PHOTOCHEMISTRY

THE PHOTO-INDUCED OXIDATION OF 2-PROPANOL AND METHANOL BY HYDROGEN PEROXIDE IN NEUTRAL AQUEOUS SOLUTIONS

A thesis submitted to the Faculty of
Graduate Studies and Research, University
of Manitoba, in partial fulfillment of the
requirements for the degree of
MASTER OF SCIENCE

by

Patrick Gregory Huminicki
Winnipeg, Manitoba
September, 1978.

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Patrick G. Huminicki

ABSTRACT

The photo-induced oxidation of 2-propanol by hydrogen peroxide in neutral deaerated aqueous solution has been investigated. Under these conditions 2-propanol is oxidized to acetone. The yields are linearly dependent on 2-propanol concentration in the range 0.10 M to 1.0 M 2-propanol and show a reciprocal square root effect on the ultraviolet light intensity.

A mechanism analogous to the mechanism used to explain the radiation chemical results is used to explain these results. Initially, OH radicals abstract hydrogen atoms from 2-propanol to form either $(CH_3)_2\dot{C}OH$ or $CH_3CHOH\dot{C}H_2$. Acetone is formed by the reaction of $(CH_3)_2\dot{C}OH$ with H_2O_2.

$$(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + OH$$

The radical $CH_3CHOH\dot{C}H_2$ may abstract the α -hydrogen from 2-propanol or undergo a bimolecular termination reaction:

$$CH_3CHOH\dot{C}H_2 + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH$$

$$2\ CH_3CHOH\dot{C}H_2 \rightarrow \text{2,5-Hexanediol, or } (CH_3)_2CO + (CH_3)_2CHOH$$

The photo-induced oxidation of methanol was studied to see if the results are similar to those for 2-propanol. Methanol is oxidized to formaldehyde. For methanol which can form only one kind of radical ($\dot{C}H_2OH$) the yields are independent of methanol concentration and show a reciprocal square root effect on the ultraviolet light intensity. The contrast with the results from 2-propanol is clearly evident.

The results and conclusions of this study are consistent with the results of the previous investigation employing γ -radiation for initiation.

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1. INTRODUCTION

1.1 Some Photochemistry

Photochemistry is the section of science that is associated with the study of chemical processes that are produced in a system when nonionizing electromagnetic radiation is absorbed. The radiation which is of general interest to photochemists ranges from the ultraviolet region through the visible to the infrared region of the electromagnetic spectrum. The wavelength of the radiation in this range is from approximately 100 nm to 1000 nm. The energy that is associated with wavelengths in this range is similar to the magnitude of chemical bond strengths. In the region above 1000 nm the radiation energy is too small to cause an electronic excitation of an atom or a molecule or dissociation of an atom or group of atoms from a molecule. In the region below 100 nm the energy of the radiation is large enough to cause ionization and is to be considered in the field of radiation chemistry.

Electromagnetic radiation is known to travel in the form of wave packets or quanta each having associated with it a discrete amount of energy determined by the equation $E = h\nu$, where h is Planck's constant and ν is the frequency of the electromagnetic radiation determined by $\nu = c/\lambda$, where c is the speed of light and λ is the wavelength of the radiation. Therefore the energy range associated with the region of the electromagnetic spectrum from 100 nm to 1000 nm is 1.2×10^{13} erg einstein^{-1} to 1.2×10^{12} erg einstein^{-1} respectively, where an einstein is defined as a mole of quanta.

Since molecules and ions absorb photons on a one to one basis, the amount of light absorbed by a sample is directly proportional to the concentration of the molecules in the sample that can absorb light of that frequency. That is the decrease in intensity of the monochromatic light as it passes through a homogeneous absorbing region should be related to the number of absorbing molecules in the region.

This behavior is described by a logarithmic relation known as the Beer-Lambert Law. The more familiar version of the relation is written

$$A = \log_{10} \frac{Io}{I_t} = \epsilon c l$$

where Io is the intensity of the source of monochromatic light representing the number of einsteins of light incident per unit time at the front of a column of a single absorbing species, c is the concentration of that species in units mole l^{-1}, and l is the path-length of the sample in cm through which the light passes in the sample cell. I_t is the intensity of the emergent light and ϵ is the molar extinction coefficient with units mole^{-1} l cm^{-1} which is a characteristic number for each kind of molecule at a given wavelength λ.

The fundamental principle governing photochemical reactions of molecules and the absorption of quanta of energy was stated by Einstein "Each quantum of radiation absorbed by a molecule activates one molecule in the primary step of a photochemical process" and is called the principle of quantum activation. This is summarized by the reaction

$M + h\nu \rightarrow M^*$ where M represents an absorbing species, $h\nu$ the energy of a quantum of radiation, and M^* the activated molecule.

It is essential to note that the primary step of light absorption by a species does not necessarily lead to a chemical reaction. The excited molecule may become deactivated through several modes of decay one of which is the chemical reaction of interest.

Consider the general reaction of a molecule M^* which undergoes photodecomposition by the primary process

$M^* \rightarrow A + \text{other products}$

where A is the particle of interest formed as the immediate effect of light absorption by M. The rate of the primary photochemical process is written as:

$$\frac{d[A]}{dt} = \phi a Ia$$

and ϕa called the primary quantum yield is the number of particles of A produced per quantum absorbed by M and has units mole einstein^{-1} or particles quantum^{-1}. Ia is the rate of energy absorption.

While ϕa refers to the number of particles of the species that are produced in the primary step following light absorption, a second quantity called the chemical quantum yield, $\phi(x)$, of a photochemical reaction is the number of molecules of reactant consumed or product formed per quantum of light absorbed. The value $\phi(x)$ can exceed unity and in many cases does in chain reactions.

The value of $\phi(x)$ can be determined by the expression

$\phi(x) = \frac{d[x]}{dt\ Ia}$ where $\frac{d[x]}{dt}$ is the rate of change of concentration with time and Ia the energy absorbed. A high value for $\phi(x)$ indicates that many molecules are formed or used up per quantum of light absorbed.

1.2 Previous Studies on Free Radical Induced Oxidation of Simple Organic Solutes.

Metal Ion / H_2O_2 Initiation

The oxidation of 2-propanol and methanol in aqueous solution has been studied by Merz and Waters (1) using Fenton's reagent.

The mechanism proposed for the oxidation of the alcohols — methanol, ethanol and 2-propanol — by hydrogen peroxide in the presence of excess ferrous salt was as follows:

Initiation:

{ 1 } $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$

Oxidation chain:

{ 2 } $RCH_2OH + OH \rightarrow R\dot{C}HOH + H_2O$

{ 3 } $R\dot{C}HOH + H_2O_2 \rightarrow RCHO + OH + H_2O$

Low alcohol termination:

{ 4 } $Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-$

High alcohol termination:

{ 5 } $2\ R\dot{C}HOH \rightarrow RCHO + RCH_2OH$

This mechanism was proposed to explain how polyhydric alcohols, α-hydroxy acids, and carbohydrates may be rapidly oxidized by hydrogen peroxide in the presence of ferrous salts as shown by Fenton.

The reactions of simple organic solutes with the Fenton and Ti(III)/H_2O_2 systems have recently been studied using fast flow e.s.r. techniques. The reaction of Ti(III) ions with hydrogen peroxide produces hydroxyl radicals (2) by a reaction analogous to that of the Fenton system.

Thermal Initiation

Burghart, *et al*, (3) have investigated a system where oxygen-free nitrogen was passed through 2-propanol containing hydrogen peroxide at 78°C. They observed that the concentration of H_2O_2 and 2-propanol decreased rapidly and acetone was produced. Burghart, *et al*., concluded that both the reaction of 2-propanol with H_2O_2 and the decomposition of H_2O_2 followed a free radical chain mechanism shown as follows:

{6} $H_2O_2 \xrightarrow{\text{thermal}} 2\ OH$

{7} $OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O$

{8} $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + OH + H_2O$

No termination of the oxidative chain was proposed for the deoxygenated system. In an oxygenated system termination would occur by the reaction:

{9} $(CH_3)_2\dot{C}OH + O_2 \rightarrow (CH_3)_2CO + HO_2$

which also leads to inhibition of the chain.

Photochemical Initiation

Barrett, et al., (4) investigated the photolysis of hydrogen peroxide in aqueous alcohol solutions. The initiation reaction was given as

{6} $H_2O_2 \xrightarrow{h\nu} 2\ OH$

The hydroxyl radicals formed react entirely with the alcohol as follows: (using 2-propanol as an example)

{7} $(CH_3)_2CHOH + \dot{O}H \rightarrow (CH_3)_2\dot{C}OH + H_2O$

The propagating step was given as

{8} $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + OH$

with acetone being the product. The chain yield for peroxide removal reached a maximum value at an alcohol concentration near 2 M in the case of each alcohol. As the alcohol concentration was raised beyond

2 M in each case the chain yields diminished gradually to a minimum value in the pure alcohol.

Barrett,*et al*., attributed this decrease to a cage effect whereby the alcohol radicals may either diffuse from the cage and cause a chain decomposition of the peroxide or interact with one another within the original solvent cage by the following processes.

1) disproportionation

{10} $2(CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH$

or (2) dimerization

{11} $2\ (CH_3)_2\dot{C}OH \rightarrow$ diol

As the alcohol concentration is increased beyond 2 M the alcohol radicals tend to interact preferentially within the cage, therefore fewer radicals diffuse from the cage to react with hydrogen peroxide with a resultant decrease in the quantum yield for disappearance of H_2O_2. Barrett also reported that results for methanol where "similar" to those for the photo-initiated reaction of hydrogen peroxide with ethanol but included no data for methanol.

Radiation Chemical Initiation

The effect of γ-rays on oxygen-free solutions containing ethanol and hydrogen peroxide were studied by Seddon and Allen (27). The ethanol concentration was varied from 1.75×10^{-3} M to 10.5×10^{-3} M and the concentration of H_2O_2 was varied from 1.22×10^{-4} M to

1.97×10^{-4} M. During these irradiations hydrogen peroxide disappeared with a very high yield, evidently by a chain reaction with the alcohol. Such a chain would be expected from the following reactions:

{13} $H_2O \rightarrow e^-_{aq}, H, OH, H_2O_2, H_2, H_3O^+, OH^-_{aq}$

{35} $H + C_2H_5OH \rightarrow CH_3\dot{C}HOH + H_2$

{36} $OH + C_2H_5OH \rightarrow CH_3\dot{C}HOH + H_2O$

{37} $e^-_{aq} + H_2O_2 \rightarrow OH + OH^-$

{38} $CH_3\dot{C}HOH + H_2O_2 \rightarrow CH_3CHO + H_2O + OH$

{39} $2\ CH_3\dot{C}HOH \rightarrow$ diol or $CH_3CHO + C_2H_5OH$

This reaction scheme predicts the yield of peroxide disappearance should rise linearly with the H_2O_2 concentration and the reciprocal square root of the intensity and should be independent of the alcohol concentration. Results obtained by Seddon and Allen showed that these points were followed. Seddon and Allen concluded that disproportionation to acetaldehyde and ethanol occurs in about 30% of the chain-breaking reactions. Taub and Dorfman (28) estimate about 20%.

Irradiation of deaerated aqueous solutions of 10^{-2}M 2-propanol and 10^{-2} M N_2O have been done by Allan and Beck (5) in order to determine the primary yields of hydrogen atoms and hydrated electrons. They found that H_2O_2 reached a low steady-state concentration in the dose range investigated (doses $< 10^{17}$ e.v./ml), and increased with increasing dose rate, high yields of acetone, and non-linearity of the acetone yield dose dependencies. They accounted for the disappearance of H_2O_2 by a chain process initiated by the reaction of the radical

$(CH_3)_2\dot{C}OH$ with H_2O_2:

{8} $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + OH$

which also accounts for the high yields of acetone and the non-linearity of the acetone yield-dose dependencies observed for solutions irradiated at low dose rates.

Allan and Beck have suggested that the OH radical may not react specifically at the α position of 2-propanol.

{7} $OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O$

{12} $OH + (CH_3)_2CHOH \rightarrow CH_3\dot{C}H_2CHOH + H_2O$

The fate of the α -radical is determined by the propagation reaction {8} or a disproportionation reaction forming acetone and 2-propanol.

{10} $2(CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH$

The diol from the combination of 2 α radicals, {11} was not observed as a product.(6) Allan and Beck do not discuss possible reactions of the β -radical formed in {12}.

Burchill and Ginns (7) have investigated the radiation-induced oxidation of 2-propanol by hydrogen peroxide in neutral deaerated aqueous solutions. They found that the rate of H_2O_2 reduction is independent of its concentration in the range 5×10^{-2} M to 10^{-3} M H_2O_2, a stoichiometric equivalence of acetone formation and peroxide reduction yields, and have demonstrated that both yields increase linearly with increasing alcohol concentration in the range 0.13 M to 1.05 M 2-propanol.

Dose-rate experiments also clearly showed an increase in G(Acetone) with decreasing dose-rate. Burchill and Ginns explained the chain reaction between 2-propanol and hydrogen peroxide by the following reaction scheme:

{13} $H_2O \rightarrow H_2,\ H_2O_2,\ H,\ OH,\ e^-_{aq},\ H_3O^+_{aq},\ OH^-_{aq}$

followed by,

{14} $H + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2$

{15} $H + (CH_3)_2CHOH \rightarrow CH_3CHOH\dot{C}H_2 + H_2$

{7} $OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O$

{12} $OH + (CH_3)_2CHOH \rightarrow CH_3CHOH\dot{C}H_2 + H_2O$

which contains the radicals $(CH_3)_2\dot{C}HOH$ and $CH_3CHOH\dot{C}H_2$. The radical $(CH_3)_2\dot{C}OH$ can undergo the propagation reaction,

{8} $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + OH$

Reaction 8 predicts that for each acetone molecule formed one peroxide molecule will be used, which was confirmed by the results.

The radical conversion reaction

{25} $CH_3CHOH\dot{C}H_2 + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH$

has been included in the reaction scheme and was suggested, in part, by the form of the experimental results. The linear dependence of the radiolytic yields on alcohol concentration suggests that the chain length is determined by the competition between a radical terminating reaction,

{17} $2\ CH_3CHOH\dot{C}H_2 \rightarrow$ 2,5-Hexanediol or $(CH_3)_2CHOH + (CH_3)_2CO$

and the reaction of that radical $CH_3CHOH\dot{C}H_2$ with the 2-propanol {25}.

Chain termination by reaction {11} would lead to competition with the propagating reaction{ 8 }and would lead to some dependence of chain length on H_2O_2 which is inconsistent with the results. Burchill and Ginns considered the possibility of reaction {25} as the rate controlling propagation step, since this appears to predict the appropriate kinetic form of the results.

Summary

The most important features of the radical induced oxidation of simple alcohols, by hydrogen peroxide can be summarized as follows;

1) A simple reaction scheme has been used to explain experimental results. Using 2-propanol as an example:

{6} $H_2O_2 \xrightarrow{h\nu} 2\ OH$

{7} $OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O$

{8} $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + OH$

{10} $2(CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH.$

2) An expression for the rate of acetone formation can be derived using the usual steady state approximations.

{18} $$\frac{d}{dt}\left[(CH_3)_2CO\right] = k_8 \left(\frac{\phi_6 Ia}{k_{10}}\right)^{1/2} H_2O_2$$

3) The expression predicts that the rate of acetone production is;

i) dependent upon H_2O_2 concentration,

ii) dependent upon the rate of energy absorption,

iii) independent of alcohol concentration.

4) Studies of the γ -radiation induced chain oxidation of aqueous 2-propanol by Burchill and Ginns (7) show clearly a dependence of yields on the concentration of 2-propanol and, at low alcohol concentrations, no dependence of H_2O_2 concentrations, which is inconsistent with the simple reaction scheme described above. Burchill and Ginns have done extensive studies on the γ -radiation initiated oxidation of 2-propanol and methanol by H_2O_2 in aqueous solution. The reaction scheme they proposed accounted satisfactorily for their results.

Barrett, et al.(4) had reported results for 2-propanol which are similar to those for radiation-initiated reactions of H_2O_2 with 2-propanol but had proposed a different mechanism to account for them. Barrett also reported that results for methanol were "similar" to the results obtained for 2-propanol but included no data for methanol. Results obtained by Burchill and Ginns (7), for the radiation-initiated reaction of methanol, in fact, show a significant difference in behavior from 2-propanol.

The primary purpose of this work was to determine whether or not results obtained by Barrett, et al., (4) for 2-propanol could be reproduced and if the mechanism proposed by Burchill and Ginns (7) could account qualitatively and quantitatively for the photo-initiated reactions. A secondary purpose was to see whether or not the results obtained by Barrett, et al., (4) for methanol were really "similar" to those for 2-propanol.

If the experimental results for both 2-propanol and methanol are comparable using both γ -irradiation and photo-initiation, this would lend support to the reaction scheme proposed by Burchill and Ginns (7) and rule out any explanation based on the phenomena peculiar to photochemistry, such as "cage effects" as used in Barrett's explanation for his results.

2. EXPERIMENTAL

2.1 Materials

Triply distilled water was prepared by first distilling laboratory distilled water from an alkaline potassium permanganate solution and then secondly from an acid potassium dichromate solution, through a 60cm reflux column filled with pyrex cut glass tubing. The distillation set up is described by Hickling (8).

2-propanol (Fisher Certified) used for preparing the stock irradiation solutions was used without further purification.

Methanol (Fisher Certified) was also used as received.

Hydrogen Peroxide (Fisher Certified) was supplied in 30% unstabilized aqueous solution and diluted as required.

Potassium Ferrioxalate $K_3Fe(C_2O_4)_3.3H_2O$ was prepared by mixing solutions of 1.5 M $K_2C_2O_4$ and 1.5 M $FeCl_3$ in a 3:1 ratio. The resulting precipitate was recrystallized three times from warm water and was dried in a current of warm air (45°C). The solid, being photosensitive to visible light while wet, was prepared and stored in a dark room.

All other chemicals used for actinometry and spectrophotometric analysis were of reagent grade quality and were used as received.

2.2 Reaction Vessel

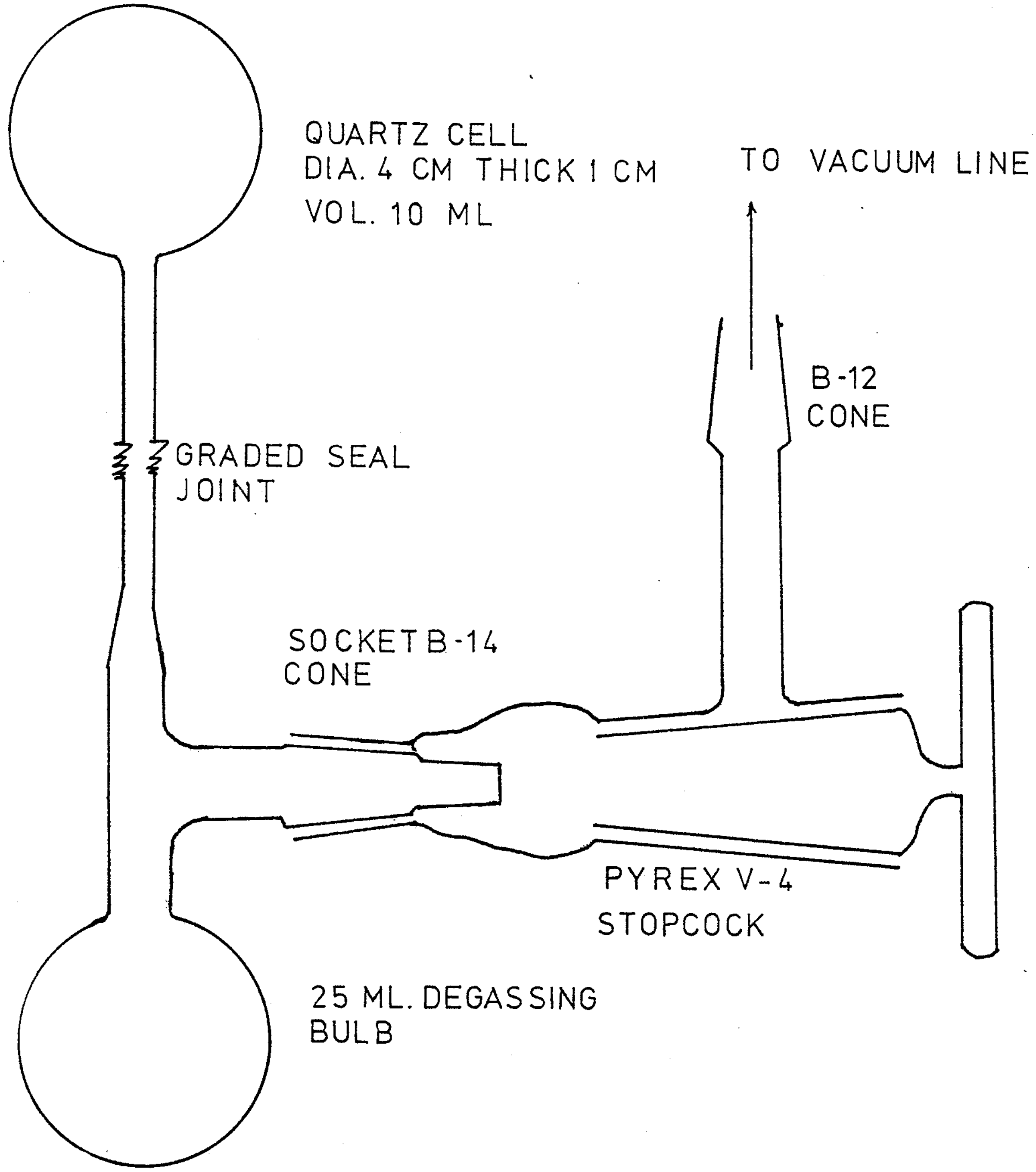
One end of the cell consisted of a pyrex bulb of 25ml volume. The other end consisted of a cylindrical quartz optical cell with a 1.00cm path length and a diameter of 4.00cm. This was attached to the 25ml bulb by means of a graded seal. The volume of the optical cell was 10ml, (Figure 1).

2.3 Ultraviolet Source and Optics

The source of the ultraviolet light was a Hanovia Z1500 - 108 mercury low pressure lamp shaped in the form of a flat spiral. The lamp was also designed to absorb the 184.9nm line from the mercury emission spectrum by means of a Vycor envelope. The lamp was surrounded by a black metal rectangular box used as a safeguard against high voltage and biologically destructive ultraviolet light. Within the box the lamp was fastened to an aluminum metal support which in turn was secured to a Cenco optical bench. Light for experimentation purposes was allowed to pass through a 4cm diameter opening cut out of one side of the box and fitted with a manually operated shutter which could be opened or closed rapidly. The moveable quartz cell holder was fastened at the desired distance from the lamp and consisted of a collimator 4cm in diameter, on the side of which was fastened a V-shaped cavity into which the quartz cell

Fig. 1

Reaction Vessel


QUARTZ CELL
DIA. 4 CM THICK 1 CM
VOL. 10 ML
TO VACUUM LINE
B-12
CONE
GRADED SEAL
JOINT
SOCKET B-14
CONE
PYREX V-4
STOPCOCK
25 ML. DEGASSING
BULB

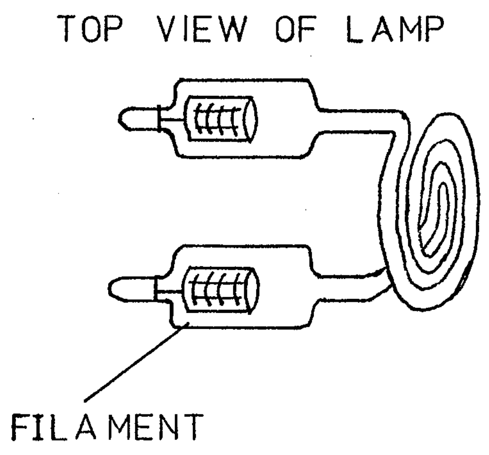
could be firmly positioned. The cell holder was designed such that when the cell was placed in the cavity it was forced flush against the collimator so that all the light passing through the collimator would also pass through the cell. To minimize the inhomogeneity of the light reaching the cell, the cell holder was kept at a distance of approximately 20cm from the mercury resonance lamp. Power and current to the lamp was maintained by a transformer and current regulator produced by Englehard Industries. When placed in series with the lamp a constant current of 60 milliamperes could be maintained. The current was constantly monitored by means of an ammeter in the circuit. Heat produced by the lamp was not regulated as the manufacturer felt this was unnecessary.

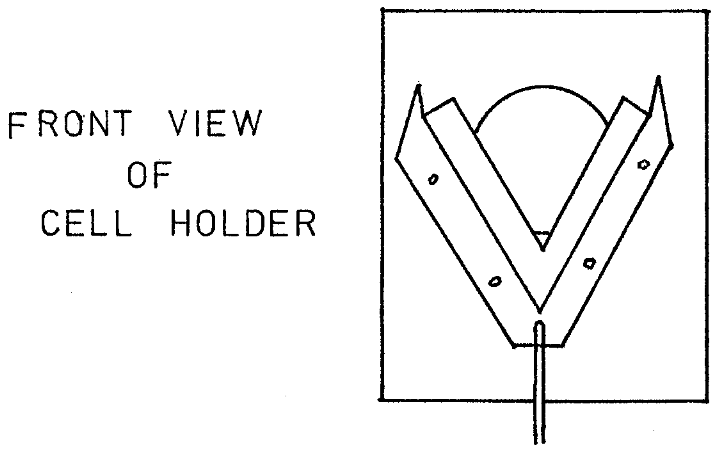
For experiments that required variations in the light intensity the following procedure was followed. First the cell holder was moved closer to the light source. Then a collimator with a 4cm diameter opening was placed between the cell holder and the light source. The opening of the collimator was covered with wire gauze which reduced the intensity of the light reaching the cell. Further reductions in light intensity were accomplished by adding additional layers of wire mesh over the opening in the collimator. Each layer of wire mesh was found to reduce the light intensity by about 40% when placed over the opening of the collimator. A diagram of the operational experimental apparatus is shown in figure (2).

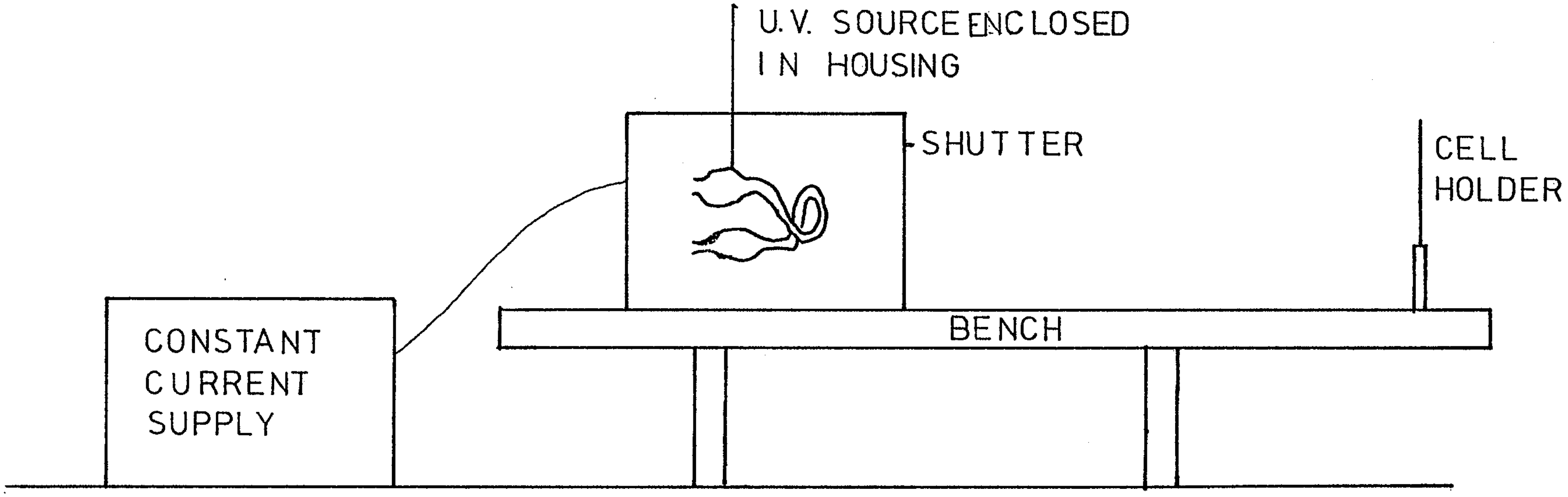
Fig. 2

Ultraviolet source

and optics


TOP VIEW OF LAMP
FILAMENT


FRONT VIEW
OF
CELL HOLDER


U.V. SOURCE ENCLOSED
IN HOUSING
SHUTTER
CELL
HOLDER
CONSTANT
CURRENT
SUPPLY
BENCH

2.4 General Considerations

Precautions were taken to counter possible experimental problems. First the light beam may be non-homogeneous. If this happens the rate of chemical reaction will vary from region to region within the reaction cell. This type of problem must be especially guarded against in the experiments undertaken in this work. The reactions studied are chain reactions and the chemical quantum yields of the products are nonlinearly dependent on some power of the light intensity. This problem can be minimized if care is taken to limit the absorption of the absorbing media to less than 50% (9). In this study this precaution was utilized. The absorbing medium was made to absorb only 38% of the light.

Non-homogeneity associated with the spacial distribution of the light source was reduced by placing the reaction cell a sizeable distance from the light source. This gave light originating from any part of the source approximately the same path length to any part of the reaction cell.

Secondly the apparatus was designed to make the light reaching the photochemical cell approximately parallel. This was accomplished by placing the reaction cells far from the light source. In addition, reaction cells with a short path length, 1.00cm, were used. This meant that any non-parallel light reaching the cell essentially traversed the entire length of the cell.

Lastly, reduction of the absorbing species, if carried out too far, would cause a decrease in I_a, which in turn would be accompanied by a change in the overall quantum yield for an intensity dependent chain reaction. Experimentally this problem was essentially resolved by preventing the reduction of the absorbing species from being carried out further than 10%.

2.5 Sample Preparation

All glassware used for experimental work was cleaned thoroughly by the following method:
The glassware was first cleaned by rinsing with a solution made by adding a few crystals of potassium permanganate to concentrated sulphuric acid, and then with a solution of concentrated nitric acid to which a small volume of hydrogen peroxide had been added. Finally the glassware was rinsed several times with each of tap water, distilled water and triply distilled water. After cleaning, the irradiation cells were dried in a drying oven at about 100°C before they were filled with the sample to be irradiated.

A stock solution was prepared by the following procedure:
An aliquot of 30% unstabilized hydrogen peroxide was transferred to a 100ml volumetric flask. The organic solute such as 2-propanol, of the correct volume, was pipetted into the same volumetric flask. The organic solute was added volumetrically in most cases, but in some

cases where the volume was small, or the organic solute too volatile, the solutes were weighed directly into the volumetric flask. The solution was then brought up to volume by the addition of triply distilled water.

Ten ml aliquots of the stock solution to be irradiated were pipetted into the degassing bulbs of the irradiation cells. Six samples to be irradiated were normally prepared. Each cell was sealed with "Apiezen N" grease and the vessels were attached by a tap assembly to a vacuum line for degassing. The vacuum line was constructed of all pyrex glass tubing with a mechanical vacuum pump and a mercury diffusion pump. Each sample was degassed by freezing the sample in a solid carbon dioxide/acetone slush, pumping, and then thawing. Four freeze-pump-thaw cycles were all that were required to complete the degassing of the samples. Each cell was then inverted so that all of the liquid sample in the degassing bulb flowed into the optical cell. The degassed samples were placed in the cell holder directly in front of the housing containing the ultraviolet lamp. The samples were irradiated at room temperature for the appropriate length of time by opening and closing the shutter mechanism. On completion of the irradiation aliquots were immediately removed for analysis.

2.6 Analytical Techniques

Spectrophotometric techniques of analysis were used. At room temperature measurements were made using a Carl Zeiss PMQ II spectrophotometer.

Acetone

The method used to determine acetone, the chief product from the oxidation of 2-propanol, was that reported by Berntsson (10). To an aliquot of standard acetone or irradiated solution in a 25ml flask, 1ml of NaOH solution (106.25g/250ml) was added. After diluting to about 10mls with triply distilled water 0.25ml of salicylaldehyde was added followed by another 10mls of NaOH solution. The solution was made to volume with triply distilled water. The mixture was shaken to obtain complete mixing and allowed to stand for two hours for color development. The absorbance was read at 474 nm against a water blank. A calibration curve using Fisher Certified acetone was linear over the concentration range used (Figure 3). An extinction coefficient of $1.79 \times 10^{4} M^{-1} cm^{-1}$ was determined. The presence of 2-propanol had no measurable effect on the extinction coefficient.

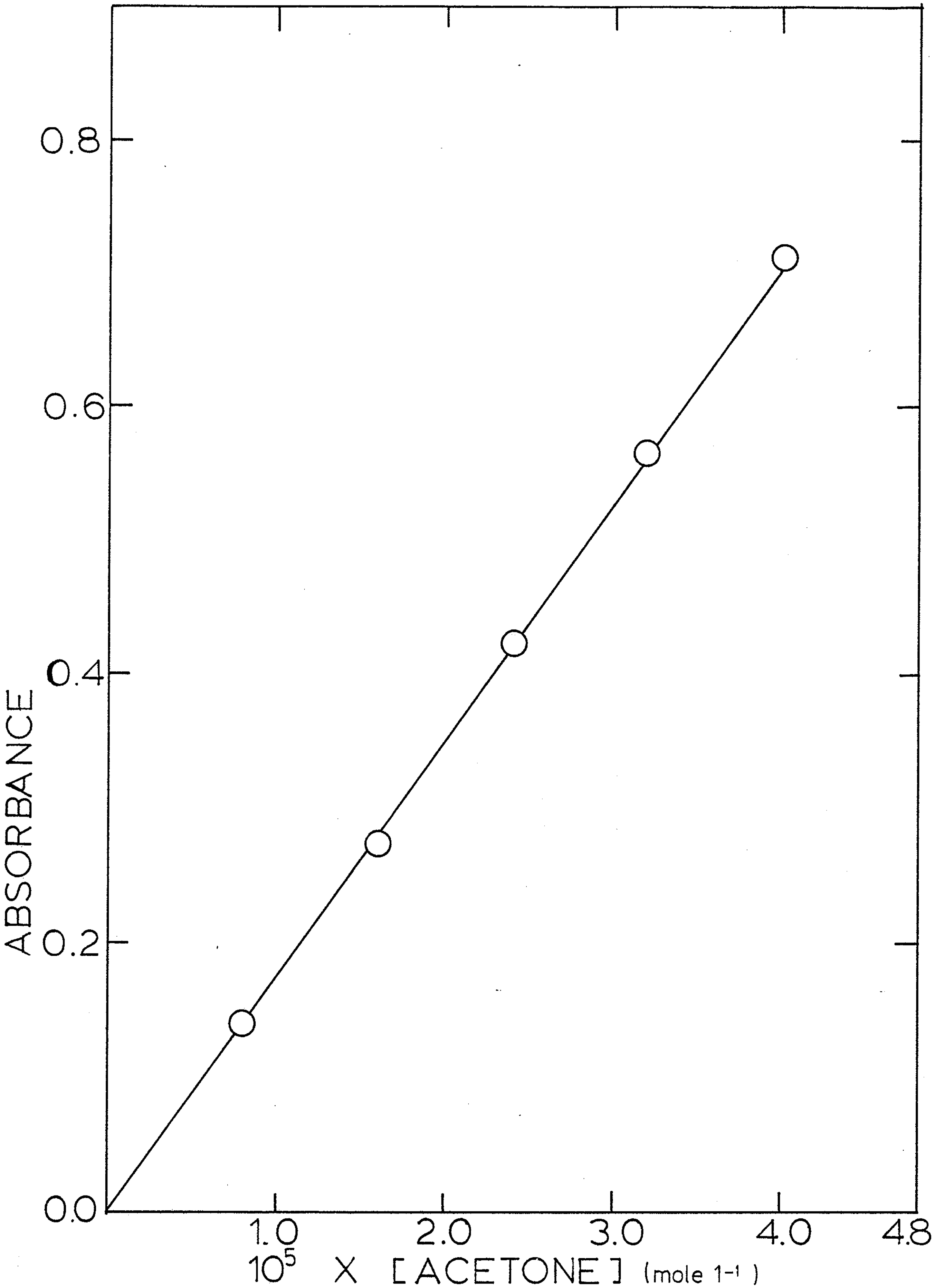
Formaldehyde

The method used for the determination of formaldehyde, produced from the oxidation of methanol, was that reported by Bricker and Johnson (11). Aliquots (0.25ml) of chromotropic acid solution, made by dissolving 2.5 grams of dry powder in 25ml of water, were added to

Fig. 3

Variation of absorbance with acetone concentration for the calibration of acetone in salicylaldehyde, measured at 474 nm.

(23a)



various quantities of stock formaldehyde solutions in 18 x 150mm glass stoppered test tubes. Concentrated sulphuric acid, (2.5ml), was slowly poured into each of the test tubes with continuous shaking. The test tubes were then stoppered and placed in a beaker of boiling water for thirty minutes. The test tubes and their contents were cooled and the contents quantitatively transferred into 25ml volumetric flasks. The volumes were adjusted to 25ml with triply distilled water and allowed to reach room temperature. The absorbance of each solution was read at 570 nm against a reagent blank. Calibration curves using (40% w/v HCHO U.S.P.) resulted in a measured extinction coefficient of $1.54 \times 10^4 M^{-1} cm^{-1}$ (Figure 4).

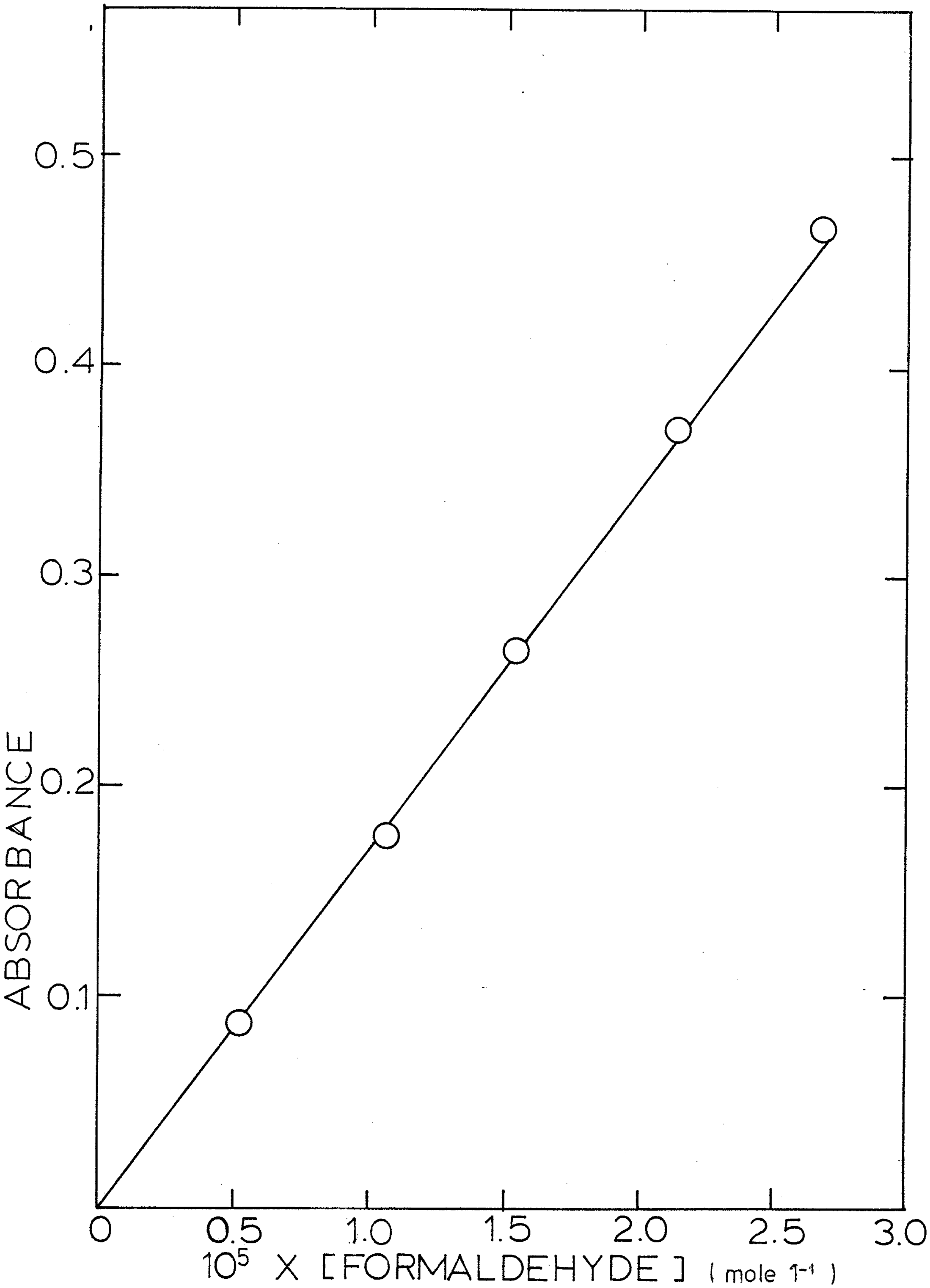
The chromotropic acid (technical reagent) was purified before use, by dissolving 10 grams in 100ml of water, filtering off the insoluble material, evaporating the filtrate to 3 to 10 ml, and then adding about 250ml of ethanol. A nearly white crystalline material separated, was collected and dried, then used in the preparation of the chromotropic acid reagent solution.

Hydrogen Peroxide

The method used for the determination of hydrogen peroxide was that reported by Allen, *et al*., (12) 5ml of potassium hydrogen phthalate reagent, made by adding 12.5g of the solid to enough water to produce 500ml of solution, was added to an aliquot of standard peroxide solution

Fig. 4

Variation of absorbance with formaldehyde
concentration for the calibration of
formaldehyde in chromotropic acid
measured at 570 nm.


ABSORBANCE
0.1
0.2
0.3
0.4
0.5
0
0.5
1.0
1.5
2.0
2.5
3.0
10^5 X [FORMALDEHYDE] (mole l^{-1})

or irradiated solution in a 25ml volumetric flask. To this 5ml of iodide reagent, made by adding 45.5g KI, 1.25g NaOH, 0.125g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ to enough water to make 500ml of solution, was added and the mixture made to volume with triply distilled water and shaken. The solution was measured spectrophotometrically at 350 nm against a reference identical to the solution but lacking in hydrogen peroxide. The solutions did not have to stand for color development, since this took place almost instantaneously. The substance measured was the triiodide ion, I_3^-, produced by the reaction,

$$\{19\} \quad H_2O_2 + 3I^- + 2\,H_3O^+ \rightarrow 4\,H_2O + I_3^-$$

Calibration curves resulted in a measured extinction coefficient $2.09 \times 10^4 M^{-1} cm^{-1}$. The Beer-Lambert plot is shown in figure (5). Peroxide solutions were standardized volumetrically against standard ceric sulphate using ferroin indicator.

2.7 Actinometry

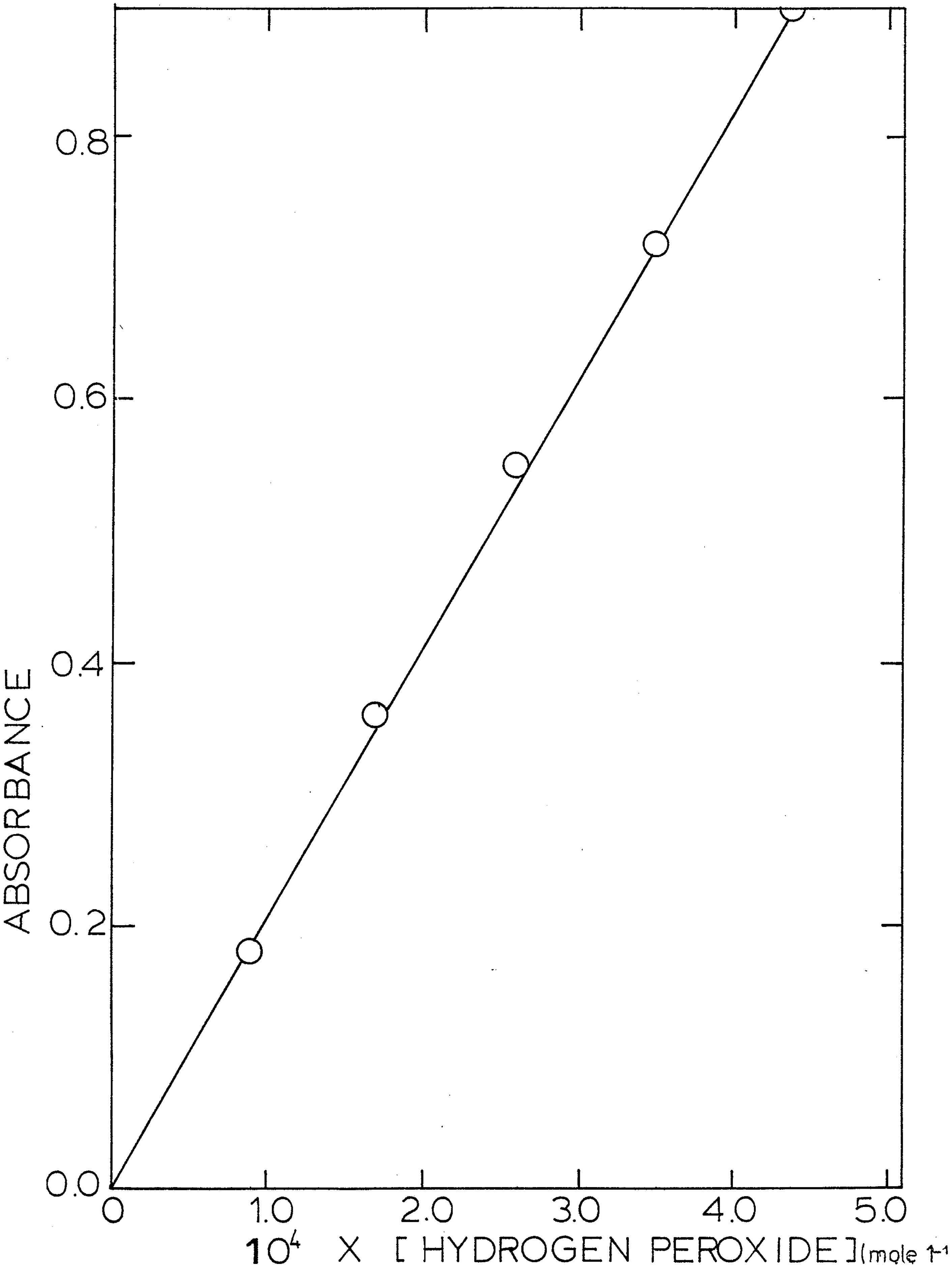
The incident radiation intensities from the ultraviolet source were measured using the ferrioxalate method devised by Hatchard and Parker (13). The reaction of concern is the photochemical decomposition of potassium ferrioxalate to ferrous oxalate in acid solution

$$\{20\} \quad 2\,Fe(C_2O_4)_3^{3-} + h\nu \rightarrow 2\,FeC_2O_4 + 3\,C_2O_4^{2-} + 2\,CO_2 \quad (14)$$

The intensity of the light source is related to the concentration of the ferrous ion formed.

Fig. 5

Variation of absorbance with hydrogen
peroxide concentration for the
calibration of hydrogen peroxide
measured at 350 nm.


ABSORBANCE
0.0
0.2
0.4
0.6
0.8
0
1.0
2.0
3.0
4.0
5.0
10⁴ X [HYDROGEN PEROXIDE](mole l⁻¹

The method may be used for radiation with wavelengths ranging from 253.7 nm to 480.0 nm. The quantum yield for 253.7 nm is 1.25. A solution containing 6.0×10^{-3} moles of potassium ferrioxalate per litre of 0.20 M H_2SO_4 solution will absorb all the radiation incident on a cell of 1cm path length.

The majority of the light emitted from the mercury resonance lamp is of wavelength 253.7 nm, but a small amount is in the visible region. Hydrogen peroxide in solution does not absorb radiation in the visible region but the ferrioxalate solution is photosensitive in the visible region. To determine the effect of the visible radiation on the actinometer solution, the solution was first irradiated directly from the ultraviolet source. Then a pyrex glass plate about 5mm thick was fixed in the path of the beam resulting in the absorption of the 253.7 nm wavelength before the beam reached the actinometer solution. By subtracting the ferrous ion yield with the use of the filter from that obtained without the use of a filter and carrying out the calculations the value for the intensity of wavelength 253.7 nm was obtained.

The irradiations were carried out in silica cells, cylindrically shaped, 4.00cm in diameter and path length 1.00cm. The volume of the actinometer solution used was 10ml, thus duplicating the volumes used in the irradiation of the alcohol/hydrogen peroxide solutions. No stirring mechanism was employed since only about 10% of ferrioxalate complex was decomposed.

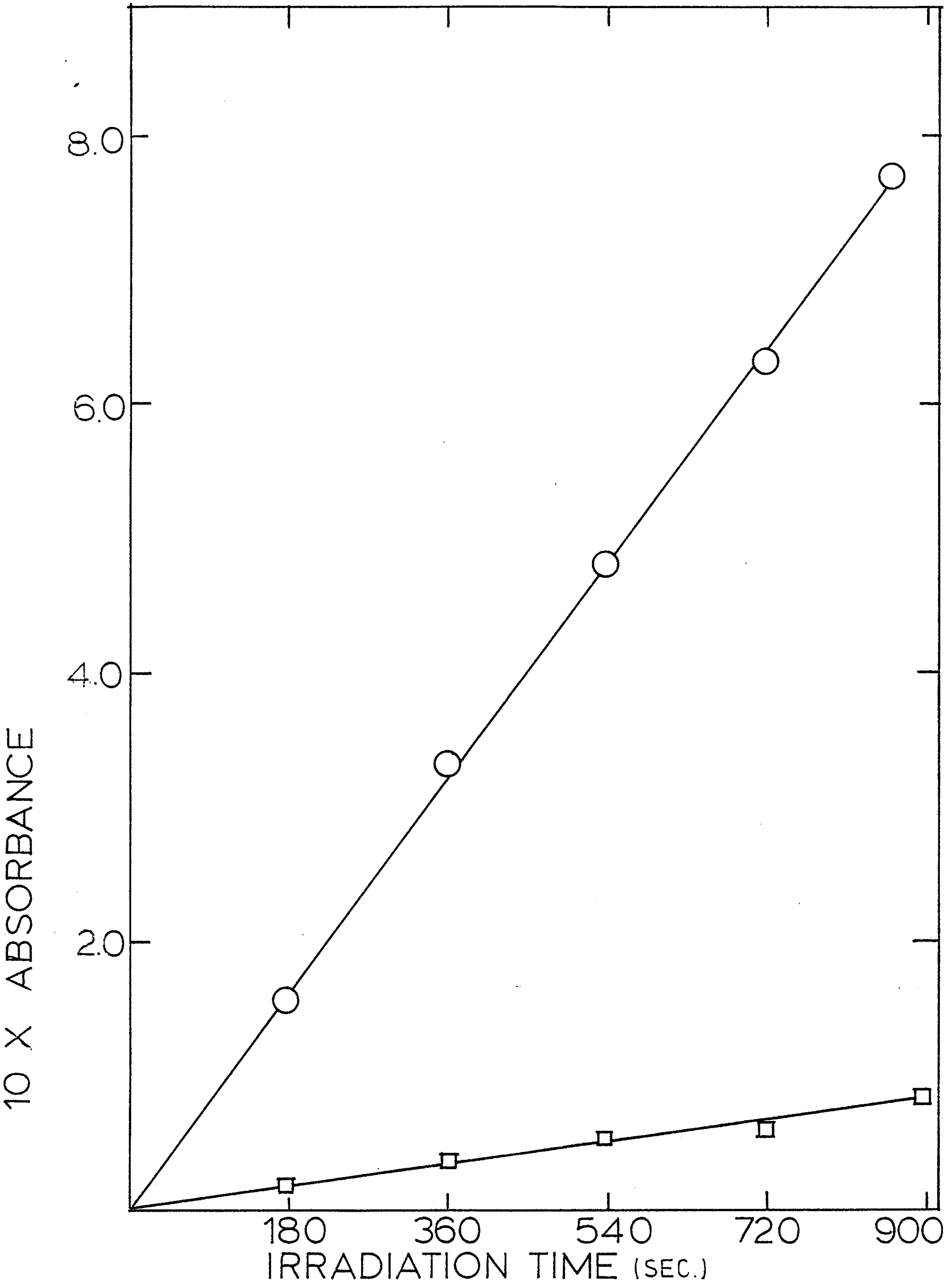
Preparation of the actinometer solution and method of ferrous ion determination is outlined as follows: The potassium ferrioxalate was prepared in a dark room as described previously in this chapter. A 6.0 x 10^{-3} M ferrioxalate solution in 0.20 M H_2SO_4 was prepared. 10ml aliquots of the solution were then irradiated and the ferrous ion determined as follows. A 3ml aliquot of the irradiated solution was added to a 25ml volumetric flask. To this was added 2ml of a 0.1% aqueous solution of 1, 10-phenanthroline. Then 2ml of a solution 6 M in sodium acetate and 0.2 M in H_2SO_4 was added to buffer the solution to a PH of 3.5. The solutions were diluted to 25ml with water and allowed to stand for thirty minutes, then measured spectrophotometrically at 510 nm in 1.00cm cells against an unirradiated blank. Because of the sensitivity of the ferrioxalate to light, all actinometry experiments were carried out in a dark room illuminated with a red photographic safe light. The results of a typical analysis are tabulated in table (I) and shown graphically in figure (6).

Table I

(A) Direct Irradiation			(B) Pyrex Plate Filter		
Sample No.	Irradiation Time (sec)	Absorbance	Sample No.	Irradiation Time (sec)	Absorbance
1	180	0.156	1	180	0.019
2	360	0.327	2	360	0.036
3	540	0.476	3	540	0.053
4	720	0.626	4	720	0.060
5	900	0.768	5	900	0.081

Fig. 6

The reduction of Fe$(C_2O_4)^{3-}$ solutions
containing 6.0 x 10^{-3} M Fe$(C_2O_4)^{3-}$
irradiated at 253.7 nm.


8.0
6.0
4.0
2.0
10 X ABSORBANCE
180
360
540
720
900
IRRADIATION TIME (SEC.)

The incident light intensity was calculated as follows:

{29} $$I_{253.7} = \frac{1}{\phi_{253.7}} \times \frac{1}{\epsilon} \times \frac{\Delta A}{\Delta t} \times \frac{25}{3}$$

$\phi_{253.7} = 1.25$ $\qquad$ $\epsilon = 1.12 \times 10^{4}$ 1 mole^{-1} cm^{-1}

{41} $$\frac{\Delta A}{\Delta t} = \frac{\Delta Aa}{\Delta t} - \frac{\Delta Ab}{\Delta t}$$

$$= 8.46 \times 10^{-4} - 0.82 \times 10^{-4}$$

$$= 7.64 \times 10^{-4} \text{ sec}^{-1}$$

$$\therefore I_{253.7} = \frac{1}{1.25} \times \frac{1}{1.12} \times 7.64 \times 10^{-4} \times \frac{25}{3}$$

$$= 4.55 \times 10^{-7} \text{ einstein } 1^{-1} \text{ sec}^{-1}$$

To determine Ia the energy absorbed by the system the Beer-Lambert Law previously described in Chapter I was used:

$$\log \frac{Io}{It} = \epsilon cl = A$$

{42} $$\therefore [H_2O_2] = \frac{AI_3^-}{\epsilon I_3^- \, 1} \times \text{dilution factor}$$

The triiodide method was used to determine $[H_2O_2]$, previously described in this chapter.

$$\therefore [H_2O_2] = \frac{1.15}{2.59 \times 10^4 \times 1} \times \frac{0.025}{100 \times 10^{-6}}$$

$[H_2O_2] = 1.11 \times 10^{-2}$ M (Note: $[I_3^-] = [H_2O_2]$

$$\log \frac{Io}{It} = \epsilon \times [H_2O_2] \times 1$$

where ϵ = 18.7 1 mole^{-1} cm^{-1} which is the molar extinction coefficient for H_2O_2 at 253.7 nm

$$\log \frac{Io}{It} = 18.7 \times 1.11 \times 10^{-2} \times 1$$

$$= 2.08 \times 10^{-1}$$

{43} % transmission = antilog (-A)

= 61.9%

% absorbed = 38.1%

{44} $Ia = 0.381 \times 4.55 \times 10^{-7}$

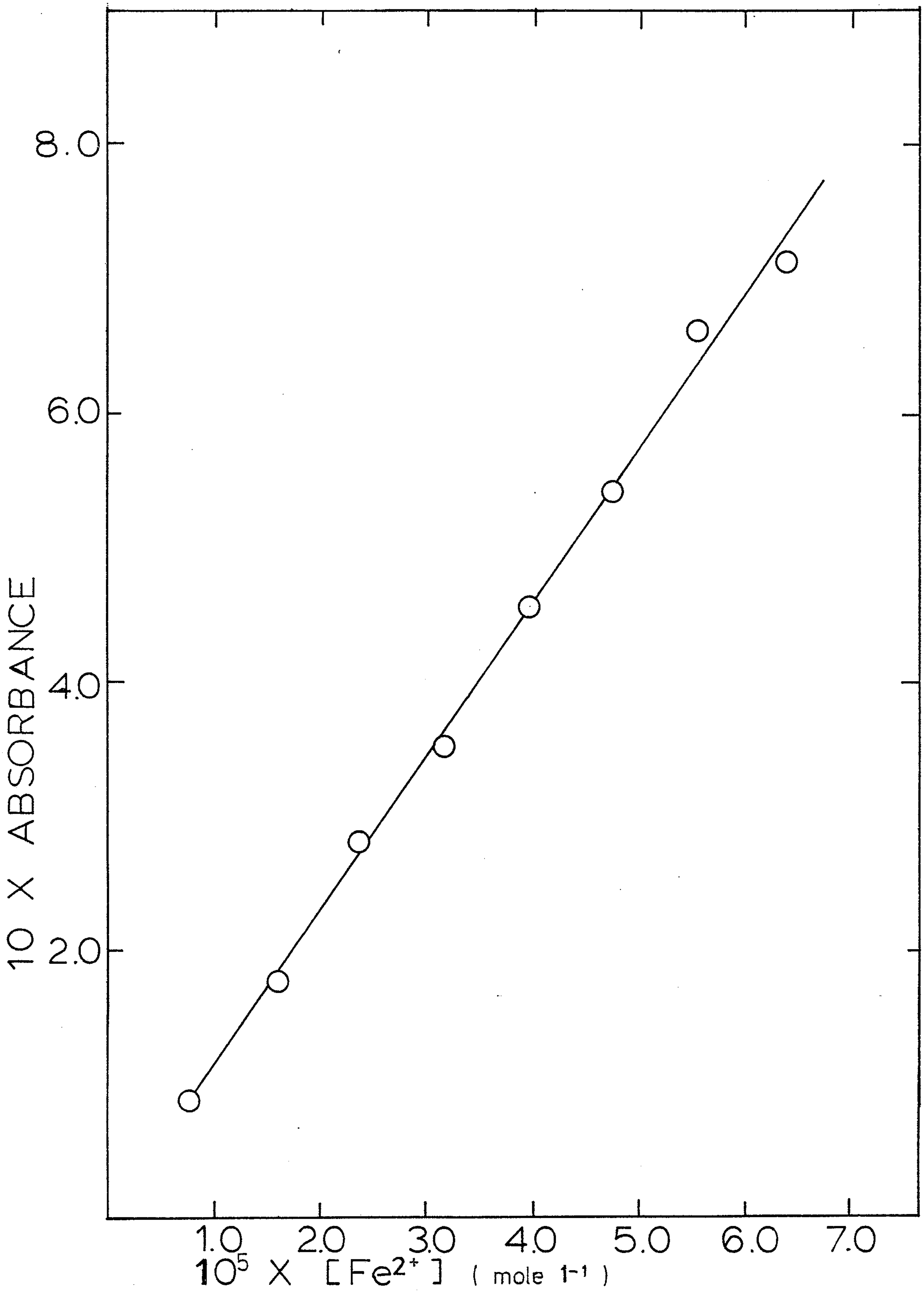
$= 1.73 \times 10^{-7}$ einstein l^{-1} sec^{-1}

A standard 4.0×10^{-4} M ferrous chloride solution in 0.2 M H_2SO_4 was prepared for the standard calibration graph of the ferrioxalate actinometer. Analizing for Fe^{2+} in the described method yielded a value for the molar extinction coefficient of 1.12×10^{4} l $mole^{-1}$ cm^{-1} (Figure 7).

7

Fig. 7

Ferrous — 1, 10 — phenanthroline
complex extinction coefficient
calibration curve measured
at 510 nm.


8.0
6.0
4.0
2.0
10 X ABSORBANCE
1.0
2.0
3.0
4.0
5.0
6.0
7.0
10^5 X $[Fe^{2+}]$ (mole l^{-1})

3. RESULTS AND DISCUSSION - 2-PROPANOL

3.1 Results

The chain oxidation of 2-propanol initiated by the photodecomposition of hydrogen peroxide in deaerated aqueous hydrogen peroxide solution has been investigated. The chain reaction has been studied over a wide range of 2-propanol concentrations and a 10-fold variation of the light intensity. Effects on the value for the quantum yield ϕ(Acetone) were monitored so as to determine the character of the system under these conditions.

Spectrophotometric techniques of analysis were used to determine the chemical quantum yield for acetone. The following trial demonstrates how the results were obtained. A 10ml sample containing 5.0×10^{-1} M 2-propanol and 1.1×10^{-2} M H_2O_2 was pipetted into each of the degassing cells and degassed. The samples were then irradiated and aliquots of 1ml were removed for the acetone analysis. The results of the analysis are tabulated in table II and shown graphically in Figure (8).

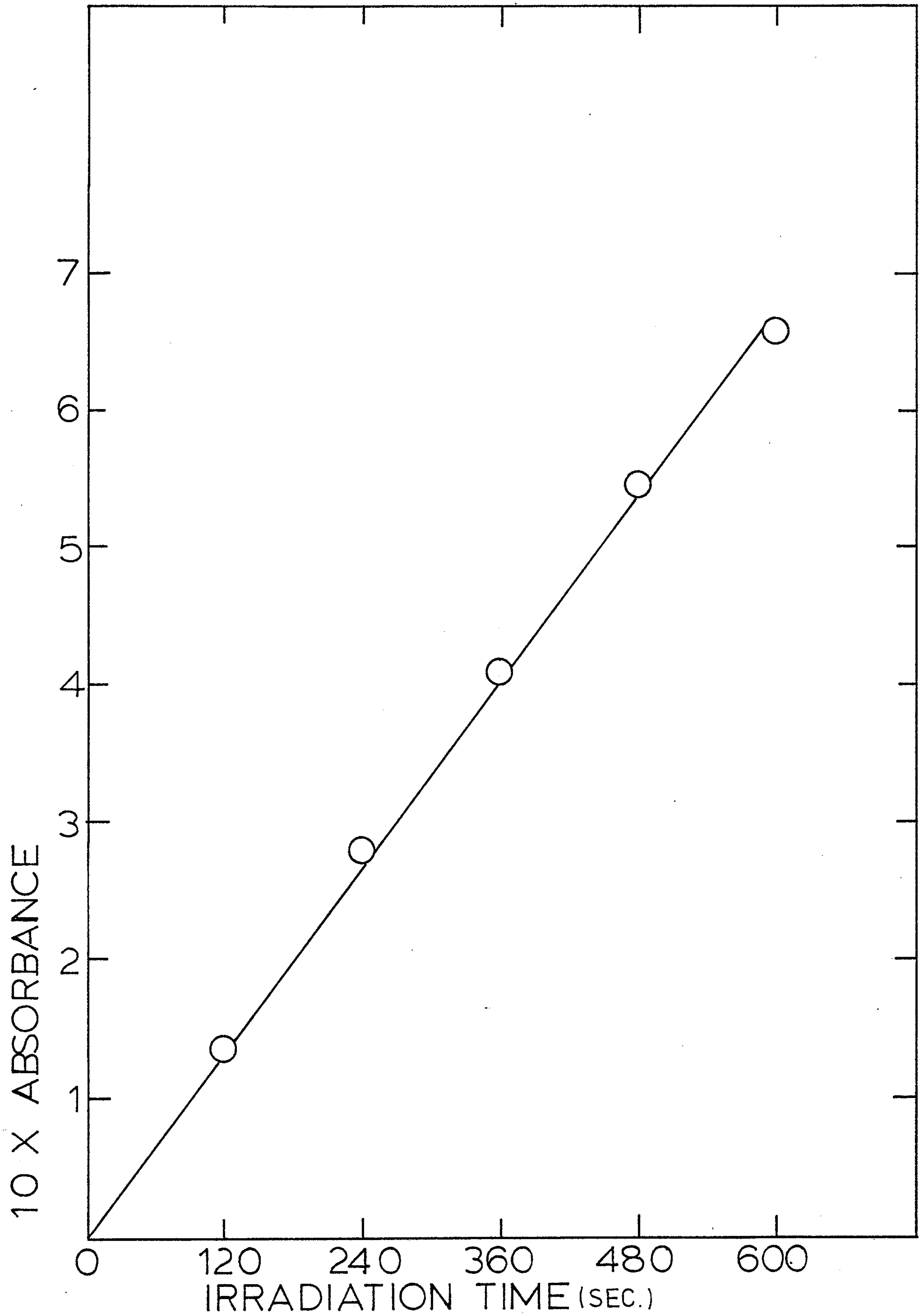
Table II

Formation of acetone with respect to irradiation time.

Sample No.	Irradiation Time (secs)	Acetone Analysis Absorbance
1	120	0.137
2	240	0.280
3	360	0.407
4	480	0.545
5	600	0.660

Fig. 8

The oxidation of 2-propanol for solutions
containing 5.00×10^{-1} M 2-propanol and
1.11×10^{-2} M H_2O_2
irradiated at 253.7 nm with
$Ia = 1.73 \times 10^{-7}$ einstein litre^{-1} sec^{-1}


10 X ABSORBANCE
1
2
3
4
5
6
7
0
120
240
360
480
600
IRRADIATION TIME (SEC.)

The quantum yield for the formation of acetone was calculated.

{21} $$\phi(\text{Acetone})\ I_a = \frac{d\,[\text{Acetone}]}{dt}$$

{22} $$\phi(\text{Acetone}) = \frac{\Delta\ \text{absorbance}}{\Delta\ \text{time}} \times \frac{1}{\epsilon} \times \frac{1}{I_a} \times \text{dilution factor}$$

From Table II, using the least mean square method,

$$\frac{\Delta\ \text{absorbance}}{\Delta\ \text{time}} = 1.09 \times 10^{-3}\ \text{sec}^{-1}$$

Substituting for acetone formation

$$\phi(\text{Acetone}) = 1.09 \times 10^{-3} \times \frac{1}{1.79 \times 10^{4}} \times \frac{1}{1.73 \times 10^{-7}} \times \frac{1}{1} \times \frac{25}{1}$$

$$\phi(\text{Acetone}) = 8.79$$

The 1.1×10^{-2} M H_2O_2 solutions absorb about 38% of the light incident on the optical cell, therefore Ia = .38 Io

From (Figure 8) the absorbance is linear with respect to irradiation time. This indicates that the concentration of acetone also increases linearly with irradiation time. For all experiments the reduction of peroxide was not carried further than 10%.

Table III

Relationship between 2-propanol concentration and ϕ(Acetone) with $I_a = 1.73 \times 10^{-7}$ einstein 1^{-1} sec^{-1}

2-propanol mole 1^{-1}	ϕ(Acetone)
1.0×10^{-1}	5.44
2.5×10^{-1}	6.62
5.0×10^{-1}	8.47
7.5×10^{-1}	10.66
10×10^{-1}	12.60

From the results in table III it can be seen that ϕ(Acetone) increases linearly with 2-propanol concentration over the range 1.0×10^{-1} M to 1.0 M. This is shown graphically in figure (9). Note that the magnitude of the quantum yields are indicative of a chain process.

The effect of change in intensity on the quantum yield ϕ(Acetone) is shown in table IV.

Table IV

Relationship between ϕ(Acetone) and intensity at $[\text{2-propanol}] = 5.0 \times 10^{-1}$ M

Ia einstein l^{-1} $\sec^{-1}$	$Ia^{-\frac{1}{2}}$ $\text{einstein}^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$ $\sec^{\frac{1}{2}}$	ϕ(Acetone)
1.39×10^{-6}	0.849×10^{3}	7.27
8.23×10^{-7}	1.10×10^{3}	7.36
4.69×10^{-7}	1.46×10^{3}	7.78
1.73×10^{-7}	2.40×10^{3}	8.47

The four experiments with intensities varying about 8-fold indicate that there is a linear relationship between the quantum yield for acetone formation and the reciprocal of the square root of the absorbed intensity. This is shown graphically in figure (10).

Table (V) shows the effect on ϕ(Acetone) for larger variation of 2-propanol concentration.

Fig. 9

Variation of ϕ(Acetone) values

vs 2-propanol concentrations for

1.1×10^{-2} M H_2O_2 solutions irradiated

at 253.7 nm with

$Ia = 1.73 \times 10^{-7}$ einstein l^{-1} sec^{-1}

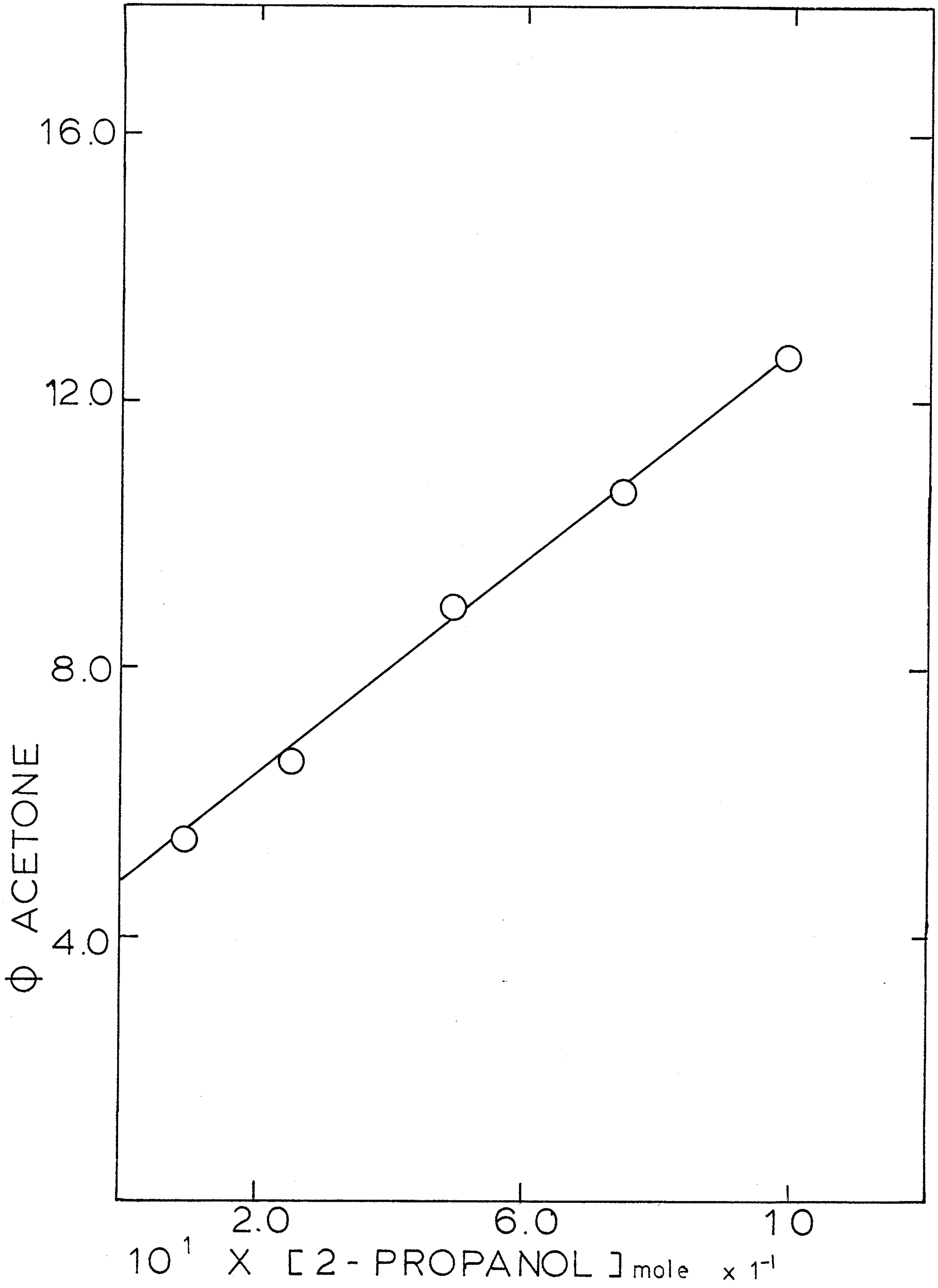

16.0
12.0
8.0
4.0
Φ ACETONE
2.0
6.0
10
10¹ X [2-PROPANOL] mole x l⁻¹

Fig. 10

Relationship between ϕ(Acetone)
and $Ia^{-\frac{1}{2}}$ for a solution of
5.0×10^{-1} M 2-propanol and 1.1×10^{-2} M H_2O_2

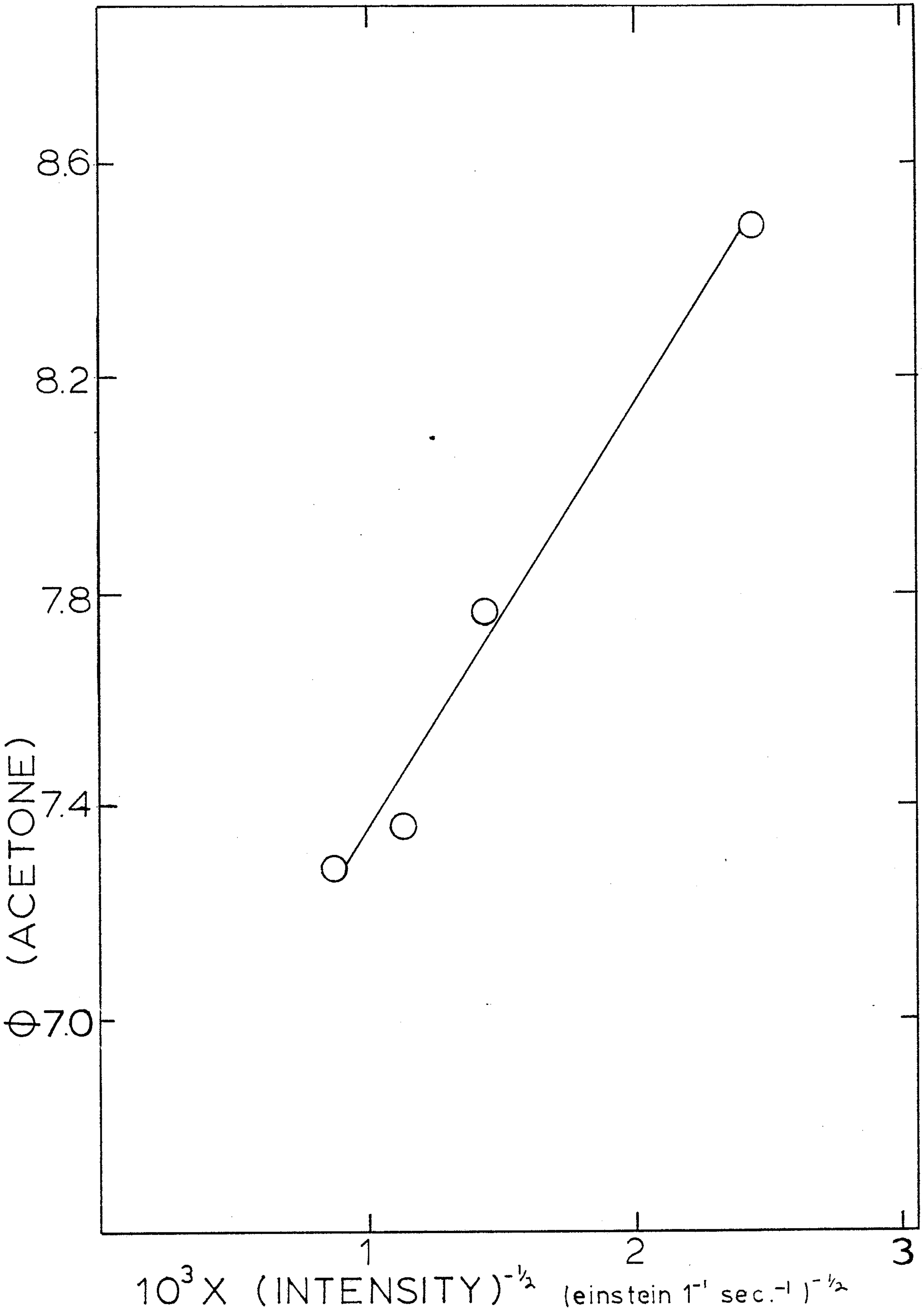

8.6
8.2
7.8
7.4
7.0
Φ (ACETONE)
1
2
3
10^3 X (INTENSITY)$^{-1/2}$ (einstein 1^{-1} sec.$^{-1}$)$^{-1/2}$

Table V

ϕ(Acetone) yields for various concentrations of 2-propanol

2-Propanol mole l^{-1}	mole percent 2-Propanol	ϕ(Acetone)
0.10	0.18	5.44
1.00	1.9	12.6
5.00	12.7	24.6
7.00	21.3	22.0
9.70	40.3	17.6
11.30	56.2	12.4
12.40	78.8	8.9
pure	100	8.6

The results in table (V) are shown graphically in figure (11). It is seen that ϕ(Acetone) increases with increasing mole percent of 2-propanol reaching a maximum value of approximately 25 at a concentration in the region of 5.0 M (12.7 mole percent). As the concentration of 2-propanol is increased above 5.0 M, ϕ(Acetone) decreases to a limiting value of 8.6 in pure 2-propanol as solvent.

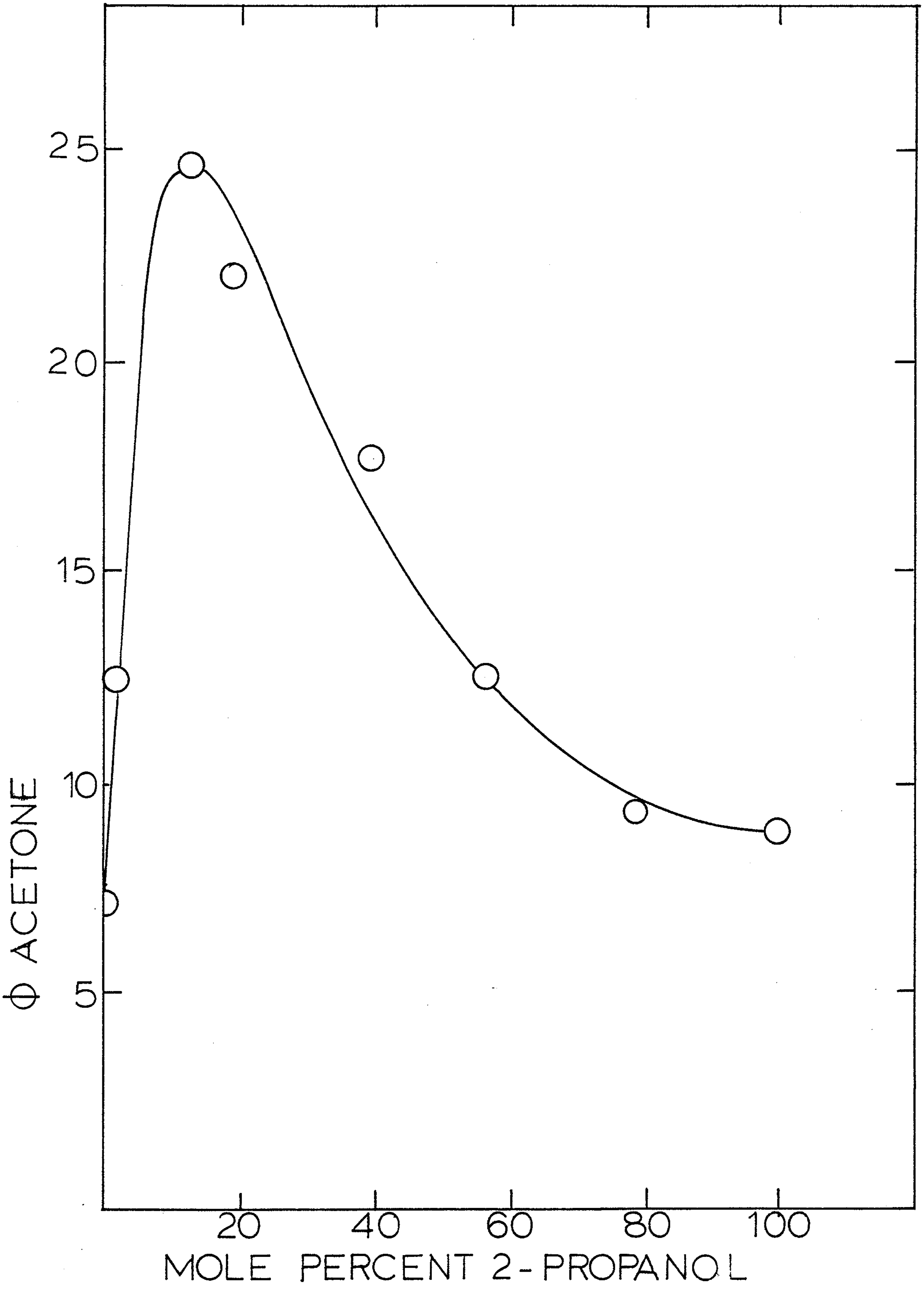
3.2 Discussion

0.1 M - 1.0 M 2-propanol in 1.1×10^{-2} M H_2O_2

The significant features of the experimental results of aqueous

Fig. 11

The relationship between
ϕ(Acetone) vs mole percent
2-propanol for 1.1 x 10^{-2} M H_2O_2
solutions irradiated at 253.7 nm.


25
20
15
10
5
Φ ACETONE
20
40
60
80
100
MOLE PERCENT 2-PROPANOL

solutions of H_2O_2 containing 2-propanol in this region are that the yields of acetone are linearly dependent upon the 2-propanol concentration and the results show a reciprocal dependence on the square root of the intensity.

It may be assumed that the 253.7 nm radiation from the ultra violet source interacts only with the hydrogen peroxide

{6} $H_2O_2 + h\nu \rightarrow 2\ OH$

The OH radicals will then react only with the 2-propanol since the $k_{OH} + H_2O_2 < k_{OH} +$ 2-propanol and the concentration of 2-propanol is greater than the concentration of the H_2O_2. Previous authors working on this system have assumed that the OH radical reacted only by abstracting a hydrogen atom from the α -position of the alcohol (1, 3, 4).

{7} $OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O$

The chain reaction has been attributed to the propagating reaction

{8} $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + OH$

and termination was attributed to the bimolecular reaction of $(CH_3)_2\dot{C}OH$

{19} $2\ (CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH$

This reaction scheme would give no dependence on the concentration of 2-propanol. However, the experiments undertaken in this study and those by Burchill and Ginns (7) show that the reaction rate is linearly dependent upon the 2-propanol concentration.

Therefore the simple reaction scheme assumed by prior authors for the chain oxidation of 2-propanol by hydrogen peroxide cannot be

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correct . A new mechanism must be outlined to explain the dependence of yields on 2-propanol and a chain term independent of 2-propanol concentration as shown in figure (9).

As mentioned, previous authors have assumed that hydrogen abstraction from the 2-propanol by OH radicals occurs only at the α site. However the following arguments will show clearly that this cannot be the only case, but that hydrogen atom abstraction from the β position of the 2-propanol may also occur via the reaction;

$\{23\} \quad OH + (CH_3)_2CHOH \rightarrow CH_3CHOH\dot{C}H_2 + H_2O$

and therefore reaction {12} must also be included in the mechanistic scheme.

Burchill and Ginns (7) have proposed a mechanism which includes reaction {12} and a radical conversion reaction.

$\{25\} \quad (CH_3)_2CHOH + CH_3CHOH\dot{C}H_2 \rightarrow (CH_3)_2\dot{C}OH + (CH_3)_2CHOH$

The inclusion of these reactions as well as reactions, {13}, {14}, {15}, {7}, {17}, into the mechanistic scheme, gave a satisfactory quantitative explanation to their results. In the following discussion reference is made to their results and they are compared to the photochemical results of this study to determine whether or not the proposed mechanism can account for the results obtained in the photochemical experiments.

Burchill and Ginns (7) have included reactions {12} and {7} in the mechanistic scheme, first, because of the form of their experimental results and, secondly, because an extensive review of the literature lends support to the occurrence of {12} and {7}. The following is a brief summary of the literature.

Livingstone and Zeldes (16) observed the e.s.r. spectra of both the α and β radicals in a solution of 2-propanol containing 25% H_2O and 1% H_2O_2 which was irradiated by ultraviolet light. They attributed the formation of the α and β radical to the abstraction of H atoms from the alcohol by the OH radical.

Anbar and Meyerstein (17) have shown the reactivity of the α -hydrogen in 2-propanol towards hydrogen atoms to be 110 times higher than that of the β -hydrogen. It has been argued that if abstraction by H atoms at the β -position in 2-propanol is significant, then abstraction by the OH radical may be even more significant because of its greater exothermicity (7).

The inclusion of the radical conversion reaction proposed by Burchill and Ginns;

$$\{25\} \quad CH_3CHOH\dot{C}H_2 + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH$$

into the mechanistic scheme is supported by the form of the experimental results. The photochemical yields of acetone formation show a linear dependence upon 2-propanol concentration, which is similar to the linear dependence of the radiolytic yields for 2-propanol concentration observed by Burchill and Ginns (7). This indicates that the chain length is determined by the competition between a radical terminating reaction and the reaction of that radical with 2-propanol. Therefore if the radical conversion reaction {25} and the possible termination by dimerization of β radicals.

{17} $2\ CH_3CHOH\dot{C}H_2 \rightarrow$ 2,5-Hexanediol, or acetone + 2-propanol

are included in the reaction scheme, with {25} as the rate determining step the kinetics work out to be in excellent agreement with the experimental results.

Although the inclusion of the radical $CH_3CHOH\dot{C}H_2$, along with the radical $(CH_3)_2\dot{C}HOH$, the conversion reaction {25} and the termination reaction {17} predict the kinetics of the system, this is not enough evidence to conclude reactions {25} and {17} do take place.

J.K. Thomas has studied the reactions of methyl radicals in water (21). The presence of the methyl radical was demonstrated by the production of methane from the reaction.

{26} $\dot{C}H_3 + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + CH_4$

The $CH_3CHOH\dot{C}H_2$ radical may be regarded as similar to $\dot{C}H_3$ therefore it is not unreasonable to predict that the $CH_3CHOH\dot{C}H_2$ radical can undergo a similar reaction.

In pure 2-propanol containing H_2O_2 Livingstone and Zeldes (23) have observed an e.s.r. spectrum attributed to the $(CH_3)_2\dot{C}OH$ radical. In a solution containing 75% 2-propanol, 25% H_2O, and a small amount of H_2O_2 they observed the spectral lines due to the $CH_3CHOH\dot{C}H_2$ radical (24). This demonstrates the possibility that although reaction {25} may be slow, it is possible that in pure 2-propanol β -radicals may be converted to α -radicals via reaction {25} before they can be detected.

At high 2-propanol concentrations reaction {25} may no longer be the rate controlling step. Chain yields would then be determined by reaction {8} in competition with reaction {10}. This scheme would lead to plateauing, which is seen in figure (11), showing a maximum value for ϕ(Acetone) $\approx$ 25. In comparison with the radiolytic yields observed by Burchill and Ginns, figure (11) for photochemical initiation is comparable to their figure (3) for radiation initiation which shows a maximum value for G(acetone) $\approx$ 100.

The radical conversion reaction {25} proposed by Burchill and Ginns (7) as a necessary step in their mechanistic scheme for a satisfactory explanation of the radiation-chemical results, can also be included in a reaction scheme explaining the photochemical results because of the similarity of the observations obtained by the two different methods of initiation.

Dimerization by reaction {17} suggests 2,5-Hexandiol as a reaction product. Burchill and Ginns (7) have demonstrated its presence qualitatively in the radiation-induced oxidation of 2-propanol by hydrogen peroxide in aqueous solution.

The results of this study indicate a reciprocal square root effect of the dose rate upon oxidation yields. This again suggests a bimolecular chain termination of radicals.

In this system there are other possibilities for bimolecular termination besides reaction {17}. Other possibilities are:

{27} $2\ OH \rightarrow H_2O_2$

{10} $2\ (CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH$

{11} $2\ (CH_3)_2\dot{C}OH \rightarrow$ diol

Termination by OH would lead to a competition between the initiation reaction {7} and the termination reaction {27}. This would lead to an alcohol dependent term, which is suggested by the experimental results. However it is considered that reaction {27} plays little role in the termination of the chain. Since the rate of reaction between $(CH_3)_2CHOH$ and OH is very large (15) and the steady state concentration is much smaller than the concentration of 2-propanol,we can assume that essentially all of the OH will react with the 2-propanol before it can be involved in termination.

The second alternate termination process is by reactions {10} and {11}. Termination of the chain reaction by the bimolecular combination of $(CH_3)_2\dot{C}OH$ radicals would lead to competition between the terminating reactions {10} and {11} and the chain propagating reaction {8}. This would show a dependence of chain oxidation yields on the concentration of H_2O_2.

The radiation-induced oxidation of alcohols has been described by Burchill-Ginns (7). Their experiments showed conclusively that the yields of acetone formation were independent of hydrogen peroxide concentrations for the same systems studied in this report. On this basis bimolecular termination by the $(CH_3)_2\dot{C}OH$ radical is very remote.

This implies that only reaction {17} would be a significant termination reaction. This would result in a competition between the possible rate controlling propagation step {25} and the bimolecular termination reaction {17}. This leads to the following chain mechanism in which initiation occurs via hydrogen atom abstraction from 2-propanol to form both $(CH_3)_2\dot{C}OH$ and $CH_3CHOHC\dot{H}_2$ radicals:

{6} $H_2O_2 \xrightarrow{h\nu} 2\ OH$

{7} $OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O$

{12} $OH + (CH_3)_2CHOH \rightarrow CH_3CHOH\dot{C}H_2 + H_2O$

{8} $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + OH$

{25} $(CH_3)_2CHOH + CH_3CHOH\dot{C}H_2 \rightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH$

{17} $2\ CH_3CHOH\dot{C}H_2 \rightarrow$ 2,5-Hexandiol or $(CH_3)_2CO + (CH_3)_2CHOH$

which is a mechanism entirely analogous to that proposed for radiation initiation by Burchill and Ginns (7).

Using the assumption of steady state for the intermediate radicals the following expression for ϕ(Acetone) can be derived:

{28} $$\phi(\text{Acetone}) = \frac{2k_7}{k_{12}}\phi_6 + \left(1 + \frac{k_7}{k_{12}}\right) \cdot k_{25} \left(\frac{\phi_6}{\text{Ia}\ k_{17}}\right)^{\frac{1}{2}} [\text{2-propanol}]$$

The expression shows a linear dependence on the concentration of 2-propanol and a reciprocal square root dependence on the intensity. The term $\left(\frac{\phi_6}{\text{Ia}\ k_{17}}\right)^{\frac{1}{2}}$ appearing in the rate expression is a consequence of a bimolecular termination. The term [2-propanol] appears in the rate expression because the propagation rate controlling step {25} is in competition with the bimolecular termination step {17}.

The portion of expression {28} $\frac{2k_7}{k_{12}}\phi_6$ predicts an alcohol independent chain yield which is consistent with the results represented in figure (9). The extrapolated limit at zero 2-propanol concentration is the alcohol independent portion of the yield $\frac{2k_7}{k_{12}} \phi_6$ and is equal to 4.6. Assuming a value $\phi 6 = 0.5$ (22) the value of $\frac{k_7}{k_{12}}$ can be obtained. The calculated value of this ratio is $\frac{k_7}{k_{12}} = 4.6$. This is in good agreement with the value 5.2 obtained by Burchill and Thompson (18) for the same ratio. The fact that the value of the ratio, $\frac{k_7}{k_{12}}$, obtained by the two different modes of initiation, radiation and photolysis, is in such close agreement, provides further strong evidence in favor of the mechanism proposed by Burchill and Ginns (7).

The portion of expression $\{28\}$ $\left(1 + \frac{k_7}{k_{12}}\right) \cdot k_{25} \left(\frac{\phi_6}{Ia\ k_{17}}\right)^{\frac{1}{2}}$ [2-propanol] predicts a linear dependence of ϕ(Acetone) on 2-propanol concentration. The expression $\left(1 + \frac{k_7}{k_{12}}\right) \cdot k_{25} \left(\frac{\phi_6}{Ia\ k_{17}}\right)^{\frac{1}{2}}$ corresponds to the slope of figure (9). The expression shows a reciprocal square root dependence on the ultra-violet light intensity. Figure (10) shows that the acetone yields are a linear function of $\left(\frac{1}{Ia}\right)^{\frac{1}{2}}$. The observed reciprocal square root dependence of the yield on the intensity is consistent with a bimolecular termination reaction such as $\{17\}$. If at the highest intensity (1.39×10^{-6} einstein l^{-1} sec^{-1}) used, bimolecular termination takes place via reaction $\{17\}$ a value for the rate constant for the radical conversion reaction $\{25\}$ may be estimated. Using $1 + \frac{k_7}{k_{12}} = 5.6$ and assuming $k_{17} = 1 \times 10^9 M^{-1} sec^{-1}$ (7) a value of $k_{25} = 75\ M^{-1} sec^{-1}$ may be calculated from the slope of figure (9). Burchill and Ginns originally obtained a value of $53 \pm 10\ M^{-1} sec^{-1}$ (recalculated as $51 \pm 2\ M^{-1} sec^{-1}$ by Burchill and Thompson). The value of k_{25} obtained from this work is higher, but well within the same order of magnitude. Burchill and Ginns also suggested that their value should be treated as a lower limit. This further indicates the consistency of the mechanism in explaining the experimental results.

The rate constant for reaction $\{26\}$ observed by J.K.Thomas shows that k_{25} is small compared to k_{26}, ($k_{26} = 1.34 \times 10^3 M^{-1} sec^{-1}$, $k_{25} = 75\ M^{-1} sec^{-1}$). This may be explained in terms of ordered transition states, the highly ordered transition state for reaction $\{25\}$ as compared to reaction $\{26\}$ may be such that the rate of reaction $\{25\}$ will be slow compared to reaction $\{26\}$.

3.3 Further Evidence

Burchill and Thompson (18), using selectively deuterated alcohols have demonstrated that abstraction from both the α and β positions contribute to the overall mechanism for the radiation-induced oxidation of 2-propanol by hydrogen peroxide. Experiments determining acetone yields for a constant initial hydrogen peroxide concentration of 0.01 M and various concentrations of $(CH_3)_2CHOH$, $(CH_3)_2CDOH$ and $(CD_3)_2CHOH$ irradiated in a Co^{60} Gammacell have been done. The results showed a large increase in the chain yield for acetone on β deuteration of 2-propanol, which implies a direct indication of the involvement of the β position in the reaction scheme. Burchill and Thompson calculated a ratio of α to β abstraction of 5.2 for the undeuterated alcohol.

Further evidence for the lack of specificity of hydrogen atom abstraction from 2-propanol is provided by a pulse radiolytic study of the site of OH radical attack on aliphatic alcohols in aqueous solutions carried out by Asmus, et al. (19) Tetranitromethane was used as an electron acceptor and reacts with the α radical via the reaction,

$$\{23\} \quad (CH_3)_2\dot{C}OH + C(NO_2)_4 \rightarrow C(NO_2)_3^- + NO_2 + H^+ + (CH_3)_2CO$$

and the comparitive radical $\dot{C}O_2^-$,

$$\{24\} \quad \dot{C}O_2^- + C(NO_2)_4 \rightarrow C(NO_2)_3^- + NO_2 + CO_2$$

The formation of the stable nitroform anion was observed at 350 nm in deaerated aqueous solutions containing N_2O (2×10^{-2} M), $C(NO_2)_4$ (1.2×10^{-4} M) and OH radical scavenger $(CH_3)_2CHOH$ (2×10^{-4} M). Using the formate anion as a standard and assuming 100% α attack it was shown that hydrogen atom abstraction at the α position occurred only 85.5% of the time for 2-propanol. This value is very close to that measured by Burchill and Ginns (7) — 86%.

The reactions with H_2O_2 of free radicals derived from 2-propanol, have been investigated by e.s.r. using in-cavity photolysis with acetone photo-sensitization to generate the radicals in flowing aqueous solutions (32). Variation in the ratio $\frac{[\beta]}{[\alpha]}$ is attributed to the selective oxidation of one radical by H_2O_2, propagating a secondary chain reaction,

{8} $(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2CO + H_2O + \dot{O}H$

{7} $\dot{O}H + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O$

{12} $\dot{O}H + (CH_3)_2CHOH \rightarrow CH_3CHOH\dot{C}H_2 + H_2O$

{35} $CH_3CHOH\dot{C}H_2 + H_2O_2 \rightarrow$

Burchill and Jones (32) found that their results and conclusions were consistent with the mechanism proposed for the radiation-induced oxidation of 2-propanol by H_2O_2 (7, 18) and with the experimental observations from the photo-induced reaction, and e.s.r. studies using electron beam irradiation, photoinitiation, and Ti(III) initiation. Since this two-radical model is consistent with the results obtained in this study, it must apply equally well to the present study.

Using their equation 15, which is an expression that gives the ratio $\frac{[\beta]}{[\alpha]}$ in the radiation-induced oxidation of 2-propanol by H_2O_2, Burchill and Jones (32), calculated that reaction {25} is not negligible at the lower rates of initiation used in the radiation-chemical study done by Burchill and Ginns (7). The similarity of results obtained in this study to those observed by Burchill and Ginns at comparable dose rates, suggests that reaction {25} is not negligible in the photo-induced oxidation of 2-propanol by H_2O_2.

Walling and Kato (20) carried out experiments on a similar system using Fenton's reagent to initiate the chain reaction. Systems containing approximately 0.1N $HClO_4$, 0.02 M ferrous perchlorate and 0.01 M - 0.5 M 2-propanol, to which was added enough hydrogen peroxide to oxidize a small portion of the ferrous ion and alcohol. They found as one of the products 2,5-Hexanediol, the expected product of the coupling of radicals of the type $CH_3CHOH\dot{C}H_2$.

Burchill and Jones (32) have calculated for 2-propanol = 0.5 M and hydrogen peroxide concentration (0.01 M), $\frac{[\beta]}{[\alpha]}$ = 26 for a dose rate of 1.8 x 10^{19} e.v. 1^{-1} s^{-1}, a rate of initiation comparable to that used here. Therefore reaction {17} would be a significant terminating process.

Walling and Kato (20) calculated $\frac{k_7}{k_{12}}$ = 6.2, close to the value 5.2 calculated by Burchill and Thompson (18) and to 4.6 calculated in this work. Asmus, et al., (19) obtained a relative yield of 85.5% for α abstraction from 2-propanol, which is quite close to the 86% value obtained by Burchill and Ginns (7). The fact that the low calculated values for $\frac{k_7}{k_{12}}$, obtained by several different modes of initiation, radiation, photolysis, metal ion and electron pulse, are in such close agreement in each case provides further strong evidence for general applicability of the two-radical model proposed by Burchill and Ginns (7).

3.4 Alcohol concentrations greater than 1.0 M

As the concentration of 2-propanol was increased beyond 1.0 M the value of ϕ(Acetone) increased less rapidly, reaching a maximum value for ϕ(Acetone) $\approx$ 25 at 2-propanol concentration 5.0 M, as shown in figure (11). The yield then decreased with further alcohol concentration to a value 8.60 for pure 2-propanol as solvent. Radiation-initiated results obtained by Burchill and Ginns (7) for the same system, (their figure 3) show a qualitative similarity to the photo-induced results, that is, a rise in G(Acetone) to a maximum value $\approx$ 100 in the region 3.7 M and, in excess of 4.0 M, G(Acetone) decreased to a limiting value of 16±1 in pure 2-propanol as solvent. Similar results have been obtained by Barrett, et al. They attributed the variation of ϕ(Acetone) to a cage effect where the OH radicals react with the alcohol molecules in the primary "photochemical cage". Since the "photochemical cage" is non-existent in the radiation initiated system it can be assumed that their explanation is not acceptable.

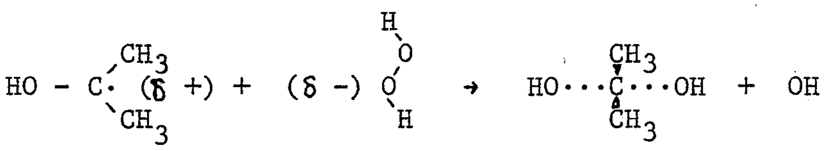
The reduction in chain yields could be explained by a reduction in primary radical yields as the system changes from pure water to pure 2-propanol. However the primary quantum yield of peroxide homolysis is said to remain constant in this concentration range, (4) making this an unsatisfactory explanation.

A possible explanation for the levelling of the curve in the region 5.0 M 2-propanol has been suggested by Burchill and Ginns (7). They suggested this might be attributed to the increase in the rate of reaction {25} with an increase in 2-propanol concentration. If the reaction rate becomes increasingly rapid, reaction {25} may no longer be the rate-controlling step and the chain yields would be determined by reaction {8} which becomes the rate-controlling propagation step, in competition with the terminating reaction {10}. At high 2-propanol concentrations this would lead to a situation of simple $(CH_3)_2\dot{C}OH$ radical kinetics where the rate of reaction would become independent of the 2-propanol concentration. This scheme would lead to plateauing and first order dependence for hydrogen peroxide reduction.

They found a significant dose rate effect on the yields of acetone, which approached but never did reach linearity for an inverse square root dependence on the dose rate. The evidence still suggests that reaction {8} is the main rate controlling propagation reaction at high 2-propanol concentration. The lack of a simple inverse square-root dependence for the dose rate effect, suggests that mixed termination between reactions {17} and {10} may be occurring in concentrated 2-propanol solutions. Livingstone and Zeldes (16) have shown that the β radical exists in detectable amounts in 75% 2-propanol and 25% H_2O.

At the same time it was proposed that the rate constant for reaction {8} decreases with increasing 2-propanol concentration as a result of the decrease in dielectric constant:

{8}



$$HO-\overset{CH_3}{\underset{CH_3}{C\cdot}}\ (\delta +) + (\delta -)\ \overset{H-O}{\underset{H}{O}} \rightarrow HO\cdots\overset{CH_3}{\underset{CH_3}{C}}\cdots OH + OH$$

The reaction of $(CH_3)_2\dot{C}OH$ with H_2O_2 involves the formation of a polar transition state and would be expected to decrease in rate with decreasing dielectric constant, since the rate of reaction between two dipoles decreases under these conditions (25). Therefore at high alcohol concentration the activation energy for the formation of the polar activated complex increases, resulting in a decrease in the rate constant k_8 and therefore a decrease in the chain yield.

To examine this proposal Burchill and Jones (32) have measured the concentrations of α and β radicals for solutions containing 0.68 M acetone, 0.029 M H_2O_2, and varying concentrations of 2-propanol. They suggest that the decrease in $\frac{[\beta]}{[\alpha]}$ (from 1.4 at low 2-propanol concentration to 0.13 at 0.5 mole fraction 2-propanol) is much too great to be accounted for by the inclusion of reaction $\{25\}$, as shown by their equation 10, although it would make some contribution. The most probable reason for this decrease is a decrease in k_8. In the photo-initiated reaction of H_2O_2 in pure 2-propanol (24) only the spectrum of the α radical was observed, but with addition of water the spectrum of the β radical became increasingly prominent. This could be accounted for by a combination of an increase in k_8 with increasing water content, thus increasing $\frac{[\beta]}{[\alpha]}$ and a decrease in the rate of reaction $\{25\}$ which would show a similar effect.

3.5 Summary

The value $\frac{k_7}{k_{12}} = 5.2$ calculated by Burchill and Thompson (18) suggests that the abstraction of hydrogen atoms from 2-propanol by OH radicals is less specific as to the site of reaction than previously believed. The value $\frac{k_7}{k_{12}} = 4.6$ calculated for this work indicates that their proposal generalizes to the photo-initiated system as well. Using

Fenton's reagent, Walling and Kato (20) calculated a value for $\frac{k_7}{k_{12}} = 6.22$ for the oxidation of 2-propanol. Asmus, et al., using a pulsed electron beam to initiate the oxidation of 2-propanol by hydroxyl radicals in aqueous solutions, determined that the attack at the α position by OH radicals occurred only 85.5% of the time. This implies that the proposal made by Burchill and Ginns (7), that is that H atom abstraction from 2-propanol can occur at both the α and β sites, which does occur in the radiation and photo-initiated systems, quite likely may also occur in systems initiated by Fenton's reagent and a pulsed electron beam.

Burchill and Ginns (7) also proposed that the radical formed by abstraction of a β -hydrogen, $CH_3CHOH\dot{C}H_2$, can react with 2-propanol to abstract the α -hydrogen forming the β -radical $(CH_3)_2\dot{C}OH$. They estimate a lower limit for the rate constant for this reaction, 53±10 litre mole^{-1} sec^{-1}, which was recalculated by Burchill and Thompson giving a value for this reaction equal to 51±2 litre mole^{-1} sec^{-1}, agreeing quite well with the result, 75 litre mole^{-1} sec^{-1}, obtained in this work.

This comparative study clearly indicates that the mechanism proposed by Burchill and Ginns (7), to explain results obtained in the radiation-initiated oxidation of 2-propanol by hydrogen peroxide in aqueous solutions, is consistent, since the mechanism explains satisfactorily the oxidation of 2-propanol by hydrogen peroxide, for several modes of initiation.

4. RESULTS AND DISCUSSION - METHANOL

4.1 Results

Experiments have been done to determine what effects that varying the methanol concentration and ultraviolet light intensity had on the oxidation of methanol to formaldehyde in deaerated aqueous solutions containing 1.1×10^{-2} M hydrogen peroxide. The chain reactions have been studied over a wide range of methanol concentration and a 10-fold variation of the light intensity. The value ϕ(Formaldehyde) was monitored so as to determine the character of the system under these conditions.

The results of the following trial demonstrate how the values ϕ(Formaldehyde) were obtained.

A 10ml sample containing 5.0×10^{-1} M methanol and 1.1×10^{-1} M H_2O_2 was pipetted into each of the degassing bulbs and degassed 4 times. The samples were then irradiated by an ultraviolet source (253.7 nm) and aliquots of 0.5ml were removed for the formaldehyde analysis. The results of the analysis are tabled in table VI and shown graphically in figure (12).

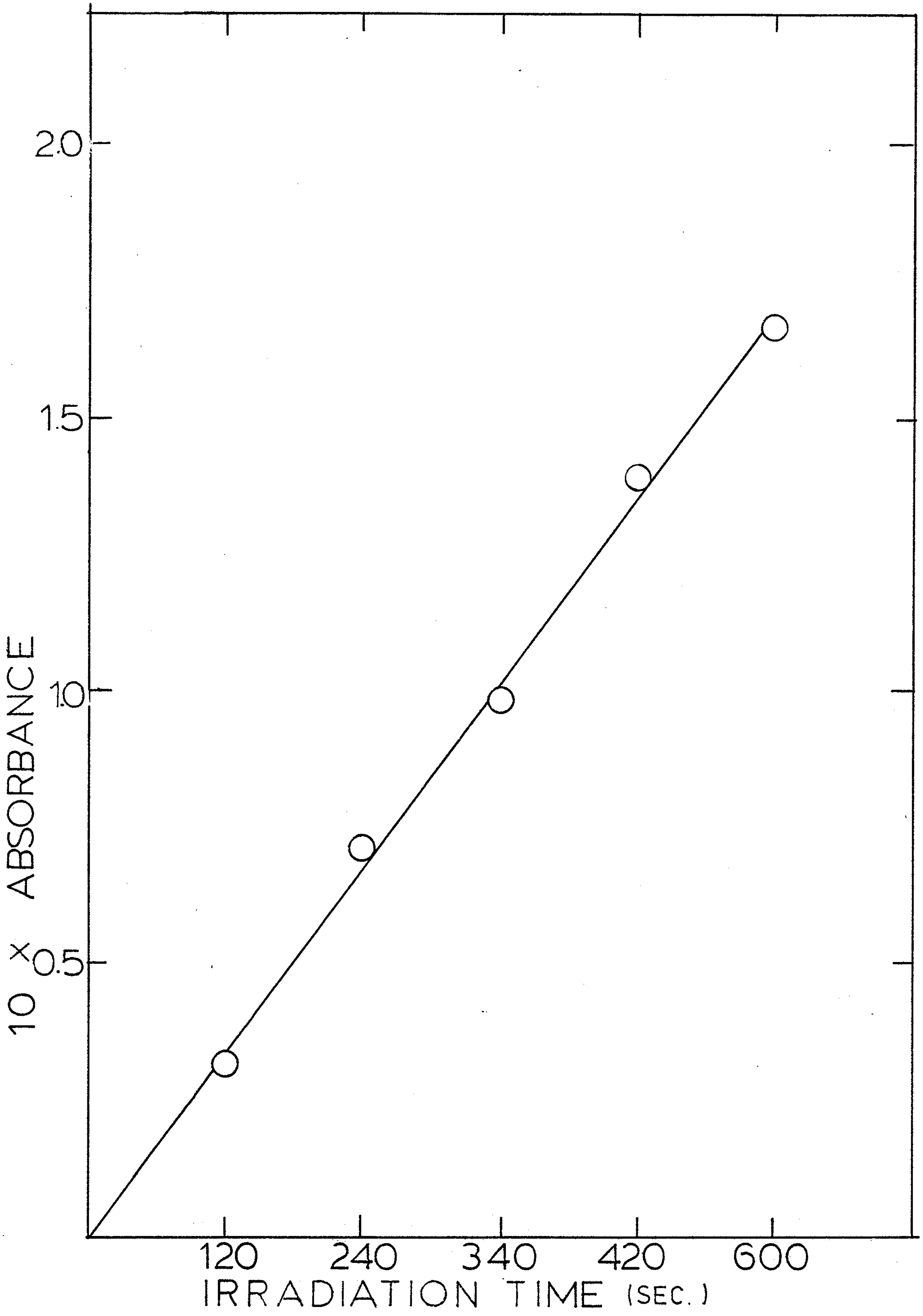
Table VI

Formation of formaldehyde with respect to irradiation time

Sample No.	Irradiation Time (secs)	Formaldehyde Analysis Absorbance
1	120	0.032
2	240	0.071
3	360	0.099
4	480	0.139
5	600	0.166

Fig. 12

The oxidation of methanol
for solutions containing 5.0 x 10^{-1} M
methanol and 1.1 x 10^{-2} M H_2O_2
irradiated at 253.7 nm with
Ia = 1.50 x 10^{-7} einstein $litre^{-1}$ sec^{-1}


2.0
1.5
1.0
0.5
10 × ABSORBANCE
120
240
340
420
600
IRRADIATION TIME (SEC.)

The quantum yield for the formation of formaldehyde can be determined by the expression:

$$\{30\} \qquad \phi(\text{Formaldehyde}) = \frac{\Delta \text{absorbance}}{\Delta \text{ time}} \times \frac{1}{\epsilon} \times \frac{1}{I_a} \times \text{dilution factor}$$

From Figure (12)

$$\frac{\Delta \text{absorbance}}{\Delta \text{ time}} = 2.76 \times 10^{-4} \text{ sec}^{-1}$$

Therefore:

$$\phi(\text{Formaldehyde}) = 2.76 \times 10^{-4} \times \frac{1}{1.54 \times 10^{4}} \times \frac{1}{1} \times \frac{1}{1.50 \times 10^{-7}} \times \frac{25}{0.50}$$

$$\phi(\text{Formaldehyde}) = 5.90$$

From figure (12) the absorbance is seen to be linear with respect to irradiation time, therefore the concentration of formaldehyde is also linear with respect to irradiation time. For all methanol solutions the reduction of peroxide was not carried further than 10%.

Table VII

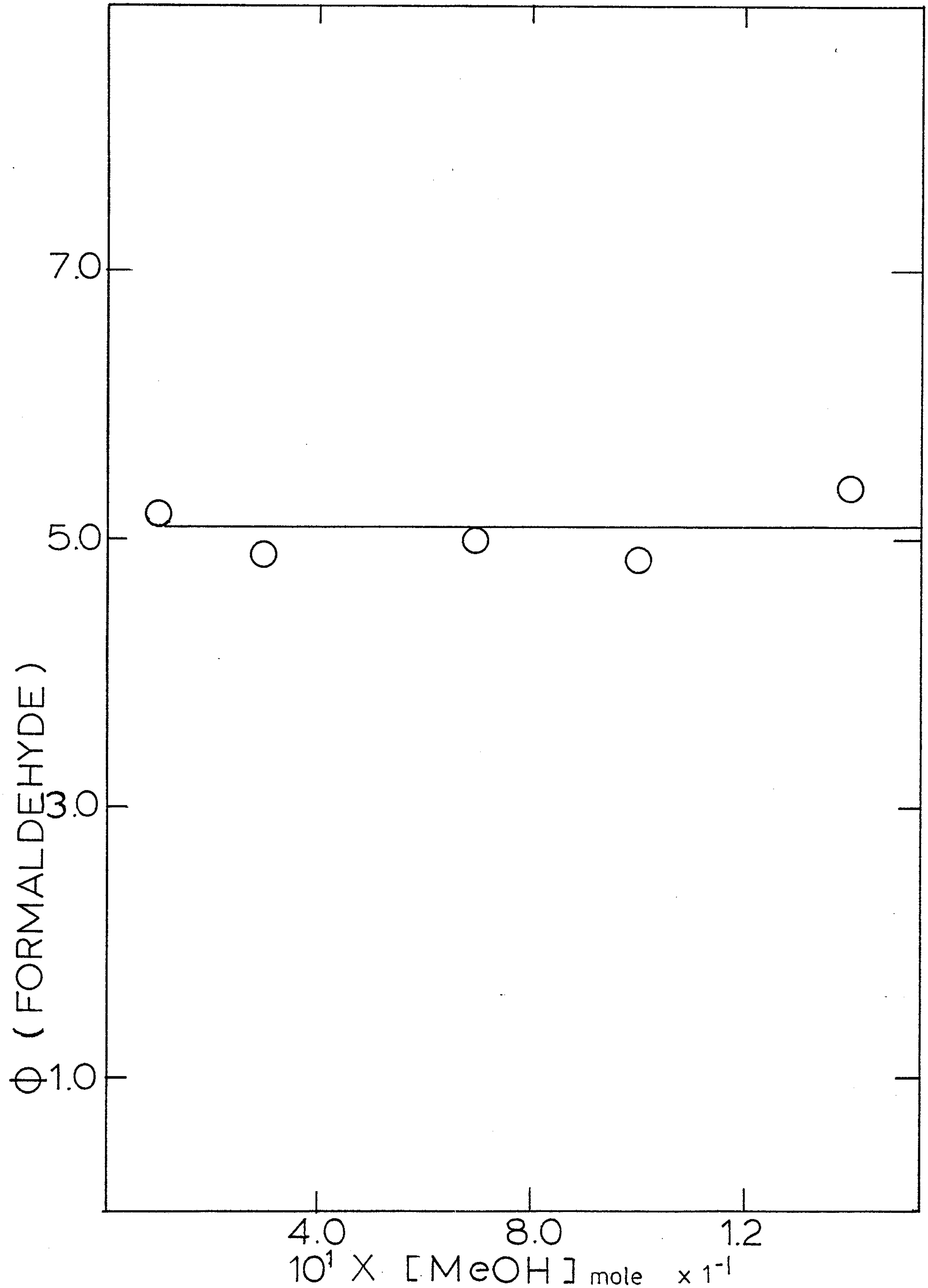
Relationship between methanol concentration and ϕ(Formaldehyde)

Methanol mole 1^{-1}	ϕ(Formaldehyde)
0.10	5.19
0.30	4.90
0.75	4.96
1.00	4.82
1.50	5.40

From the results in table VII it can be concluded that the oxidation yields are independent of the methanol concentration over the

Fig. 13

The relationship between ϕ(Formaldehyde) vs methanol concentrations for 1.1×10^{-2} M H_2O_2 solutions irradiated at 253.7 nm with $Ia = 1.50 \times 10^{-7}$ einstein l^{-1} sec^{-1}


7.0
5.0
3.0
1.0
Φ (FORMALDEHYDE)
4.0
8.0
1.2
10¹ X [MeOH] mole x 1⁻¹

range 1.0 x 10^{-1} M to 1.5 M. This is shown graphically in figure (13). Note that the value of ϕ(Formaldehyde) $\approx$ 5.0 indicates a chain reaction.

The effect of change in intensity on the quantum yield ϕ(Formaldehyde) is shown in table VIII.

Table VIII

Relationship between ϕ(Formaldehyde) and intensity at [methanol] = 5.0 x 10^{-1} M

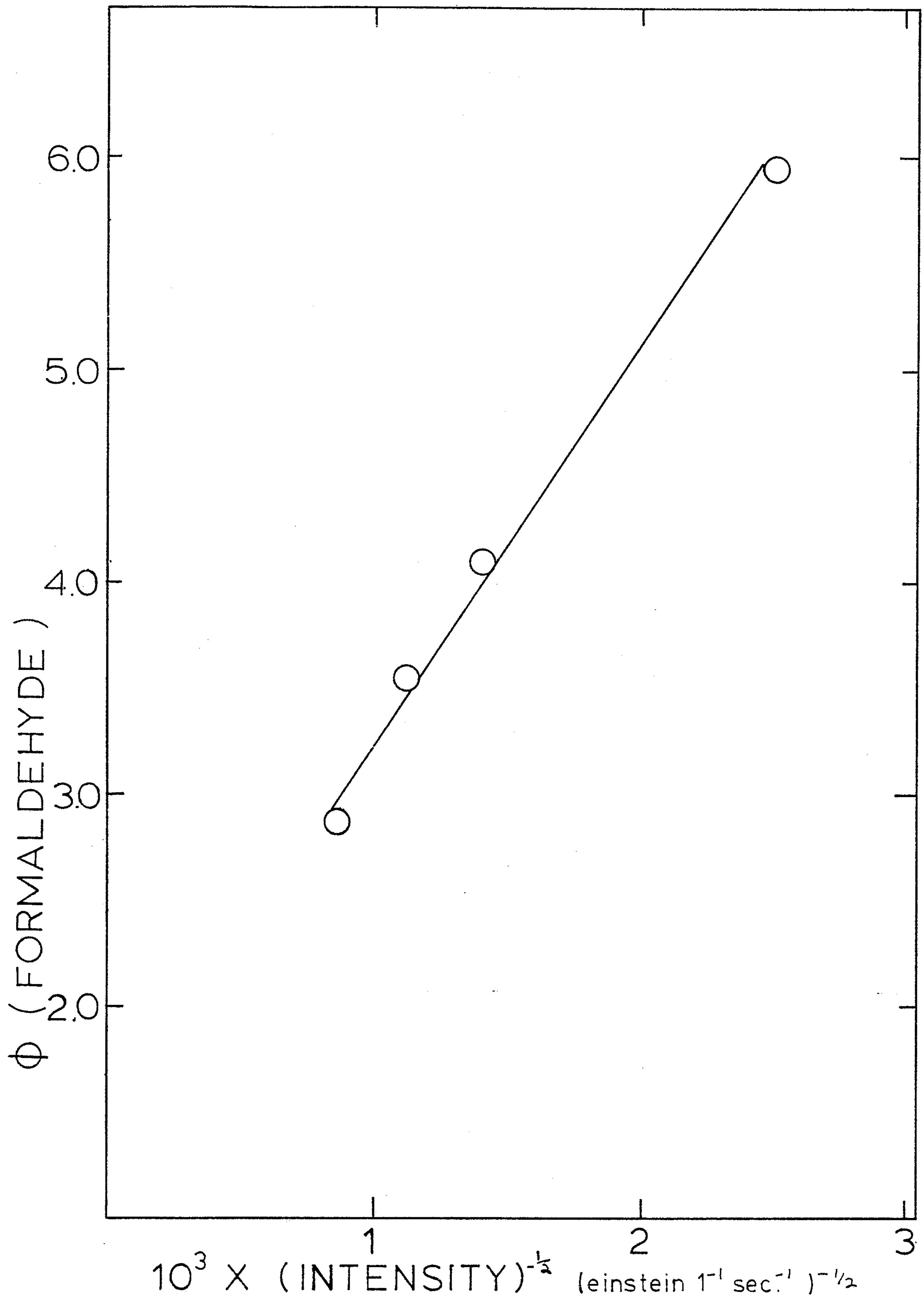
Ia einstein l^{-1} sec^{-1}	$Ia^{-\frac{1}{2}}$ $einstein^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$ $sec^{\frac{1}{2}}$	ϕ(Formaldehyde)
1.39 x 10^{-6}	0.849 x 10^{3}	2.89
8.23 x 10^{-7}	1.10 x 10^{3}	3.51
4.69 x 10^{-7}	1.46 x 10^{3}	4.13
1.50 x 10^{-7}	2.59 x 10^{3}	5.90

The four experiments with intensities varying about 10-fold indicate that there is a linear relationship between the quantum yield for formaldehyde formation and the reciprocal square root of the absorbed intensity. This is shown graphically in figure (14).

Table IX shows the effect of ϕ(Formaldehyde) vs mole percent methanol.

Fig. 14

Relationship between ϕ(Formaldehyde)
and $Ia^{-\frac{1}{2}}$ for a solution of
5.0×10^{-1} M methanol and 1.1×10^{-2} M H_2O_2



6.0
5.0
4.0
3.0
2.0
Φ (FORMALDEHYDE)
1
2
3
10³ X (INTENSITY)^-½ (einstein 1⁻¹ sec.⁻¹)^-½

Table IX

ϕ(Formaldehyde) vs mole percent methanol

Methanol mole 1^{-1}	mole percent Methanol	ϕ(Formaldehyde)
0.30	0.55	4.90
1.00	1.8	4.82
3.00	5.8	4.50
5.00	10.1	4.50
6.00	14.4	3.90
15.00	41.0	3.60
20.00	64.5	3.57
pure	100	3.58

The results in table IX show that in varying the methanol concentration over a wide range the value of ϕ(Formaldehyde) decreases at high alcohol concentration, figure (15). The results do not display a significant intermediate maximum as was shown by the results for 2-propanol.

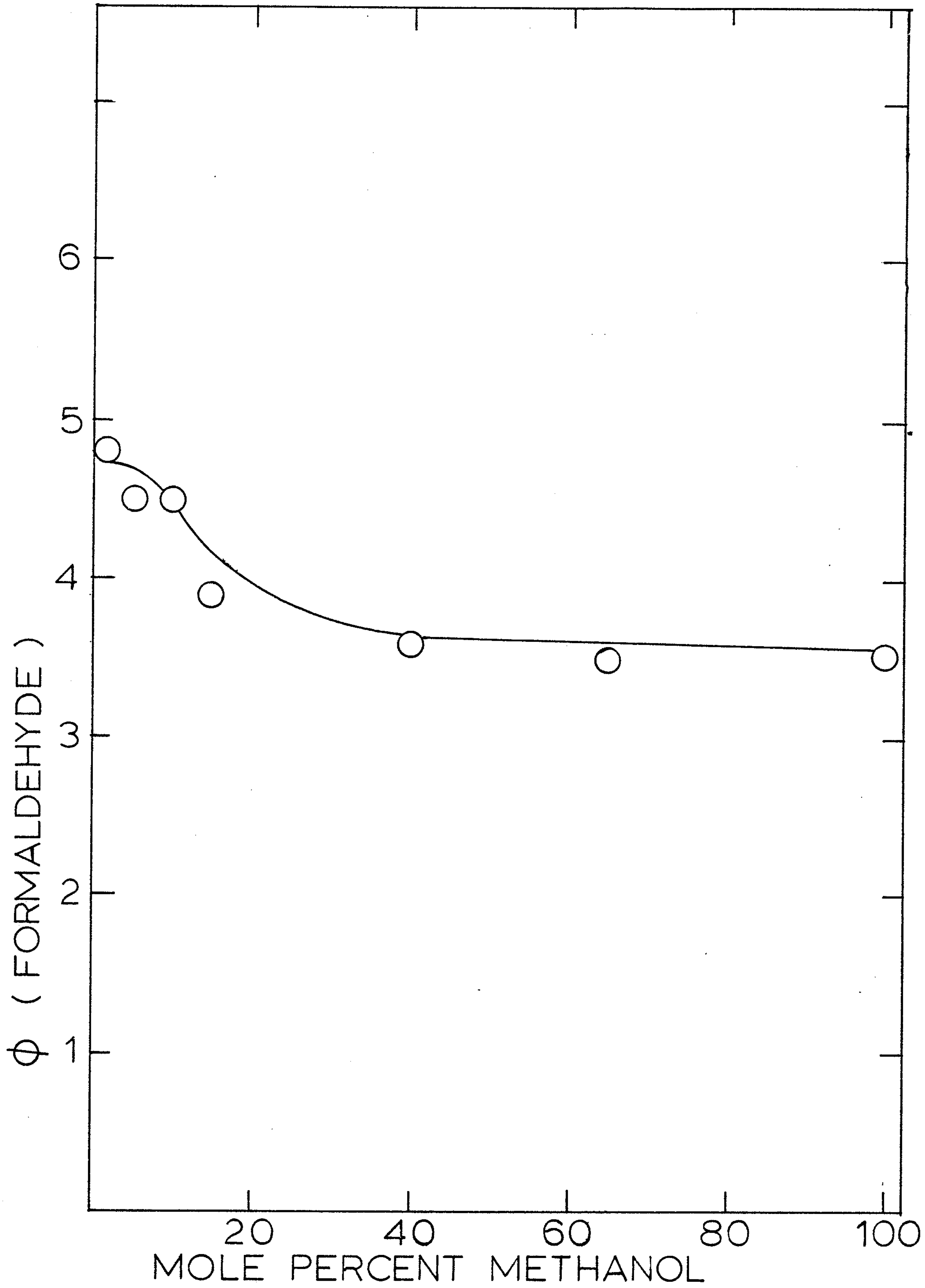
4.2 Discussion

Methanol 0.1 M - 1.5 M / 1.1 x 10^{-2} M H_2O_2

Barrett, et al., (4) have stated that their results for methanol

Fig. 15

The relationship between ϕ(Formaldehyde) vs mole percent methanol for 1.1×10^{-2} M H_2O_2 solutions irradiated at 253.7 nm.


φ (FORMALDEHYDE)
1
2
3
4
5
6
20
40
60
80
100
MOLE PERCENT METHANOL

were similar to those for 2-propanol but did not include any data in their report. Their statement could be interpreted to mean an increase of ϕ(Formaldehyde) results from increasing methanol concentration at low alcohol concentrations, reaching a maximum in the region of 4.0 M and decreasing to a limiting value at high alcohol concentration. The results obtained in this study show that ϕ(Formaldehyde) is independent of the methanol concentration in the region 0.1 M - 1.5 M, figure (13) and show no intermediate maximum, figure (15), which is in contrast to the results obtained for 2-propanol. The only similarity between ϕ(Acetone) and ϕ(Formaldehyde) is at high alcohol concentration where both show a decrease in quantum yields with increase in alcohol concentration. At low methanol concentration the results also show a reciprocal dependence of the square root of the intensity, figure (14).

The contrast in the results obtained when methanol at low concentration is oxidized by hydrogen peroxide in aqueous solutions, can be attributed to the fact that only one kind of radical, $\dot{C}H_2OH$, may be formed by abstraction of a hydrogen atom from a C-H bond in methanol. Since the β -radical cannot form when methanol is the oxidizable substrate, there are no reactions analogous to, $\{12\}$, $\{25\}$ and $\{17\}$. Therefore in the case of methanol the Burchill-Ginns mechanism (7) reduces to a simpler mechanistic scheme. Radiation from the ultraviolet source interacts with hydrogen peroxide $\{6\}$. The OH radicals react with the methanol producing only one kind of radical, $\dot{C}H_2OH$. The kinetics of the oxidation of methanol should be determined by the following reaction scheme:

{6} $H_2O_2 + h\nu \rightarrow 2\,OH$

{31} $OH + CH_3OH \rightarrow \dot{C}H_2OH + H_2O$

{32} $\dot{C}H_2OH + H_2O_2 \rightarrow CH_2O + H_2O + OH$

{33} $2\,\dot{C}H_2OH \rightarrow$ ethylene glycol or $CH_2O + CH_3OH$

Applying the normal steady state approximations the expression for the yield of formaldehyde is shown to be:

{34} $$\phi(CH_2O) = k_{32}\left(\frac{\phi_6}{Ia\ k_{33}}\right)^{1/2}[H_2O_2]$$

This expression predicts that the yields of CH_2O are independent of methanol concentration, for moderate to large chain lengths, which is in agreement with the experimental results, figure (12), also that ϕ(Formaldehyde) is dependent upon the hydrogen peroxide concentration. The expression also includes a reciprocal square root dependence on the intensity which is in agreement with the experimental results, figure (13).

Burchill and Ginns (30) have investigated the radiation-induced oxidation of methanol by hydrogen peroxide in deaerated aqueous solutions. Comparing their results to results obtained in this study, qualitative similarity is observed. That is, at a constant initial concentration of H_2O_2 (0.01 M) initial $G(-H_2O_2)$ values are independent of methanol concentration in the range 0.2 to 2.0 M and then decrease as the methanol concentration is further increased. A reciprocal square root dependence on the dose rate is also observed. Burchill and Ginns attribute the contrast in results between 2-propanol and methanol to the fact that only one kind of radical $\dot{C}H_2OH$ may be formed when methanol is the oxidizable substrate. Therefore they are suggesting that the chain oxidation of methanol conforms to a simple mechanistic scheme. This proposal is supported by the form of the experimental results obtained in this work. Assuming a value $k_{33} = 1.2 \times 10^{9}\ M^{-1}\ sec^{-1}$ (29) for the bimolecular termination reaction $\{33\}$, a rate constant for the chain propagating reaction may be estimated as $k_{32} = 0.9 \times 10^{4}\ M^{-1}\ sec^{-1}$. Burchill and Ginns obtain a value $k_{32} = (4.0 \pm 0.4) \times 10^{4}\ M^{-1}\ sec^{-1}$ for the same reaction.

The mechanistic scheme used to explain the chain oxidation of methanol suggests that ethylene glycol may be a product of the termination reaction $\{33\}$. Barrett and Baxendale (31) said that the major product of radical combination is ethylene glycol in the photolysis of methanol water solutions. Burchill and Ginns (30) using γ -radiation to initiate the oxidation of methanol for the same system found (G(Glycol) $\approx$ 0.5) which represents a small amount, approximately 20% of the termination reaction.

Methanol concentration $>$ 1.5 M

At high methanol concentration the yields of formaldehyde are reduced to a limiting value $\approx$ 3.60 in pure methanol. Barrett (4) attributed the variation of quantum yields for ethanol to a "photochemical cage" effect and the results with 2-propanol and methanol were said to be similar. Examination of the results in this work show clearly that methanol is not similar to 2-propanol, but when compared to results obtained by Burchill and Ginns (30) for the radiation induced oxidation of methanol qualitative similarity is seen. The fact that methanol does not display a significant intermediate maximum yield can be explained by the following argument. Burchill and Ginns (7) have suggested that the increasing yields with increasing 2-propanol concentration (for solute concentration < 3 M) reflects the increasing rate of reaction {25}. With methanol (30) where only one kind of radical can be formed, there is no reaction analogous to {25} and, correspondingly, no increase in yield with increasing methanol concentration. The close similarity of the results observed in these experiments to those obtained by Burchill and Ginns, suggests that the Burchill Ginns explanation for the lack of an intermediate maximum for methanol, in general, applies to the photochemical system as well.

Furthermore, Burchill and Thompson (18), have determined apparent first-order rate constants for peroxide removal for four different alcohol concentrations for both CH_3OH and CD_3OH and observed no significant effect on deuteration of the methyl group. This supplies evidence that reaction {32} (and its analogue, {8}) for 2-propanol, does not involve the rupture of a C-H bond as a rate-determining process and is in accord with the prediction made on the basis of their equation 15. Since equation {34} is analogous to their equation 15, it may be implied that their explanation also holds true in the photo-induced system.

The reduction in Φ(Formaldehyde) at high methanol concentration, figure (15), is similar to the decrease in initial $G(-H_2O_2)$ values observed by Burchill and Ginns (30). They explain that the decrease is a result of a decrease in the rate constant for reaction {32} which is due to a decrease in dielectric constant. The explanation for the same effect offered by Barrett, et al., (4) is that the reduction of yields is due to a "photochemical cage" effect. This cannot be true since there is no analogue to the primary solvent cage in radiation-induced reactions, therefore it may be assumed that the Burchill-Ginns explanation for reduced yields applies to the photo-induced oxidation of methanol as well. Hence methanol, with no mechanism for an increase in yields, would have the rate constant for the propagating reaction {32} decrease, and with it the chain length would show a continuous decrease with increasing methanol concentration. This has been observed in the results.

At high alcohol concentrations ϕ(Acetone) decreases from ~25 to 8.60 for 2-propanol and ϕ(Formaldehyde) decreases from ~5.0 to 3.60 for methanol, a much less dramatic decrease than for 2-propanol. This may in part be explained in terms of the decrease in the dielectric constant, (water 80.36, methanol 33.62 and 2-propanol 18.3 (26)). The decrease in dielectric constant going from H_2O to alcohol is larger for 2-propanol than for methanol. This suggests that the rate constant k_8 may decrease a greater amount than the rate constant k_{32}: Hence a larger decrease in ϕ(Acetone) compared to ϕ(Formaldehyde).

4.3 Summary

Burchill and Ginns have demonstrated that a one-radical model accounts satisfactorily for the features of the radiation-induced oxidation of methanol. Because of the similarity of results obtained for the photo-induced oxidation of methanol it may be concluded that a similar one-radical model also applies to the photo-induced system.

5. SUMMARY

The chain oxidation of 2-propanol by hydrogen peroxide has been investigated. Previous authors (1,3,5) have explained their results by assuming a one-radical model. Burchill and Ginns (7) have demonstrated that this is not a satisfactory explanation. The simple mechanism predicts that the yields are dependent on peroxide concentration and independent of alcohol concentration. Burchill and Ginns found that the yields are independent of peroxide concentration and dependent on alcohol concentration. They proposed a two-radical model which satisfactorily explained their experimental results.

Results obtained for the photo-initiated oxidation of 2-propanol by hydrogen peroxide in this work demonstrate qualitative and quantitative similarity to the results obtained by Burchill and Ginns. It has also been demonstrated that the two-radical model is a satisfactory explanation for the results in this system.

Table X

Comparison of Numerical Results

Author	Initiation	$\frac{k_7}{k_{12}}$	k_{25} (M^{-1} s^{-1})	10^{-4}x k_{32} (M^{-1} s^{-1})	% attack at α -position by OH
Burchill Ginns (7)	radiation	6.2	53±10	4.0	86
Burchill Thompson (18)	radiation	5.2	51±2		
Burchill Huminicki	photochemical	4.6	75	0.9	
Walling Kato (20)	Fenton's reagent	6.2			
Asmus (19)	pulsed electron beam				85.5

The numerical values in table (X) are consistent with the mechanism proposed for the radiation-induced oxidation of 2-propanol and methanol by hydrogen peroxide (7,30).

Barrett reported the variation of peroxide quantum yields for ethanol and said 2-propanol and methanol were "similar". Barrett attributed the variations in quantum yields to a "photochemical cage" effect. The results in this study, figure 15, show clearly that methanol is not similar to 2-propanol, that is the yields are independent of alcohol concentration and show no significant intermediate maximum. Comparison with the radiation-induced results reported by Burchill and Ginns show good qualitative and quantitative agreement. The parallel between the radiation chemical results and the photochemical results reported here makes Barrett's explanation unlikely since there is no analogue to the photochemical "cage" in radiation chemistry.

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