) Stock solution of Thiourea \((\text{H}_2\text{NCSNH}_2)\) \text{mol.wt.}=76.12

0.01 \text{mol.dm}^{-3} \text{ solution of thiourea was prepared in 50% aqueous propanol.}

e) Stock solution of Allylthiourea \((\text{H}_2\text{C}=\text{CHCH}_2\text{NHCSNH}_2)\) \text{mol.wt.}=116.19

0.01 \text{mol.dm}^{-3} \text{ solution of allylthiourea was prepared in 50% aqueous propanol.}

(iii) Stock solution of sodium hydroxide:

The stock solution of sodium hydroxide was prepared in 50% aqueous propanol by dissolving a known amount of sodium hydroxide in propanol. This solution was standardized before use by titrating with standard oxalic acid. The concentration of sodium hydroxide was kept constant as 1x10^{-2} \text{mol.dm}^{-3}.

(iv) Stock solution of oxalic acid:

A known amount of oxalic acid was dissolved in 50% 2-propanol for the preparation of 1x10^{-2} \text{mol.dm}^{-3} solution.

(v) Stock solution of sodium acetate:

0.01 \text{mol.dm}^{-3} \text{ solution of sodium acetate was prepared in 50% aqueous 2-propanol. Sodium acetate was used as a buffer solution.}
(vi) *Stock solution of Acridine*:

The stock solution of acridine of concentration $1.0 \times 10^{-3}$ mol.dm$^{-3}$ was prepared in 50% (v/v) 2-propanol. This solution was used to determine the acidity of the reacting solutions.

### 3.3 Measurement of Light Intensity

The intensity of light beam was measured by means of photocell,$^{242}$ which was connected with an ammeter. The current measured by ammeter, after the passing light is directly proportional to the *amount* of light striking at the cathod.

$$I = k I_0$$

Where $k = \text{photocell constant} = 20$; $I_0 = \text{amount of light in lumen}$.

According to this relation current $I$ is a function of amount of light. The response of the photocell was recorded on ammeter. The energy of photon is given by:

$$E = N h \nu$$

$$= N h c / \lambda \quad \text{(3.3.1)}$$

where

- $N = \text{Avogadro's number} = 6.023 \times 10^{23}$
- $h = \text{planck's constant} = 6.627 \times 10^{-27} \text{ ergs s.}$
- $\lambda = \text{wave length of light} = 660 \text{ nm.}$
- $\nu = \text{frequency of light used.}$
- $c = \text{velocity of light} = 2.998 \times 10^{10} \text{ cm/s.}$
The intensity of light is given as:

\[ I_o = \frac{1}{k} = \frac{x}{k} \text{ lumen} \quad 3.3.2 \]

Where \( x \) is the effective value of current recorded on the ammeter.

\[ I_o = \frac{x}{20} \text{ lumen (since } k=20) \]

One lumen = \( \frac{1}{680} \) light watts.

\[ = 0.00147 \text{ light watts.} \]

Therefore \( I_o = \frac{x}{20} \times \frac{0.00147}{2.066 \times 10^5} \text{ Einstein.s}^{-1} \quad [\text{Ref. 242}] \)

### 3.4 MEASUREMENT OF ACIDITY OF THE SOLUTION

Acidity of the solution can be determined in terms of Hammett\(^{133,243}\) acidity function \( H_o \), given as below:

\[ H_o = -\log h_o \]

While \( h_o = \frac{[H^+] f_{B^*} f_B}{f_{BH^*}} \quad 3.4.1 \)

Where \( f_B, f_{BH^*} \) and \( f_{H^*} \) are the activity coefficients of a base indicator B, its protonated form are BH\(^*\) and the hydrogen ion H\(^*\).

An optical method described earlier by Uddin\(^{133}\) was used for the determination of acidity of the reaction solution.
The acidity of the solution was determined by using Hammett's\textsuperscript{37,133,243} relation given as:

\[ H_0 = pK_a - \log \frac{(d_1 - d)}{(d - d_2)} \quad 3.4.2 \]

Where \( d_1 \) and \( d_2 \) are optical density of the indicator in extreme acidic and basic solutions respectively. \( d \) is the optical density of the solutions of intermediate acidity. For the present work Weller's value for aqueous acridine solution was taken as 5.45.

The best acidity range selected for the present work was varying from 4.16 to 7.59.

\textbf{3.5 MEASUREMENT OF EXTINCTION CO-EFFICIENT OF METHYLENE BLUE}

The values of extinction co-efficient given by Matsumoto,\textsuperscript{116} Kayser,\textsuperscript{43} Parker\textsuperscript{104} and Sommer\textsuperscript{79} are given in the Table-3.

Extinction coefficients of methylene blue were determined in water, hydrochloric acid, absolute propanol and 50\% aqueous propanol. The calculated values of molar extinction coefficient are tabulated in Table-5. The value of molar extinction coefficient is in agreement with the values given by Matsumoto,\textsuperscript{116} Kayser,\textsuperscript{43} Parker\textsuperscript{104,191} & Sommer\textsuperscript{79,86}.

The spectrum of the solutions of methylene blue in absolute propanol and in 50\% aqueous propanol are given in Figures 1 and 2.
The determination of extinction coefficient of methylene blue in 2-propanol is described below.

The optical densities of various concentrations of methylene blue solution in aqueous 2-propanol were measured at 660 nm (Table-6).

A plot of absorbance vs wave-length is shown in Figure 3. The extinction coefficient is determined by using the Beer-Lambert relation.

\[ \text{O.D.} = \epsilon \cdot c \cdot l \]  \hspace{1cm} 3.5.1

Where O.D. is the optical density and \( \epsilon \) is the concentration of methylene blue. \( l \) is the path length of cell. The observed optical density of the methylene blue at 2x10\(^{-6}\) mol.dm\(^{-3}\) is 0.1307. \( \epsilon \) is the molar absorbtivity. The calculated value of molar absorbtivity is 6.533x10\(^{4}\) mol\(^{-1}\).d\(^{3}\).cm\(^{-1}\).

3.6 EXPERIMENTAL PROCEDURE

Experimental samples were prepared using calibrated micropipets. 30 ml of reaction solution containing known volumes of methylene blue, reductant and buffer solution in propanol were introduced into the cell. The cell was then fitted with the nitrogen retractable bubbler and the outlet tap. The cell was kept in dark and well stirred magnetically during the flushing and irradiation periods. Oxygen free nitrogen was bubbled or 30 minutes through reaction cell before the irradiation.
The 250 w high pressure mercury lamp was switched on for 45 minutes before exposing the reaction solution a monochromatic light of 660 nm. Photocell responses from the deflection on the scale of the galvanometer were noted with no cell in the beam ($D_0$), with the cell containing solvent ($D_m$) and with the cell containing reaction solution ($D_n$). Simultaneous observations were taken on the reference galvanometer. The intensity of light was measured from the ammeter. The quantum yield was calculated as described in Section 4.
CHAPTER - 4

RESULTS
4.0 RESULTS

4.1 ABSORPTION SPECTRA OF METHYLENE BLUE

The effect of different solvents on the $\lambda_{\text{max}}$ of methylene blue and on molar extinction coefficient is reported in Table-5. The variation of absorbances of methylene blue in 1:1 aqueous 2-propanol were recorded for the determination of extinction coefficient.

Absorption spectra of methylene blue in pure and 1:1 aqueous 2-propanol are represented in Figure 1.

Influence of concentration of methylene blue in 1:1 aqueous 2-propanol is represented in Figure 2.

**TABLE - 5**

**Effect of different solvents on the $\lambda_{\text{max}}$ of methylene blue.**

$[\text{Methylene blue}] = 2.0 \times 10^{-6} \text{ mol.dm}^{-3}$

<table>
<thead>
<tr>
<th>SOLVENTS</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (mol$^{-1}$.dm$^3$.cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>664.4</td>
<td>$4.90 \times 10^4 \pm 0.41$</td>
</tr>
<tr>
<td>HCl (3.46 $\times 10^{-2}$mol.dm$^{-3}$)</td>
<td>665</td>
<td>$1.10 \times 10^5 \pm 0.62$</td>
</tr>
<tr>
<td>Propanol 50%</td>
<td>660</td>
<td>$6.53 \times 10^4 \pm 0.82$</td>
</tr>
<tr>
<td>Propanol 100%</td>
<td>650</td>
<td>$8.00 \times 10^5 \pm 1.2$</td>
</tr>
</tbody>
</table>
TABLE - 6

Absorbance measurements at various concentrations of methylene blue in 50% propanol.

\[ \lambda_{\text{max}} = 660 \text{ nm} \]

<table>
<thead>
<tr>
<th>[Methylene blue] ( \times 10^5 ) mol.dm(^{-3} )</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.130</td>
</tr>
<tr>
<td>0.40</td>
<td>0.298</td>
</tr>
<tr>
<td>1.00</td>
<td>0.650</td>
</tr>
<tr>
<td>1.50</td>
<td>0.980</td>
</tr>
<tr>
<td>2.00</td>
<td>1.301</td>
</tr>
</tbody>
</table>

4.2 CALCULATION OF THE QUANTUM YIELD

The quantum yield for the reaction of methylene blue with reductants was calculated as follow:

Light intensity of the beam reaching front window.

\[ I_0 \text{ Einst. s}^{-1} \]

Intensity behind front window \[ = I_1 \text{ " "} \]

Intensity behind solution \[ = I_2 \text{ " "} \]

Intensity behind back window \[ = I_3 \text{ " "} \]

Then \[ I_a = I_1 - I_2 \] \hspace{1cm} 4.2.1

Where \( I_a \) = intensity of light absorbed in the solution.
Now \( I_a = \beta D_a \) \[4.2.2\]

Where \( \beta \) is the proportionality factor. Deflection is proportional to the intensity of the beam.

\[
I_a = \beta D_a = \frac{\beta (D_a - D_n)}{(1 - \alpha)} \tag{4.2.3}
\]

Where \( D_a \) = photocell response for without cell in the beam.

\( D_m \) = photocell response for the solvent in the cell.

\( D_n \) = photocell response for the solution in the cell.

\( \alpha \) = fraction of light lost at each window.

The deflection of light entering the solution = \( D_a (1 - \alpha) \)

and \( D_m = D_a (1 - \alpha)^2 \) \[4.2.4\]

also \( D_n = D_a (1 - \alpha)^2 - D_a (1 - \alpha) \) \[4.2.5\]

\[
D_m - D_n = D_a (1 - \alpha) \tag{4.2.6}
\]

Quantum yields \( \phi \) can be defined as:

\[
\phi = \frac{\text{number of moles of reactants converted into product}}{\text{number of moles of light absorbed}} \tag{4.2.7}
\]
\[
\phi = \frac{d[MBH^*]}{dt}_{b} \quad [I_a]_b
\]

where the subscript 'b' stands for the light beam.

\[
= \frac{\text{change in conc. of methylene blue per unit volume of light beam per unit time}}{\text{absorption of light per unit volume of the beam}}
\]

or

\[
= \frac{d[HBH^*]}{dt} = \phi [I_a]_b
\]

as the volume of the beam in the solution is \(V_b\), for the whole solution.

\[
\frac{d[MBH^*]}{dt} = \frac{V_b}{V} \frac{d[MBH^*]}{dt}_b
\]

\[
= \phi V_b [I_a]_b (1/V)
\]

Since \([I_a]_b\) is the light absorbed in unit volume, the value \(V_b [I_a]_b\) is the total light absorbed in the solution i.e. \(I_a\).

\(V\) is the volume of reaction mixture in the cell, hence equation 4.2.9 becomes:

\[
\frac{d[MBH^*]}{dt} = \phi \frac{1_a}{V}
\]

Applying Beer-Lambert's law to equation 4.2.1

\[
I_a = I_1 - I_2
\]

\[
= I_1 - I_1 \exp (-\varepsilon^* [MBH^*]) L
\]

Where \(\varepsilon^* = 2.303 \varepsilon\), the exponential extinction coefficient.

\(L\) = length of the path of the beam in the cell.
On simplification of equation (4.2.11) and substituting the value \( I_1 = I_o (1-\alpha) \), the intensity of the beam entering the solution:

\[
I_o = I_o (1-\alpha) \{1 - \exp[-\varepsilon^* (MBH^*)] L\}
\]

or \( \exp[-\varepsilon^* [MBH^*]] L = \left\{\frac{1}{1 - \frac{I_o}{I_o (1-\alpha)}}\right\} \)

Taking log of both sides, we get:

\[
-\varepsilon^* [MBH^*] L = \ln \left\{1 - \frac{I_o}{I_o (1-\alpha)}\right\} \quad 4.2.12
\]

On differentiating equation (4.2.12) for \([MBH^*]\) and \(I_o\) we get:

\[
-\varepsilon^* d[MBH^*] L = -\frac{dI_o}{I_o (1-\alpha)\left\{1 - \frac{I_o}{I_o (1-\alpha)}\right\}}
\]

\[
= -\frac{dI_o}{I_o (1-\alpha) - I_o} \quad 4.2.13
\]

Now substituting \( d[MBH^*] \) from equation 4.2.1 in equation 4.2.13, we get:

\[
-\varepsilon \left\{\frac{I_o \phi}{v} \right\} dI_o = -\frac{dI_o}{I_o (1-\alpha) - I_o}
\]

or \( \{\varepsilon^* L_o \phi\} \frac{dt}{v} = \frac{dI_o}{I_o \left\{I_o (1-\alpha) - I_o\right\}} \quad 4.2.14 \)
on integration of equation we get:

\[
\int \left\{ \frac{e^{-\frac{L\phi}{\nu}}}{v} \right\} \, dt = \int \frac{dI_s}{I_o \{I_o (1-\alpha) - I_s\}}
\]

\[
e^{\frac{L\phi}{v}} \cdot t + C = \frac{1}{I_o (1-\alpha)} \left\{ \ln I_s - \ln [I_o (1-\alpha) - I_s] \right\}
\]

\[
= -\frac{1}{I_o (1-\alpha)} \ln \left\{ \frac{I_s (1-\alpha) - I_s}{I_s} \right\} \quad 4.2.15
\]

Where \(C\) = constant of integration, if \(t = 0\), \(I_s = I_{ai}\)

where \(i\) stands for initial.

From equation 4.2.13 we get:

\[
I_a = \frac{\beta (D_m - D_m)}{(1-\alpha)}
\]

and \(C = -\frac{1}{I_o (1-\alpha)} \ln \left\{ \frac{I_s (1-\alpha) - I_s}{I_s} \right\} \quad 4.2.16
\]

at time \(t\), \(I_s = I_{at} = \frac{\beta (D_m - D_m)}{(1-\alpha)} \quad 4.2.17
\]

Then equation (4.2.15) becomes:

\[
= -\frac{1}{I_o (1-\alpha)} \ln \left\{ \frac{I_s (1-\alpha) - I_s}{I_s} \right\}
\]

\[
e^{\frac{L\phi}{v}} \cdot t = -\frac{1}{I_v (1-\alpha)} \ln \left\{ \frac{[I_o (1-\alpha) - I_v]}{[I_v (1-\alpha) - I_{at}]} \right\} \quad 4.2.18
\]
From equation (4.2.2), \( I_0 = \beta D_0 \) and from equation (4.2.4), \( D_m = D_0 (1-\alpha)^2 \)

and as such \( I_{at} = \beta (D_m - D_{ni})/(1-\alpha) \) \hspace{1cm} 4.2.19

and \( I_a = \beta (D_m - D_{ni})/(1-\alpha) \) \hspace{1cm} 4.2.20

Substituting equation (4.2.19) and (4.2.20) in equation (4.2.18), we get:

\[
\frac{I_o (1-\alpha) \phi e^* L}{v} t = \ln \left( \frac{D_{ni} - D_m}{D_m} \right) - \ln \left( \frac{D_{ni} - D_{ri}}{D_{ri}} \right) \hspace{1cm} 4.2.21
\]

Taking \( \log \) to the base 10, equation (4.2.21) becomes:

\[
\frac{I_o (1-\alpha) \phi e^* L}{v} t = 2.303 \log \left( \frac{D_{ni} - D_m}{D_m} \right) - 2.303 \log \left( \frac{D_{ni} - D_{ri}}{D_{ri}} \right) \hspace{1cm} 4.2.22
\]

Where \( e^* \) = molar extinction coefficient of methylene blue.

\[
\log \left( \frac{D_{ni} - D_m}{D_m} \right) = \frac{I_o (1-\alpha) \phi e^* L}{2.303 \times v} + \log \left( \frac{D_{ni} - D_{ri}}{D_{ri}} \right) \hspace{1cm} 4.2.23
\]

The plot of \( \log \left( \frac{D_{ni} - D_m}{D_m} \right) \) against time \( t \) should be a straight line having slope and intercept as:

Slope = \( \frac{I_o (1-\alpha) \phi e^* L}{2.303 \times v} \) \hspace{1cm} 4.2.24

or \( \phi = \frac{2.303 \times v \times \text{slope}}{I_o (1-\alpha) e^* L} \) \hspace{1cm} 4.2.25

Intercept = \( \log \left( \frac{D_{ni} - D_m}{D_m} \right) \)
The molar extinction coefficient for methylene blue in 50% 2-propanol at 660 nm was $6.533 \times 10^4$ dm$^3$.mol$^{-1}$.cm$^{-1}$.

Where $L$ is the path length of 7 cm, traveled by the beam in the cell $v$ is the volume of the solution which is 0.03 dm$^3$; $I_o$ is the intensity of light and $\alpha$ is the fraction of light lost at each window measured during the course of experiment.

Finally the quantum yield was calculated from the following expression:

$$\phi = \frac{2.303 \times 0.03 \times v \times \text{slope}}{I_o (1 - \alpha) \times 7 \times 6.533 \times 10^4}$$

$$\phi = \frac{1.9544 \times 10^{-1} \times \text{slope}}{I_o (1 - \alpha)}$$  \hspace{1cm} 4.2.26

Representative plots of $\log \left( \frac{D_{in} - D_{int}}{D_{in}} \right)$ vs time are shown in Figures 4(a) and 4(b).
4.3 DETERMINATION OF QUANTUM YIELD

The reduction of methylene blue with urea, thiourea, allylurea, allyl thiourea and phenyl urea was carried out in an inert condition. The reduction process was studied in buffered and 50% v/v 2-propanol. The apparatus and the procedure were described in section-3. The effect of deoxygenation of the solution by bubbling of nitrogen on the quantum yield was studied at various time intervals. The data are shown in Tables 7-11.

From the calculated values of quantum yield it is concluded that time of passing the nitrogen through test solution has not any significant effect on the quantum yield. Nitrogen was bubbled for thirty minutes before each run. The reacting solution was irradiated with Hg light of wave length 660 nm. The photocell response was observed in various experimental conditions with the help of galvanometer. These conditions were as follow:

i. no cell was placed in the path of beam

ii. cell containing solvent.

iii. cell containing reaction solution.
**TABLE - 7**

Variation in the quantum yield with time of perging the nitrogen gas in urea.

\[
\text{[Methylene blue]} = 2.00 \times 10^{-6} \text{ mol.dm}^{-3} \\
\text{Temperature} = 30 \pm 0.1 \degree C
\]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Quantum yield at concentration of urea</th>
<th>1.66 x 10^{-3} mol.dm^{-3}</th>
<th>5.00 x 10^{-3} mol.dm^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( H_o = 4.06 )</td>
<td>( H_o = 7.59 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( H_o = 4.06 )</td>
<td>( H_o = 7.59 )</td>
</tr>
<tr>
<td>10</td>
<td>0.0879</td>
<td>0.0205</td>
<td>0.1643</td>
</tr>
<tr>
<td>20</td>
<td>0.0890</td>
<td>0.0208</td>
<td>0.1640</td>
</tr>
<tr>
<td>30</td>
<td>0.1499</td>
<td>0.0210</td>
<td>0.1950</td>
</tr>
<tr>
<td>40</td>
<td>0.1499</td>
<td>0.0205</td>
<td>0.1740</td>
</tr>
<tr>
<td>50</td>
<td>0.1022</td>
<td>0.0210</td>
<td>0.1950</td>
</tr>
<tr>
<td>60</td>
<td>0.1499</td>
<td>0.0210</td>
<td>0.1641</td>
</tr>
</tbody>
</table>

**TABLE - 8**

Variation in the quantum yield with time of perging the nitrogen gas in Allylurea.

\[
\text{[Methylene blue]} = 2 \times 10^{-6} \text{ mol.dm}^{-3} \\
\text{Temperature} = 30 \pm 0.1 \degree C
\]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Quantum yield at concentration of allylurea</th>
<th>1.66 x 10^{-3} mol.dm^{-3}</th>
<th>5.00 x 10^{-3} mol.dm^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( H_o = 4.06 )</td>
<td>( H_o = 7.59 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( H_o = 4.06 )</td>
<td>( H_o = 7.59 )</td>
</tr>
<tr>
<td>10</td>
<td>0.032</td>
<td>0.0114</td>
<td>0.092</td>
</tr>
<tr>
<td>20</td>
<td>0.039</td>
<td>0.0120</td>
<td>0.092</td>
</tr>
<tr>
<td>30</td>
<td>0.042</td>
<td>0.0130</td>
<td>0.104</td>
</tr>
<tr>
<td>40</td>
<td>0.040</td>
<td>0.0125</td>
<td>0.098</td>
</tr>
<tr>
<td>50</td>
<td>0.040</td>
<td>0.0130</td>
<td>0.095</td>
</tr>
<tr>
<td>60</td>
<td>0.040</td>
<td>0.0130</td>
<td>0.095</td>
</tr>
</tbody>
</table>
**TABLE - 9**

Variation in the quantum yield with time of perging the nitrogen gas in phenylurea.

[Methylene blue] = 2.00 x 10^{-6} mol.dm^{-3}

Temperature = 30 ± 0.1 °C

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>1.66 x 10^{-3} mol.dm^{-3}</th>
<th>5.00 x 10^{-3} mol.dm^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₀ = 4.06</td>
<td>H₀ = 7.59</td>
</tr>
<tr>
<td>10</td>
<td>0.0665</td>
<td>0.0290</td>
</tr>
<tr>
<td>20</td>
<td>0.0690</td>
<td>0.0308</td>
</tr>
<tr>
<td>30</td>
<td>0.0730</td>
<td>0.0300</td>
</tr>
<tr>
<td>40</td>
<td>0.0700</td>
<td>0.0340</td>
</tr>
<tr>
<td>50</td>
<td>0.0700</td>
<td>0.0340</td>
</tr>
<tr>
<td>60</td>
<td>0.0730</td>
<td>0.0315</td>
</tr>
</tbody>
</table>

**TABLE - 10**

Variation in the quantum yield with time of perging the nitrogen gas in thiourea.

[Methylene blue] = 2.00 x 10^{-6} mol.dm^{-3}

Temperature = 30 ± 0.1 °C

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>1.66 x 10^{-3} mol.dm^{-3}</th>
<th>5.00 x 10^{-3} mol.dm^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₀ = 4.06</td>
<td>H₀ = 7.59</td>
</tr>
<tr>
<td>10</td>
<td>0.149</td>
<td>0.027</td>
</tr>
<tr>
<td>20</td>
<td>0.154</td>
<td>0.029</td>
</tr>
<tr>
<td>30</td>
<td>0.158</td>
<td>0.038</td>
</tr>
<tr>
<td>40</td>
<td>0.158</td>
<td>0.038</td>
</tr>
<tr>
<td>50</td>
<td>0.154</td>
<td>0.038</td>
</tr>
<tr>
<td>60</td>
<td>0.154</td>
<td>0.030</td>
</tr>
</tbody>
</table>
TABLE - 11

Variation in the quantum yield with time of perging the 
nitrogen gas in allylthiourea.

[Methylene blue] = 2.00 x 10^{-6} \text{ mol.dm}^{-3}

Temperature = 30 \pm 0.1 ^\circ \text{C}

| Time (min.) | Quantum yield at concentration of allylthiourea. |  
|            | 1.66 x 10^{-3} \text{ mol.dm}^{-3} | 5.00 x 10^{-3} \text{ mol.dm}^{-3} |
|            | \text{H}_0 = 4.06 | \text{H}_0 = 7.59 | \text{H}_0 = 4.06 | \text{H}_0 = 7.59 |
| 10         | 0.0665          | 0.0294          | 0.1048          | 0.079           |
| 20         | 0.0697          | 0.0272          | 0.1048          | 0.082           |
| 30         | 0.0730          | 0.0308          | 0.1296          | 0.089           |
| 40         | 0.0730          | 0.0308          | 0.1296          | 0.082           |
| 50         | 0.0700          | 0.0290          | 0.1285          | 0.082           |
| 60         | 0.0700          | 0.0290          | 0.1285          | 0.082           |

4.4 PRESENTATION OF EXPERIMENTAL DATA

The photo-reduction of methylene blue was carried out in the presence of reducing agents such as, urea, allylurea, phenylurea, thiourea and allylthiourea in 50% 2-propanol. The results are tabulated in the following order:

1. Influence of acidity on the quantum yield of photo-reduction of methylene blue in aqueous 2-propanol.
2. Influence of concentration of reductants on quantum yield.
3. Influence of concentration of methylene blue on quantum yield.
4.5 INFLUENCE OF ACIDITY ON THE QUANTUM YIELD OF PHOTO-REDUCTION OF METHYLENE BLUE IN AQUEOUS 2-PROPANOL.

Methylene blue in presence of buffer solution and without any reducing agent photo-reduced to leucodye by the visible light at 30 ± 0.1 °C. Slow bleaching was observed even in absence of reducing agent (Table-12). The quantum yield was observed of order of 10⁻³ at various acidities. The values of quantum yield summarized in Table-12 were observed approximately twice in highly acidic medium as compared to the highly basic medium. The plots of reciprocal of quantum yield versus 1/h₀ show a straight line relation with a intercept which is equal to the value of quantum yield at infinite value of h₀. The variation of (ϕ₁ - ϕ)/(ϕ - ϕ₂) with 1/h₀ was also studied by plotting graph between (ϕ₁ - ϕ)/(ϕ - ϕ₂) versus 1/h₀. The graph shows a straight line relationship between two quantities passing through origin.
TABLE - 12

Quantum yield of photo-reduction of methylene blue in absence of reductant at different acidities.

\[
\text{[Methylene blue]} = 2.00 \times 10^{-6} \text{ mol.dm}^{-3} \\
\text{Temperature} = 30.0 \pm 0.1^\circ\text{C}
\]

<table>
<thead>
<tr>
<th>Acidity (H₀)</th>
<th>(\phi \times 10^3)</th>
<th>(1/\rho_0 \times 10^{-5})</th>
<th>((\phi_i - \phi)/(\phi - \phi_2))</th>
<th>(1/\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>7.63</td>
<td>0.01148</td>
<td>****</td>
<td>131.06</td>
</tr>
<tr>
<td>4.33</td>
<td>7.45</td>
<td>0.02142</td>
<td>0.0314</td>
<td>134.022</td>
</tr>
<tr>
<td>4.86</td>
<td>7.25</td>
<td>0.07244</td>
<td>0.2432</td>
<td>144.71</td>
</tr>
<tr>
<td>6.01</td>
<td>5.27</td>
<td>1.02330</td>
<td>0.7777</td>
<td>166.113</td>
</tr>
<tr>
<td>6.88</td>
<td>4.77</td>
<td>7.5861</td>
<td>1.9918</td>
<td>193.05</td>
</tr>
<tr>
<td>7.07</td>
<td>4.32</td>
<td>11.7400</td>
<td>8.9459</td>
<td>251.89</td>
</tr>
<tr>
<td>7.59</td>
<td>3.95</td>
<td>38.9105</td>
<td>****</td>
<td>253.164</td>
</tr>
</tbody>
</table>

* Nitrogen was perfused for 20 minutes in each set.

4.5.1 Influence of Acidity on the quantum yields of Photo-reduction of Methylene blue with urea in aqueous 2-propanol.

The influence of acidity of methylene blue solution in 50% 2-propanol on quantum yield was also observed in presence of urea. The quantum yields were determined at two concentrations of urea i.e. 1.66 \(\times 10^{-3}\) mol.dm\(^{-3}\) and 2.5\(\times 10^{-2}\) mol.dm\(^{-3}\). The acidities were varied by using acetate buffer. A significant decrease in the quantum yields was observed with the rise in basic property of solution. The results are tabulated in Table-13. The temperature was maintained constant at 30 \(\pm 0.1^\circ\text{C}\). The acidities were
varied from 4.06 to 7.59. The plots of quantum yield versus acidities for methylene blue with urea are shown in Figure 11. The plots of reciprocal of quantum yield versus $1/h_0$ show a straight line relationship in Figure 16. The values of slopes and intercepts give the value of quantum yield at infinite acidity $1/\phi_0$. The variation of $(\phi_1 - \phi)/(\phi - \phi_2)$ with $1/h_0$ was also studied and graph between $(\phi_1 - \phi)/(\phi - \phi_2)$ was plotted against $1/h_0$ are shown in Figure 21. The graph shows a straight line relationship between two quantities passing through origin. The values of slopes are given in Table-19.

4.5.2 Influence of Acidity on the quantum yield of photo-reduction of Methylene blue with N. Allylurea in aqueous 2-propanol.

The quantum yield were determined by irradiating the deoxygenated reaction solutions at various acidities, for fixed concentration of methylene blue, and the reductant N. allylurea. The acidity of reaction solutions was varied and controlled using the acetate buffer solution. The results are shown in Table-14. When the quantum yield was plotted against acidity, at a fixed concentration of methylene blue and N-allylurea, the curves were obtained as shown in Figure 12. The quantum yield was found to decrease with an increase in the acidity of the solution $H_0$. Table-14 and Figure 12 shows the dependence of quantum yield on acidity. The plots of $1/\phi$ versus $1/h_0$ are
straight lines as shown in Figure 17. Taking \( \phi_1 \) and \( \phi_2 \) at the extreme values of low and high acidities, \((\phi_1 - \phi)/(\phi - \phi_2)\) was plotted against \(1/h_0\). Figure 22 shows the plots of \((\phi_1 - \phi)/(\phi - \phi_2)\) versus \(1/h_0\) are straight lines passing through the origin.

**TABLE - 13**

*Quantum yield of photo-reduction of methylene blue in presence of urea at different acidities.*

<table>
<thead>
<tr>
<th>Acidity (H(_0))</th>
<th>(\phi)</th>
<th>(\phi/h_0 \times 10^{-6})</th>
<th>((\phi_1 - \phi)/(\phi - \phi_2))</th>
<th>(1/\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.2880</td>
<td>0.01148</td>
<td>***</td>
<td>3.4722</td>
</tr>
<tr>
<td>4.33</td>
<td>0.2830</td>
<td>0.02142</td>
<td>0.0294</td>
<td>3.1340</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2600</td>
<td>0.07244</td>
<td>0.1904</td>
<td>3.8460</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1700</td>
<td>1.0233</td>
<td>2.0701</td>
<td>5.8820</td>
</tr>
<tr>
<td>6.88</td>
<td>0.1370</td>
<td>7.5861</td>
<td>5.5926</td>
<td>7.2990</td>
</tr>
<tr>
<td>7.07</td>
<td>0.1270</td>
<td>11.7400</td>
<td>11.5000</td>
<td>7.8740</td>
</tr>
<tr>
<td>7.59</td>
<td>0.1130</td>
<td>38.9105</td>
<td>***</td>
<td>8.8490</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acidity (H(_0))</th>
<th>(\phi)</th>
<th>(\phi/h_0 \times 10^{-6})</th>
<th>((\phi_1 - \phi)/(\phi - \phi_2))</th>
<th>(1/\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.2202</td>
<td>0.01148</td>
<td>***</td>
<td>04.540</td>
</tr>
<tr>
<td>4.33</td>
<td>0.2110</td>
<td>0.02142</td>
<td>0.0700</td>
<td>04.740</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2030</td>
<td>0.07244</td>
<td>0.1400</td>
<td>0.0493</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1320</td>
<td>1.0233</td>
<td>1.6960</td>
<td>07.570</td>
</tr>
<tr>
<td>6.88</td>
<td>0.1090</td>
<td>7.5861</td>
<td>3.8340</td>
<td>09.170</td>
</tr>
<tr>
<td>7.07</td>
<td>0.0943</td>
<td>11.7400</td>
<td>8.8040</td>
<td>10.600</td>
</tr>
<tr>
<td>7.59</td>
<td>0.0800</td>
<td>38.9105</td>
<td>***</td>
<td>14.920</td>
</tr>
</tbody>
</table>

* Nitrogen was purged for 20 minutes in each set.
TABLE - 14

Quantum yield of photoreduction of methylene blue in presence of Allylurea at different acidities.

\[
\text{[ Methylene blue ] } = 2.00 \times 10^{-6} \text{ mol.dm}^{-3}
\]
\[
\text{[ Allylurea ] } = 2.5 \times 10^{-2} \text{ mol.dm}^{-3}
\]
Temperature : $30 \pm 0.1^\circ\text{C}$

<table>
<thead>
<tr>
<th>Acidity ($H_0$)</th>
<th>$\phi$</th>
<th>$l/h_0 \times 10^6$</th>
<th>$(\phi_1-\phi)/(\phi_2-\phi)$</th>
<th>$1/\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.3180</td>
<td>0.01148</td>
<td>****</td>
<td>3.220</td>
</tr>
<tr>
<td>4.33</td>
<td>0.3000</td>
<td>0.02142</td>
<td>0.0769</td>
<td>3.330</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2730</td>
<td>0.07244</td>
<td>0.2174</td>
<td>3.660</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1410</td>
<td>1.0233</td>
<td>2.3600</td>
<td>7.092</td>
</tr>
<tr>
<td>6.88</td>
<td>0.0880</td>
<td>7.5861</td>
<td>10.450</td>
<td>9.260</td>
</tr>
<tr>
<td>7.07</td>
<td>0.0820</td>
<td>11.7400</td>
<td>14.750</td>
<td>12.195</td>
</tr>
<tr>
<td>7.59</td>
<td>0.0660</td>
<td>38.9105</td>
<td>****</td>
<td>15.151</td>
</tr>
</tbody>
</table>

\[
\text{[ Methylene blue ] } = 2.00 \times 10^{-6} \text{ mol.dm}^{-3}
\]
\[
\text{[ Allylurea ] } = 1.66 \times 10^{-2} \text{ mol.dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Acidity ($H_0$)</th>
<th>$\phi$</th>
<th>$l/h_0 \times 10^6$</th>
<th>$(\phi_1-\phi)/(\phi_2-\phi)$</th>
<th>$1/\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.2850</td>
<td>0.0115</td>
<td>****</td>
<td>3.5087</td>
</tr>
<tr>
<td>4.33</td>
<td>0.2720</td>
<td>0.0214</td>
<td>0.0572</td>
<td>3.6760</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2170</td>
<td>0.0724</td>
<td>0.3186</td>
<td>4.4050</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1070</td>
<td>1.0233</td>
<td>2.8709</td>
<td>9.3450</td>
</tr>
<tr>
<td>6.88</td>
<td>0.0735</td>
<td>7.5861</td>
<td>7.3916</td>
<td>13.600</td>
</tr>
<tr>
<td>7.07</td>
<td>0.0617</td>
<td>11.7400</td>
<td>1.3712</td>
<td>16.200</td>
</tr>
<tr>
<td>7.59</td>
<td>0.0450</td>
<td>38.9105</td>
<td>****</td>
<td>22.220</td>
</tr>
</tbody>
</table>

*Nitrogen was purged for 20 minutes in each set.*
**TABLE - 15**

Quantum yield of photo-reduction of methylene blue in presence of phenylurea at different acidities.

\[
\text{[ Methylene blue ]} = 2.00 \times 10^{-6} \text{ mol.dm}^{-3} \\
\text{[ Phenylurea ]} = 2.5 \times 10^{-2} \text{ mol.dm}^{-3} \quad \text{Temperature : } 30 \pm 0.1^\circ\text{C}
\]

<table>
<thead>
<tr>
<th>Acidity (H(_o))</th>
<th>(\phi)</th>
<th>(I/I_o \times 10^6)</th>
<th>((\phi_1-\phi)/(\phi-\phi_2))</th>
<th>(1/\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.2900</td>
<td>0.0115</td>
<td>****</td>
<td>3.4482</td>
</tr>
<tr>
<td>4.33</td>
<td>0.2800</td>
<td>0.0214</td>
<td>0.0537</td>
<td>3.5714</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2500</td>
<td>0.0724</td>
<td>0.2409</td>
<td>3.8800</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1680</td>
<td>1.0233</td>
<td>1.6486</td>
<td>5.9523</td>
</tr>
<tr>
<td>6.88</td>
<td>0.1280</td>
<td>7.5861</td>
<td>4.7009</td>
<td>7.4000</td>
</tr>
<tr>
<td>7.07</td>
<td>0.1080</td>
<td>11.7400</td>
<td>13.0000</td>
<td>8.7000</td>
</tr>
<tr>
<td>7.59</td>
<td>0.0940</td>
<td>38.9105</td>
<td>****</td>
<td>10.6380</td>
</tr>
</tbody>
</table>

\[
\text{[ Methylene blue ]} = 2.00 \times 10^{-6} \text{ mol.dm}^{-3} \\
\text{[ Phenylurea ]} = 1.66 \times 10^{-2} \text{ mol.dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Acidity (H(_o))</th>
<th>(\phi)</th>
<th>(I/I_o \times 10^6)</th>
<th>((\phi_1-\phi)/(\phi-\phi_2))</th>
<th>(1/\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.2600</td>
<td>0.0115</td>
<td>****</td>
<td>3.8460</td>
</tr>
<tr>
<td>4.33</td>
<td>0.2480</td>
<td>0.0214</td>
<td>0.0655</td>
<td>4.0322</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2174</td>
<td>0.0724</td>
<td>0.2795</td>
<td>4.6000</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1280</td>
<td>1.0233</td>
<td>1.3400</td>
<td>7.8120</td>
</tr>
<tr>
<td>6.88</td>
<td>0.0930</td>
<td>7.5861</td>
<td>5.9642</td>
<td>10.2000</td>
</tr>
<tr>
<td>7.07</td>
<td>0.0800</td>
<td>11.7400</td>
<td>11.0700</td>
<td>11.6600</td>
</tr>
<tr>
<td>7.59</td>
<td>0.0650</td>
<td>38.9105</td>
<td>****</td>
<td>15.3846</td>
</tr>
</tbody>
</table>

* Nitrogen was purged for 20 minutes in each set.
### TABLE - 16

Quantum yield of photo-reduction of methylene blue in presence of Thiourea at different acidities.

\[ \text{[Methylene blue]} = 2.00 \times 10^{-6} \text{ mol.dm}^{-3} \]
\[ \text{[Thiourea]} = 2.5 \times 10^{-2} \text{ mol.dm}^{-3} \]

Temperature: $30 \pm 0.1^\circ C$

<table>
<thead>
<tr>
<th>Acidity (H_0)</th>
<th>$\phi$</th>
<th>$1/\text{H}_0 \times 10^6$</th>
<th>$(\phi_1 - \phi)/(\phi_2 - \phi)$</th>
<th>$1/\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.3160</td>
<td>0.0115</td>
<td>****</td>
<td>3.1640</td>
</tr>
<tr>
<td>4.33</td>
<td>0.3080</td>
<td>0.0214</td>
<td>0.0360</td>
<td>3.2460</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2730</td>
<td>0.0724</td>
<td>0.2349</td>
<td>3.6630</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1680</td>
<td>1.0233</td>
<td>1.8970</td>
<td>5.9520</td>
</tr>
<tr>
<td>6.88</td>
<td>0.1285</td>
<td>7.5861</td>
<td>4.9470</td>
<td>7.7820</td>
</tr>
<tr>
<td>7.07</td>
<td>0.1060</td>
<td>11.7400</td>
<td>13.1250</td>
<td>9.4340</td>
</tr>
<tr>
<td>7.59</td>
<td>0.0900</td>
<td>38.9105</td>
<td>****</td>
<td>11.1110</td>
</tr>
</tbody>
</table>

\[ \text{[Methylene blue]} = 2.00 \times 10^{-6} \text{ mol.dm}^{-3} \]
\[ \text{[Thiourea]} = 1.66 \times 10^{-2} \text{ mol.dm}^{-3} \]

<table>
<thead>
<tr>
<th>Acidity (H_0)</th>
<th>$\phi$</th>
<th>$1/\text{H}_0 \times 10^6$</th>
<th>$(\phi_1 - \phi)/(\phi_2 - \phi)$</th>
<th>$1/\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.2800</td>
<td>0.0115</td>
<td>****</td>
<td>3.5714</td>
</tr>
<tr>
<td>4.33</td>
<td>0.2770</td>
<td>0.0214</td>
<td>0.0136</td>
<td>3.6100</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2520</td>
<td>0.0724</td>
<td>0.1435</td>
<td>3.9680</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1400</td>
<td>1.0233</td>
<td>1.6867</td>
<td>7.1428</td>
</tr>
<tr>
<td>6.88</td>
<td>0.0840</td>
<td>7.5861</td>
<td>7.2592</td>
<td>11.9047</td>
</tr>
<tr>
<td>7.07</td>
<td>0.0680</td>
<td>11.7400</td>
<td>19.2720</td>
<td>14.7050</td>
</tr>
<tr>
<td>7.59</td>
<td>0.0570</td>
<td>38.9105</td>
<td>****</td>
<td>17.5438</td>
</tr>
</tbody>
</table>

* Nitrogen was purged for 20 minutes in each set.
**TABLE - 17**

Quantum yield of photo-reduction of methylene blue in presence of Allylthiourea at different acidities.

<table>
<thead>
<tr>
<th>Methylene blue</th>
<th>Allylthiourea</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2.0 \times 10^{-6} \text{ mol.dm}^{-3} )</td>
<td>( 2.5 \times 10^{-2} \text{ mol.dm}^{-3} )</td>
<td>( 30 \pm 0.1^\circ\text{C} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acidity (H(_o))</th>
<th>( \phi )</th>
<th>( 1/\phi \times 10^{-6} )</th>
<th>( (\phi - \phi) / (\phi - \phi) )</th>
<th>( 1/\phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.3306</td>
<td>0.0115</td>
<td>****</td>
<td>3.0200</td>
</tr>
<tr>
<td>4.33</td>
<td>0.3197</td>
<td>0.0214</td>
<td>0.0546</td>
<td>3.1280</td>
</tr>
<tr>
<td>4.86</td>
<td>0.2960</td>
<td>0.0724</td>
<td>0.1969</td>
<td>3.3780</td>
</tr>
<tr>
<td>6.01</td>
<td>0.1700</td>
<td>1.0233</td>
<td>2.1063</td>
<td>5.8823</td>
</tr>
<tr>
<td>6.88</td>
<td>0.1800</td>
<td>7.5861</td>
<td>2.5220</td>
<td>5.5555</td>
</tr>
<tr>
<td>7.07</td>
<td>0.1600</td>
<td>11.7400</td>
<td>4.2972</td>
<td>6.2500</td>
</tr>
<tr>
<td>7.59</td>
<td>0.1203</td>
<td>38.9105</td>
<td>****</td>
<td>8.3120</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acidity (H(_o))</th>
<th>( \phi )</th>
<th>( 1/\phi \times 10^{-6} )</th>
<th>( (\phi - \phi) / (\phi - \phi) )</th>
<th>( 1/\phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>0.3010</td>
<td>0.0115</td>
<td>****</td>
<td>3.3220</td>
</tr>
<tr>
<td>4.33</td>
<td>0.2880</td>
<td>0.0214</td>
<td>0.0539</td>
<td>3.4720</td>
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<tr>
<td>4.86</td>
<td>0.2483</td>
<td>0.0724</td>
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<td>4.0270</td>
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<tr>
<td>6.01</td>
<td>0.1538</td>
<td>1.0233</td>
<td>1.3780</td>
<td>6.5020</td>
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<tr>
<td>6.88</td>
<td>0.0800</td>
<td>7.5861</td>
<td>6.6970</td>
<td>12.500</td>
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<tr>
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<td>0.0550</td>
<td>11.7400</td>
<td>30.7500</td>
<td>18.181</td>
</tr>
<tr>
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<td>****</td>
<td>21.270</td>
</tr>
</tbody>
</table>

* Nitrogen was purged for 20 minutes in each set.
TABLE - 18

Equations obtained from the plots of $1/\phi$ vs $1/ h_o \times 10^6$.

<table>
<thead>
<tr>
<th>Reductants</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.66 \times 10^{-2}$ mol.dm$^{-3}$</td>
</tr>
<tr>
<td>Urea</td>
<td>$Y = 0.2520 X + 5.9232$</td>
</tr>
<tr>
<td>Allylurea</td>
<td>$Y = 0.4553 X + 6.5479$</td>
</tr>
<tr>
<td>Phenylurea</td>
<td>$Y = 0.2764 X + 5.8675$</td>
</tr>
<tr>
<td>Thiourea</td>
<td>$Y = 0.3512 X + 5.9325$</td>
</tr>
<tr>
<td>Allylthiourea</td>
<td>$Y = 0.4612 X + 5.9571$</td>
</tr>
</tbody>
</table>

TABLE - 19

Equations obtained from the plots of $(\phi_1/\phi)/(\phi_2/\phi_3)$ vs $1/ h_o \times 10^6$.

<table>
<thead>
<tr>
<th>Reductants</th>
<th>Equations at concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.66 \times 10^{-2}$ mol.dm$^{-3}$</td>
</tr>
<tr>
<td>Urea</td>
<td>$Y = 0.6832 X$</td>
</tr>
<tr>
<td>Allylurea</td>
<td>$Y = 1.0997 X$</td>
</tr>
<tr>
<td>Phenylurea</td>
<td>$Y = 0.8990 X$</td>
</tr>
<tr>
<td>Thiourea</td>
<td>$Y = 1.4410 X$</td>
</tr>
<tr>
<td>Allylthiourea</td>
<td>$Y = 2.1038 X$</td>
</tr>
</tbody>
</table>

4.5.3 *Influence of Acidity on the quantum yield of photo-reduction of Methylene blue with phenylurea in aqueous 2-propanol.*

Table-15 summarizes the effect of acidity on quantum yield for methylene blue, along with concentration of $2.0 \times 10^{-6}$ mol.dm$^{-3}$ and $1.66 \times 10^{-2}$ mol.dm$^{-3}$ of phenylurea in aqueous 2-propanol. Acetate buffer was used to control the acidity of the reaction solutions. All the results are tabulated in Table-15.
It is observed that the quantum yield is decreased when the acidity value of the reaction solution is increased. The plots of quantum yield ($\phi$) versus ($H_0$) shown in Figure 13, indicate that the quantum yield as with N-allylurea depends upon the acidity.

The quantum yields observed with N-allylurea are higher than the values obtained with N-phenylurea, in the same range of acidity and concentrations of reductants. This may be due to the fact that N-allylurea is more effective than N-phenylurea.

The plots of $1/\phi$ against $1/h_0$ are shown in Figure 18, which are straight lines. Taking $\phi_1$ and $\phi_2$ at the extreme of low and high values of acidities, the plot of $(\phi_1 - \phi)/(\phi - \phi_2)$ against the reciprocal of $h_0$ ($1/h_0$) shown in Figure 23 are straight lines passing through the origin.

**4.5.4 Influence of Acidity on the quantum yield of photo-reduction of Methylene blue with thiourea in aqueous 2-propanol.**

The values of quantum yield at fixed concentration of the dye and reductant concentrations at a temperature of 30 ± 0.1 °C are summarized in Table-16. The results indicate that there is a decrease in the values of quantum yield as the acidity increases. The plots of acidity ($H_0$) against quantum yield ($\phi$) at two different values of concentration of reductant are shown in Figure 14. The plots of reciprocal of quantum yield ($1/\phi$) against $1/h_0$ are shown in
Figure 19. The values of quantum yield at infinite acidity ($\phi_a$) are found to be 0.1682 and 0.2126 at concentrations of $1.66\times10^{-2}$ mol.dm$^{-3}$ and $2.5\times10^{-2}$ mol.dm$^{-3}$, respectively. Taking $\phi_1$ and $\phi_2$ the extreme values of quantum yield at low and high acidity, plots of $(\phi_1 - \phi)/(\phi - \phi_2)$ versus $1/h_o$ are illustrated in Figure 24.

4.5.5 Influence of Acidity on the quantum yield of photo-reduction of Methylene blue with allylthiourea in aqueous 2-propanol.

The values of quantum yields of photo-bleaching of methylene blue with allylthiourea in aqueous 2-propanol at a temperature of $30 \pm 0.1$ °C are summarized in Table-17.

It is observed that in the same range of acidity and concentrations of the reductants the value of quantum yield in presence of allylthiourea are higher then the values obtained with thiourea. The greater reactivity may be due to the presence of more reactive allyl group along with the thiourea.

The plots of reciprocal of quantum yields $(1/\phi)$ against reciprocal of acidity $(1/h_o)$ at different concentrations of allylthiourea are shown in Figure 20, which shows a straight line relationship between these two quantities. The intercept of the plot gives the value of quantum yield at infinite acidity ($\phi_a$) as shown in Table-18. The value of quantum yield at infinite acidity at concentrations at $1.66\times10^2$ mol.dm$^{-3}$ and $2.5\times10^{-2}$ mol.dm$^{-3}$ comes out to be 0.1674 and 0.2461, respectively.
The plots of \((\phi_1 - \phi)/(\phi - \phi_2)\) against reciprocal of acidity \((1/\text{H}_0)\) as shown in Figure 25 are straight lines passing through origin, where \(\phi_1\) and \(\phi_2\) are the quantum yields at low and high acidity values respectively. The values of slope are given in Table-19.

4.6 THE EFFECT OF CONCENTRATION OF THE REDUCTANTS ON QUANTUM YIELD OF PHOTOREDUCTION OF METHYLENE BLUE IN AQUEOUS 2-PROpanOL

The effect of each reductant i.e. urea, thiourea, allylurea, allylthiourea and phenylurea on quantum yield was observed at two different acidities 4.06 and 7.59. The temperature was maintained constant at 30 ± 0.1 °C. The concentration of methylene blue in buffered propanol was remained constant in each run. The concentrations of each reductants were in the range from 0.3333x10^-3 mol.dm^-3 to 6.666x10^-3 mol.dm^-3. The results are tabulated in Tables 33-37 show an increase in the value of quantum yield as the concentration of each reductant increases. The reciprocal of quantum yield were plotted against \(1/|\text{AH}_2|\) at both acidities. The plots show a straight line with positive slopes shown in Figures 31-37.

The values of quantum yields at infinite concentration of each reductant are obtained from the intercepts and are tabulated in Table-25.
4.6.1 Effects of urea concentration on the quantum yield of photoreduction of methylene blue in aqueous 2-propanol.

The effect of concentration of urea on the photoreduction of methylene blue in aqueous 2-propanol was observed at two different acidities 4.06 and 7.59. The temperature was maintained constant to 30 ± 0.1 °C. The concentration of methylene blue was $2 \times 10^{-6}$ mol.dm$^{-3}$, while the concentration of urea was varied from $3.33 \times 10^{-4}$ mol.dm$^{-3}$ to $6.66 \times 10^{-3}$ mol.dm$^{-3}$. A significant rise in the values of quantum yield was observed due to increase in the concentration of urea at acidity 4.06 and 7.59 shown in Table-20. A 20 fold rise in the concentration of urea has increased the value of quantum yield at a factor of 3.72 and 10.71 at acidity 4.06 and 7.59 respectively.

The plots of reciprocal of quantum yields $(1/\phi)$ versus reciprocal of concentration of urea at two acidities are shown in Figure 31 and 36. The graph shows a straight line relationship between $1/\phi$ and $1/[\text{urea}]$. The values of slope and intercept are given in Table-25. The intercept gives the value of quantum yield at infinite concentration of urea. The value of quantum yield at infinite concentration of urea $\phi_i$ is calculated as 0.079 at acidity 4.06.
4.6.2 Effects of alylurea concentration on the quantum yield of photo-reduction of methylene blue in aqueous 2-propanol.

The quantum yields of photo-reduction of methylene blue at various concentrations of N-allylurea were determined at two different acidities 4.06 and 7.59. Under all similar experimental conditions an increase in the concentrations of allylurea results in a significant rise in the quantum yield at both values of acidity shown in Table-22. A Twenty fold rise in the concentration of allylurea has increased the value of quantum yield in a factory of 5.02 at lower acidity, while the increase in quantum yield at higher acidity was found to be in a factor of 4.26. The relationship between quantum yield and concentration of allylurea is shown at two acidities in Figures 32 and 36. A straight line plot is obtained at both acidities, the values of slopes and intercepts are given in Table-25. The quantum yield at infinite concentration of allylurea is obtained from the intercept of each plot. The value of quantum yield at infinite concentration of allylurea at lower acidity is found to be 0.100. The value of quantum yield at infinite concentration of allylurea was greater than that of urea. This may be due to the presence of allyl group along with urea. The presence of allyl group has increased the reduction process of methylene blue.
4.6.3 **Effects of phenylurea concentration on the quantum yield of methylene blue in aqueous 2-propanol.**

The effect of concentration of phenylurea on the photo-reduction of methylene blue in aqueous 2-propanol was observed at 30 ± 0.1 °C. All the results of photo-reduction of methylene blue at various concentrations of phenylurea in terms of quantum yield are tabulated in Table-24. The results summarized in Table-24 show that quantum yield increases with increase in the concentration of reductant. In contrast to the earlier results regarding the values of quantum yield obtained due to interaction of urea and allylurea, under all similar experimental conditions phenylurea gives a greater value of quantum yield. The increase in the magnitude of quantum yield in photo-reduction process of methylene blue due to phenylurea as compared to the urea is approximately 3.43 ± 0.157 at acidity 4.06 and 7.58. The value of quantum yield at infinite concentration of phenylurea is obtained by the graph 1/ϕ versus 1/[AH2].

The value of quantum yield at infinite concentration of phenylurea at lower acidity is found to be 0.23 ± 0.001.
4.6.4 Effects of thiourea concentration on the quantum yield of photo-reduction of methylene blue in aqueous 2-propanol.

The photo-reduction of methylene blue in aqueous 2-propanol was observed in the presence of different concentrations of thiourea. The temperature and the concentration of methylene blue were kept constant. The photo-reduction was carried out at two acidities. The variation in the quantum yield at different concentrations of thiourea are tabulated in Table-21. Results show that twenty fold rise in the concentration of thiourea has increased the value of quantum yield in a magnitude of 3.11 ± 0.005. The plots of reciprocal of quantum yield (1/φ) versus concentration of thiourea 1/[AH₂] at acidity 4.06 are shown in Figures 34, 35, while Figure 37 represents the relation of quantum yield with concentration of reductant at acidity 7.59.

The intercept of the plot gives the value of quantum yield at infinite concentration of thiourea. The values of quantum yield of reductant at infinite concentration are found to be 0.1612 ± 0.0001 at lower acidity while 0.076 ± 0.0007 at higher acidity.
4.6.5 **Effects of allylthiourea concentration on the quantum yield of photo-reduction of methylene blue in aqueous 2-propanol.**

The values of quantum yields of photo-bleaching of methylene blue with various concentrations of allylthiourea in aqueous 2-propanol at temperature $30 \pm 0.1 \, ^\circ\text{C}$ are summarized in Table-22. An increase in the concentration of allylthiourea has increased the value of quantum yield at different acidities of solution. The values in Table-22 show that a rise in the value of quantum yield in lower acidity value i.e. 4.06 is much higher than that obtained in higher acidity value i.e. 7.59. In contrast to the values of quantum yield obtained by thiourea, allylthiourea has greater tendency to give electron in the photo-reduction of methylene blue hence gives greater values of quantum yield.

The average rise in the magnitude of quantum yield due to allylthiourea is found to be $2.01 \pm 0.9$. The quantum yield at infinite concentration of allylthiourea at acidity 4.06 and 7.59 are obtained by intercept of Figure 35 and 37 respectively. The value of quantum yield at infinite concentration of allylthiourea at acidity 4.06 and 7.59 is found to be $0.24 \pm 0.007$ and $0.09 \pm 0.007$ at acidity 4.06 and 7.59, respectively.
TABLE - 20

Variation of Quantum Yield with Concentration of Urea at different Acidities.

\[ \text{[Methylene Blue]} = 2 \times 10^{-6} \text{ mol.dm}^{-3} \]
\[ \text{Temperature.} = 30 \pm 0.1 \, ^\circ\text{C} \]

<table>
<thead>
<tr>
<th>[Urea] ( \times 10^3 ) mol.dm(^{-3} )</th>
<th>Quantum Yield at ( H_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3333</td>
<td>0.025</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.028</td>
</tr>
<tr>
<td>0.8330</td>
<td>0.030</td>
</tr>
<tr>
<td>3.3300</td>
<td>0.075</td>
</tr>
<tr>
<td>6.6660</td>
<td>0.093</td>
</tr>
<tr>
<td></td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td>0.0070</td>
</tr>
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<td></td>
<td>0.0130</td>
</tr>
<tr>
<td></td>
<td>0.0180</td>
</tr>
<tr>
<td></td>
<td>0.0300</td>
</tr>
</tbody>
</table>

TABLE - 21

Variation of Quantum Yield with Concentration of Thiourea at different Acidities.

\[ \text{[Methylene Blue]} = 2 \times 10^{-6} \text{ mol.dm}^{-3} \]
\[ \text{Temperature.} = 30 \pm 0.1 \, ^\circ\text{C} \]

<table>
<thead>
<tr>
<th>[Thiourea] ( \times 10^3 ) mol.dm(^{-3} )</th>
<th>Quantum Yield at ( H_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3333</td>
<td>0.039</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.044</td>
</tr>
<tr>
<td>0.8330</td>
<td>0.061</td>
</tr>
<tr>
<td>3.3300</td>
<td>0.114</td>
</tr>
<tr>
<td>6.6660</td>
<td>0.196</td>
</tr>
<tr>
<td></td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td>0.086</td>
</tr>
</tbody>
</table>
TABLE - 22

Variation of Quantum Yield with Concentration of Allylurea at different Acidities.

<table>
<thead>
<tr>
<th>[Methylene Blue]</th>
<th>= 2 x 10^{-6} \text{mol.dm}^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature.</td>
<td>= 30 \pm 0.1 \degree \text{C}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[Allylurea] x 10^3 \text{mol.dm}^{-3}</th>
<th>Quantum Yield at H_0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>0.3333</td>
<td>0.034</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.038</td>
</tr>
<tr>
<td>0.8330</td>
<td>0.042</td>
</tr>
<tr>
<td>3.3300</td>
<td>0.084</td>
</tr>
<tr>
<td>6.6660</td>
<td>0.130</td>
</tr>
</tbody>
</table>

TABLE - 23

Variation of Quantum Yield with Concentration of Allylthiourea at different Acidities.

<table>
<thead>
<tr>
<th>[Methylene Blue]</th>
<th>= 2 x 10^{-6} \text{mol.dm}^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature.</td>
<td>= 30 \pm 0.1 \degree \text{C}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[Allyl thiourea] 10^3 \text{mol.dm}^{-3}</th>
<th>Quantum Yield at H_0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>0.3333</td>
<td>0.130</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.134</td>
</tr>
<tr>
<td>0.8330</td>
<td>0.142</td>
</tr>
<tr>
<td>3.3300</td>
<td>0.182</td>
</tr>
<tr>
<td>6.6660</td>
<td>0.400</td>
</tr>
</tbody>
</table>
TABLE - 24

Variation of Quantum Yield with Concentration of Phenylurea at different Acidities.

[ Methylene Blue ]  \( = 2 \times 10^{-6} \text{ mol.dm}^{-3} \)

Temperature.  \( = 30 \pm 0.1 ^\circ \text{C} \)

<table>
<thead>
<tr>
<th>[Phenylurea]x10^3 mol.dm^{-3}</th>
<th>Quantum Yield at H_o</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>0.3333</td>
<td>0.080</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.1300</td>
</tr>
<tr>
<td>0.8330</td>
<td>0.1500</td>
</tr>
<tr>
<td>3.3300</td>
<td>0.1700</td>
</tr>
<tr>
<td>6.666</td>
<td>0.2136</td>
</tr>
</tbody>
</table>

TABLE - 25

Equations obtained by the plots of 1/\( \phi \) vs 1/[AH_2].

<table>
<thead>
<tr>
<th>Reductants</th>
<th>H_o = 4.06</th>
<th>H_o = 7.59</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urca</td>
<td>( Y = 10.508 X + 12.649 )</td>
<td>( Y = 102.59 X + 3.2877 )</td>
</tr>
<tr>
<td>Allylurea</td>
<td>( Y = 7.4134 X + 9.9641 )</td>
<td>( Y = 61.839 X + 19.28 )</td>
</tr>
<tr>
<td>Phenylurea</td>
<td>( Y = 2.3796 X + 4.3171 )</td>
<td>( Y = 58.549 X + 4.1817 )</td>
</tr>
<tr>
<td>Thiourea</td>
<td>( Y = 7.1583 X + 6.2035 )</td>
<td>( Y = 15.264 X + 13.035 )</td>
</tr>
<tr>
<td>Allylthiourea</td>
<td>( Y = 1.4824 X + 4.0428 )</td>
<td>( Y = 7.3352 X + 10.229 )</td>
</tr>
</tbody>
</table>
4.7 EFFECT OF CONCENTRATION OF METHYLENE BLUE ON THE QUANTUM YIELD OF PHOTO-REDUCTION IN AQUEOUS 2-PROPA-NOL

The effect of methylene blue concentration on the quantum yield was studied at various concentrations of methylene blue ranging from 0.333x10^{-6} to 1.6666x10^{-6} mol.dm^{-3} in 50% aqueous propanol (Table-26). The temperature and acidity of the reacting solutions were kept constant i.e. 30 ± 0.1 °C and 4.06 respectively.

The results of quantum yield corresponding to various concentrations of methylene blue are tabulated in Table-26. The effect was studied in presence of various reductants and it was observed that variation in the concentration of dye has not any significant change in the value of quantum yield of the reaction. Results show that quantum yield is practically independent of the dye concentration in the range of 0.33 x 10^{-6} – 1.66 x 10^{-6} mol. dm^{-3}. The results were also supported by Matsumoto.116

4.7.1 Effect of concentration of Methylene blue on the quantum yield of photo-reduction in presence of urea.

Photo-reduction of methylene blue is carried out in presence of urea. The reaction was performed at various concentrations of methylene blue ranging 0.33 x 10^{-6} to 1.66 x 10^{-6} mol.dm^{-3}, to study the effect of concentration of
methylene blue on the quantum yield. The methylene blue of various concentrations was photo-reduced by $3.33 \times 10^{-4}$ mol.dm$^{-3}$ urea, at $30 \pm 0.1$ °C. The results summarized in Table-26 show the value of quantum yield at acidity of 4.06. There is no significant change in the value of quantum yield, which shows that the variation in the quantum yield is not influenced by the concentration of methylene blue.

4.7.2 Effect of concentration of Methylene blue on the quantum yield of photo-reduction in presence of allylurea.

Methylene blue of various concentrations was photo-reduced in presence of allylurea, the composition of solvent, temperature and acidity each experiment were maintained constant. From the values of quantum yield in Table-26, it is seen that the values of quantum yield are higher than those found in the photo-reduction process by urea. However, there is no any significant change in the values of quantum yields observed against various concentrations of methylene blue. However, in present investigation a non-linear response was obtained between quantum yield and concentration of methylene blue. This shows that the quantum yield is independent of the concentration of methylene blue.
4.7.3 Effect of concentration of Methylene blue on the quantum yield of photo-reduction in presence of phenylurea.

The quantum yields of photo-reduction of methylene blue at its various concentrations were evaluated at constant concentration of phenylurea, temperature, acidity and solvent composition. The values of quantum yield summarized in Table-26 show no significant relation between the quantum yield and the concentration of methylene blue. However, it is observed that the increase in the quantum yield under all similar experimental conditions is only due to the increase in the electron donating nature of the substituent. In contrast to the values of quantum yield due to urea and allylurea, the phenylurea has enhanced the rate of photo-reduction process at an average value of 10 ± 0.22.

4.7.4 Effect of concentration of Methylene blue on the quantum yield of photo-reduction in presence of thiourea.

Methylene blue at its various concentrations ranging 0.33 to 1.66 x 10⁻⁶ mol.dm⁻³ at constant temperature 30 ± 0.1 °C is photo-reduced by 3.33 x 10⁻⁴ mol.dm⁻³ thiourea. The acidity of reaction mixture was maintained at a value of 4.06. The rate of change in the photo-reduction process was calculated in terms of the quantum yield. The values of quantum yield are tabulated in Table-26. These values show an insignificant effect on quantum yield pertaining to the concentration of methylene blue. Earlier reports also
reveal the same behaviour where the variation in the concentration of dye did’nt produce any significant response in relation to these concentration for photochemical reduction.\textsuperscript{238,239}  

4.7.5 Effect of concentration of Methylene blue on the quantum yield of photo-reduction in presence of allylthiourea.

The quantum yield of photo-reduction in the presence of allylthiourea was influenced by the concentration of methylene blue in a similar fashion as mentioned in previous section. For instance, the quantum yield values showed no appreciable variation in the presence of different concentrations of methylene blue as tabulated in Table-26. The reason for such response has already explained in previous section on the basis of literature cited.\textsuperscript{238,239}

**TABLE - 26**

Variation of quantum yield as a function of concentration of methylene blue at acidity (H\textsubscript{0}) = 4.06.

<table>
<thead>
<tr>
<th>[Reductant]</th>
<th>Quantum yield ($\phi$) x 10$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Methylene blue] 10$^6$ mol.dm$^{-3}$</td>
</tr>
<tr>
<td>Urea</td>
<td>1.7250  3.1670  1.1650  0.0265  0.6663</td>
</tr>
<tr>
<td>Allylurea</td>
<td>4.6400  4.0500  1.1280  4.3300  4.1690</td>
</tr>
<tr>
<td>Phenylurea</td>
<td>9.9200  2.7070  1.2330  15.0580 20.683</td>
</tr>
<tr>
<td>Thiourea</td>
<td>3.1950  0.9544  0.9153  0.4216  0.2009</td>
</tr>
<tr>
<td>Allylthiourea</td>
<td>1.3885  0.2685  0.5411  0.8782  0.7486</td>
</tr>
</tbody>
</table>

[Reductant] = 3.33 x 10$^{-4}$ mol.dm$^{-3}$
Temperature = 30 ± 0.1 °C
4.8 EFFECT OF VARIATION OF THE TEMPERATURE ON QUANTUM YIELD OF PHOTO-REDUCTION IN AQUEOUS 2-PROPA NOL

The effect of temperature on quantum yield was observed by the selected reductants. The influence of temperature was observed at two acidities i.e. 4.06 and 7.59. The concentration of methylene blue was kept constant at each experimental run, while reductant’s concentrations were taken as 1.66x10^{-3} \text{ mol.dm}^{-3} and 5x10^{-3} \text{ mol.dm}^{-3}, respectively. The reduction of dyes with each reductant and acidity was studied at temperatures ranging 20^\circ C to 40^\circ C (interval of 5^\circ C). The results are tabulated in Tables-27-31.

The temperature coefficients for every five degree increase in temperature were found at two acidities. It was found that the average temperature coefficients at the two acidities 4.06 and 7.59 were 1.818 and 1.643. The values of quantum yield tabulated in Table-27-31 were used to evaluate the activation parameters as a function concentration of reductants and acidity of the medium. The plots of $\log \phi$ against reciprocal of the absolute temperature were drawn. From the Arrhenius relation, the values of energy of activation ($E_a$) were evaluated.
4.8.1 Effect of variation of temperature on the quantum yield of photo-reduction in presence of urea.

The photo-reduction of 2.00 x 10^{-6} mol.dm^{-3} methylene blue was carried out at different temperatures ranging from 20 to 40°C. The effect of varying concentration of reductant on the quantum yield was also determined at various temperatures.

The photo-reduction process of methylene blue by urea at various temperatures were studied as a function of acidity ([H+], which was maintained by acetate buffer. The rate of photo-reduction of methylene blue was measured as a function of quantum yield. The values of quantum yield at acidities 4.06 and 7.59 in presence of urea are tabulated in Table-27. The quantum yield of the photo-reduction increased with both temperature and the concentration of urea. A plot of log quantum yield (log \( \phi \)) versus 1/T is used to calculate the energy of activation shown in Figure 26. The value of intercept obtained is used to calculate entropy to activation \( \Delta S^* \), free energy of activation \( \Delta G^* \) and enthalpy of activation \( \Delta H^* \). The values of activation parameters at two different concentrations of urea are given in Table-38 and 39. The temperature coefficients for every five degree increase in temperature were found at two acidities are shown in Table-32. The average value of temperature coefficient for the photo-reduction of methylene blue with urea at acidities 4.06 and 7.59 are found to be 1.72 \( \pm \) 0.0015 and 2.03 \( \pm \) 0.0016, respectively.
4.8.2 Effect of variation of temperature on the quantum yield of photo-reduction in presence of allylurea.

The values of quantum yield obtained in photo-reduction of methylene blue with allylurea at different temperatures and acidity are tabulated in Table-28. The result shows that the quantum yield of the reaction increases with temperature at extreme acidic and basic media. Whereas the values of quantum yield in higher acidity value 7.59 is approximately five times less than the values found at acidity 4.06.

The average value of temperature coefficient for the photo-reduction of methylene blue in the presence of allylurea was found to be $1.88 \pm 0.001$ and $1.62 \pm 0.002$ at lower and higher value of acidity respectively shown in Table-33.

Using the Arrhenius law, the activation energy ($E_a^*$) values calculated from the plots of log quantum yield versus $1/T$ are given in Table-38, 39. Other activation parameters such as $\Delta H^*$, $\Delta S^*$ and $\Delta G^*$ were also evaluated for different acidity of the media.

4.8.3 Effect of variation of temperature on the quantum yield of photo-reduction in presence of phenylurea.

The reduction of methylene blue with phenylurea was also influenced by temperature. The experiments were performed at two acidities which were
maintained constant using acetate buffer at 4.06 and 7.59 respectively. The concentration of methylene blue was kept constant for each experimental run. The reactions were carried out at two different concentrations of phenylurea $1.66 \times 10^{-3}$ and $5 \times 10^{-3}$ mol.dm$^{-3}$ at five different temperatures from 20 to $40 \pm 0.1$ °C. It was observed that quantum yield apparently increased with increase in temperature, results are shown in Table-29. The plots of log quantum yield versus reciprocal of absolute temperature at two acidities given in Figure 28 are straight lines with negative slopes. The value of slope was used to calculate the energy of activation for the photo-reduction process. Other activation parameters were also found from usual relationship summarized in Table-38, 39. The results show that the values of energy of activation, enthalpy of activation ($\Delta H^*$) and free energy of activation ($\Delta G^*$) were found to decrease in higher concentrations of phenylurea, which favoured the enhancement of photo-reduction process at higher concentration of phenylurea. The values of temperature coefficient are tabulated in Table-34.

4.8.4 Effect of variation of temperature on the quantum yield of photo-reduction in presence of thiourea.

Effect of temperature on the photo-reduction of methylene blue with thiourea was also investigated under similar experimental conditions as mentioned in section 4.8. The results tabulated in Table-30 show that the quantum yield
apparently increased with rise in temperature. In general, it is concluded from the results that a twenty degree rise in temperature has produced a tenfold increase in the value of quantum yield at an acidity value of 4.06. A similar behaviour was observed in lower acidity while determining effect of rise in temperature on the quantum yield.

The temperature coefficients for every five degree variation in temperature at different acidities were also calculated and summarized in Table-35. It was found that the average temperature coefficient at two different acidities 4.06 and 7.59 were 1.89 ± 0.004 and 1.93 ± 0.007 respectively. This leads to the conclusion that the reaction is more dominating at higher acidity.

The plots between log quantum yield and reciprocal of absolute temperature show a linear relationship with a negative slope, as shown in Figure 29. The reaction was studied at different temperatures to evaluate the activation parameters. The values of activation energy Table-38, 39 for the photoreduction of methylene blue and thiourea were evaluated as 84.14 ± 0.02 kJ.mol⁻¹ and 97.94 ± 0.004 kJ.mol⁻¹ at acidity value of 4.06 and 7.59 respectively.
4.8.5 Effect of variation of temperature on the quantum yield of photo-reduction in presence of allylthiourea.

The influence of temperature on the photo-reduction process of methylene blue in the presence of allylthiourea at two different acidities and concentrations of allylthiourea was found to be almost similar compared to the previously explained systems in section 4.8. While determining the temperature coefficient values for the reduction process, the average value at acidity 4.06 was found to be $1.76 \pm 0.0015$ and at 7.59 it was $1.58 \pm 0.0027$. This behaviour predicts that the reaction is relatively enhanced at lower value of acidity. This behaviour may be correlated with the structural differences in various reducing species. Arrhenius relationship was verified by plotting graphs between log quantum yield and reciprocal of absolute temperature at two different acidities shown in Figure 30. The values of energy of activation were calculated from the slope of each plots. All other activation parameters were calculated at 30°C by Eyring relationship the value of activation parameters are given in Table-38 and 39.
### TABLE - 27

Influence of Temperature on the Quantum Yield.

| Methylene Blue | = 2.00×10^{-6}\text{mol.dm}^{-3} |
| Urea | = 1.66×10^{-3}\text{mol.dm}^{-3} |

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Quantum Yield at H₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>20</td>
<td>0.0230</td>
</tr>
<tr>
<td>25</td>
<td>0.0290</td>
</tr>
<tr>
<td>30</td>
<td>0.0420</td>
</tr>
<tr>
<td>35</td>
<td>0.1250</td>
</tr>
<tr>
<td>40</td>
<td>0.1500</td>
</tr>
</tbody>
</table>

| Methylene Blue | = 2×10^{-6}\text{mol.dm}^{-3} |
| Urea | = 5×10^{-3}\text{mol.dm}^{-3} |

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Quantum Yield at H₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>20</td>
<td>0.0380</td>
</tr>
<tr>
<td>25</td>
<td>0.0420</td>
</tr>
<tr>
<td>30</td>
<td>0.1040</td>
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<td>35</td>
<td>0.1367</td>
</tr>
<tr>
<td>40</td>
<td>0.1616</td>
</tr>
</tbody>
</table>
TABLE - 28

Influence of Temperature on the Quantum Yield.

<table>
<thead>
<tr>
<th>Methylene Blue</th>
<th>$= 2.00 \times 10^{-6}$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allylurea</td>
<td>$= 1.66 \times 10^{-3}$ mol dm$^{-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>Quantum Yield at $H_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>20</td>
<td>0.019</td>
</tr>
<tr>
<td>25</td>
<td>0.031</td>
</tr>
<tr>
<td>30</td>
<td>0.0816</td>
</tr>
<tr>
<td>35</td>
<td>0.0802</td>
</tr>
<tr>
<td>40</td>
<td>0.1849</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Methylene Blue</th>
<th>$= 2 \times 10^{-6}$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allylurea</td>
<td>$= 5 \times 10^{-3}$ mol dm$^{-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>Quantum Yield at $H_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>20</td>
<td>0.0355</td>
</tr>
<tr>
<td>25</td>
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</tr>
<tr>
<td>30</td>
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<td>0.1778</td>
</tr>
<tr>
<td>40</td>
<td>0.2028</td>
</tr>
</tbody>
</table>
TABLE - 29

Influence of Temperature on the Quantum Yield.

<table>
<thead>
<tr>
<th>Methylene Blue</th>
<th>Phenylurea</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.00 \times 10^{-6}$ mol.dm$^{-3}$</td>
<td>$1.66 \times 10^{-3}$ mol.dm$^{-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>Quantum Yield at $H_0$</th>
<th>4.06</th>
<th>7.59</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0253</td>
<td>0.0074</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.0560</td>
<td>0.0144</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.1499</td>
<td>0.0200</td>
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<td>35</td>
<td>0.1816</td>
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</tr>
<tr>
<td>40</td>
<td>0.2287</td>
<td>0.0360</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Methylene Blue</th>
<th>Phenylurea</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 10^{-6}$ mol.dm$^{-3}$</td>
<td>$5 \times 10^{-3}$ mol.dm$^{-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>Quantum Yield at $H_0$</th>
<th>4.06</th>
<th>7.59</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0578</td>
<td>0.039</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.1330</td>
<td>0.045</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.1880</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>0.2180</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.2520</td>
<td>0.650</td>
<td></td>
</tr>
</tbody>
</table>
**TABLE - 30**

*Influence of Temperature on the Quantum Yield.*

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Quantum Yield at $H_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>20</td>
<td>0.0198</td>
</tr>
<tr>
<td>25</td>
<td>0.0590</td>
</tr>
<tr>
<td>30</td>
<td>0.0730</td>
</tr>
<tr>
<td>35</td>
<td>0.1374</td>
</tr>
<tr>
<td>40</td>
<td>0.2032</td>
</tr>
</tbody>
</table>

| Methylene Blue | = $2.00 \times 10^{-6}$ mol.dm$^{-3}$ |
| Thiourea       | = $1.66 \times 10^{-3}$ mol.dm$^{-3}$ |

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Quantum Yield at $H_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.06</td>
</tr>
<tr>
<td>20</td>
<td>0.0280</td>
</tr>
<tr>
<td>25</td>
<td>0.0708</td>
</tr>
<tr>
<td>30</td>
<td>0.1296</td>
</tr>
<tr>
<td>35</td>
<td>0.1874</td>
</tr>
<tr>
<td>40</td>
<td>0.2224</td>
</tr>
</tbody>
</table>

| Methylene Blue | = $2 \times 10^{-6}$ mol.dm$^{-3}$ |
| Thiourea       | = $5 \times 10^{-3}$ mol.dm$^{-3}$ |
### TABLE - 31

**Influence of Temperature on the Quantum Yield.**

| Methylene Blue | = 2.00x10^{-6} mol.dm^{-3} |
| Allylthiourea | = 1.66x10^{-3} mol.dm^{-3} |

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Quantum Yield at H₀</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0310</td>
<td>0.0120</td>
</tr>
<tr>
<td>25</td>
<td>0.0600</td>
<td>0.0180</td>
</tr>
<tr>
<td>30</td>
<td>0.1580</td>
<td>0.0380</td>
</tr>
<tr>
<td>35</td>
<td>0.1890</td>
<td>0.0588</td>
</tr>
<tr>
<td>40</td>
<td>0.2300</td>
<td>0.0680</td>
</tr>
</tbody>
</table>

| Methylene Blue | = 2x10^{-6} mol.dm^{-3} |
| Allylthiourea | = 5x10^{-3} mol.dm^{-3} |

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Quantum Yield at H₀</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.082</td>
<td>0.0150</td>
</tr>
<tr>
<td>25</td>
<td>0.128</td>
<td>0.0220</td>
</tr>
<tr>
<td>30</td>
<td>0.205</td>
<td>0.0400</td>
</tr>
<tr>
<td>35</td>
<td>0.22</td>
<td>0.0620</td>
</tr>
<tr>
<td>40</td>
<td>0.2448</td>
<td>0.1002</td>
</tr>
</tbody>
</table>
TABLE - 32

Values of temperature co-efficient in presence of Urea.

\[
[\text{urea}] = 1.66 \times 10^{-3} \text{ mol.dm}^{-3}
\]

<table>
<thead>
<tr>
<th>(H_o)</th>
<th>(\phi_{25}/\phi_{20})</th>
<th>(\phi_{30}/\phi_{25})</th>
<th>(\phi_{35}/\phi_{30})</th>
<th>(\phi_{40}/\phi_{35})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>1.2608</td>
<td>1.4482</td>
<td>2.9761</td>
<td>1.2000</td>
</tr>
<tr>
<td>7.59</td>
<td>1.8275</td>
<td>1.2264</td>
<td>2.0770</td>
<td>1.2600</td>
</tr>
</tbody>
</table>

\[
[\text{urea}] = 5.00 \times 10^{-3} \text{ mol.dm}^{-3}
\]

<table>
<thead>
<tr>
<th>(H_o)</th>
<th>(\phi_{25}/\phi_{20})</th>
<th>(\phi_{30}/\phi_{25})</th>
<th>(\phi_{35}/\phi_{30})</th>
<th>(\phi_{40}/\phi_{35})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>1.1052</td>
<td>2.5360</td>
<td>1.3140</td>
<td>1.1820</td>
</tr>
<tr>
<td>7.59</td>
<td>2.1052</td>
<td>2.5360</td>
<td>1.3140</td>
<td>1.1820</td>
</tr>
</tbody>
</table>

TABLE - 33

Values of temperature co-efficient in presence of Allylurea.

\[
[\text{Allylurea}] = 1.66 \times 10^{-3} \text{ mol.dm}^{-3}
\]

<table>
<thead>
<tr>
<th>(H_o)</th>
<th>(\phi_{25}/\phi_{20})</th>
<th>(\phi_{30}/\phi_{25})</th>
<th>(\phi_{35}/\phi_{30})</th>
<th>(\phi_{40}/\phi_{35})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>1.6310</td>
<td>2.6320</td>
<td>0.9830</td>
<td>2.3050</td>
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<tr>
<td>7.59</td>
<td>1.2650</td>
<td>1.2660</td>
<td>1.9730</td>
<td>2.000</td>
</tr>
</tbody>
</table>

\[
[\text{Allylurea}] = 5.00 \times 10^{-3} \text{ mol.dm}^{-3}
\]

<table>
<thead>
<tr>
<th>(H_o)</th>
<th>(\phi_{25}/\phi_{20})</th>
<th>(\phi_{30}/\phi_{25})</th>
<th>(\phi_{35}/\phi_{30})</th>
<th>(\phi_{40}/\phi_{35})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>1.3740</td>
<td>1.8030</td>
<td>2.0200</td>
<td>1.1406</td>
</tr>
<tr>
<td>7.59</td>
<td>1.8330</td>
<td>1.2540</td>
<td>1.3760</td>
<td>1.5979</td>
</tr>
</tbody>
</table>
### TABLE - 34

Values of temperature co-efficient in presence of phenylurea.

\[ [\text{phenylurea}] = 1.66 \times 10^{-3} \text{ mol.dm}^{-3} \]

<table>
<thead>
<tr>
<th>( H_0 )</th>
<th>( \phi_{25}/\phi_{20} )</th>
<th>( \phi_{30}/\phi_{25} )</th>
<th>( \phi_{35}/\phi_{30} )</th>
<th>( \phi_{40}/\phi_{35} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>2.2134</td>
<td>2.6760</td>
<td>1.2114</td>
<td>1.2593</td>
</tr>
<tr>
<td>7.59</td>
<td>1.9459</td>
<td>1.3880</td>
<td>1.3850</td>
<td>1.2996</td>
</tr>
</tbody>
</table>

\[ [\text{phenylurea}] = 5.00 \times 10^{-3} \text{ mol.dm}^{-3} \]

<table>
<thead>
<tr>
<th>( H_0 )</th>
<th>( \phi_{25}/\phi_{20} )</th>
<th>( \phi_{30}/\phi_{25} )</th>
<th>( \phi_{35}/\phi_{30} )</th>
<th>( \phi_{40}/\phi_{35} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>2.0130</td>
<td>1.4135</td>
<td>1.1595</td>
<td>1.0642</td>
</tr>
<tr>
<td>7.59</td>
<td>1.1538</td>
<td>1.1111</td>
<td>1.1200</td>
<td>1.1607</td>
</tr>
</tbody>
</table>

### TABLE - 35

Values of temperature co-efficient in presence of Thiourea.

\[ [\text{thiourea}] = 1.66 \times 10^{-3} \text{ mol.dm}^{-3} \]

<table>
<thead>
<tr>
<th>( H_0 )</th>
<th>( \phi_{25}/\phi_{20} )</th>
<th>( \phi_{30}/\phi_{25} )</th>
<th>( \phi_{35}/\phi_{30} )</th>
<th>( \phi_{40}/\phi_{35} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>2.9790</td>
<td>1.2370</td>
<td>1.8820</td>
<td>1.4780</td>
</tr>
<tr>
<td>7.59</td>
<td>2.5500</td>
<td>1.8550</td>
<td>2.0450</td>
<td>1.3010</td>
</tr>
</tbody>
</table>

\[ [\text{thiourea}] = 5.00 \times 10^{-3} \text{ mol.dm}^{-3} \]

<table>
<thead>
<tr>
<th>( H_0 )</th>
<th>( \phi_{25}/\phi_{20} )</th>
<th>( \phi_{30}/\phi_{25} )</th>
<th>( \phi_{35}/\phi_{30} )</th>
<th>( \phi_{40}/\phi_{35} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>2.5280</td>
<td>1.8300</td>
<td>1.4460</td>
<td>1.1860</td>
</tr>
<tr>
<td>7.59</td>
<td>1.9320</td>
<td>2.2270</td>
<td>1.1890</td>
<td>1.2010</td>
</tr>
</tbody>
</table>
TABLE - 36

Values of temperature co-efficient in presence of Allylthiourea.

\[ \text{[Allylthiourea]} = 1.66 \times 10^{-3} \text{ mol.dm}^{-3} \]

<table>
<thead>
<tr>
<th>( H_0 )</th>
<th>( \phi_{25}/\phi_{20} )</th>
<th>( \phi_{30}/\phi_{25} )</th>
<th>( \phi_{35}/\phi_{30} )</th>
<th>( \phi_{40}/\phi_{35} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>2.0000</td>
<td>2.6330</td>
<td>1.1960</td>
<td>1.2170</td>
</tr>
<tr>
<td>7.59</td>
<td>1.5000</td>
<td>2.1110</td>
<td>1.5260</td>
<td>1.1720</td>
</tr>
</tbody>
</table>

\[ \text{[Allylthiourea]} = 5.00 \times 10^{-3} \text{ mol.dm}^{-3} \]

<table>
<thead>
<tr>
<th>( H_0 )</th>
<th>( \phi_{25}/\phi_{20} )</th>
<th>( \phi_{30}/\phi_{25} )</th>
<th>( \phi_{35}/\phi_{30} )</th>
<th>( \phi_{40}/\phi_{35} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.06</td>
<td>1.5610</td>
<td>1.6010</td>
<td>1.0730</td>
<td>1.1120</td>
</tr>
<tr>
<td>7.59</td>
<td>1.4660</td>
<td>1.8180</td>
<td>1.5500</td>
<td>1.6160</td>
</tr>
</tbody>
</table>
CHAPTER 5

DISCUSSION
5.0 DISCUSSION

5.1 INTRODUCTION

The photo-reduction of methylene blue in presence of reducing agents such as urea, allylurea, phenylurea, thiourea and allylthiourea were carried out under the influence of different parameters such as acidity of solution, variation of temperature, concentration of reducing agents and concentration of methylene blue. Quantum yields of the each of the photo-reduction process were calculated by using relation 4.2.26.

Linear regression method was applied for the evaluation of relationship between $1/\phi$ against $1/\text{[Reductant]}$ and $1/h_\circ \ (\phi-\phi) \ (\phi-\phi_2)$ against $1/h_\circ$ and log $\phi$ against $1/$temperature.

5.2 QUALITATIVE CHARACTERISTICS OF METHYLENE BLUE BY SPECTRAL ANALYSIS

The absorption spectra of methylene blue were recorded in the presence as well as in absence of different reductants before and after the photochemical changes, while irradiating 20 minutes of reaction mixture through 250 W Hg lamp. The changes occurred in spectra were observed as a functions of acidity of the reaction mixture and concentration of different reductants. They were carried out at two acidities i.e. 4.06 & 7.59. The details of each spectrum are given below:
5.2.1 *Spectra of methylene blue in 2-propanol.*

Spectra of methylene blue in 50% and 100% 2-propanol are shown in Figure 1. A bathochromic shift is observed in the case of spectrum of methylene blue in 50% 2-propanol along with a decrease in the value of absorbance at its \( \lambda_{\text{max}} \). It is due to the change in solvents polarity. The values of molar extinction coefficient Tabulated in Table-5 and \( \lambda_{\text{max}} \) show a bathochromic shift due to increase in polarity of solvent, which confirms the \( \pi-\pi^* \) transition in methylene blue.\(^{245}\)

5.2.2 *Spectral studies of methylene blue in 50% 2-propanol at various concentrations.*

The transient absorption spectra of nitrogen saturated 1:1 aqueous 2-propanol solution of methylene blue 2\( \times \)10\(^{-6} \) mol.dm\(^{-3} \) to 2\( \times \)10\(^{-5} \) mol.dm\(^{-3} \) are shown in Figure 2. Here, no significant change in \( \lambda_{\text{max}} \) of methylene blue was registered regarding its mixture of dimerization or trimerization nature as reported in literature.\(^{245}\) The literature reveals that the basic dyes generally follow the process of polymerization reaction.\(^{245}\) In this case the monomer and dimmer follow different absorption spectra.\(^{245,246}\) For instance, methylene blue at lower concentrations exists almost in monomer form with an absorption maxima at 660 nm. The dimeric or trimeric form of methylene blue exists at higher concentrations i.e. 5\( \times \)10\(^{-5} \) mol.dm\(^{-3} \) to 5\( \times \)10\(^{-3} \) mol.dm\(^{-3} \) with \( \lambda_{\text{max}} \) nearly at 610 nm and 580 nm respectively. Figure 2 represents the
spectrum of methylene blue at different concentrations. There is no significant shift in the $\lambda_{\text{max}}$ due to the variation in concentration of methylene blue in the concentration range of $2 \times 10^{-6}$ mol.dm$^{-3}$ to $2 \times 10^{-5}$ mol.dm$^{-3}$. Above 0.1 mol.dm$^{-3}$ concentration methylene blue exists completely as trimeric form.$^{244}$ In the present work, Beer's law holds good and well verified by the plots of methylene blue concentration versus absorbance as shown in Figure 3. The value of molar extinction coefficient was calculated to be $6.533 \times 10^{4}$ dm$^{-3}$mol.cm$^{-1}$.

5.3 VARIATION IN ABSORPTION SPECTRA OF METHYLENE BLUE WITH THE ACIDITY

The nitrogen saturated 1:1 aqueous propanol solutions of methylene blue at two acidities $H_0$ i.e. 4.06, 7.59 were analysed by spectral study. Their absorption spectra are given in Figure 5. It was found that methylene blue at $H_0$ 4.06 showed a sharp peak at $\lambda_{\text{max}}$ 660 nm, with a much suppressed shoulder at 610 nm. However this shoulder appeared considerably prominent at $H_0$=7.59 (in the basic system) as shown in Figure 5. At acidity 7.59 a broad spectrum was observed with $\lambda_{\text{max}}$ 620 nm, and a small shoulder at 660 nm, which is significantly suppressed in this buffer composition. Such a change in absorbance measurements has been supported by the literature$^{39,245,246}$ regarding the dimerization of methylene blue. The shape of the absorption curve also shows nearly a half decrease in the absorption
value at 660 nm, due to variation in $H_0$, i.e. the absorption value decreased from 0.141 to 0.068 with the variation of $H_0$ from 4.06 to 7.59. However it may be due to the photo-induced dimerization of methylene blue monomer as reported in the literature.²⁴⁵

5.4 SPECTRAL STUDIES IN THE PRESENCE OF REDUCTANTS

5.4.1 Spectra of methylene blue in presence of urea.

The absorption spectra of methylene blue were recorded in nitrogen saturated 1:1 aqueous propanol systems in presence of urea, thiourea and their derivatives. The spectra shown in Figure 6. The spectra in presence of urea of concentration of $1.66 \times 10^{-3}$ mol.dm$^{-3}$ at acidities 4.06 and 7.59 resemble with the spectrum of Figure 5 in terms of their $\lambda_{max}$ and $\varepsilon$ values. In other words, the presence of urea the absorption spectrum of methylene blue at two acidities doesn't produce any significant changes pertaining to $\lambda_{max}$ or molar extinction coefficient.

It signifies that the changes in buffer composition to maintain acidities 4.06 and 7.59 are so dominating that it doesn't allow to cause any change in $\lambda_{max}$ or absorbance in the presence of urea. The decrease in the absorbance at lower acidity value 4.06 in presence of urea conforms that photo-reductions
of methylene blue whereas no significant response is observed at higher acidity value i.e. 7.59.

5.4.2 Spectra of methylene blue in the presence of Allylurea.

The spectrum of buffered methylene blue solution in presence of 1.66x10^{-3} mol.dm^{-3} allylurea is shown in Figure 7. No spectral changes are observed in solution of acidity 4.06 except a decrease in the value of absorbance showing greater reducing tendency than urea. However, at higher acidity value i.e. 7.59 a bathochromic shift is observed i.e. λ_{max} in absence of reductant was at 620 nm while in the presence of allylurea it was shifted to wave-length of 657 nm along with a small shoulder that appeared at 620 nm.

5.4.3 Spectra of methylene blue in the presence of phenylurea.

The system showed similar behaviour to that of Figure 6, except a slight broadening in the absorption spectrum which is also supported by literature,^{245} according to which broadening is caused by the existence of dimeric form of methylene blue.

5.4.4 Spectra of methylene blue in presence of thiourea and allyl-thiourea.

In case of urea small shoulder appears at higher wave length value (hypochromic shift) whereas spectrum with all other reductants such as allylurea Figure 7), thiourea and allylthiourea Figure 10 have the value of
λ_{max} beyond a small shoulder confirming a hyperchromic shift. Such a
decrease in the absorbance value from 610 to 660 nm at H₀ 7.59
(hypochromic shift) may be due to high value of equilibrium constant and
presence of auxochromes reported by Polster et al.²⁴⁵

5.5 Influence of Acidity on Quantum Yield

The variation of quantum yield with acidity is obtained by plotting φ against
H₀. A typical inverted S shaped curves obtained in presence of different
reducing agents Figures 11-15 are more or less similar in shape showing two
equilibrria. First at the range of acidity 4.06 to 6.86 and second equilibrium
extending from acidity range 6.88 to 7.59. Higher values of quantum yield in
lower acidity value signify that the reduction is more favourable in acidic
medium due to π-π* transition¹⁶⁵,¹⁶⁷ as compared to the basic medium.

In general shape of these curves shows that the quantum yield may be
controlled by two excited species of methylene blue.

It is assumed that the triplet state is the result of the competition between

\[ \text{MBH}^+ + \text{H}^+ \rightarrow \text{MBH}^{++} \quad \text{and} \]
\[ \text{MBH}^+ + \text{AH}_2 \rightarrow \text{Products} \]

It is also assumed MBH^{++}_2T associated with AH₂ resulting the following
equilibrium

\[ \text{MBH}^{++}_2T + \text{AH}_2 \rightleftharpoons \text{MBH}^{++}_2T \cdot \text{AH}_2 \]
5.6 INFLUENCE OF CONCENTRATION OF REDUCTANTS ON QUANTUM YIELD

Methylene blue in 1:1 aqueous solution of 2-propanol with monochromatic light of 660 nm, by means of 250 Watt Hg lamp was irradiated for about 20 minutes. The deflection in the photocells on irradiation was measured under deoxygenated condition. The quantum yield calculated by equation 4.26, is discussed on the basis of acidity, concentration and structure of reducing agents. The variations in the quantum yield with the acidity Table 9 are shown by the plots of quantum yield ($\phi$) and acidity ($H_o$) at two different concentrations of reductant Figures 11-15. The variation in $\phi$ with $H_o$ is well supported by the literature.\textsuperscript{133,247}

The quantum yield increased with increasing the concentration of reducing agent. The results are summarized in Tables 13-17. These findings were also supported by Matsumoto\textsuperscript{116} and Uddin.\textsuperscript{113,247} The reciprocal of quantum yield was plotted against $1/[\text{Red}]$ at two acidities 4.06 and 7.59. A straight line relation was appeared with a positive slope. The values of quantum yield at infinite concentration of reductants and slope at two acidities are reported in Table-25.

A comparative study among the reductants also shows that the quantum yield in photo-reduction of methylene blue by reductants is affected by the subsequent groups attached with urea. For instance, under all similar
experimental conditions quantum yield of urea is smaller than that of its linear derivatives such as allyl and phenylurea. These results are supported by Yong et al. Variation in the quantum yield in photo-reduction process also depends on the energy of activation, since the energy of activation is also related with the distance and relative orientation between dye and reductant in photochemical reactions. Variation of quantum yield with the concentration of dye was also investigated. The results reported in Table-26 show that the quantum yield is practically independent of the dye concentration in the range of $0.33 \times 10^{-6}$ to $1.66 \times 10^{-6}$ mol dm$^{-3}$. A similar behaviour was reported earlier.

5.7 EFFECT OF TEMPERATURE ON THE QUANTUM YIELD

In order to study the effect of temperature on the quantum yield of photoreduction, the deaerated reaction mixtures along with reductants were irradiated for 20 minutes each, at five different temperatures from 20°C to 40°C, the results tabulated in Table 27-31, describe the variation of quantum yield as a function of concentration of reductants and acidity. The average value of temperature coefficient for the rise of 5°C in presence of allylurea has been found to be 1.88 and 1.62 for the acidities 4.06 & 7.59 respectively. The lower value of quantum yield at higher acidity $H_0$ value is also in accord with other studies.
5.7.1 *Activation parameters*

Activation parameters were determined by using Arrhenius\(^{253}\) relation as function of acidities and concentrations of reducing agents at 30\(^\circ\)C of each reductant.

A plot of \(\log \phi\) against \(1/T\) in the presence of different reductants and at acidities 4.06, 7.59 are given in Figure 26-30. The plots were found to be linear over the accessible temperature range. The resulting Arrhenius parameters \(E_a\) (energy of activation) and \(A\) (steric factor), are obtained from the value of slopes and intercept given in Table-37. The Eyring parameters, such as the activation enthalpy (\(\Delta H^*\)) and activation entropy (\(\Delta S^*\)), free energy \(\Delta G^*\) calculated by using usual relations\(^{253}\) are shown in Tables-38-39.

Considering the Tables-15 and 16, it is observed that at acidity 4.06, there is a decrease in energy of activation as the number of carbon atom connecting to amide group of urea increases. In this case energy transfer (\(E_a\)), in the presence of urea is \(= 78.60\) k.j.mol\(^{-1}\), whereas due to allyl group \(E_a=83.95\) k.j.mol\(^{-1}\). This behaviour is also supported by the earlier work.\(^{249,254}\)

Increasing the concentration of urea and allylurea from 1.66x10\(^{-3}\) M to 5x10\(^{-3}\) M, the value of activation energy has decreased at same acidity i.e. 4.06. A decrease in \(E_a\) observed due to the rise in the concentration of reductants is approximately from 16.73 to 8.368 k.j.mol\(^{-1}\). While in case of allylthiourea and thiourea a decrease in \(E_a\) is from 37.65 to 8.37 k.j.mol\(^{-1}\).
It is concluded that energy of activation is inversely related with the concentration of the reductant as well as the presence of subsequent groups.
TABLE - 37

Values of slope and intercept obtained by Arrhenius plots for different reductants.

<table>
<thead>
<tr>
<th>Reductants</th>
<th>Equations at $H_o = 4.06$</th>
<th>$H_o = 7.59$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Urea]x10^3 mol.dm^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.66</td>
<td>$Y = -4.1053 X + 1202981$</td>
<td>$Y = -3.804 X + 10.72$</td>
</tr>
<tr>
<td>5.00</td>
<td>$Y = -3.2514 X + 9.6496$</td>
<td>$Y = -2.8775 X + 7.8031$</td>
</tr>
<tr>
<td>[Allylurea]x10^3 mol.dm^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.66</td>
<td>$Y = -4.3845 X + 13.249$</td>
<td>$Y = -3.6569 X + 0.0730$</td>
</tr>
<tr>
<td>5.00</td>
<td>$Y = -3.8079 X + 11.522$</td>
<td>$Y = -3.0002 X + 8.0500$</td>
</tr>
<tr>
<td>Phenylurea]x10^3 mol.dm^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.66</td>
<td>$Y = -4.4677 X + 13.7418$</td>
<td>$Y = -3.0506 X + 8.3390$</td>
</tr>
<tr>
<td>5.00</td>
<td>$Y = -2.6290 X + 7.8542$</td>
<td>$Y = -0.9875 X + 1.9616$</td>
</tr>
<tr>
<td>Thiourea]x10^3 mol.dm^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.66</td>
<td>$Y = -4.3943 X + 13.386$</td>
<td>$Y = -5.1153 X + 15.338$</td>
</tr>
<tr>
<td>5.00</td>
<td>$Y = -4.0581 X + 12.408$</td>
<td>$Y = -3.6951 X + 11.0009$</td>
</tr>
<tr>
<td>[Allylthiourea]x10^3 mol.dm^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.66</td>
<td>$Y = -4.1272 X + 12.6498$</td>
<td>$Y = -3.7046 X + 10.735$</td>
</tr>
<tr>
<td>5.00</td>
<td>$Y = -2.1872 X + 6.4352$</td>
<td>$Y = -7.4713 X + 23.0009$</td>
</tr>
</tbody>
</table>
**TABLE - 38**

*Activation parameters for the photo-reduction of methylene blue in different reductants.*

Temperature = $30 \pm 0.1 \, ^\circ C$

Acidity ($H_0$) = 4.06

<table>
<thead>
<tr>
<th>Reductants</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.66 \times 10^{-3} \text{ mol.dm}^{-3}$</td>
</tr>
<tr>
<td><strong>Urea</strong></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (kJ.mol$^{-1}$)</td>
<td>78.61 ± 0.0053</td>
</tr>
<tr>
<td>$\Delta H^*$ (kJ.mol$^{-1}$)</td>
<td>75.805 ± 0.01</td>
</tr>
<tr>
<td>$\Delta S^*$ (J.mol$^{-1}$ K$^{-1}$)</td>
<td>4.09 ± 0.002</td>
</tr>
<tr>
<td>$\Delta G^*$ (kJ.mol$^{-1}$)</td>
<td>74.57 ± 0.001</td>
</tr>
<tr>
<td><strong>Allylurea</strong></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (kJ.mol$^{-1}$)</td>
<td>83.95 ± 0.002</td>
</tr>
<tr>
<td>$\Delta H^*$ (kJ.mol$^{-1}$)</td>
<td>81.43 ± 0.001</td>
</tr>
<tr>
<td>$\Delta S^*$ (J.mol$^{-1}$ K$^{-1}$)</td>
<td>-3.78 ± 0.001</td>
</tr>
<tr>
<td>$\Delta G^*$ (kJ.mol$^{-1}$)</td>
<td>82.28 ± 0.001</td>
</tr>
<tr>
<td><strong>Pheny lurea</strong></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (kJ.mol$^{-1}$)</td>
<td>85.54 ± 0.004</td>
</tr>
<tr>
<td>$\Delta H^*$ (kJ.mol$^{-1}$)</td>
<td>83.00 ± 0.02</td>
</tr>
<tr>
<td>$\Delta S^*$ (J.mol$^{-1}$ K$^{-1}$)</td>
<td>-7.86 ± 0.001</td>
</tr>
<tr>
<td>$\Delta G^*$ (kJ.mol$^{-1}$)</td>
<td>85.10 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Thiourea</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>84.13 ± 0.135</td>
</tr>
<tr>
<td>$\Delta H^\circ$ (kJ mol$^{-1}$)</td>
<td>81.61 ± 0.01</td>
</tr>
<tr>
<td>$\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>-4.91 ± 0.01</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (kJ mol$^{-1}$)</td>
<td>82.81 ± 0.015</td>
</tr>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>79.02 ± 0.0025</td>
</tr>
<tr>
<td>$\Delta H^\circ$ (kJ mol$^{-1}$)</td>
<td>76.50 ± 0.001</td>
</tr>
<tr>
<td>$\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>1.18 ± 0.01</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (kJ mol$^{-1}$)</td>
<td>75.90 ± 0.1</td>
</tr>
</tbody>
</table>
TABLE - 39

Activation parameters for the photo-reduction of methylene blue by different reductants.

Temperature = 30 ± 0.1 °C
Acidity (H₀) = 7.59

<table>
<thead>
<tr>
<th>Reductants</th>
<th>Concentrations</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.66x10⁻³ mol.dm⁻³</td>
<td>5.00x10⁻³ mol.dm⁻³</td>
</tr>
<tr>
<td><strong>Urea</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Eₐ</strong> (kJ.mol⁻¹)</td>
<td>72.84 ± 0.01</td>
<td>55.09 ± 0.005</td>
</tr>
<tr>
<td><strong>ΔH</strong>* (kJ.mol⁻¹)</td>
<td>70.32 ± 0.016</td>
<td>52.57 ± 0.006</td>
</tr>
<tr>
<td><strong>ΔS</strong>* (J.mol⁻¹ K⁻¹)</td>
<td>17.17 ± 0.025</td>
<td>41.33 ± 0.003</td>
</tr>
<tr>
<td><strong>ΔG</strong>* (kJ.mol⁻¹)</td>
<td>15.50 ± 0.02</td>
<td>9.51 ± 0.011</td>
</tr>
<tr>
<td><strong>Allylurea</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Eₐ</strong> (kJ.mol⁻¹)</td>
<td>70.02 ± 0.019</td>
<td>57.45 ± 0.01</td>
</tr>
<tr>
<td><strong>ΔH</strong>* (kJ.mol⁻¹)</td>
<td>67.50 ± 0.01</td>
<td>54.0 ± 0.92</td>
</tr>
<tr>
<td><strong>ΔS</strong>* (J.mol⁻¹ K⁻¹)</td>
<td>22.52 ± 0.011</td>
<td>39.30 ± 0.02</td>
</tr>
<tr>
<td><strong>ΔG</strong>* (kJ.mol⁻¹)</td>
<td>60.40 ± 0.031</td>
<td>42.80 ± 0.02</td>
</tr>
<tr>
<td><strong>Phenylurea</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Eₐ</strong> (kJ.mol⁻¹)</td>
<td>58.41 ± 0.01</td>
<td>19.00 ± 0.907</td>
</tr>
<tr>
<td><strong>ΔH</strong>* (kJ.mol⁻¹)</td>
<td>56.00 ± 0.11</td>
<td>16.40 ± 0.12</td>
</tr>
<tr>
<td><strong>ΔS</strong>* (J.mol⁻¹ K⁻¹)</td>
<td>-36.90 ± 0.04</td>
<td>-89.70 ± 0.02</td>
</tr>
<tr>
<td><strong>ΔG</strong>* (kJ.mol⁻¹)</td>
<td>66.80 ± 0.07</td>
<td>43.51 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Thiourea</td>
<td>Allylthiourea</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>$E_a$ (kJ.mol⁻¹)</td>
<td>97.90 ± 0.04</td>
<td>70.75 ± 0.001</td>
</tr>
<tr>
<td>$\Delta H^\circ$ (kJ.mol⁻¹)</td>
<td>95.42 ± 0.02</td>
<td>68.20 ± 0.03</td>
</tr>
<tr>
<td>$\Delta S^\circ$ (J.mol⁻¹ K⁻¹)</td>
<td>-21.00 ± 0.08</td>
<td>14.82 ± 0.02</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (kJ.mol⁻¹)</td>
<td>101.00 ± 0.47</td>
<td>202.00 ± 0.87</td>
</tr>
</tbody>
</table>
5.8 GENERAL MECHANISM PROPOSED FOR THE PHOTOREDUCTION OF METHYLENE BLUE WITH UREA, THIOUREA AND THEIR DERIVATIVES

The photochemistry of the dyes has been the subject of considerable interest throughout the nineteenth century. Various ultra violet and visible detectors were used to study the reduction of dyes by some reducing agents. The photochemically induced reactions between dyes and the reducing agents were well documented. However, the electron / hydrogen ion transfer mechanism between methylene blue and reducing species such as urea, Allylurea, phenylurea, thiourea and allylthiourea has not yet been investigated. The present work reveals a comparative study of the reaction of methylene blue with above reductants. Studies in the different aspects and parameters, all the above systems show similarity in the following respects, and are well verified by the plots mentioned below:

1) Plots between quantum yields ($\phi$) and acidity ($H_o$). \(^{239,246}\)
2) Plots between $1/\phi$ against $1/[AH_2]$. \(^{116}\)
3) Plots between $1/\phi$ and $(\phi_1 - \phi)/(\phi - \phi_2)$ against $1/h_o$. \(^{239,246}\)
4) Log quantum yields and $1/T$. \(^{253}\)

In the view of current findings section 4.4.1 to 4.4.4 a tentative mechanism for the photochemical reduction is suggested which includes the following steps.

$$\text{MBH}^* + h\nu \rightarrow \text{MBH}_s^* \quad \text{Rate} = [I_o] \quad 5.8-1$$

Where $I_o$ is the intensity of light quanta, and $\text{MBH}_s^*$ is the excited singlet state of $\text{MBH}^*$. 
De-excitation of the excited singlet \( ^1S \) state is followed by the emission of fluorescence radiation \( h\nu_f \).

\[
\begin{align*}
k_1 & \quad \text{MBH}^*_s \rightarrow \text{MBH}^* + h\nu_f & \quad \text{Rate} = (1 - \alpha) \ [I_0] \quad 5.8-2
\end{align*}
\]

Where \( k_1 \) = rate constant for the conversion of singlet state to ground state.

On the bases of the evidences provided by Pestemer\textsuperscript{73} and Uddin,\textsuperscript{239,246}

\[
\begin{align*}
k_2 & \quad \text{MBH}^*_s \rightarrow \quad \text{Rate} = \alpha [I_0] \quad 5.8-3
\end{align*}
\]

\( k_2 \) = rate constant for internal conversion from singlet to triplet state.

\( \alpha \) = Fraction of light absorbed.

Collisional deexcitation\textsuperscript{59,88} of the excited singlet methylene blue takes place between \( \text{MBH}^* \) and unexcited methylene blue or with the reductants, which may follow the reaction as given below;

\[
\begin{align*}
k_3 & \quad \text{MBH}^*_s + \text{MBH}^* \rightarrow \text{MBH}^* + \text{MBH}^* \quad 5.8-4
\end{align*}
\]

\( k_3 \) = quenching rate constant for singlet state with unexcited molecule.

\[
\begin{align*}
k_4 & \quad \text{MBH}^*_s + \text{AH}_2 \rightarrow \text{MBH}^* + \text{AH}_2 \quad 5.8-5
\end{align*}
\]

\( k_4 \) = quenching rate constant for singlet state with reductant.

It is also possible for triplet dye to associate with a hydrogen\textsuperscript{59,116} ion, according to following scheme ;

\[
\begin{align*}
K_1 & \quad \text{MBH}^* + H^* \underset{K_f}{\xrightarrow{\text{MBH}^*}} \text{MBH}_2^+ \quad 5.8-6
\end{align*}
\]

\[
K_f = \frac{[\text{MBH}_2^+]}{[\text{MBH}_1^*] [H^+]^2} \quad 5.8-7
\]

\( K_1 \) = Equilibrium constant for single protonated triplet state and doubly protonated state.
The triplet\textsuperscript{69,116,121,139} excited dye may be deactivated to cationic dye MBH\textsuperscript{+} by collision with reductant molecule;

\[
\begin{align*}
    k_5 \\
    MBH^*_T + AH_2 & \rightarrow MBH^+ + AH_2 
\end{align*}
\]

5.8-8

Where \( k_3, k_\eta, k_5 \) are the quenching rate constants for respective reactions.

The triplet state is supposed to react with reductants forming semi reduced dye MBH\textsuperscript{+} \_2;

\[
\begin{align*}
    k_6 \\
    MBH^*_T + AH_2 & \rightarrow MBH^+_2 + AH 
\end{align*}
\]

5.8-9

\( k_6 \) = Rate constant for the formation of MBH\textsubscript{2}.

In the triplet state the exited methylene blue may form cation MBH\textsuperscript{+} due to non radiative transition between two state of different multiplicity\textsuperscript{88,139} Which will follow the reaction as below ;

\[
\begin{align*}
    k_7 \\
    MBH^*_T & \rightarrow MBH^+ 
\end{align*}
\]

5.8-10

\( k_7 \) = Rate constant for inter system crossing (isc)\textsuperscript{TS}

The protonated triplet species are supposed to react with the reductants forming semi reduced methylene blue, which on disproportionation produces the leucomethylene blue\textsuperscript{88,139,239,246}.

\[
\begin{align*}
    k_8 \\
    MBH^{++}_{2T} + AH_2 & \rightarrow MBH^{++}_{2} + AH_2 
\end{align*}
\]

5.8-11

\( k_8 \) = quenching rate constant.

\[
\begin{align*}
    k_9 \\
    MBH^{++}_{2T} + AH_2 & \rightarrow MBH^{++}_3 + AH 
\end{align*}
\]

5.8-12

\( k_9 \) = Rate constant for the formation of MBH\textsubscript{3}. 

\[ k_{10} \]
\[ \text{MBH}^{\ast\ast}_{2T} + \text{AH}_2 \rightarrow \text{MBH}^{\ast\ast}_2 + \text{AH}_2 \quad 5.8-13 \]

\( k_{10} \) = quenching rate constant for internal conversion (ic)

Association of \( \text{MBH}_2 \) with reductant may also establish another equilibrium\textsuperscript{239,247}:

\[ \frac{k_2}{[\text{MBH}^{\ast\ast}_{2T} \cdot \text{AH}_2]} \]
\[ \begin{array}{c c c c}
\text{MBH}^{\ast\ast}_{2T} + \text{AH}_2 & \rightarrow & \text{MBH}^{\ast\ast}_{2T} \cdot \text{AH}_2 \\
\end{array} \quad 5.8-14 \]

\( k_2 \) = equilibrium constant between doubly protonated and protonated triplet complex.

Reaction with the solvent (SH) is given as\textsuperscript{239,247}:

\[ k_{11} \]
\[ \text{MBH}^{\ast\ast}_{2T} + \text{SH} \rightarrow \text{MBH}^*_3 + \text{S} \quad 5.8-15 \]

\( k_{11} \) = rate constant for the reaction with solvent.

Existed energy of the complex may also be lost by the internal conversion (ic), which may lead to the dissociation of the species.

\[ k_{12} \]
\[ \text{MBH}^{\ast\ast}_{2T} \cdot \text{AH}_2 \rightarrow \text{MBH}^* + \text{H}^* + \text{AH}_2 \quad 5.8-16 \]

\( k_{12} \) = rate constant for dissociation process.

The energy\textsuperscript{239} loss may also occur by the collision of complex with the unexcited methylene blue \( \text{MBH}^* \):

\[ k_{13} \]
\[ \text{MBH}^{\ast\ast}_{2T} \cdot \text{AH}_2 + \text{MBH}^* \rightarrow \text{MBH}^{\ast\ast}_3 + \text{AH} + \text{MBH}^* \quad 5.8-17 \]

\( k_{13} \) = rate constant for the formation of \( \text{MBH}^{\ast\ast}_3 \). \( \text{AH} \) = free radical.
By the transfer of electron, the oxidation-reduction reaction can also take place accordingly:\(^{239,247}\):

\[
\begin{align*}
&k_{14} \quad \text{MBH}^{**}_{2T} + \text{AH}_2 + \text{MBH}^+ \longrightarrow \text{MBH}^3 + \text{AH}^+ + \text{MBH}^+ \quad 5.8-18 \\
& \text{MBH}^3 + H \longrightarrow \text{MBH}^{**}_{3} \quad \text{(semi reduced methylene blue)} \quad 5.8-19
\end{align*}
\]

\( k_{14} \) = quenching rate constants for respective reactions.

\( \text{MBH}^3 \) disproportionate\(^{56}\) to give leuco dye \( \text{MBH}^{**}_{4} \), and methylene blue cation \( \text{MBH}^+ \):

\[
k_{15} \quad 2\text{MBH}^{**}_{3} \longrightarrow \text{MBH}^{**}_{4} + H^+ + \text{MBH}^+ \quad 5.8-20
\]

\( k_{15} \) = rate constant for the above disproportionation reaction.

\[
2\text{AH} \longrightarrow \text{Product} \quad 5.8.21
\]

### 5.8.1 Mechanism of photo-reduction of methylene blue at a glance.

The mechanism proposed in section 5.8 for the reduction of methylene blue under steady illumination consists of following elementary steps:

\[
\begin{align*}
&\text{MBH}^+ + h\nu \longrightarrow \text{MBH}_s^+ \quad 5.8.1 \\
&\text{MBH}^+_s \longrightarrow \text{MBH}^+ + h\nu_f \quad 5.8.2 \\
&\text{MBH}^+_s \longrightarrow \text{MBH}^+_t \quad 5.8.3 \\
&\text{MBH}^+_s + \text{MBH}^+ \longrightarrow \text{MBH}^+ + \text{MBH}^+ \quad 5.8.4 \\
&\text{MBH}^+_s + \text{AH}_2 \longrightarrow \text{MBH}^+ + \text{AH}_2 \quad 5.8.5 \\
&\text{MBH}^+_t + H^+ \longrightarrow \text{MBH}^{**}_{2T} \quad 5.8.6 \\
K_1 &= \frac{[\text{MBH}^{**}_{2T}]}{[\text{MBH}^+_t] [H^+]} \quad 5.8.7
\end{align*}
\]
\[
\begin{align*}
\text{MBH}^+_T + \text{AH}_2 & \xrightleftharpoons[k_5]{\text{MBH}^+_T} \text{MBH}^+_T + \text{AH}_2 & 5.8.8 \\
\text{MBH}^+_T + \text{AH}_2 & \xrightleftharpoons[k_6]{\text{MBH}^+_T} \text{MBH}_2^+ + \text{AH} & 5.8.9 \\
\text{MBH}^+ & \xrightleftharpoons[k_7]{\text{MBH}^+} & 5.8.10 \\
\text{MBH}_{2T}^{++} + \text{AH}_2 & \xrightleftharpoons[k_8]{\text{MBH}_{2T}^{++}} \text{MBH}_2^{++} + \text{AH}_2 & 5.8.11 \\
\text{MBH}_{2T}^{++} + \text{AH}_2 & \xrightleftharpoons[k_9]{\text{MBH}_{2T}^{++}} \text{MBH}_3^{++} + \text{AH} & 5.8.12 \\
\text{MBH}_{2T}^{++} + \text{AH}_2 & \xrightleftharpoons[k_{10}]{\text{MBH}_{2T}^{++}} \text{MBH}_{2T}^{++} + \text{AH}_2 & 5.8.13 \\
\text{MBH}_{2T}^{++} + \text{AH}_2 & \xrightleftharpoons[k_2]{\text{MBH}_{2T}^{++}} \text{MBH}_{2T}^{++} + \text{AH}_2 & 5.8.14 \\
\text{K}_2 = \frac{[\text{MBH}_{2T}^{++} \cdot \text{AH}_2]}{[\text{MBH}_{2T}^{++} \cdot \text{[AH}_2\text{]}]} \\
\text{MBH}_{2T}^{++} + \text{SH} & \xrightleftharpoons[k_{11}]{\text{MBH}_{2T}^{++}} \text{MBH}_3^{++} + \text{S} & 5.8.15 \\
\text{MBH}_{2T}^{++} + \text{AH}_2 & \xrightleftharpoons[k_{12}]{\text{MBH}_{2T}^{++}} \text{MBH}^+ + \text{H}^+ + \text{AH}_2 & 5.8.16 \\
\text{MBH}_{2T}^{++} \cdot \text{AH}_2 + \text{MBH}^+ & \xrightleftharpoons[k_{13}]{\text{MBH}_{2T}^{++}} \text{MBH}_3^{++} + \text{AH} + \text{MBH}^+ & 5.8.17 \\
\text{MBH}_{2T}^{++} \cdot \text{AH}_2 + \text{MBH}^+ & \xrightleftharpoons[k_{14}]{\text{MBH}_{2T}^{++}} \text{MBH}_2^+ + \text{AH}_2 + \text{MBH}^+ & 5.8.18 \\
\text{MBH}^+ + \text{H}^+ & \xrightleftharpoons[k_{15}]{\text{MBH}^+} \text{MBH}_3^{**} \text{reduced methylene blue} & 5.8.19 \\
2\text{MBH}_3^{**} & \xrightarrow{k_{15}} \text{MBH}_4^{**} + \text{H}^+ + \text{MBH}^+ & 5.8.20 \\
\text{2AH} & \text{Reduction} \rightarrow \text{Product} & 5.8.21
\end{align*}
\]
5.8.2 Derivation of rate equations.

(a) Relationship between \((\phi_1 - \phi)/(\phi - \phi_2)\) and \(1/h_o\)

Considering the above reactions for determining the rate of reactions, let us consider following notations for simplification.

\[
\begin{align*}
[MBH^+_1] &= a \\
[MBH^{**}_2] &= b \\
[MBH^{**}_{2T}] &= c \\
[MBH^+] &= A \\
[AH_2] &= l \\
[H] &= h_o
\end{align*}
\]

Rate of disappearance of \(MBH^+\);

\[-d[MBH^+] / dt = \frac{1}{2} \{ k_0 a l + k_9 b l + k_{11} b + k_{13} c A \} \quad -5.8-20\]

Rate of formation of the triplet state;

\[-[MBH^+_1] / dt = \alpha \{ L_0 - k_3 [MBH^+_1][AH_2] \} - k_6 [MBH^+_1][AH_2] -
\]

\[ k_7 [MBH^+_1] - k_9 [MBH^{**}_{2T}] [AH_2] - k_{10} [MBH^{**}_{2T}] [SH] - k_{12} [MBH^{**}_{2T}] [AH_2] -
\]

\[ k_{13} [MBH^{**}_{2T}][AH_2] [MBH^+] \quad 5.8-21\]

Consider the rate equations for the reactions 5.8-7 and 5.8-14, and using the above notations;

\[
\begin{align*}
K_1 &= b / a h_o \\
K_2 &= c / bl \\
b &= K_2 a h_o \\
c &= K_2 bl \text{ or } K_1 K_2 a h_o l
\end{align*}
\]
Applying steady state conditions and using the above notations;

$$\alpha [I_a] = a (k_5l + k_6l + k_7) + b (k_8l + k_9l + k_{10} + k_{11})$$

Since the quantum yield is given as;

$$\phi = \frac{d [MBH^*]}{dt}$$

Therefore $$\phi = \alpha \frac{k_6a l + k_9b l + k_{11}b + k_{13}cA}{2 a (k_5l + k_6l + k_7) + b (k_8l + k_9l + k_{10} + k_{11}) c (k_{12} + k_{13}A)}$$

5.8-22

Placing the values of b and c, the above equation can be written as;

$$\phi = \alpha \frac{a (k_6l + K_1 k_9h + K_1 k_{11} + K_2 k_{13} + K_3 l l A)}{2 (k_5l + k_6l + k_7) K_1 h o (k_8l + k_9l + k_{10} + k_{11} + k_{12} K_2 l + K_2 k_{13} A l)}$$

5.8-23

Let $$\phi = \phi_1$$ at high $$h_o$$

$$\phi = \phi_2$$ at lower $$h_o$$

Consider the equation (5.8-22), at high value of $$h_o$$, a is negligible, while b and c are the controlling factors, the relation becomes as follow;

$$\frac{1}{\phi_1} = \frac{2}{a} \frac{b (k_8l + k_9l + k_{10} + k_{11}) + c (k_{12} + k_{13}A)}{k_9b l + k_{11}b + k_{13}cA}$$

5.8-24

at lower $$h_o$$, b and c are negligible while a is the controlling term.

Therefore the above equation becomes as below;

$$\frac{1}{\phi_2} = \frac{2}{a} \frac{(k_5l + k_6l + k_7) a}{k_6a l}$$

5.8-25

Adding equation 5.8-24 and 5.8-25, and multiply L.H.S. by $$\phi$$.

The relation becomes as below;

$$\frac{(\phi / \phi_1) (k_9b l + k_{11}b + k_{13}cA) + \phi / \phi_2 k_6 a l = b(k_9l + k_{11}) + ck_{13}A}{\phi_1}$$

$$k_9b l + k_{11}b + k_{13}cA + k_6l$$
On rearranging equation becomes;

\[(\phi_1/\phi_2)k_6al - k_6al = bk_9l + k_{11}l + k_{11}b + k_{13}cA / \phi_1\]

\[\phi / \phi_1 = bk_9l + k_{11}b + k_{13}cA / \phi_1\]

and putting the value of b and c;

\[(\phi_1 - \phi_2) / (\phi_1 - \phi) = (\phi_2 / \phi_1) - \frac{k_9K_1a \cdot h_0l + k_{13}K_1K_2a h_0lA}{k_6a l}\]

\[(\phi_1 - \phi) / (\phi_1 - \phi_2) = (\phi_1 / \phi_2) - \frac{k_6}{\frac{h_oK_1}{k_9 + K_2k_{13}A}}\]

5.8-26

According to the above relation, The plot of \((\phi_1 - \phi) / (\phi - \phi_2)\) against \(1 / h_0\) is a straight line passing through the origin, with a slope whose quantity is equal to

\[
\left(\frac{\phi_1}{\phi_2}\right) - \frac{k_6}{K_1\left(k_9 + K_2k_{13}A\right)}
\]

(b) **Relationship between I / \phi and 1 / [reductant]**

Considering equation (5.8-23)

\[1 / \phi = 2 / \alpha - \frac{(k_5l + k_6l + k_7) + K_1h_0(k_5l + k_5l + k_{10} + k_{11} + K_2k_{12}l + K_2k_{13}A)l}{k_6l + K_1k_9h_0l + K_1k_{11}h_0 + K_1K_2k_{13}h_0lA}\]

Let us ignore the effect of solvent on rate constant (since its concentration remains constant throughout the work) and rearranging equation 5.8-23,

\[1 / \phi = 2 / \alpha \left(\frac{k_6l + K_1k_9h_0l + K_1K_2k_{13}h_0lA + k_5l + K_2k_{12}h_0l}{k_6l + K_1k_9h_0l + K_1K_2k_{13}h_0lA}\right) + \frac{K_1k_9h_0l + k_7 + K_1k_{10}h_0}{k_6l + K_1k_9h_0l + K_1K_2k_{13}h_0lA}\]
Consider only the primary and secondary photochemical changes, the final relation becomes as given below;

\[
1/\phi = 2/\alpha \left[ 1 + \frac{K_2k_{12}}{(k_9 + K_2k_{13}A)} + \frac{2}{\alpha} \frac{k_{10}}{(k_9 + K_2k_{13}A)} \right] - \frac{1}{l} \tag{5.8-27}
\]

having intercept
\[
= 2/\alpha \left[ 1 + \frac{K_2k_{12}}{(k_9 + K_2k_{13}A)} \right]
\]

slope
\[
= 2/\alpha \cdot \frac{k_{10}}{(k_9 + K_2k_{13}A)}
\]

If considering only the rate constant for intersystem crossing (isc) the equation can be modified as below;

\[
1/\phi = 2/\alpha \left[ 1 + \frac{K_2k_{12}}{(k_9 + K_2k_{13}A)} \right] + \frac{2}{\alpha} \frac{(k_7)}{(k_9 + K_2k_{13}A) K_1} \tag{5.8-27(a)}
\]

If only quenching due to reductants are involved, \(k_8\) must have value greater than zero, in this condition the relation will be represented as;

\[
1/\phi = 2/\alpha \left[ 1 + \frac{K_2k_{12} + k_8}{(k_9 + K_2k_{13}A)} \right] + \frac{2}{\alpha} \frac{k_{10}}{(k_9 + K_2k_{13}A)} \frac{1}{l} \tag{5.8-27(b)}
\]

If only the photophysical processes are involved, the above relation may be modified as;

\[
1/\phi = 2/\alpha \left[ 1 + \frac{K_2k_{12}}{(k_9 + K_2k_{13}A)} \right] + \frac{2}{\alpha} \frac{(k_7 + k_{10})}{(k_9 + K_2k_{13}A)} \frac{1}{l} \tag{5.8-27(c)}
\]
(c) Relationship between $1/\phi$ and $1/h_0$

Considering equation (5.8-23);

$$1/\phi = \frac{2}{\alpha} \left( 1 + \frac{k_7 + k_{10} h_0 + K_1 K_2 h_0 + K_1 K_2 k_{12} h_0}{K_1(k_9 + K_2 k_{13} A) h_0} \right)$$

On rearranging:

$$1/\phi = \frac{2}{\alpha} \left( 1 + \frac{(K_2 + K_2 k_{12})}{(k_9 + K_2 k_{13} A)} + \frac{2}{\alpha} \frac{k_5}{K_1(k_9 + K_2 k_{13} A)} \right) \cdot \frac{1}{h_0}$$

having slope $= \frac{2}{\alpha} \frac{k_5}{K_1(k_9 + K_2 k_{13} A)}$

Intercept $= \frac{2}{\alpha} \left( 1 + \frac{(K_2 + K_2 k_{12})}{(k_9 + K_2 k_{13} A)} \right)$ let it be equal to $\frac{1}{\phi_a}$

When there is no dissociation, the intercept of the above relation will be:

$$\frac{2}{\alpha} \left| 1 + \frac{K_2}{(k_9 + K_2 k_{13} A)} \right| = \frac{1}{\phi_a}$$

Finally the relation may be written as below;

$$1/\phi = \frac{1}{\phi_a} + \frac{2}{\phi_a} \frac{k_5}{K_1(k_9 + K_2 k_{13} A)} \cdot \frac{1}{h_0}$$

5.8-28 (b)
(d) **Determination of the ratios of the rate constants of photo-reduction of methylene blue by reductants.**

The ratios of the rate constants were calculated by using various equation of the general mechanism, for instance

\[ \frac{2 \times k_5 + k_6}{\alpha k_6} \]

was calculated from equation 5.8-25.

The ratio of \( \frac{k_6}{K_1(k_9 + K_2k_{13} A)} \) was obtained by the slope of equation 5.8-26,

While

\[ \frac{K_2k_{12}}{(k_9 + K_2k_{13} A)} \]

and

\[ \frac{2}{\alpha} \cdot \frac{k_{10}}{(k_9 + K_2k_{13} A)} \]

were obtained by intercept and slope of equation 5.8-27 respectively.

The ratios \( \frac{k_5}{K_1(k_9 + K_2k_{13} A)} \) and \( \frac{K_2}{k_9 + K_2k_{13} A} \)

were obtained from plots of equation 5.8-28 (a) (ignoring \( K_2 \)).

The values of slope and intercept obtained by the use of equations 5.8-27 and 5.8-28 by various plots are summarized in Tables - 18 and 25. The values of the ratios of the rate constants for the reaction of methylene blue in 50% aqueous propanol with various reductants are summarized in Table - 40 and 41.

\[ \frac{2}{\alpha} \cdot \frac{(k_5 + k_6)}{k_6} \] is concerned with the MBH\(^+\) species. At comparatively higher acidity region, the quantum yield is due to \( k_6 \).
The term \((k_9 + K_2k_{13}A)\) is exceptionally more in 50% aqueous propanol with the reductants in the order such as urea, allylurea, phenylurea, thiourea and allylthiourea, which is due to greater ability of reducing species to give off electrons to the triplet dye.

\[
\frac{k_6}{(k_9 + K_2k_{13}A)K_1}
\]

is the ratio of the rate constant responsible for the formation of products by three species i.e. triplet state, protonated triplet state and association of protonated triplet state of methylene blue with reductant.
TABLE ~ 40

Ratios of the rate constants.

<table>
<thead>
<tr>
<th>Ratios</th>
<th>Urca</th>
<th>Allylurea</th>
<th>Phenylurea</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2/\alpha [k_5 + k_6]/k_6$</td>
<td>8.85±0.001</td>
<td>15.20±0.048</td>
<td>10.70±0.0617</td>
</tr>
<tr>
<td>$(\phi_1/\phi_2) k_6/[K_1(k_9+K_2k_{13}A)]10^6$</td>
<td>0.91±0.004</td>
<td>1.30±0.0025</td>
<td>1.00±0.0328</td>
</tr>
<tr>
<td>$2/\alpha [k_{10}/(k_9+K_2k_{13}A)]10^3$</td>
<td>10.51±0.002</td>
<td>7.50±0.0866</td>
<td>2.40±0.0205</td>
</tr>
<tr>
<td>$2/\alpha [k_7/(k_9+K_2k_{13}A)K_1]10^6$</td>
<td>0.13±0.003</td>
<td>0.30±0.0071</td>
<td>0.20±0.0267</td>
</tr>
<tr>
<td>$2/\alpha [k_5/(k_9+K_2k_{13}A)]K_110^6$</td>
<td>5.92±0.012</td>
<td>6.60±0.0521</td>
<td>5.90±0.0325</td>
</tr>
<tr>
<td>$2/\alpha [1+K_2k_{12}/(k_9+K_2k_{13}A)]$</td>
<td>12.65±0.16</td>
<td>10.00±0.0359</td>
<td>4.00±0.3171</td>
</tr>
<tr>
<td>$2/\alpha [1+K_2/(k_9+K_2k_{13}A)]$</td>
<td>4.74±0.0036</td>
<td>5.20±0.2086</td>
<td>4.00±0.0377</td>
</tr>
<tr>
<td>$k_{10}/k_7$</td>
<td>83.00±0.064</td>
<td>25.00±0.3103</td>
<td>14.00±0.2695</td>
</tr>
<tr>
<td>$k_{10}K_1/k_5$</td>
<td>1.80±0.026</td>
<td>1.00±0.1322</td>
<td>0.40±0.0055</td>
</tr>
<tr>
<td>$k_7/k_5$</td>
<td>0.02±0.001</td>
<td>0.50±0.0053</td>
<td>0.03±0.0005</td>
</tr>
<tr>
<td>Ratios</td>
<td>Thiourea</td>
<td>Allylthiourea</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>$2/\alpha \left( \frac{k_5 + k_6}{k_6} \right)$</td>
<td>11.00±0.11</td>
<td>8.00±0.33</td>
<td></td>
</tr>
<tr>
<td>$\left( \phi_1/\phi_2 \right) \frac{k_6}{[K_1(k_9 + K_2 k_{13} A)]10^6}$</td>
<td>0.98±0.005</td>
<td>0.36±0.005</td>
<td></td>
</tr>
<tr>
<td>$2/\alpha \left[ k_{10}/(k_9 + K_2 k_{13} A) \right]10^3$</td>
<td>7.16±0.0017</td>
<td>1.50±0.0176</td>
<td></td>
</tr>
<tr>
<td>$2/\alpha \left[ k_7/(k_9 + K_2 k_{13} A)[K_1] \right]10^6$</td>
<td>2.00±0.0073</td>
<td>0.12±0.0007</td>
<td></td>
</tr>
<tr>
<td>$2/\alpha \left[ k_5/(k_9 + K_2 k_{13} A) [K_1] \right]10^6$</td>
<td>6.00±0.067</td>
<td>6.00±0.043</td>
<td></td>
</tr>
<tr>
<td>$2/\alpha \left[ 1 + K_2 k_{12}/(k_9 + K_2 k_{13} A) \right]$</td>
<td>6.20±0.0035</td>
<td>4.40±0.0028</td>
<td></td>
</tr>
<tr>
<td>$2/\alpha \left[ 1 + K_2/(k_9 + K_2 k_{13} A) \right]$</td>
<td>4.70±0.0034</td>
<td>4.06±0.0017</td>
<td></td>
</tr>
<tr>
<td>$k_{10}/k_7$</td>
<td>36.30±0.003</td>
<td>12.43±0.0042</td>
<td></td>
</tr>
<tr>
<td>$K_1 k_{10}/k_5$</td>
<td>1.21±0.0034</td>
<td>0.25±0.0012</td>
<td></td>
</tr>
<tr>
<td>$k_7/k_5$</td>
<td>0.03±0.0024</td>
<td>0.018±0.002</td>
<td></td>
</tr>
</tbody>
</table>

\[
\frac{k_{10}}{(k_9 + K_2 k_{13} A)}
\]

is the ratio of the rate constant between internal conversion (ic) rate of

$MBH^{* * 2T}$ and the products forming rate due to species $MBH^{* * 2T}$ and

$MBH^{* * 2T}$. $AH_2$.

\[
\frac{k_7}{(k_9 + K_2 k_{13} A)}
\]

is the ratio of the rate constant for intersystem crossing (isc) and the products forming rate due to the species $MBH^*7$.

\[
\frac{k_5}{(k_9 + K_2 k_{13} A)[K_1]}
\]

is the ratio of quenching rate constant and product formation constant.
The values obtained by various reductants tabulated in Tables 40 and 41 were found to be almost similar.

\[ \frac{K_2k_{12}}{(k_9 + K_2k_{13}A)} \] is the ratio of dissociation constant and the product forming rate due to MBH\textsuperscript{++}2T and MBH\textsuperscript{++}2T, AH\textsubscript{2}.

\[ \frac{k_{10}}{k_7} \] is the ratio of the rate constant for internal conversion and inter system crossing.

\[ \frac{k_{10}K_1}{k_5} \] is the ratio of the internal conversion and quenching rate constants

\[ \frac{k_7}{k_5} \] is the ratio of the rate constant for intersystem crossing and quenching processes. The ratio predicts that the quenching process occurs more frequently than the intersystem crossing.

5.9 JUSTIFICATION OF THE PROPOSED MECHANISM

Following tests were put forward to justify the reaction mechanism;

5.9.1 Test for equation

\[ \frac{2}{\alpha} \times \frac{k_7}{K_1(k_9 + K_2k_{13}A)} \]

Considering the equation (5.8-28), the plot of 1/ \( \phi \) vs 1/ \( h_0 \) at constant concentration of reductant gives the value of slope as below;

\[ \frac{2}{\alpha} \times \frac{k_7}{K_1(k_9 + K_2k_{13}A)} = 2.929 \times 10^{-7} \quad \text{(in case of allylurea)} \]

Where \( k_7 \) is approximately equal to 10\textsuperscript{5} s\textsuperscript{-1}, as reported by Parker\textsuperscript{104,191}, the concentration of methylene blue i.e \( A = 10^{-6} \text{ mol dm}^{-3} \).
The value of $K_1$ is $1 \times 10^{-6}$, $k_9$ and $k_{13}$ reported by Uddin and et al.\textsuperscript{133,239} are $1.0 \times 10^{11}$ and $10^{10}$ mol dm\textsuperscript{-3} s\textsuperscript{-1} respectively. The triplet quantum yield ($\alpha$) is about 0.318 and 0.29 in presence of allylurea and phenylurea respectively.

The value of slope calculated by the plot of $1/\phi$ vs $1/h_a$ Figure 17 in case of reaction between methylene blue and allylurea = $2.929 \times 10^{-7}$. Using above values, the relation will become as below;

$$\frac{2}{0.318} \times \frac{10^5}{10^{-6} \left( 10^{11} + 10^{10} K_2 10^{-6} \right)} = 2.929 \times 10^{-7}$$

$$\frac{10^{11}}{(10^{11} + K_2 10^4)} = 2.929 \times 10^{-7} \times 0.159$$

$$\frac{10^{11}}{(10^{11} + K_2 10^4)} = 4.6571 \times 10^{-8}$$

$$2.1472 \times 10^{18} = 10^{11} + K_2 10^4$$

$$K_2 = 2.1473 \times 10^{14} \text{ mol dm}^{-3} \text{ s}^{-1}$$

The value of $K_2$ calculated for the reaction of methylene blue and allylurea in present work comes out to be $\approx 2.1473 \times 10^{14}$ mol\textsuperscript{-1} dm\textsuperscript{3} s\textsuperscript{-1}, while the value reported by Uddin is also $\approx 1 \times 10^{14}$ mol dm\textsuperscript{-3} s\textsuperscript{-1}

**Calculation and verification of rate constants**

Using all above values the following ratios, obtained by various equations and plots can also be calculated;

i) \[ \frac{\phi_1}{\phi_2} \times \frac{k_6}{(k_9 + k_2 k_{13}A) K_1} \]

ii) \[ \frac{1}{\phi_2} = 2 \frac{k_5 + k_6}{\alpha k_6} \]

iii) \[ \frac{2}{\alpha} \times \frac{k_7}{K_1 (k_9 + K_2 k_{13}A)} \]
iv) \[ \frac{2}{\alpha} \times \frac{k_{10}}{(k_9 + K_2k_{13}A)} \]

v) \[ \frac{2}{\alpha} \times \left[ 1 + \frac{K_2k_{12}}{(k_9 + K_2k_{13}A)} \right] \]

5.9.2 Calculation of rate constant for the formation of \( MBH^+_2 \) i.e \( k_6 \)

The value of \( k_6 \) is calculated from the value of slope of the plot \( \phi_1 - \phi/\phi = \phi_2 \) vs \( 1/h_o \), equation (5.7-26) Figure 22, Table 19.

\[ \frac{\phi_1}{\phi_2} \times \frac{k_6}{(k_9 + K_2k_{13}A)K_1} = 1.2975 \times 10^{-6} \]

Let \((k_9 + K_2k_{13}A) = Z \)

Using the reported values \( Z = (10^{11} + 2.1472 \times 10^{14} \times 10^{10} \times 10^{-6}) \)

\( Z = 2.1472 \times 10^{18} \)

Therefore

\[ \frac{0.3180}{0.0660} \times \frac{k_6 \times 10^{-6}}{2.1472 \times 10^{18}} = 1.2975 \times 10^{-6} \]

\[ k_6 = 0.2692 \times 10^{-7} \times 10^{-6} \times 2.1472 \times 10^{18} \]

\[ k_6 = 5.7809 \times 10^5 \text{ mol}^{-1}\text{dm}^3\text{s}^{-1} \]

5.9.3 Calculation of quenching rate constant i.e \( k_5 \)

The value of \( k_5 \) is calculated with the help of equation 5.7-25,

\[ \frac{1}{\phi_2} = \frac{2}{\alpha} \frac{k_5 + k_6}{k_6} \]

\[ \frac{1}{0.066} = 6.2890 \frac{(k_5 + 5.7809 \times 10^5)}{5.7809 \times 10^5} \]

\[ (k_5 + 5.7809 \times 10^5) = 1.3927 \times 10^6 \]

\[ k_5 = 8.1465 \times 10^5 \text{ mol dm}^{-3}\text{s}^{-1} \]
5.9.4 Calculation of rate constant for inter system crossing i.e. \( k_7 \)

\[
\frac{2}{\alpha} \times \frac{k_7}{K_1(k_9 + K_2k_{13A})} = 2.29 \times 10^{-7}
\]

\[
k_7 = 10^{-6} \times 2.1472 \times 10^{18} \times 2.929 \times 10^{-7} \times 0.159
\]

\[
k_7 = 1.00 \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}
\]

5.9.5 Calculation of rate constant for internal conversion i.e. \( k_{10} \)

The value of rate constant \( k_{10} \) is calculated with the help of plot \( 1/\phi \) vs \( 1/|\text{red.}| \).

Using equation (5.8-27), and Figure 32, according to the values tabulated in Table 25, the value of slope is given as below;

\[
\frac{2}{\alpha} \times \frac{k_{10}}{(k_9 + K_2k_{13A})} = 7.4134 \times 10^{-3}
\]

\[
k_{10} = 7.4134 \times 10^{-3} \times 0.159 \times 2.1472 \times 10^{18}
\]

\[
k_{10} = 2.5309 \times 10^{15} \text{ mol}^{-1} \text{dm}^3 \text{ s}^{-1}
\]

5.9.6 Calculation of rate constant for the dissociation process i.e. \( k_{12} \)

The value of rate constant \( k_{12} \) is calculated with the help equation 5.8-28 (a) and intercept of Figure 32, Table 25.

\[
\frac{2}{\alpha} \times \frac{1 + K_2k_{12}}{(k_9 + K_2k_{13A})} = 9.9641
\]

\[
K_2k_{12} = (9.9641 \times 0.159) - 1 \times 2.1472 \times 10^{18}
\]

\[
K_2k_{12} = 0.5843 \times 2.1472 \times 10^{18}
\]

Since \( K_2 = 2.1473 \times 10^{14} \)

\[
k_{12} = 5.8426 \times 10^5 \text{ mol}^{-1} \text{dm}^3 \text{ s}^{-1}
\]
5.9.7 Calculation of quenching rate constant i.e $k_8$

If only the quenching due to reductant is involved, the equation 5.8-27 (b) can be used to calculate the value of $k_8$.

\[
\frac{[1 + \frac{K_2k_{12} + k_8}{Z}]}{Z} = (9.9641 \times 0.159)
\]

or $K_2k_{12} + k_8 = (1.5843 - 1) 2.1472 \times 10^{18}$

\[
k_8 = 1.246 \times 10^{18} - K_2k_{12}
\]

since $K_2 = 2.1473 \times 10^{14}$ mol dm$^{-3}$ s$^{-1}$

\[
k_{12} = 5.842 \times 10^3$ mol dm$^{-3}$ s$^{-1}$

Therefore $k_8 = 2.00 \times 10^{14}$ mol dm$^{-3}$ s$^{-1}$
**TABLE - 41**

Values of the rate constant for the reaction of methylene blue and reductants.

\[
|\text{Reducants}| = 2.5 \times 10^{-2} \text{ mol.dm}^{-3}
\]

Temperature = 30 ± 0.1 °C

<table>
<thead>
<tr>
<th>Rate constants (mol.(^{-1}) dm(^3).s(^{-1}))</th>
<th>Allylurea</th>
<th>phenylurea</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_2)</td>
<td>2.1473 \times 10^{14}</td>
<td>3.9795 \times 10^{14}</td>
</tr>
<tr>
<td>(k_5)</td>
<td>8.1465 \times 10^{5}</td>
<td>6.7695 \times 10^{5}</td>
</tr>
<tr>
<td>(k_6)</td>
<td>5.7809 \times 10^{5}</td>
<td>1.2476 \times 10^{6}</td>
</tr>
<tr>
<td>(k_7)</td>
<td>1.00 \times 10^{5}</td>
<td>9.999 \times 10^{4}</td>
</tr>
<tr>
<td>(k_8)</td>
<td>2.00 \times 10^{14}</td>
<td>6.700 \times 10^{13}</td>
</tr>
<tr>
<td>(k_{10})</td>
<td>2.5309 \times 10^{15}</td>
<td>1.373 \times 10^{15}</td>
</tr>
<tr>
<td>(k_{12})</td>
<td>5.84 \times 10^{3}</td>
<td>3.740 \times 10^{3}</td>
</tr>
</tbody>
</table>
Comparison with the literature values of the rate constant for the reduction of dye with reductants.

<table>
<thead>
<tr>
<th>Rate constants (mol·¹ dm³ s⁻¹)</th>
<th>Literature values</th>
<th>Observed values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2$</td>
<td>$1 \times 10^{14}$ Ref. 133&lt;br&gt;$7 \times 10^9$ Ref. 59</td>
<td>$2.15 \times 10^{14}$</td>
</tr>
<tr>
<td>$k_5$</td>
<td>$9.5 \times 10^7$ Ref. 133&lt;br&gt;$5.0 \times 10^6$ Ref. 247</td>
<td>$8.14 \times 10^5$</td>
</tr>
<tr>
<td>$k_6$</td>
<td>$3.0 \times 10^7$ Ref. 133&lt;br&gt;$=10^6$ Ref. 59</td>
<td>$5.78 \times 10^5$</td>
</tr>
<tr>
<td>$k_7$</td>
<td>$2.80 \times 10^7$ Ref. 133&lt;br&gt;$=10^5$ Ref. 104</td>
<td>$1.0 \times 10^5$</td>
</tr>
<tr>
<td>$k_8$</td>
<td>$7.85 \times 10^7$ Ref. 133</td>
<td>$2.0 \times 10^{14}$</td>
</tr>
<tr>
<td>$k_{10}$</td>
<td>$2.75 \times 10^{15}$ Ref. 133</td>
<td>$2.53 \times 10^{15}$</td>
</tr>
<tr>
<td>$k_{12}$</td>
<td>$9.99 \times 10^3$ Ref. 133</td>
<td>$5.84 \times 10^5$</td>
</tr>
</tbody>
</table>
CONCLUSIONS:

The photolysis of methylene blue in various solutions had been studied by a number of workers. Explanation of the results obtained by Matsumoto in the photolysis of methylene blue in aqueous solution, involves the formation of a labile complex between a pair of half oxidized and half reduced methylene blue molecules, or formation of a charge complex between a photo excited methylene blue and an unexcited molecule. Reduction of thionine and methylene blue by organic reductants has been noted by many workers. Ahmed and Uddin have described the reduction of thionine and methylene blue.

From the results tabulated in chapter 4, the photo reduction of methylene blue with reductants such as urea, allylurea, phenylurea, thiourea and allylthiourea lead to the following conclusions:

i) The reduction of methylene blue need not initially involve the abstraction of hydrogen from the solvent, however experiments reflects the ease of exchange of the hydrogen involved in the reduction rather than implicating the solvent in the initial reduction process.

ii) Variation in the quantum yield of the reaction depends on the concentration and the nature of reducing species.

iii) Variation in the quantum yield depends on the acidity.

iv) Reduction is more favourable in lower acidity.

v) There is no dependence of the quantum yield on the concentration of methylene blue.

vi) Photo-reduction process is influenced by temperature.

vii) Energy of activation depends on the reductant concentration.
viii) It is also concluded that the quantum yield is controlled by two equilibria.

a) One of the equilibrium exists between triplet state of methylene blue with proton and protonated triplet state of methylene blue.

\[ MBH^+ + H^+ \rightleftharpoons MBH^{++} \]

b) secondly between protonated triplet state of methylene blue with reductants and associated complex (\( MBH^{++}_{2T}.AH_2 \)).

\[ MBH^{++}_{2T} + AH_2 \rightleftharpoons MBH^{++}_{2T}.AH_2 \]
5.11 COMPARISON WITH EARLIER WORK

5.11.1 Kinetics of the similar reaction

The maximum quantum yield obtained in the present work for the reaction between methylene blue with allylurea and allylthiourea was 0.318 and 0.3306 respectively. These values may be compared with the value (0.35) obtained by Uddin,239,247 for the reaction between thionine and N. phenylglycine. However the Pestemer73, reported 0.27 for the reaction of thionine with allylthiourea. The maximum quantum yield obtained by Sawkar52 and Ahmed238 for the reaction of thionine with allylthiourea and anetholc was 0.22 and 0.458 respectively.

The values of quantum yield for the reaction between methylene blue and phenylurea obtained at different acidities are higher as compared to the urea and allylurea Table 15. The higher values of the quantum yield due to phenyl group was also observed by several workers.255 According to them proton transfer reaction takes place more effectively due to interacting phenyl group.

The comparison of the present findings can also be made with the straight line graph plotted between 1/\(\phi\) against 1/\(h_o\), and 1/\(\phi\) against 1/\(1/\mu_\text{red.}\) by Pestemcr,73 Ahmed,238 and Uddin.239,247

The linear plots of \((\phi_1-\phi) / (\phi - \phi_2)\) against 1/\(h_o\) passing through origin obtained in the present work are similar to those obtained by Uddin. 239,247

The variation in the quantum yield with concentration of the reductant also followed the same pattern as reported earlier.247 The variation of quantum yield with acidities were also verified by the Sawkar52 and Uddin.239,247 However, Ahmed238 and Matsumoto189 observed no dependence of the quantum yield on the concentration of the dye as well
as in the present work. The shape of the plots of quantum yield against acidity reported by Pestemer,\textsuperscript{73} Ahmed\textsuperscript{238} and Uddin\textsuperscript{239,247} is similar to the shape of plots obtained in the present work.

5.11.2 **Comparison due to variation in temperature**

A temperature co-efficient of 1.89 and 1.67 were observed for the reaction of methylene blue and thiourea per five degree rise in temperature at acidity 4.06, while the concentration of thiourea was $1.66 \times 10^{-3}$ mol.dm$^{-3}$ and $5.00 \times 10^{-3}$ mol.dm$^{-3}$. The value obtained by Uddin was approximately equal to 1.3 in the reactions of thionine and thiourea.$^{239}$ Similarly Kostryukova et al.$^{101}$ reported the value as 1.2 for the reaction of thionine and thiourea.

The influence of temperature on the reaction of thionine with thiourea and allylthiourea was also found by Weber.$^{255}$ He proposed that the number of effective collisions of the excited thionine with the reductant increases with the rise in temperature and concentration of reductant. Currently a three fold rise in the concentration of reductant has decreased the average value of temperature co-efficient from 1.76 to 1.33 for allylthiourea at lower acidity i.e. 4.06. This behaviour was also supported by the Weber.$^{255}$

In the present work the activation energy ($E_a$) for the reaction of methylene blue and allylthiourea calculated by Arrhenius relation$^{253}$ was found to be 18.81 k.cal.mol$^{-1}$, a three fold rise in the concentration of allylthioure at acidity of 4.06 has decreased the value of energy of activation to 9.9735 k.cal.mol$^{-1}$, in the presence of acetate buffer Table 38. Koizumi et al.$^{89}$ reported the value of energy of activation ($E_a$) for the photobleaching of toludine blue in the presence of phosphate buffer at pH 7.74 as 4.20 k.cal.mol$^{-1}$, lower value of ($E_a$) may be due to ten fold rise in the concentration of toludine blue. This shows that
increase in the concentration has decreased the value of energy of activation ($E_a$).

Abuin et al.$^{256}$ calculated the activation energy for the photocleavage of butane 2-one from triplet state approximately 12.71 k.cal.mol$^{-1}$.

The flash kinetic measurements of temperature dependence for bromophenone triplet decay was studied by Peter et al.$^{257}$, They reported the energy of activation ($E_a$) 5.30 k.cal.mol$^{-1}$ calculated by Arrhenius plot for triplet decay and entropy of activation ($\Delta S^*$) -3 and -5 eu. While using Eyring plots.$^{253}$ The exited singlet state energy level of methylene blue in water intercalated into a polynucleotide respectively, were 43.02 and 42.30 k.cal.mol$^{-1}$, whereas triplet energy in benzene /ethanol was reported to be 34.41 k.cal.mol$^{-1}$ by Wilkinson et al.$^{68}$

Ohno et al.$^{67}$ reported the triplet energy dependent on the extent of protonation in water. The triplet energy reported for the monoprotonated and unprotonated triplet were as 22.94 and 33.22 k.cal.mol$^{-1}$ respectively.

The association constant of most of the bases decreases as the temperature is increased. The values of the association constants:

$$\begin{align*}
K_1 &= \frac{[MBH^{++}_2]}{[MBH^+_T][H^+]} \\
K_2 &= \frac{[MBH^{++}_2 \cdot AH_2]}{[MBH^{++}_2][AH_2]} 
\end{align*}$$

Could be assumed to decrease with the increase in temperature. However, the quantum yield of the reactions of methylene blue with reductants was found to increase with the increase in temperature (see Section 4.8). It
seems therefore that the reaction follows according to equation given below:

\[ \text{MBH}^{**}_{2T} \cdot \text{AH}_2 + \text{MBH}^+ \rightarrow \text{MBH}^{**}_3 + \text{AH} + \text{MBH}^+ \]

5.12 FUTURE PERSPECTIVES

The present work deals with reactions of methylene blue with urea, allylurca, phenylurea thiourea and allylthiourea in 50% aqueous propanol. The selected acidity range is from 4.06 to 7.59.

Photochemical changes in the present work were monitored by means of photocell. The experimental set up can also be designed in such a pattern that could be studied by different advanced techniques such as laser flash photolysis or by photothermal grating spectroscopy.

The photochemical characteristics of dyes and the use of dyes in photovoltaic cell as well as in solar cell would be very advantageous and may be helpful to solve the energy problems at present.

In the present work, the isodielectric media was used to study the photochemical changes in the reaction. It would be interesting if we study the reaction in various dielectric constants, more viscous aromatic solvents, or in solvents which are capable to donate hydrogen atoms, this will provide to understand the variation in the photochemical reaction due to change in medium and the nature of the solvent. The selection of medium and its effect on the above reaction may also be helpful to determine the isokinetic temperature of the reaction in various solvents.

The use of aprotic solvents such as cyclohexane, dibutyle ether, diethyl ether, tetra hydrofurane, dimethyl sulfoxide acetoniitrile (of spectroscopic
quality) can provide more information about the electronic spectra as well as nature of reaction mechanism.

It would also be interesting to study the reaction between dye and inorganic reductants and some metal complexes.

The isolation of the photochemical products by GLC, Mass and NMR may provide some valuable information regarding the mechanism of the reaction.

Photochemical reduction of other dyes of thiazine class might be compared with the phenothiazine series. The effect of the ionic strength, pH and different buffers such as borate and phosphate on the quantum yield may also be advantageous.

The photochemical changes in the presence of some quenching agents may also be useful for the degradation of environmental pollution which is the most important issue of the century.

The photo electrochemical and electrochemical measurements of the dye in presence of semi conductors can be measured with the help of voltametric analyser and cyclic voltameters. Mechanism of photocurrent generated and the redox potential of the excited state dye can also be discuss by cyclic voltammeter. Moreover effect of pH value, concentration of electron donor and acceptor on the generation of photocurrent may also provide the information for the making of voltaic cell. The quantum yield of the reaction can be calculated with the help of photocurrent generated.
FIGURES
Figure 1. Spectra of Methylene blue in different composition of 2-propanol.
Figure 2. Spectra of Methylene blue in 50% 2-Propanol.
Figure 3. Plot of Absorbance vs Concentration of Methylene blue.
Figure 4(a). Plot of $\log(D_m - D_m'/D_m)$ against Time

Figure 4(b). Plot of $\log(D_m - D_n/D_m)$ against Time
Figure 5. Spectra of Methylene blue in Absence of Reducing agent at different Acidity.
Figure 6. Spectra of Methylene blue in presence of Urea.
Figure 7. Spectra of Methylene blue in presence of Allylurea.

[Allylurea] = 1.66x10^{-3} M

- O.D at 4.06
- O.D at 7.59
Figure 8. Spectra of Methylene blue in presence of Phenyl Urea.
Figure 9. Spectra of Methylene blue in presence of Thiourea.
Figure 10. Spectra of Methylene blue in presence of Allylthiourea.
Figure 11. Variation in Quantum Yield with Acidity at different concentration of urea.
Figure 12. Variation in Quantum yield with Acidity at different Concentration of allylurea.
Figure 13. Variation in Quantum yield with Acidity at different concentration of phenylurea.
Figure 14. Variation in Quantum Yield with Acidity at different concentration of thiourea.
Figure 15. Variation in Quantum Yield with Acidity at different concentration of Allylthiourea.
Figure 16 - Plot of \( 1/\text{Quantum Yield} \) vs \( 1/h_o \)
( Reductant = Urea )

Figure 17 - Plot of \( 1/\text{Quantum yield} \) vs \( 1/h_o \)
( Reductant = Allylurea )
Figure 18. Plot of $1/\Phi$ Quantum yield vs $1/h_o$
(Reductant = Phenylurea)

Figure 19. Plot of $1/\Phi$ Quantum yield vs $1/h_o$
(Reductant = Thiourea)
Figure 20. Plot of $1/\text{Quantum Yield}$ vs $1/h_o$ (Reductant = Allylthiourea)
Figure 21. Plot of $\frac{\phi_1 - \phi}{\phi - \phi_2}$ vs $1/h_0$
(Reductant = Urea)

Figure 22. Plot of $\frac{\phi_1 - \phi}{\phi - \phi_2}$ vs $1/h_0$
(Reductant = Allylurea)
Figure 23 - Plot of \( \frac{(\phi_1 - \phi)}{(\phi - \phi_2)} \) vs \( \frac{1}{h} \).
(Reductant = Phenyl Urea)

Figure 24 - Plot of \( \frac{(\phi_1 - \phi - \phi_2)}{(\phi_2)} \) vs \( \frac{1}{h} \).
(Reductant = Thiourea)
Figure 25 - Plot of $(\phi_1 - \phi)/(\phi - \phi_2)$ vs $1/h_0$

(Reductant = Allylthiourea)
Figure 26(a)- Plot of $\log \phi$ vs $1/T$
[Urea] = $1.66 \times 10^{-3}$ mol. dm$^{-3}$

Figure 26(b)- Plot of $\log \phi$ vs $1/T$
[Urea] = $5.00 \times 10^{-3}$ mol. dm$^{-3}$
Figure 27(a) - Plot of $\log \phi$ Vs $1/T$

$[\text{Allylurea}] = 1.66 \times 10^{-3}$ mol. dm$^{-3}$

Figure 27(b) - Plot of $\log \phi$ Vs $1/T$

$[\text{Allylurea}] = 5.66 \times 10^{-3}$ mol. dm$^{-3}$
Figure 28 (b) - Plot of log ϕ vs 1/T

[Phenylurea] = 5.00 \times 10^{-3} \text{ mol. dm}^{-3}
Figure 29(a) - Plot of log $\phi$ vs $1/T$
[Thiourea] = $1.06 \times 10^{-3}$ mol dm$^{-3}$

Figure 29(b) - Plot of log $\phi$ vs $1/T$
[Thiourea] = $5.00 \times 10^{-3}$ mol dm$^{-3}$
Figure 30(a) - Plot of $\log \phi$ vs $1/T$

$[\text{Allylthiourea}] = 1.66 \times 10^{-3}\text{ mol. dm}^{-3}$

Figure 30(b) - Plot of $\log \phi$ vs $1/T$

$[\text{Allylthiourea}] = 5.00 \times 10^{-3}\text{ mol. dm}^{-3}$
Figure 31 - Plot of $1/\phi$ vs $1/\text{[Urea]}$
Acidity = 4.06

Figure 32 - Plot of $1/\phi$ vs $1/\text{[Allylurea]}$
Figure 33 - Plot of $1/\phi$ vs $1/[\text{Phenylurea}]$
Acidity = 4.06

Figure 34 - Plot of $1/\phi$ vs $1/[\text{Thiourea}]$
Acidity = 4.06
Figure 35 - Plot of $1/\phi$ vs $1/\text{[Allyli thiourea]}$

Acidity = 4.06
Figure 36 - Plot of $1/\phi$ vs $1/\text{[Reductant]}$

$H_3 = 7.52$

Figure 37 - Plot of $1/\phi$ vs $1/\text{[Reductant]}$

$H_8 = 7.59$
Symbols used in Text.

\( p \) = \( -\log \)  
\( pK_a \) = \( -\log k_a \)  
\( k_a \) = Dissociation constant.  
\( \text{pH} \) = \( -\log \) (Hydrogen ion).  
\( \text{O.D} \) = Optical density / absorbance.  
\( \text{OD}_a \) = Optical density of acidic form of the dye.  
\( \text{OD}_b \) = Optical density of basic form of the dye.  
\( \text{f} \) = Activity coefficient of dye.  
\( \phi/Q.Y. \) = Quantum yield.  
\( \phi_s \) = Quantum yield at infinite concentration.  
\( \phi_a \) = Quantum yield of highest acidity.  
\( \phi_b \) = Quantum yield of lowest acidity.  
\( \phi_{ic} \) = Quantum yield of internal conversion.  
\( \phi_{isc} \) = Quantum yield of intersystem crossing.  
\( \phi_{et} \) = Quantum yield of electron transfer process.  
\( \phi_{O_2} \) = Quantum yield of singlet oxygen production.  
\( \lambda \) = Wave length of the light.  
\( \lambda_{max} \) = Wave length of light for maximum absorption.  
\( \nu \) = Frequency of light.  
\( C \) = Velocity of light: \( 2.998 \times 10^8 \) m/sec.
nm = Nanometer : 10^{-9} meters.
I = Intensity of light.
I_0 = Intensity of incident light.
I_T = Intensity of transmitted light.
I_1 = Intensity of light behind front window.
I_2 = Intensity of light behind solution.
I_3 = Intensity of light behind back window.
I_a = Light absorbed by solution.
I_{at} = Light absorbed by solution in time t.
\alpha = Fraction of light lost at each window.
E = Energy of photons.
\epsilon = Molar extinction co-efficient.
\epsilon^* = Exponential extinction co-efficient=2.303\epsilon
\epsilon_{\text{max}} = Molar extinction co-efficient at maximum absorption of light.
d = Extinction of solution in intermediate acidity.
d_1 = Extinction of solution in extreme acidic solution.
D_2 = Extinction of solution in extreme basic solution.
D_0 = Photocell response on galvanometer when no cell is in the beam.
D_m = Photocell response on galvanometer when solvent is in the cell.
D_n = Photocell response on galvanometer when solution is in the cell.
D_a = The deflection equivalent of the light absorbed.
\(D_{ni}\) = The deflection equivalent of light when reaction starts.

\(D_{nt}\) = The deflection equivalent of light after time \(t\).

\(h\) = Planck's constant = \(6.627 \times 10^{-27}\) ergs sec.

\(N\) = Avogadro's number = \(6.02 \times 10^{23}\).

\(h_o\) = Acidity of the solution = active hydrogen ion concentration.

\(H_o\) = Hammett acidity function = -log \(h_o\).

\(L\) = Pathlength of the beam in cell.

\(V\) = Volume of the cell.

\(S-S\) = Singlet to singlet transmittance.

\(T-T\) = Triplet to triplet transmittance.

\(S_r\) = First singlet state.

\(S_2\) = Second singlet state.

\(T_1\) = First triplet state.

\(T_2\) = Second triplet state.

\(D\) = Ground state of dye.

\(D^*\) = Excited state of dye.

\(D_T^*\) = Triplet excited state of dye.

\(D^+\) = Monoprotonated dye.

\(D^{**}\) = Excited state of monoprotonated dye.

\(D^{t+}\) = Triplet state of monoprotonated dye.

\(D^3/D^t\) or \(D_t\) = Triplet state of dye.
D^1 / D_8 = Singlet state of dye.
M = Monomer of dye.
S_0 / D_H = Semiquinone of the dye.
3S* = Excited triplet state of semiquinone.
SD = Semi reduced dye.
DH_2 / L = Leuco dye.
MB = Ground state of methylene blue.
MBH^+ = Singly protonated state of methylene blue.
MBH^{++} = Doubly protonated state of methylene blue.
MBH^{+++} = Triply protonated state of methylene blue.
MB^+ = First excited state of methylene blue.
MBH^0 = Basic form of methylene blue.
MBH^' = Intermediate radical of methylene blue.
MBH_2 = Leucodye.
MBH^r_3 = Singlet state of monoprotonated methylene blue.
MBH^r_T = Triplet state of monoprotonated methylene blue.
MBH^{++}_2T = Triplet state of diprotonated methylene blue.
LMB = Leuco methylene blue.
Th^+ = Ground state of Thionine.
3Th^' = Triplet state of monoprotonated thionine.
3Th^{+2} = Triplet state of diprotonated thionine.
HDH = Hydrogen atom adduct.
AHi = Reductant.
u = Urea.
Au = Allylurea.
Pu = Phenylurea.
Tu = Thiourea.
ATu = Allythiourea.
[Red]/[AHi] = Concentration of electron donor.
V0 = Velocity of the reaction.
fB = Activity co-efficient of base indicator.
fBM = Activity co-efficient of protonated forms of base indicator.
f(H+) = Activity co-efficient of hydrogen ion.
k, k1, k2 = Dissociation constants.
k = Rate constant of semi-reduced dye.
kd = Rate constant of disproportionation of semidye.
kL = Rate constant of leucodye.
kε = Rate constant of electron transfer reaction.
kq = Rate constant for semi-quinone formation.
k1 - k10 = Rate constants for different process of the reduction of methylene blue.
kA & kB = Rate constants for different processes of the reduction of methylene blue.
kR (μ) = Reactive rate constant.
\[ k_s (\mu) = \text{Overall rate constant.} \]

\[ E = \text{Free energy of activation} \]

\[ \Delta H^* = \text{Enthalpy change} \]

\[ \Delta G^* = \text{Free energy change} \]

\[ \Delta S^* = \text{Entropy change} \]
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REFERENCES


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